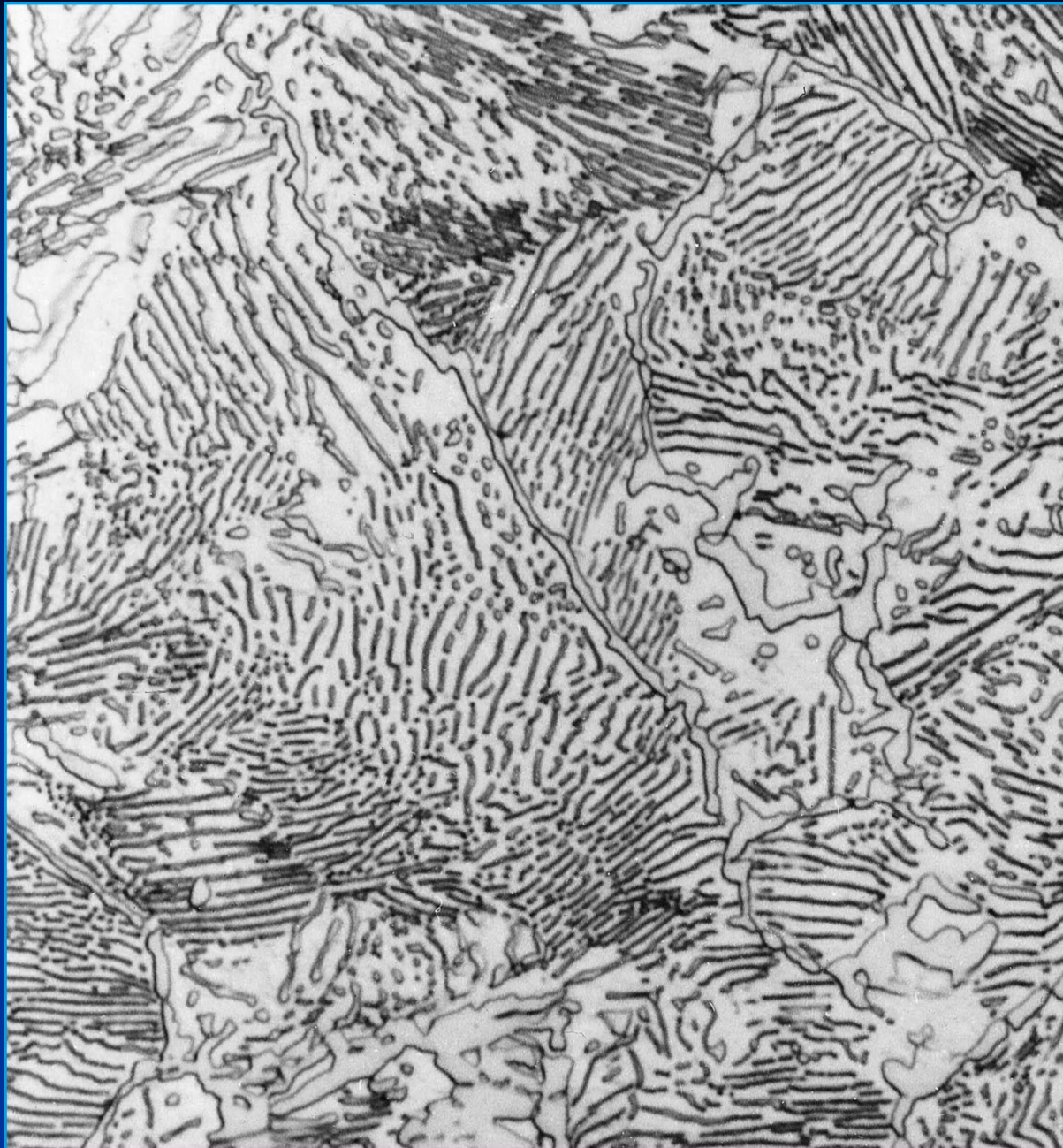


# Phase Transformations in Metals

Development of Microstructure and  
Alteration of Mechanical Properties



A photomicrograph of a pearlitic steel that has partially transformed to spheroidite. 2000 $\times$ . (Courtesy of United States Steel Corporation.)

# Introduction

- The development of microstructure in alloys involves phase transformation:
  - Phase transformation need time, and cooling rate greatly modify the phase transformation.

# Phase Transformation

## Basic Concepts

- **Phase transformation** as well as the **transformation rate** are important to develop a specific microstructure which in turn affect the mechanical properties of materials.
- For example, the tensile strength of Fe-C eutectoid alloy can be 700 MPa to 2000 MPa depending on heat treatment condition.

# Basic Concepts

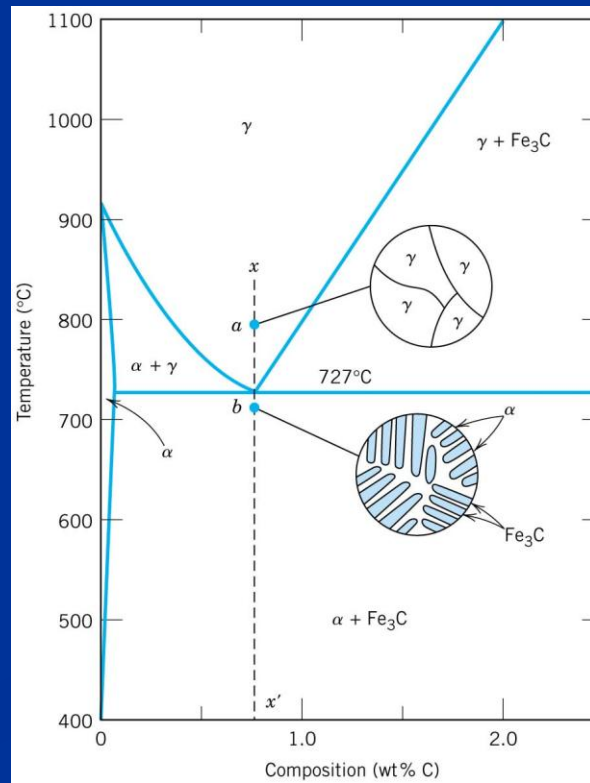
- Three classifications of phase transformations:
  - No change in composition, simple diffusion-dependent transformation
  - Composition change, diffusion-dependent transformation
  - Diffusionless transformation

# The 1st kind of phase transformation

- No change in composition, simple diffusion-dependent transformation
  - Solidification
  - Allotropic transformation ( $\alpha \rightarrow \gamma$ )
  - Recrystallization and grain growth
- No change in composition of phases.

# The 2nd kind of phase transformation

- Composition change, diffusion-dependent transformation
  - Eutectoid reaction ( $\gamma \rightarrow$  pearlite)



**FIGURE 9.23** Schematic representations of the microstructures for an iron-carbon alloy of eutectoid composition (0.76 wt% C) above and below the eutectoid temperature.

# The 3rd kind of phase transformation

- Diffusionless transformation
  - Metastable phase
  - Martensitic transformation

# The Kinetics of Phase Transformation

- The progress of a phase transformation can be broken down into two distinct stages:
  - Nucleation
  - Growth
- There are two types of nucleation :
  - Homogeneous
  - Heterogeneous
- The growth begins once an embryo has exceeded the critical size,  $r^*$

# Solidification: Nucleation Processes

## ■ Homogeneous nucleation

- nuclei form in the bulk of liquid metal
- requires supercooling (typically 80-300°C max)

