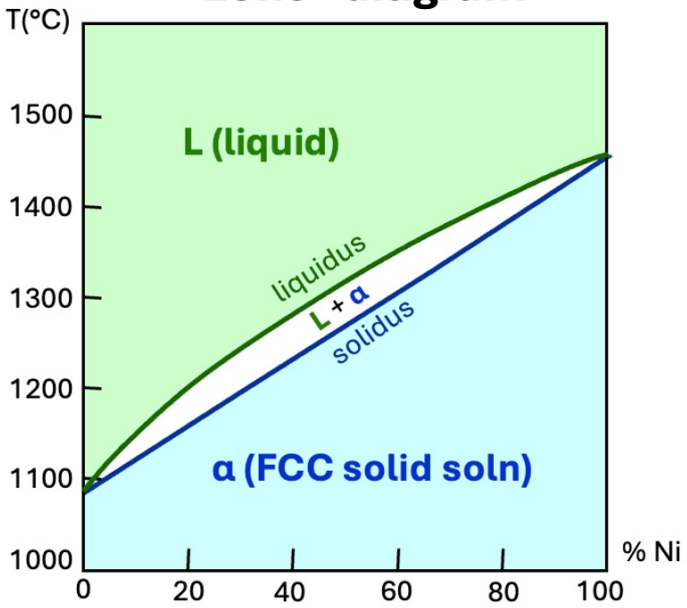
Lecture 7:
Phase Transformations

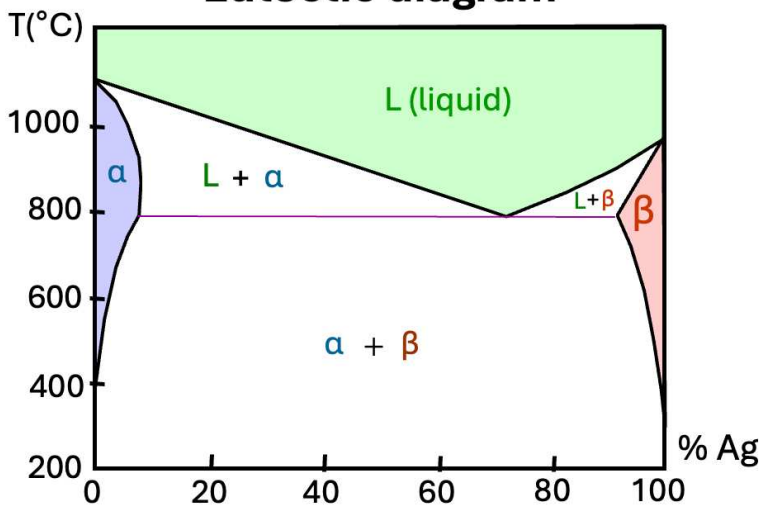
Prof. Nathan Szymanski
nszymanski@seas.ucla.edu
Department of Materials Science & Engineering

Make sure you understand last week's lecture!