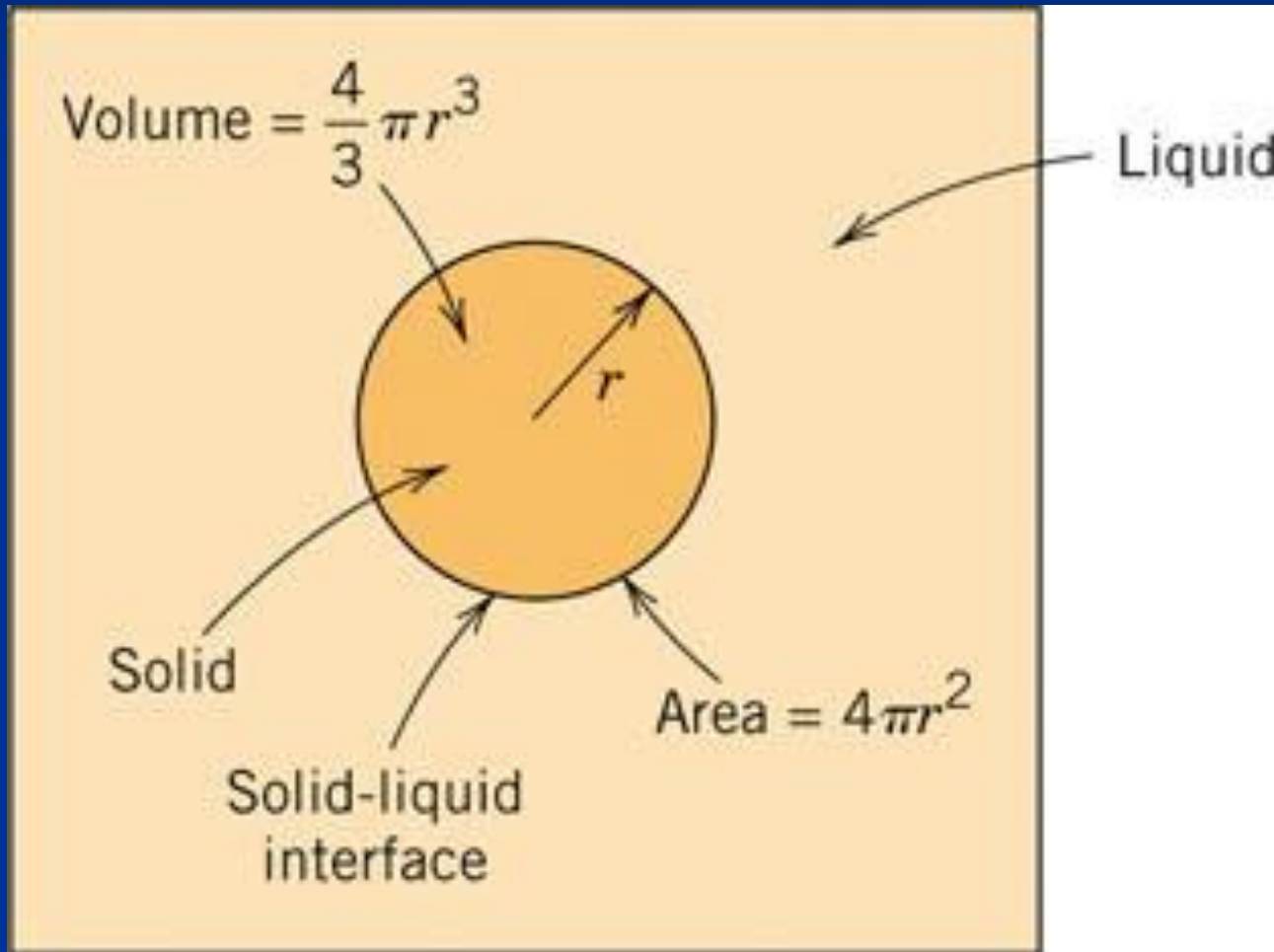
## ■ Heterogeneous nucleation

- much easier since stable “nucleus” is already present
  - Could be wall of mold or impurities in the liquid phase
- allows solidification with only 0.1-10°C supercooling

# The Kinetics of Phase Transformation

- Homogeneous nucleation
  - Nuclei of the new phase form uniformly throughout the parent phase.
  - Will occur spontaneously only when free energy change  $\Delta G$  is negative.
  - Fig. 10.1 solidification of a pure material from liquid phase.

# The Kinetics of Phase Transformation

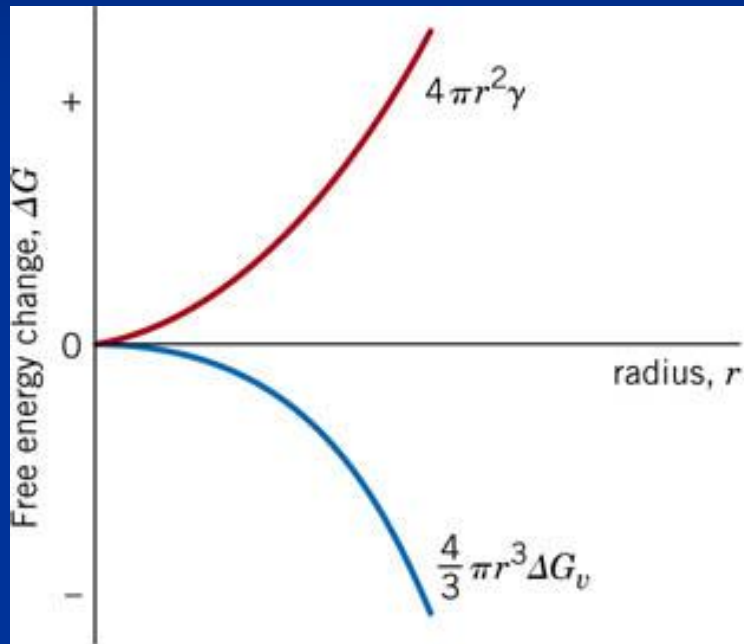


# The Kinetics of Phase Transformation

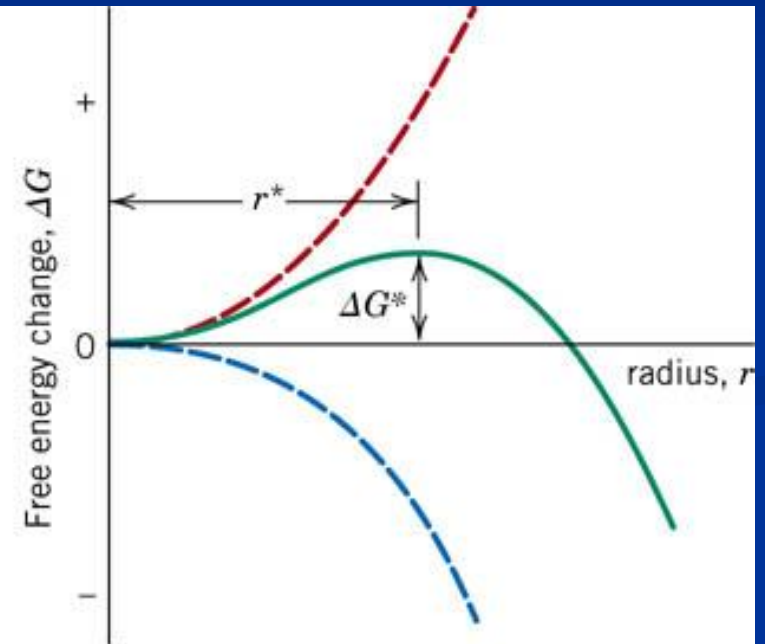
- There are two contributions to the total free energy change that accompany a solidification transformation:
  - Free energy difference between the solid and liquid phase: **Volume free energy** :  $\Delta G_v < 0$
  - Formation of the solid-liquid phase boundary: **surface free energy** :  $\gamma > 0$

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

# The Kinetics of Phase Transformation

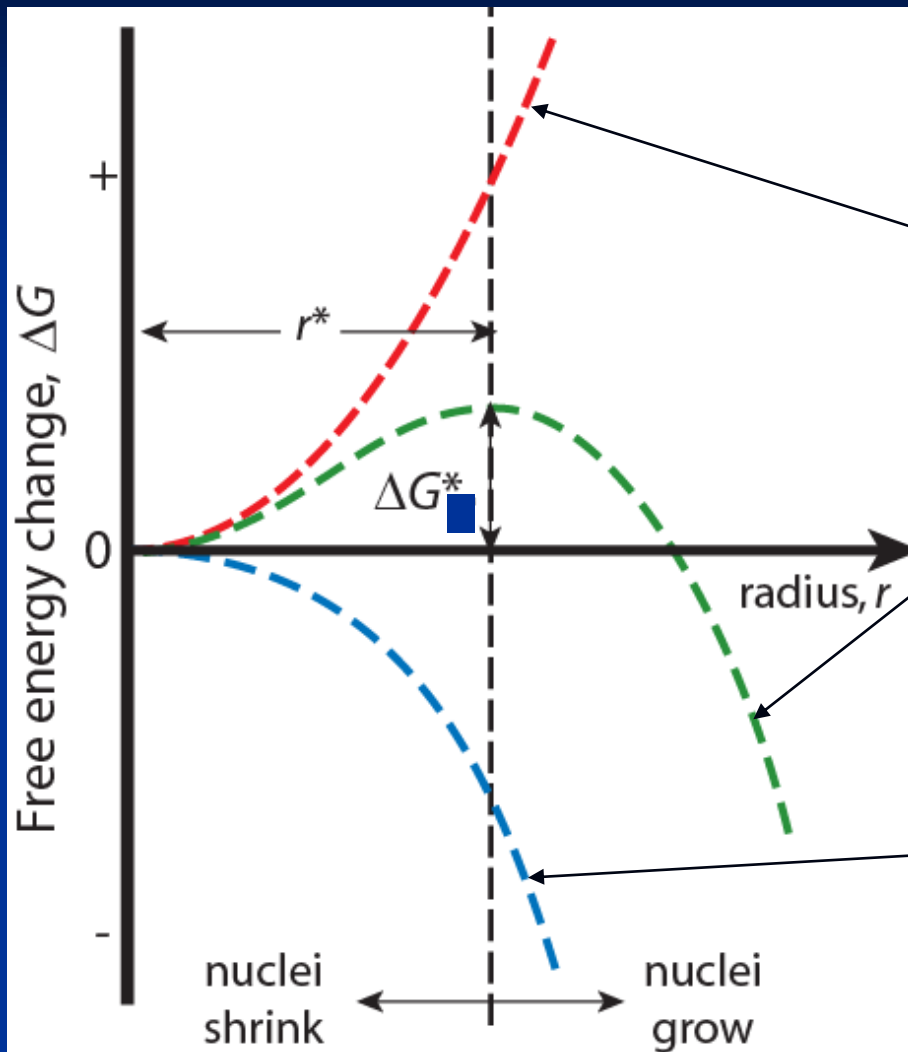


(a)



(b)

# Homogeneous Nucleation & Energy Effects



**Surface Free Energy**- destabilizes the nuclei (it takes energy to make an interface)

$$\Delta G_S = 4\pi r^2 \gamma$$

$\gamma$  = surface tension

$$\Delta G_T = \text{Total Free Energy}$$

$$= \Delta G_S + \Delta G_V$$

**Volume (Bulk) Free Energy** – stabilizes the nuclei (releases energy)

$$\Delta G_V = \frac{4}{3} \pi r^3 \Delta G_v$$

$$\Delta G_v = \frac{\text{volume free energy}}{\text{unit volume}}$$

$r^*$  = critical nucleus: nuclei  $< r^*$  shrink; nuclei  $> r^*$  grow (to reduce energy)

# The Kinetics of Phase Transformation

- The subcritical particle is an embryo, whereas the particle of radius greater than  $r^*$  is termed a nucleus.
- Since  $r^*$  and  $\Delta G^*$  appear at the maximum on the free energy-versus-radius curve of Fig. 10.2b, derivation of expressions for these two parameters is a simple matter.  $\rightarrow$  equation 10.3 and 10.4

# The Kinetics of Phase Transformation

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



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

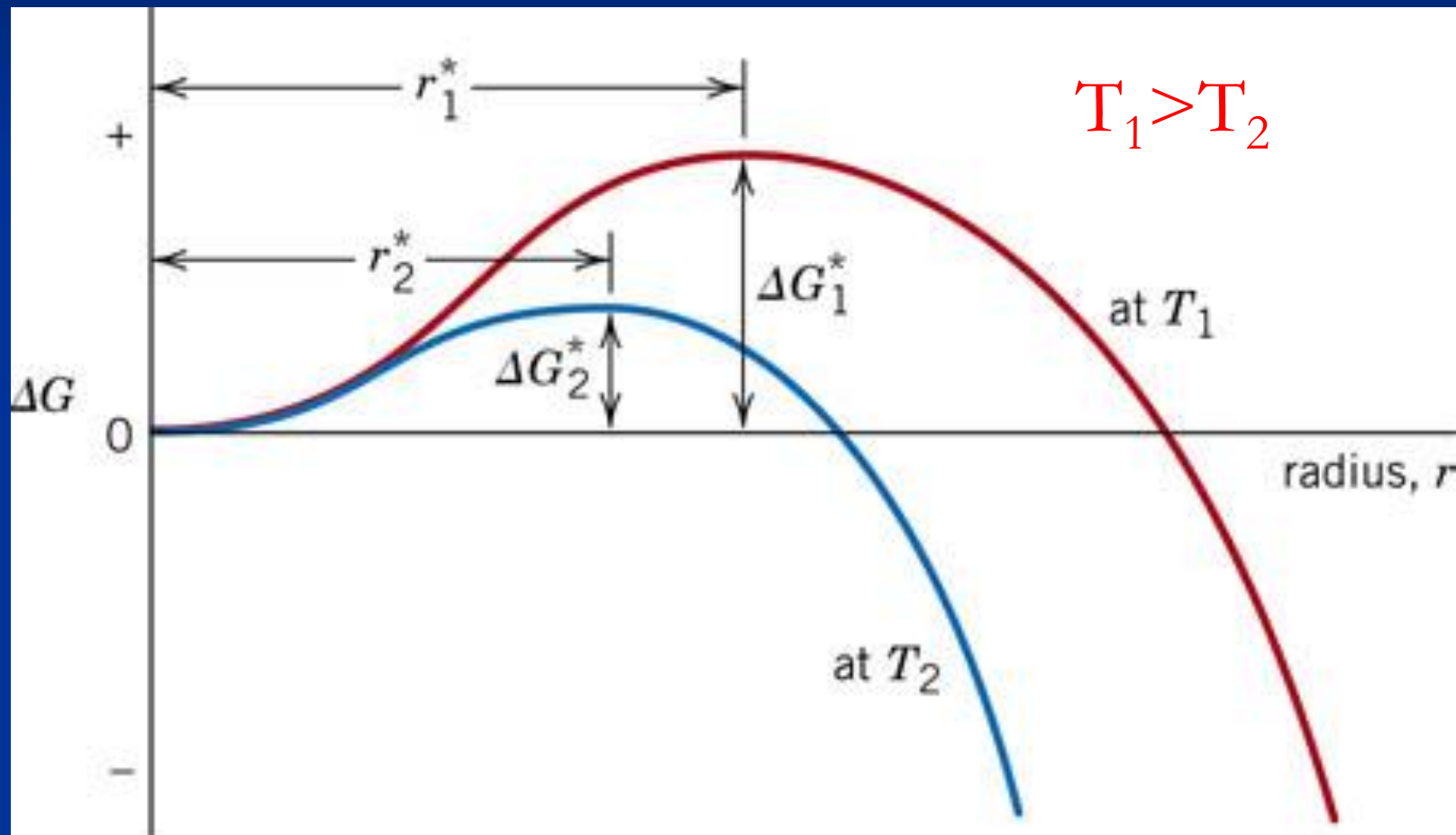
$$\Delta G_v = \frac{\Delta H_f (T_m - T)}{T_m}$$

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



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

# The Kinetics of Phase Transformation



# The Kinetics of Phase Transformation

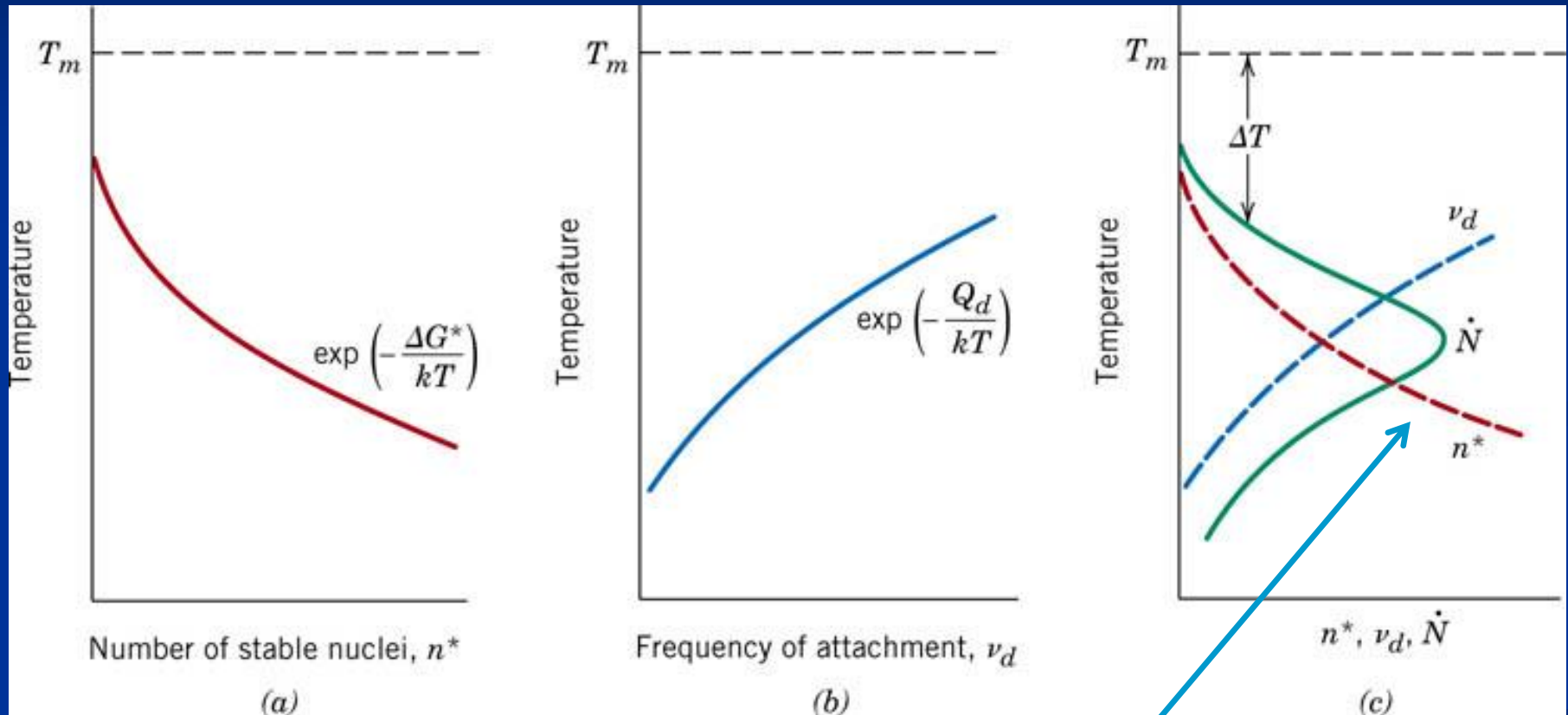
- The number of stable nuclei  $n^*$  (radii greater than  $r^*$ ) is a function of temperature:

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

- Another temperature-dependent parameter is also important for nucleation: rate of diffusion, the frequency atoms from the liquid attach to the solid nucleus.