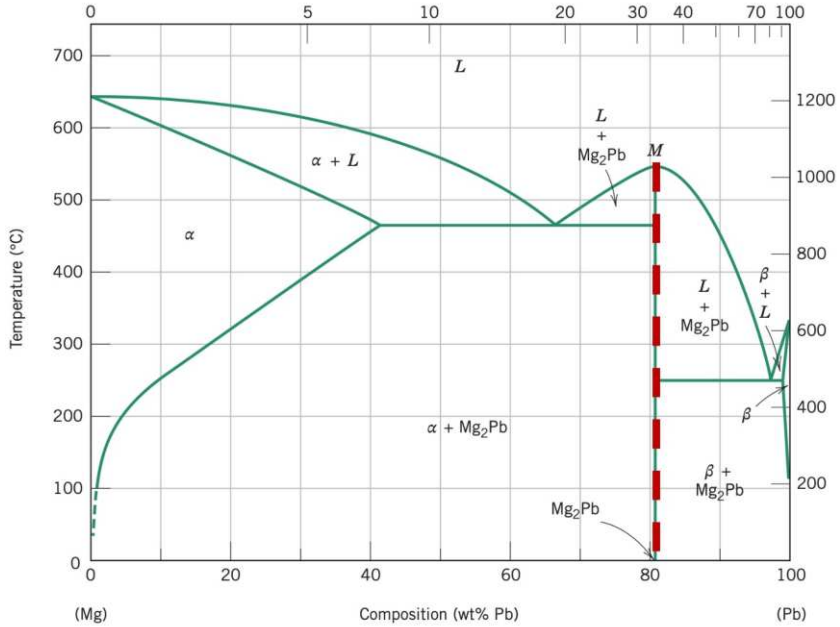
"Lens" diagram

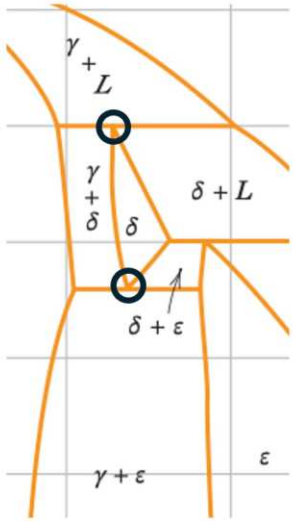


Eutectic diagram



Intermetallic formation



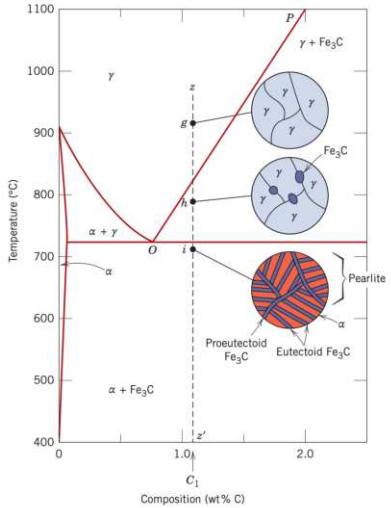


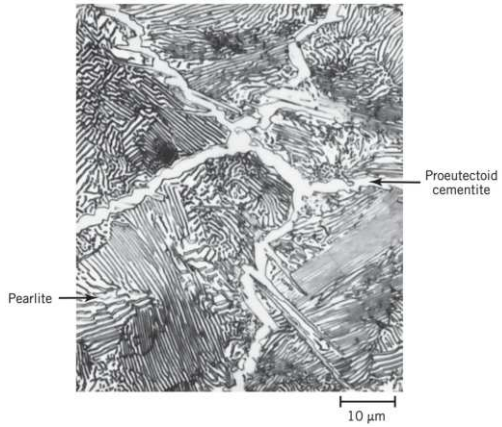
$$\delta \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \gamma + \varepsilon$$

Eutectoid reaction:
One solid solution → Two solid phases upon cooling

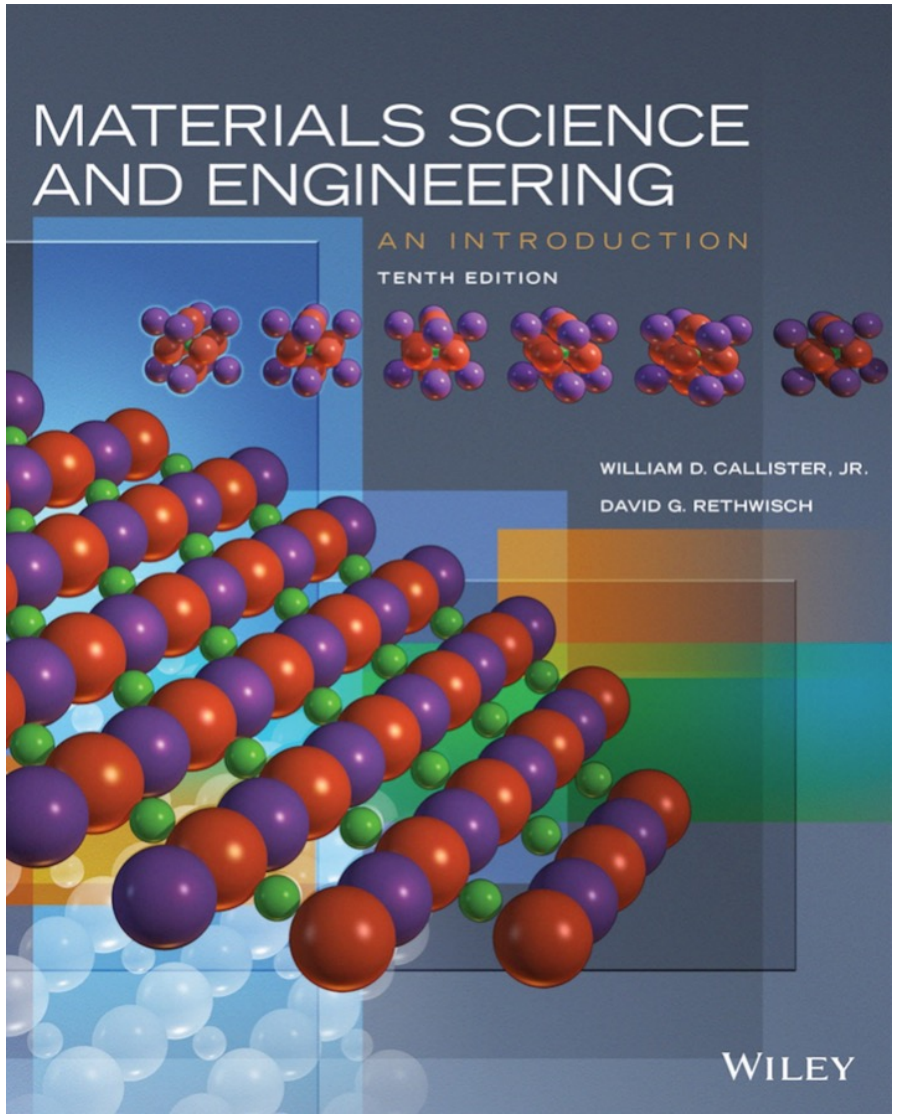
$$\delta + L \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \varepsilon$$