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

# The Kinetics of Phase Transformation



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

# The Kinetics of Phase Transformation

<i>Metal</i>	$\Delta T$ (°C)
Antimony	135
Germanium	227
Silver	227
Gold	230
Copper	236
Iron	295
Nickel	319
Cobalt	330
Palladium	332

**Source:** D. Turnbull and R. E. Cech, “Microscopic Observation of the Solidification of Small Metal Droplets,” *J. Appl. Phys.*, **21**, 808 (1950).

# The Kinetics of Phase Transformation

## Example Problem

- Computation of critical nucleus radius and activation free energy
- Computing the number of atoms in a critical nucleus.

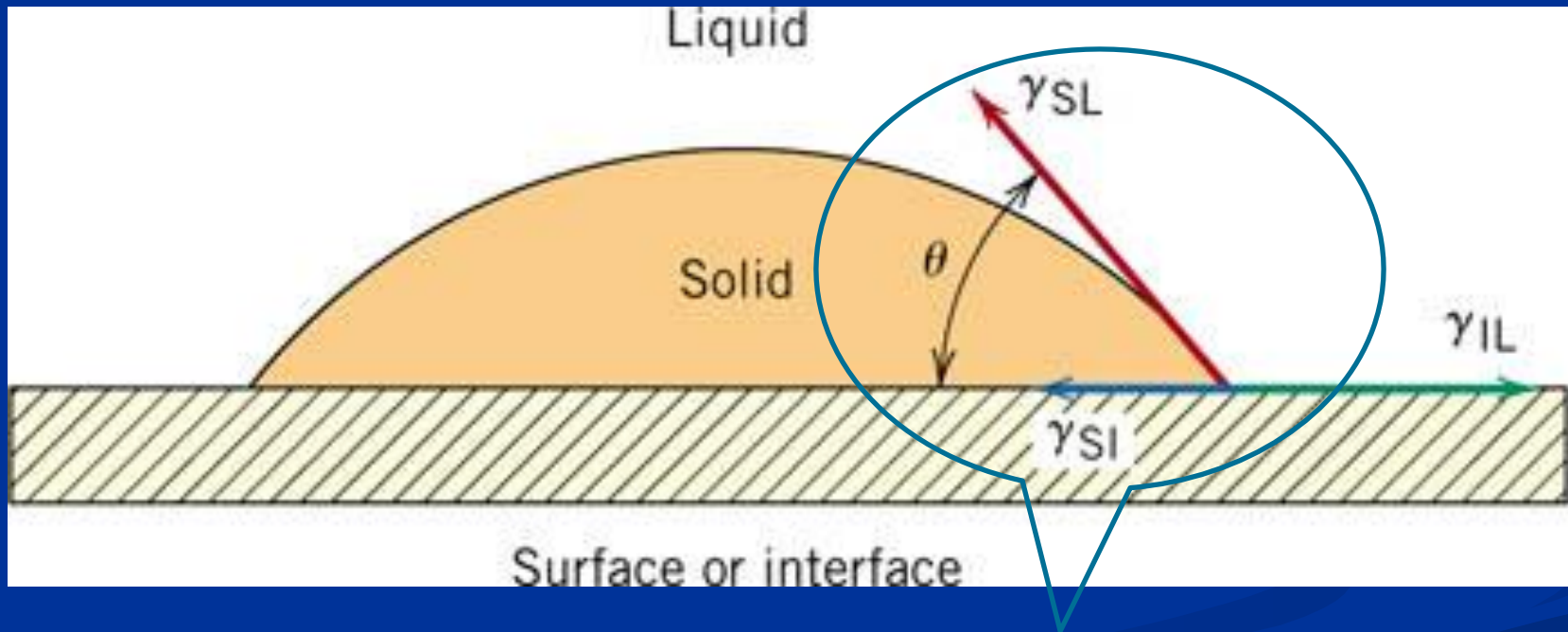
# The Kinetics of Phase Transformation

## ■ Heterogeneous Nucleation

- The activation energy (energy barrier) for nucleation ( $\Delta G^*$ ) is lowered when nuclei form on preexisting surfaces or interfaces.
- The surface free energy  $\gamma$  is reduced.

# The Kinetics of Phase Transformation

## Heterogeneous Nucleation



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

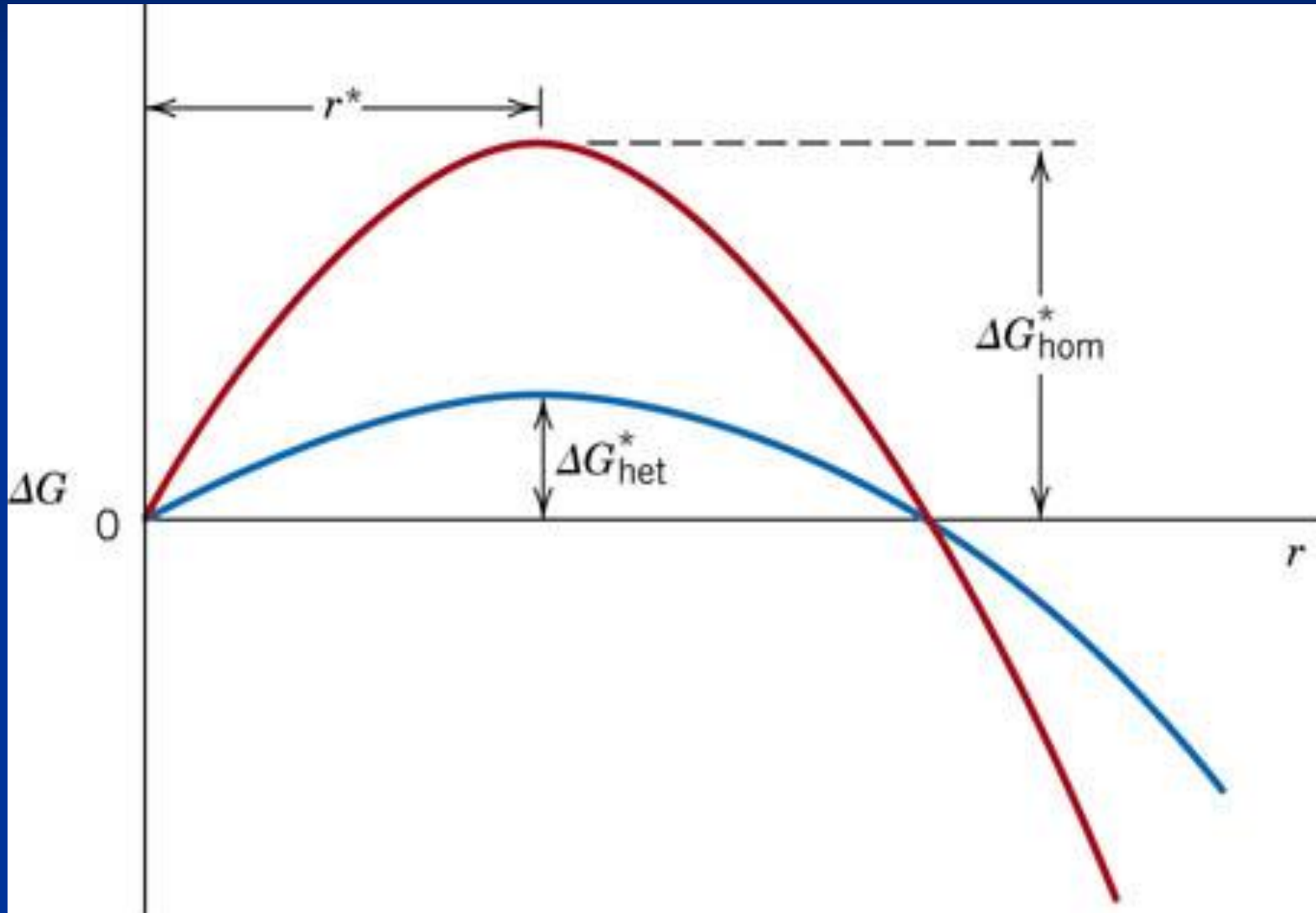
# The Kinetics of Phase Transformation

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

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

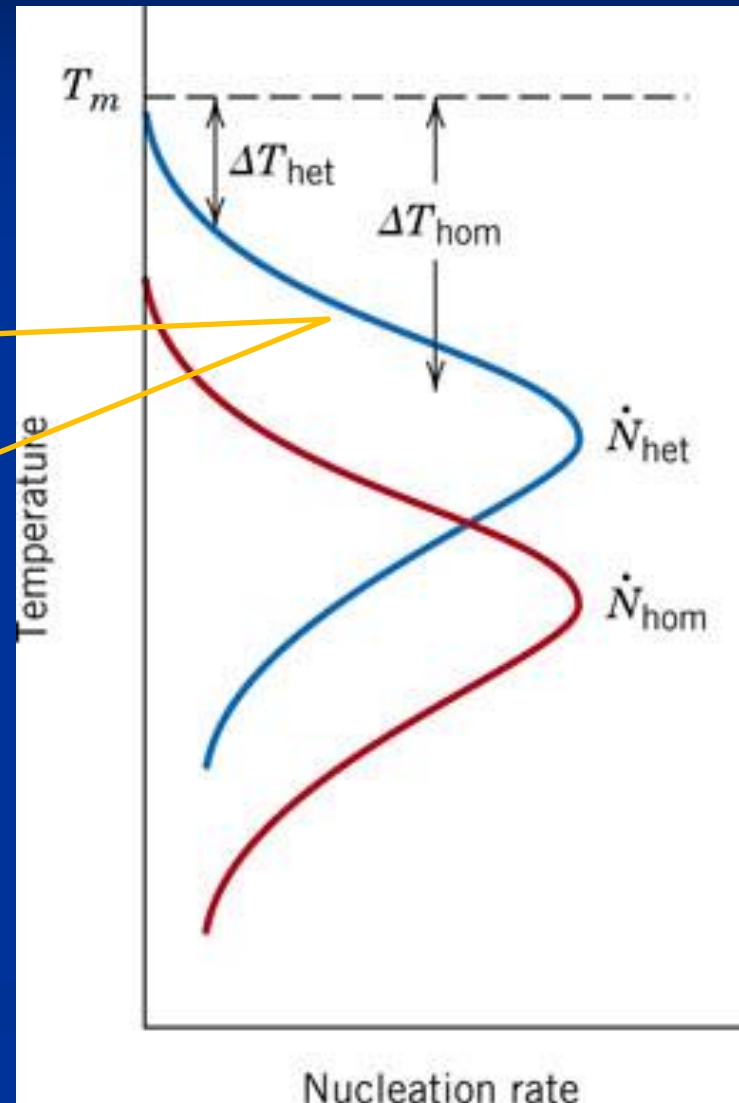
$$\theta=30-90^\circ, \quad S(\theta)=0.01\sim 0.5$$

# The Kinetics of Phase Transformation



# The Kinetics of Phase Transformation

The nucleation rate is shifted to higher temperature for heterogeneous.



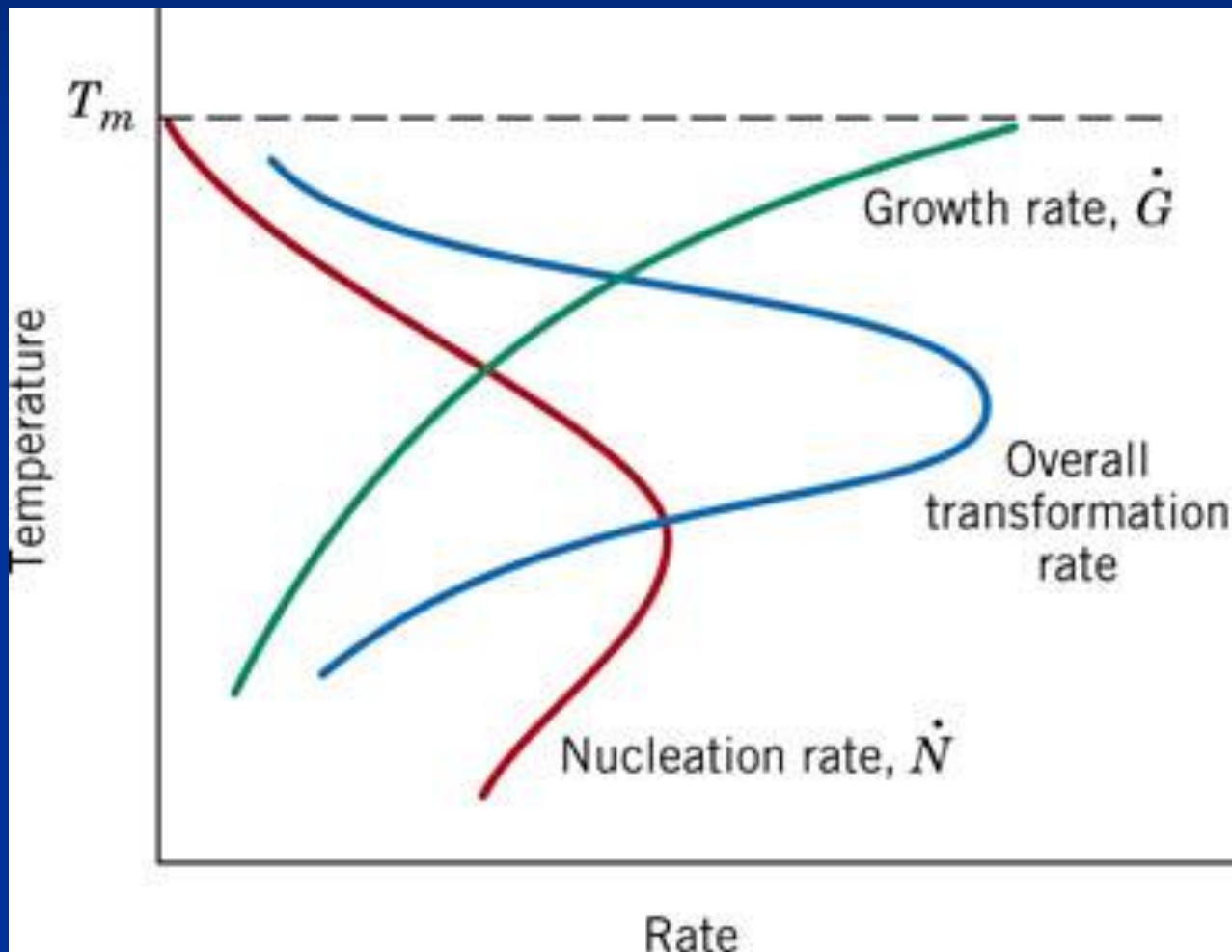
# The Kinetics of Phase Transformation

- The growth rate is determined by the rate of diffusion and its temperature dependence is the same.