Peritectic reaction:
Solid + liquid → one solid solution upon cooling





Reading for today's lecture

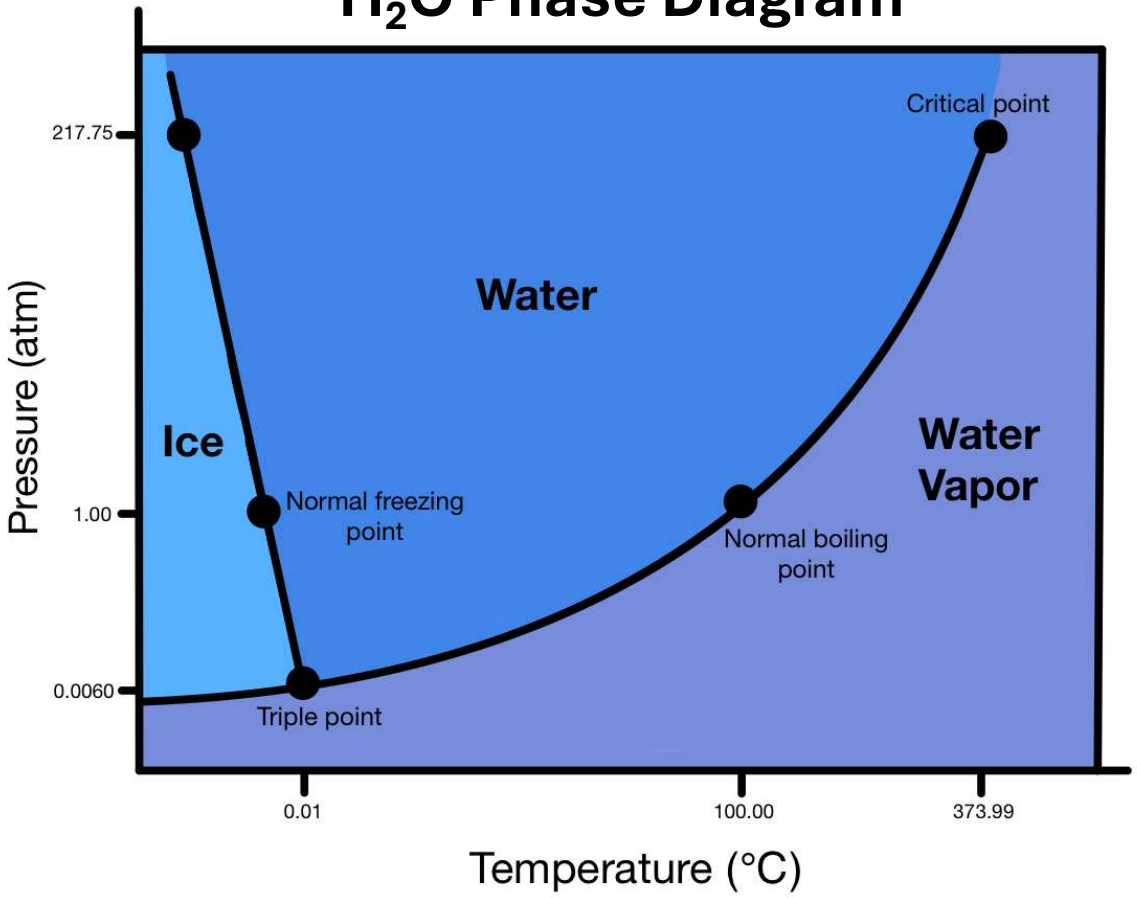


Chapter 10 Phase Transformations: Development of Microstructure and Alteration of Mechanical Properties

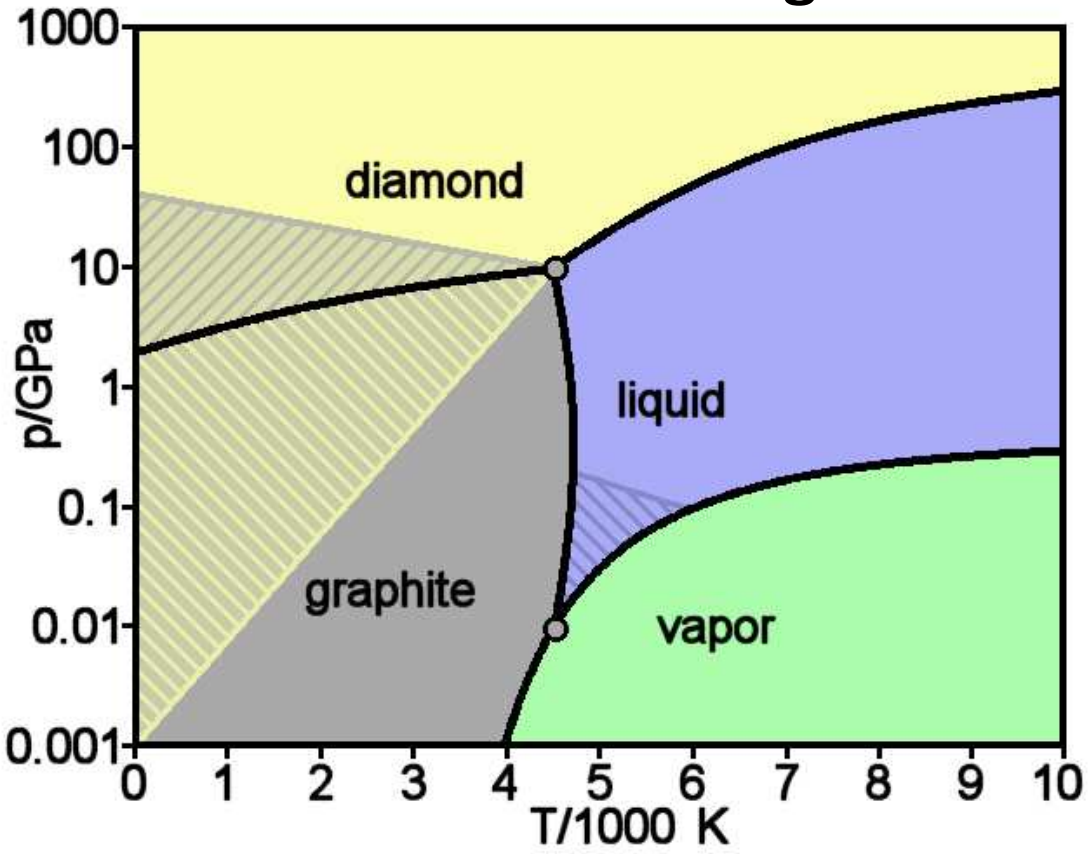
This discussion will closely follow **Chapter 10** of Callister, **pages 304-343** of the 10th edition.