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

- The overall phase transformation rate is equal to some product of N and G

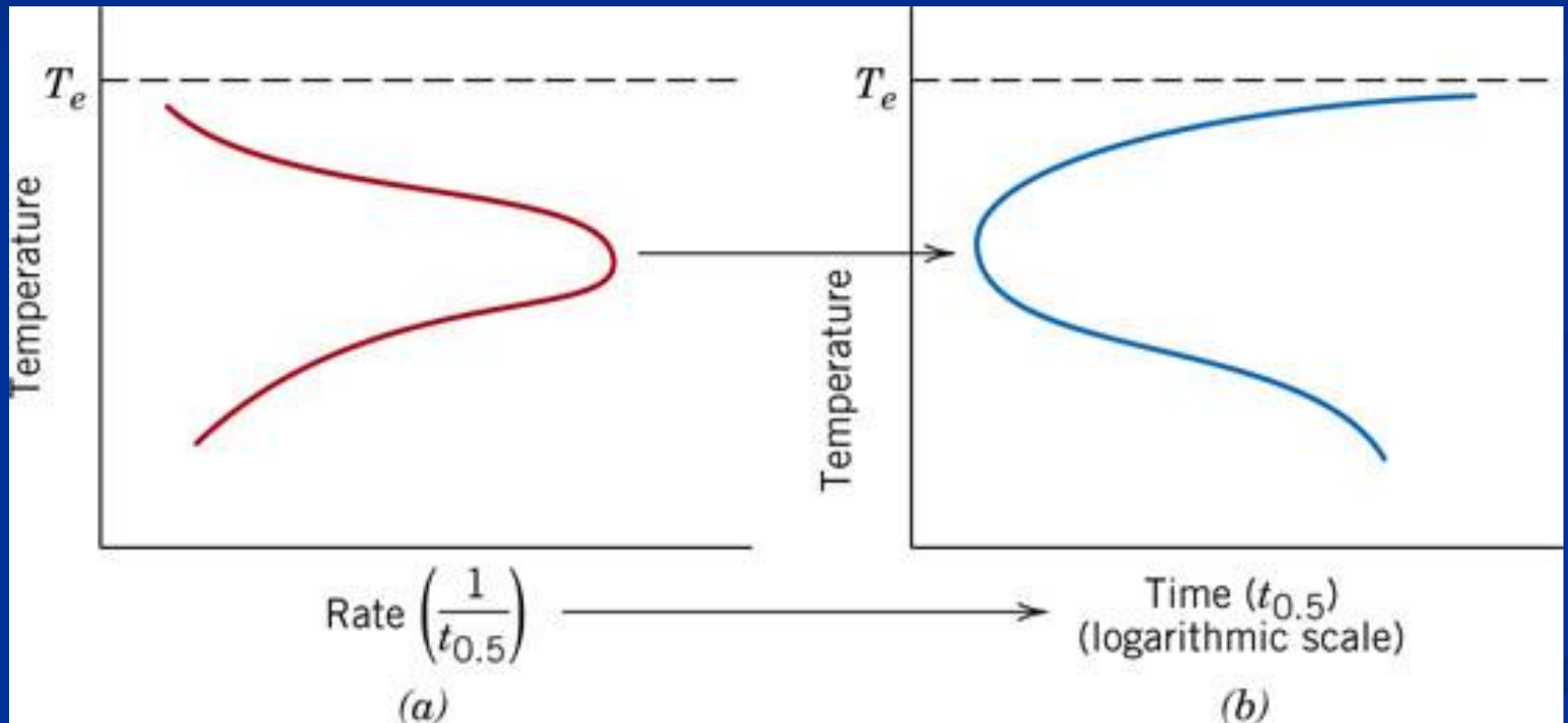
# The Kinetics of Phase Transformation



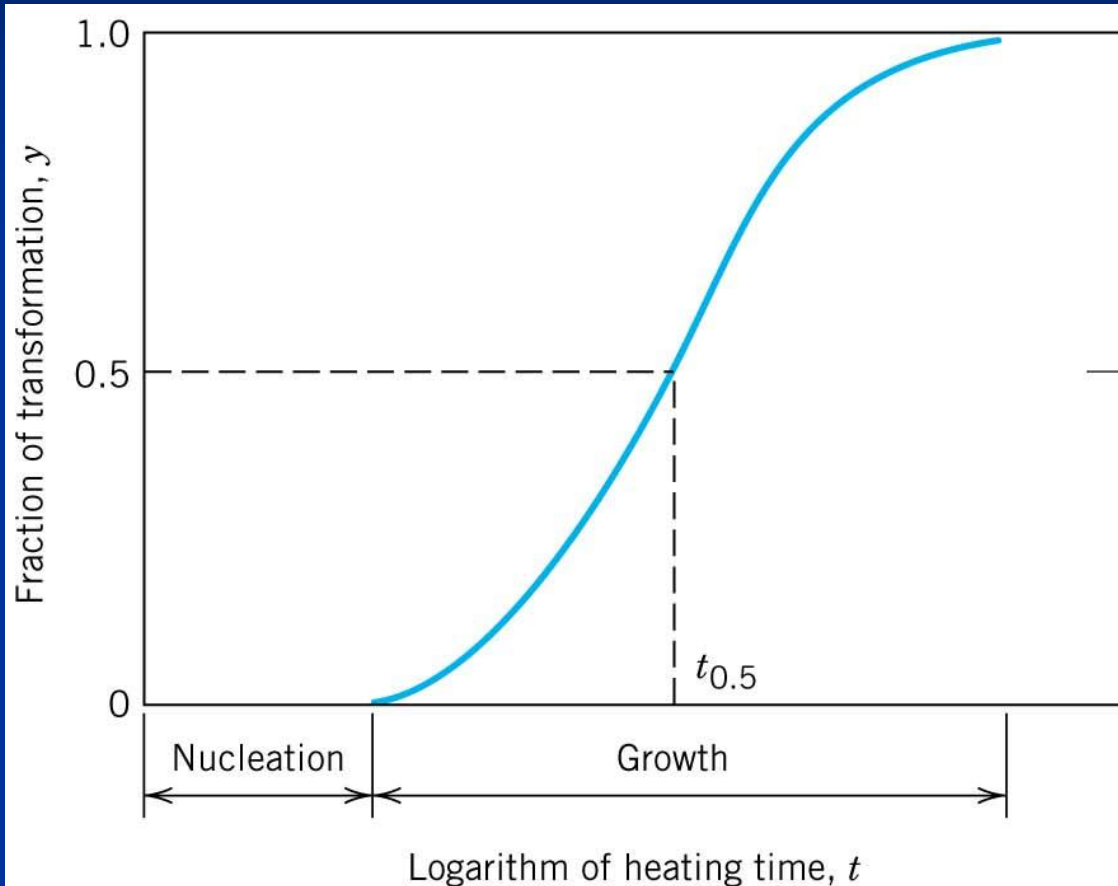
# The Kinetics of Phase Transformation

- The rate of transformation and the time required for the transformation (say 50%) is inversely proportional to one another.
- Rate of transformation :  $r = 1 / t_{0.5}$
- $t_{0.5}$  = time required for halfway to completion.

## 10.3 The Kinetics of Phase Transformation



# Rate of transformation



**FIGURE 10.1** Plot of fraction reacted versus the logarithm of time typical of many solid-state transformations in which temperature is held constant.

# The Kinetics of Phase Transformation-

## Kinetic considerations of solid-state transformation

- Rate of transformation :  $r = 1 / t_{0.5}$
- $t_{0.5}$  = time required for halfway to completion.
- Temperature will affect the rate of transformation:

$$r = A \cdot e^{\left(-\frac{Q}{RT}\right)}$$

- $Q$  = activation energy
- Phase transformation is a thermal activated process.

# The Kinetics of Phase Transformation-

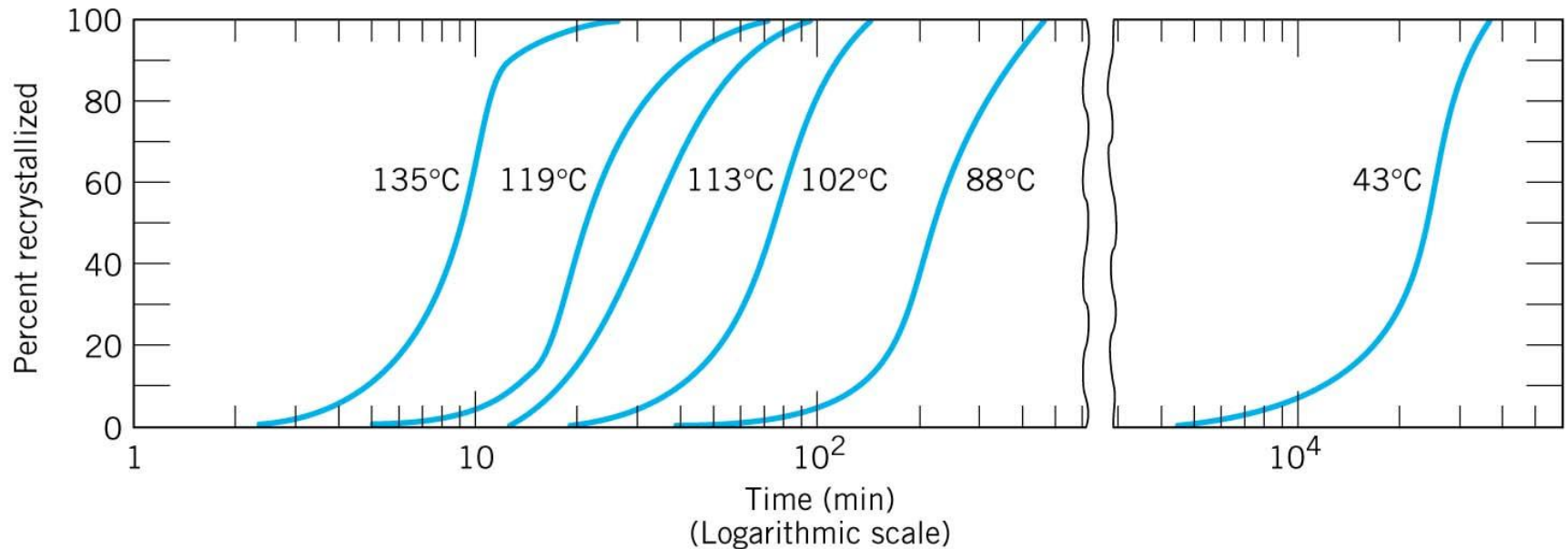
## Kinetic considerations of solid-state transformation

- Solid-state transformation did not occur instantly.
  - Need composition redistribution or atomic rearrangement
  - Energy increase for nucleation or new phase boundaries.
  - Time-dependent process (kinetics): *Avrami equation*.