Recall: phase diagrams tell us which phase we expect to form at equilibrium

H_2O Phase Diagram

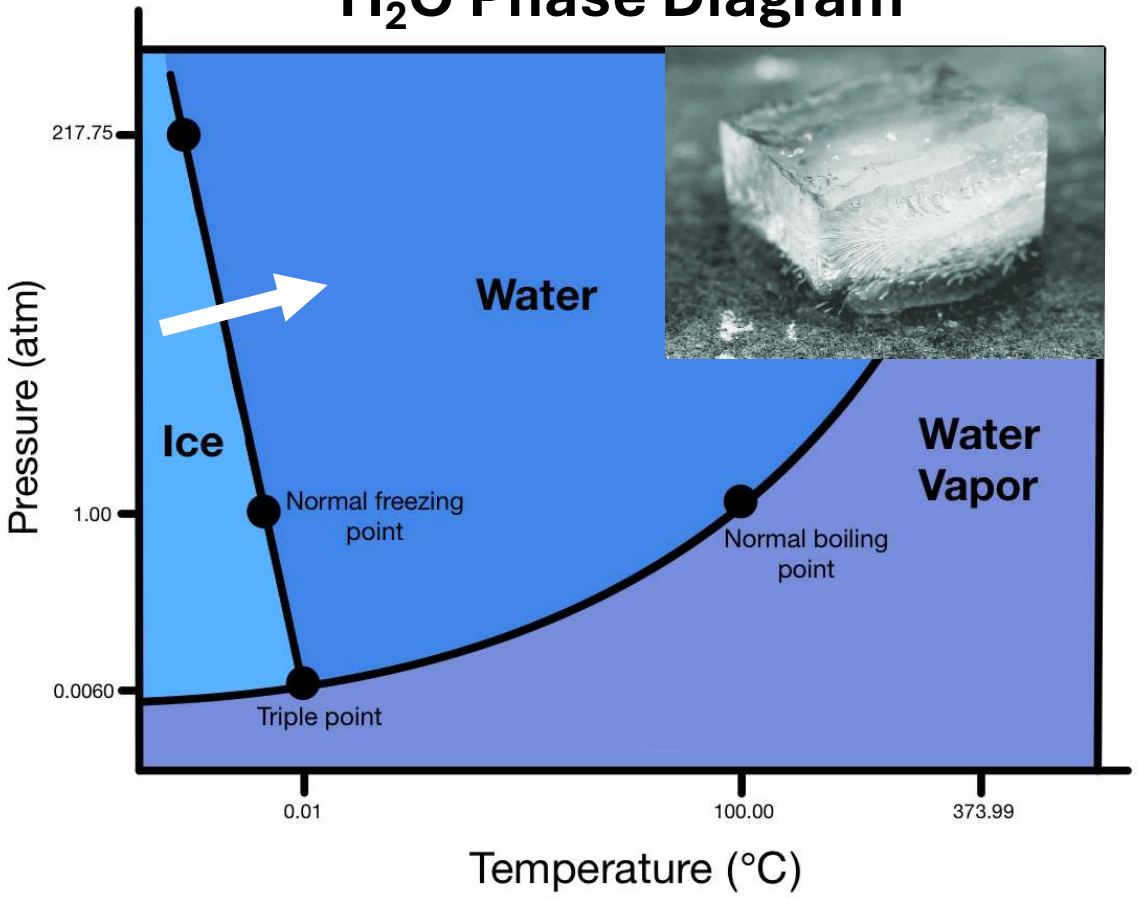


Carbon Phase Diagram

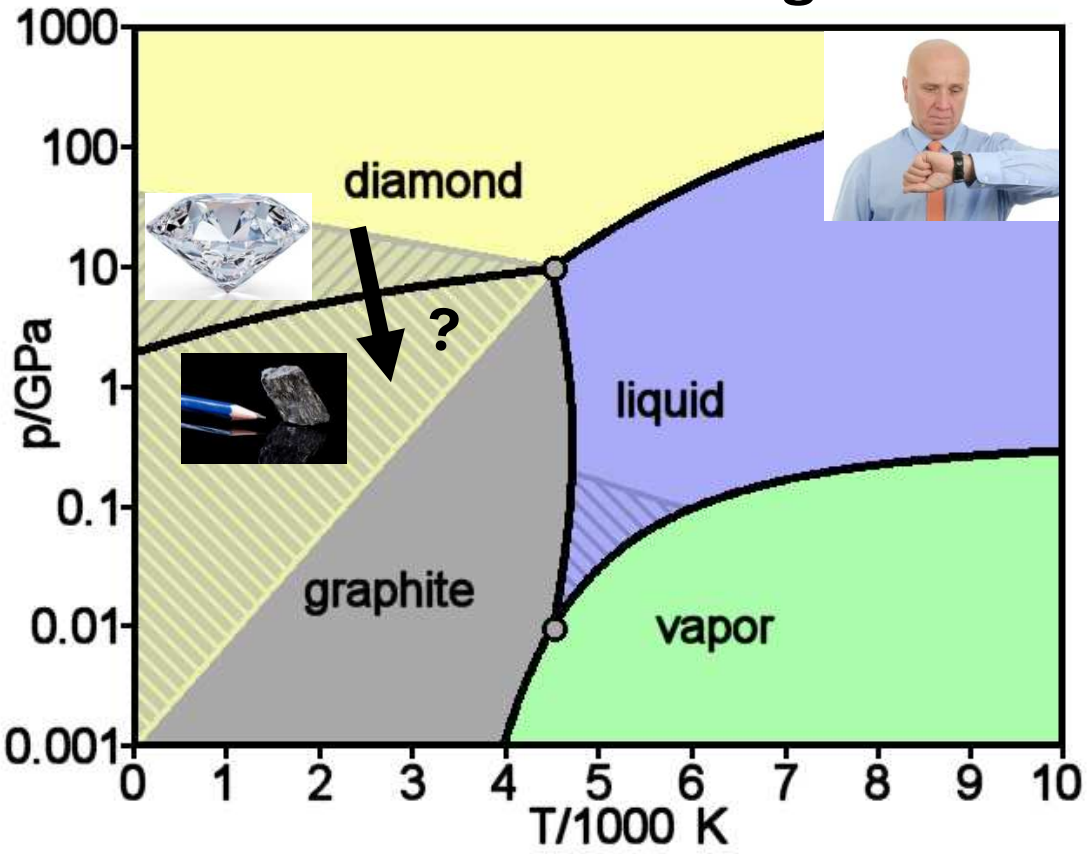


They don't tell us *how* the transformations between these phases take place

H_2O Phase Diagram

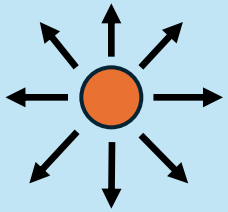


Carbon Phase Diagram

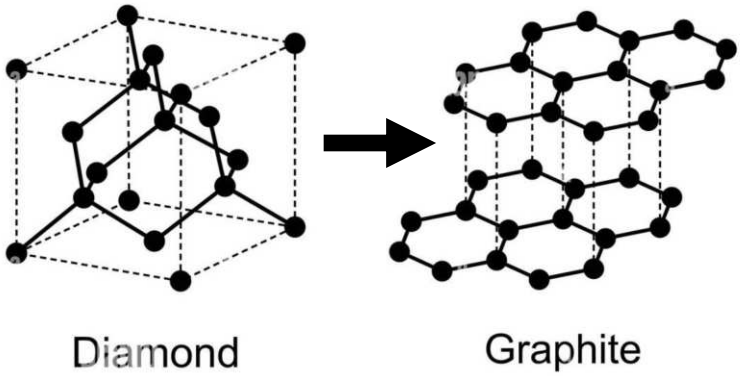


Transformations are often initiated by nucleation

Matrix of initial material (*e.g.*, diamond)