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

k, n = time-independent constant ; k relates to r.

# Rate of transformation



**FIGURE 10.2** Percent recrystallization as a function of time and at constant temperature for pure copper. (Reprinted with permission from *Metallurgical Transactions*, Vol. 188, 1950, a publication of The Metallurgical Society of AIME, Warrendale, Pennsylvania. Adapted from B. F. Decker and D. Harker, "Recrystallization in Rolled Copper," *Trans. AIME*, **188**, 1950, p. 888.)



# Metastable versus Equilibrium states

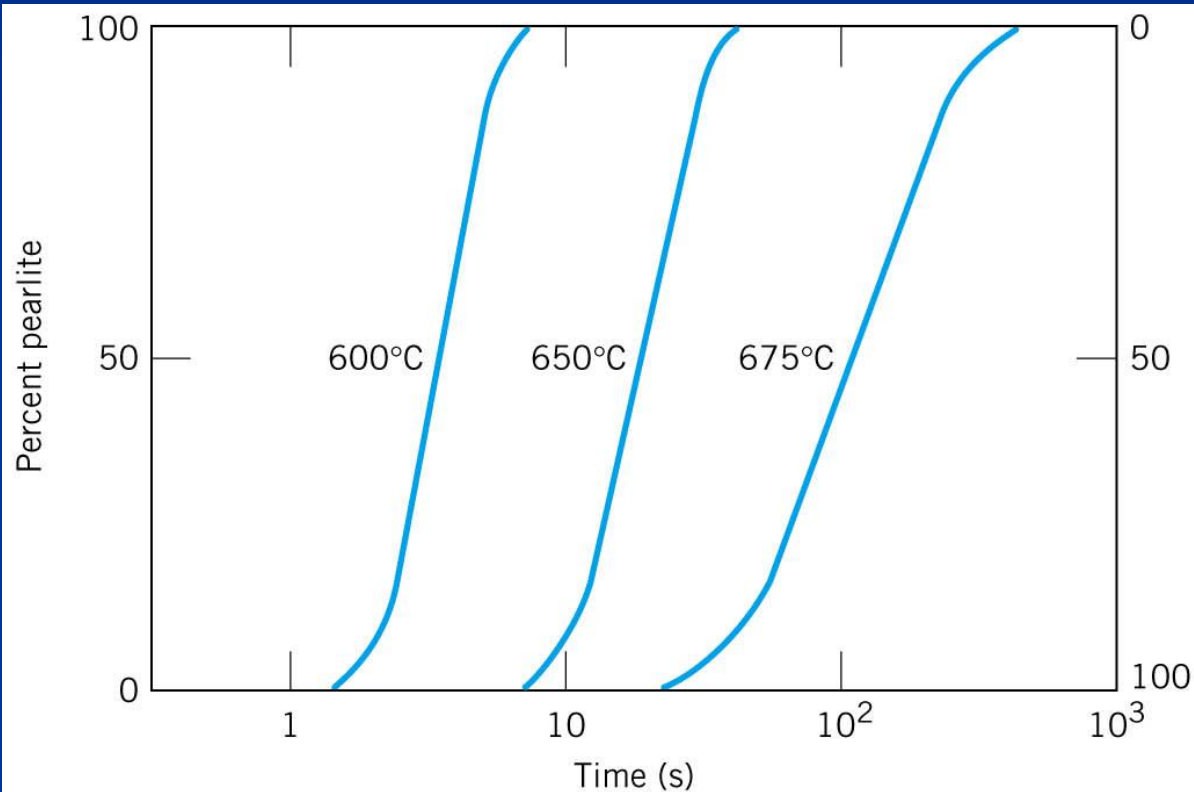
- Phase transformation is a time-dependent process, long time is required to reach equilibrium stage.
  - Speed or rate of cooling is designed to produce specific microstructure which the phase may not be the equilibrium one. → metastable phase.
  - Supercooling or superheating happens very often in practical purpose.

# Microstructure and Property Changes in Fe-C Alloys

## 10.5 Isothermal Transformation Diagrams

- Eutectoid reaction, at 727°C
  - $\gamma \rightarrow$  pearlite ( $\alpha + \text{Fe}_3\text{C}$ )
- See Fig. 10.12
- The lower the temperature, the fast the phase transforms.

# Isothermal Transformation Diagrams

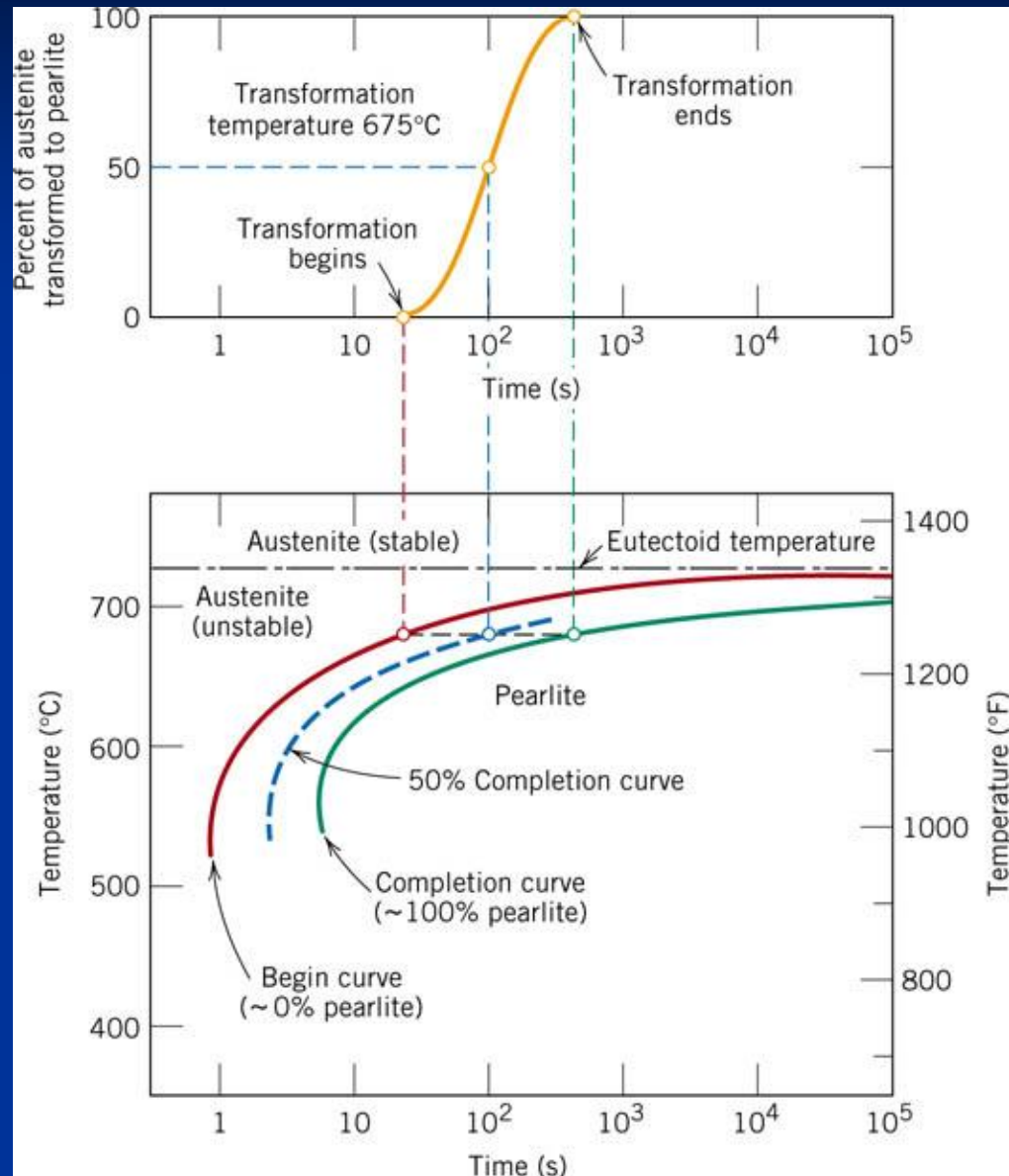


**FIGURE 10.3** For an iron-carbon alloy of eutectoid composition (0.76 wt% C), isothermal fraction reacted versus the logarithm of time for the austenite-to-pearlite transformation.