Initial **nucleus** of the new material (e.g., graphite) forms and grows

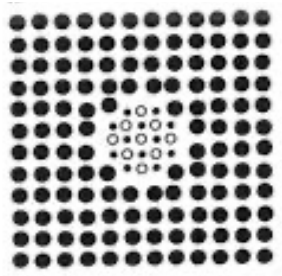


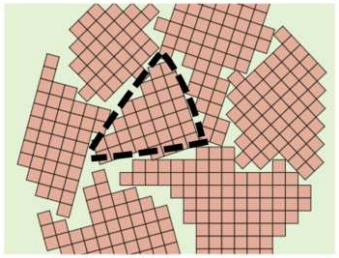
For example: A seed of graphite has to nucleate within diamond. ***Very slow!***

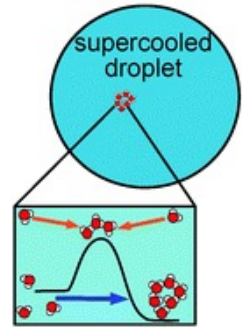
But nucleation is not always favorable

Matrix of initial material (*e.g.*, diamond)

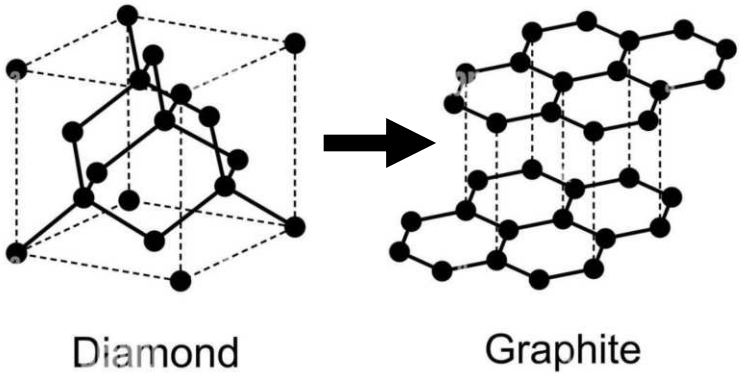
Initial **nucleus** of the new material (e.g., graphite) forms and grows