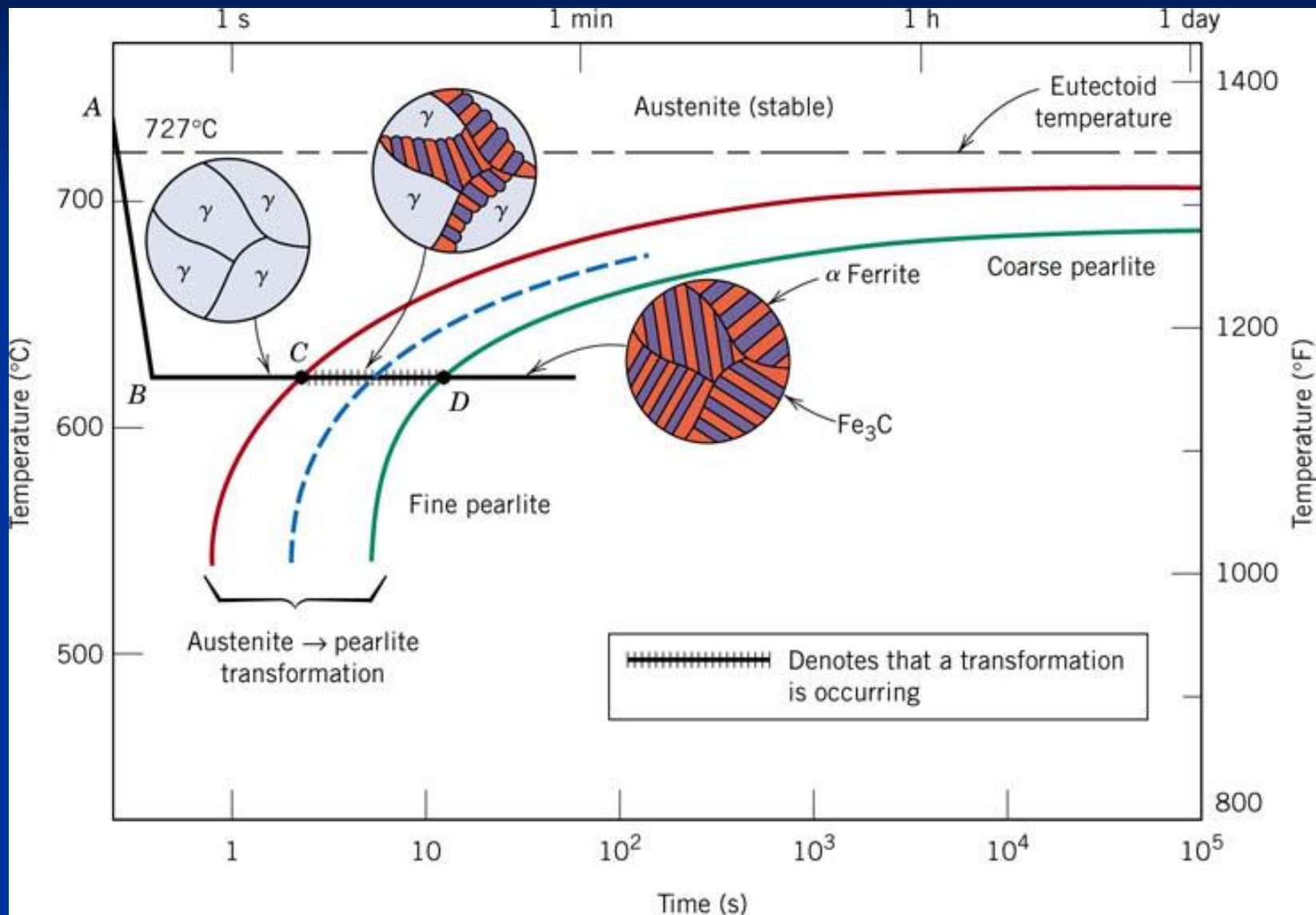
# Isothermal Transformation Diagrams

- $T \sim < 727^{\circ}\text{C}$  (slightly lower):
  - Phase transformation needs longer time
  - Microstructure becomes coarse pearlite.
- $T \ll 727^{\circ}\text{C}$  (much lower):
  - Phase transformation is quick.
  - Microstructure is fine pearlite.
- See Fig. 10.13, which is called isothermal transformation diagram. (Time-temperature-transformation, T-T-T plot)

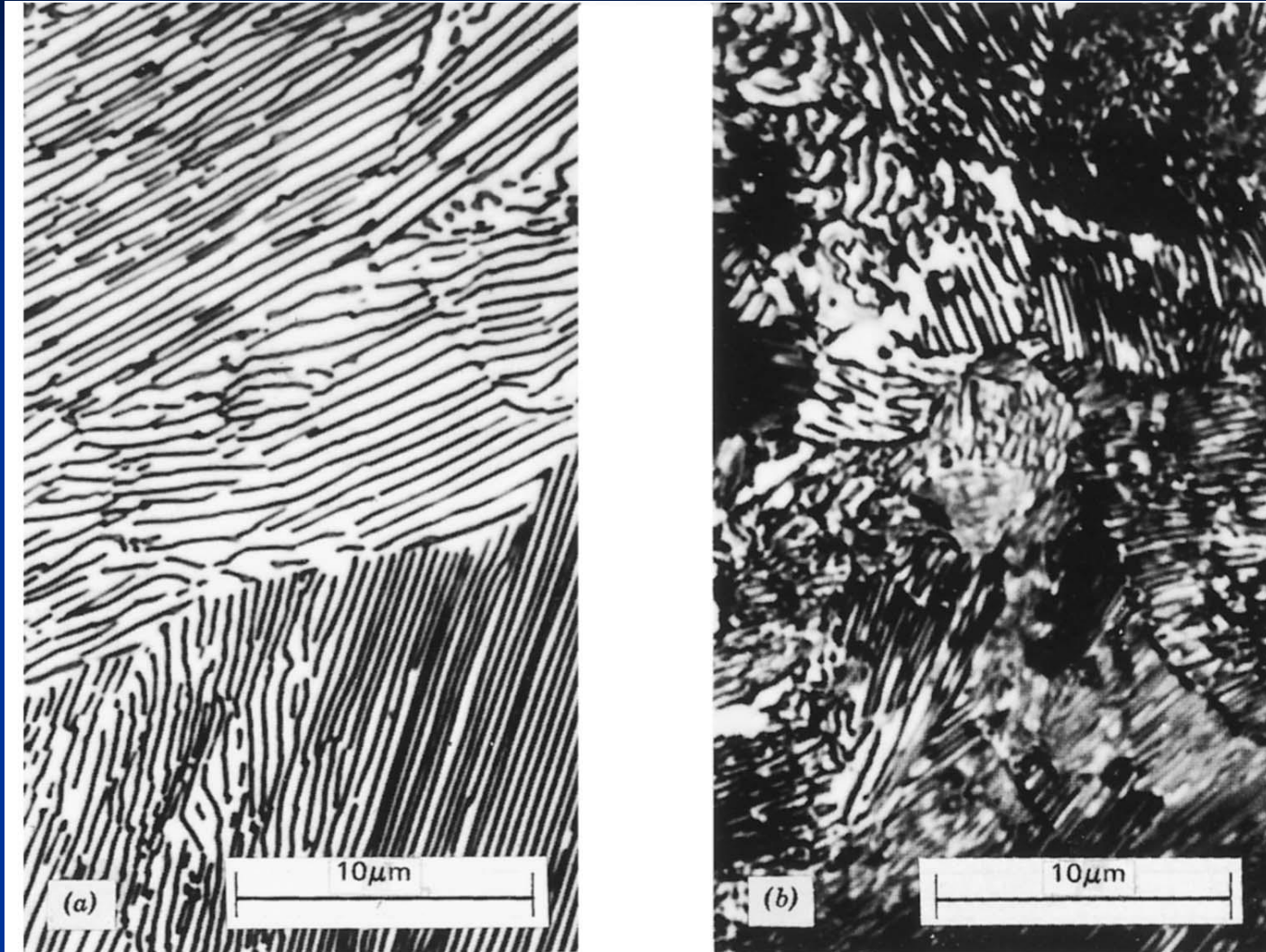
# T-T-T plot



# Cooling curve ABCD in T-T-T plot for eutectoid reaction



# (a) Coarse pearlite and (b) fine pearlite



**FIGURE 10.6** Photomicrographs of (a) coarse pearlite and (b) fine pearlite. 3000 $\times$ . (From K. M. Ralls et al., *An Introduction to Materials Science and Engineering*, p. 361. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

# End of section (1)

- You have learned:
  - What is eutectoid phase transformation
  - Phase transformation needs time
  - Cooling rate affect phase transformation, and eventually microstructure.
  - T-T-T plot to show how can the coarse pearlite and fine pearlite be formed.