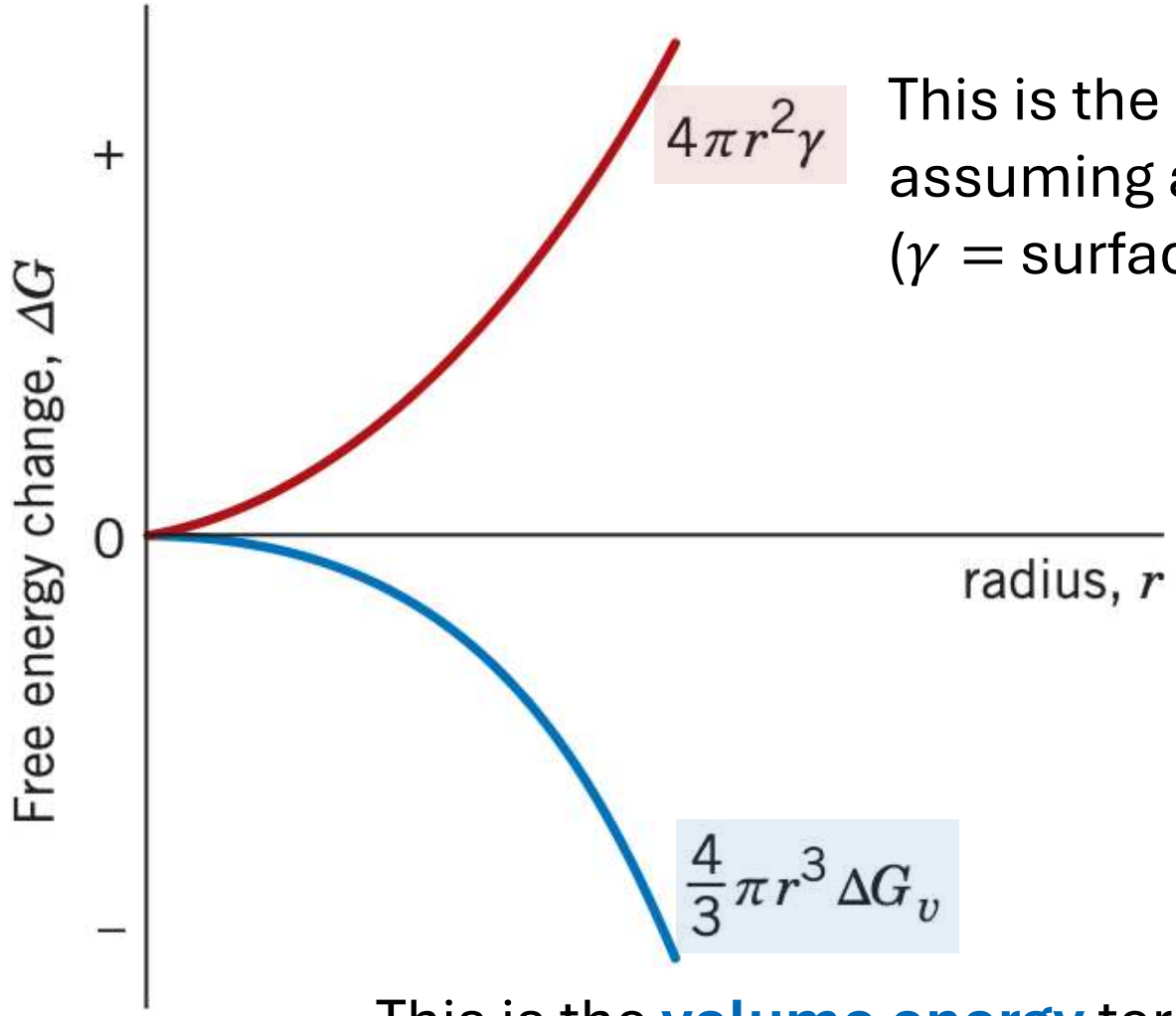
Even though this new material is more stable than the original one, its surface (or interface) has **unpassivated bonds → unstable**



For example: A seed of graphite has to nucleate within diamond. ***Very slow!***

In reality, there is some tradeoff between the **bulk energy decrease** and **surface energy increase**

Thermodynamics of nucleation



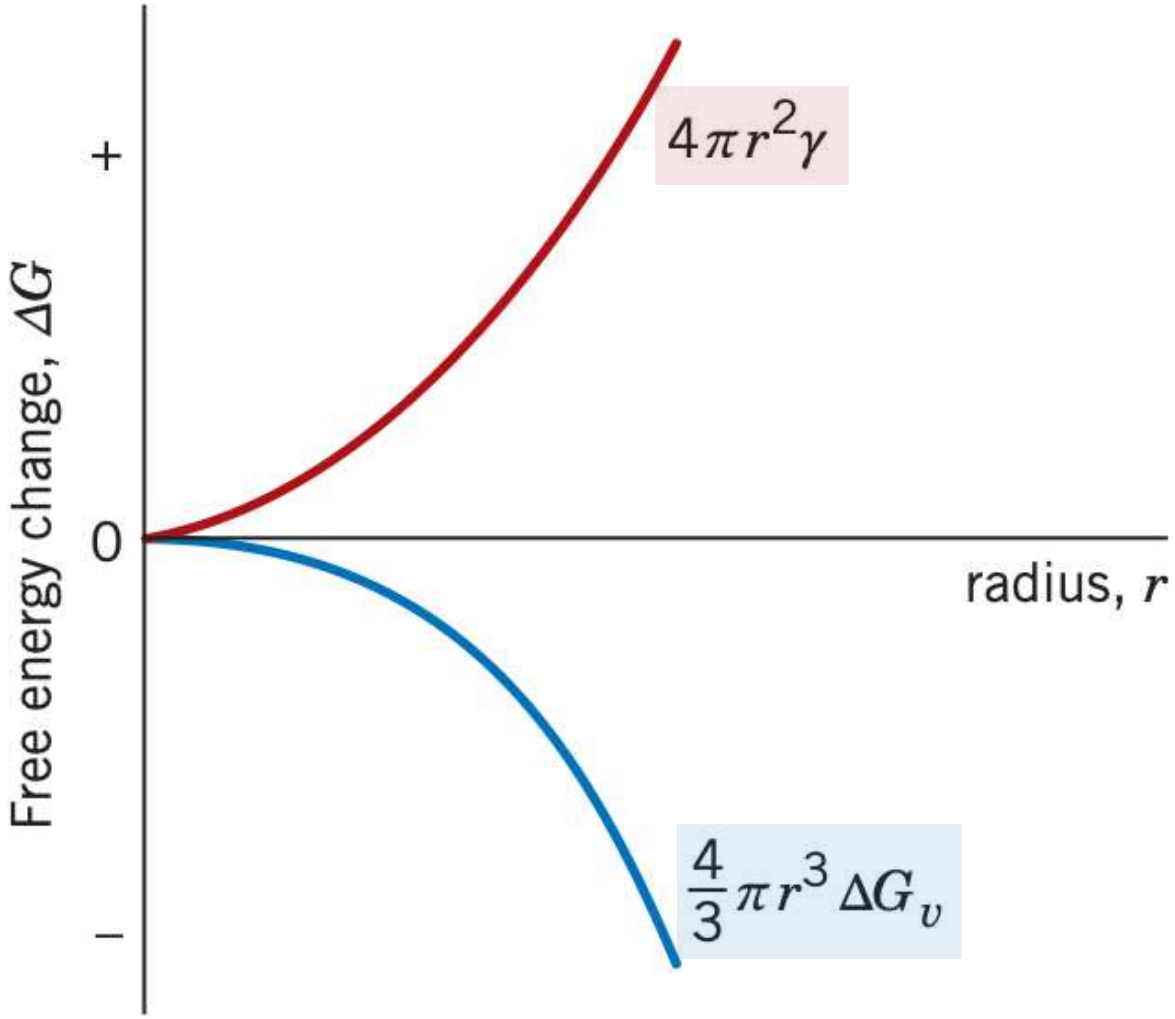
This is the **surface energy** term, assuming a spherical nucleus (γ = surface tension)

This is the **volume energy** term, assuming a spherical nucleus

In reality, there is some tradeoff between the **bulk energy decrease** and **surface energy increase**

(ΔG_v = free energy difference between original and new phase)

Thermodynamics of nucleation



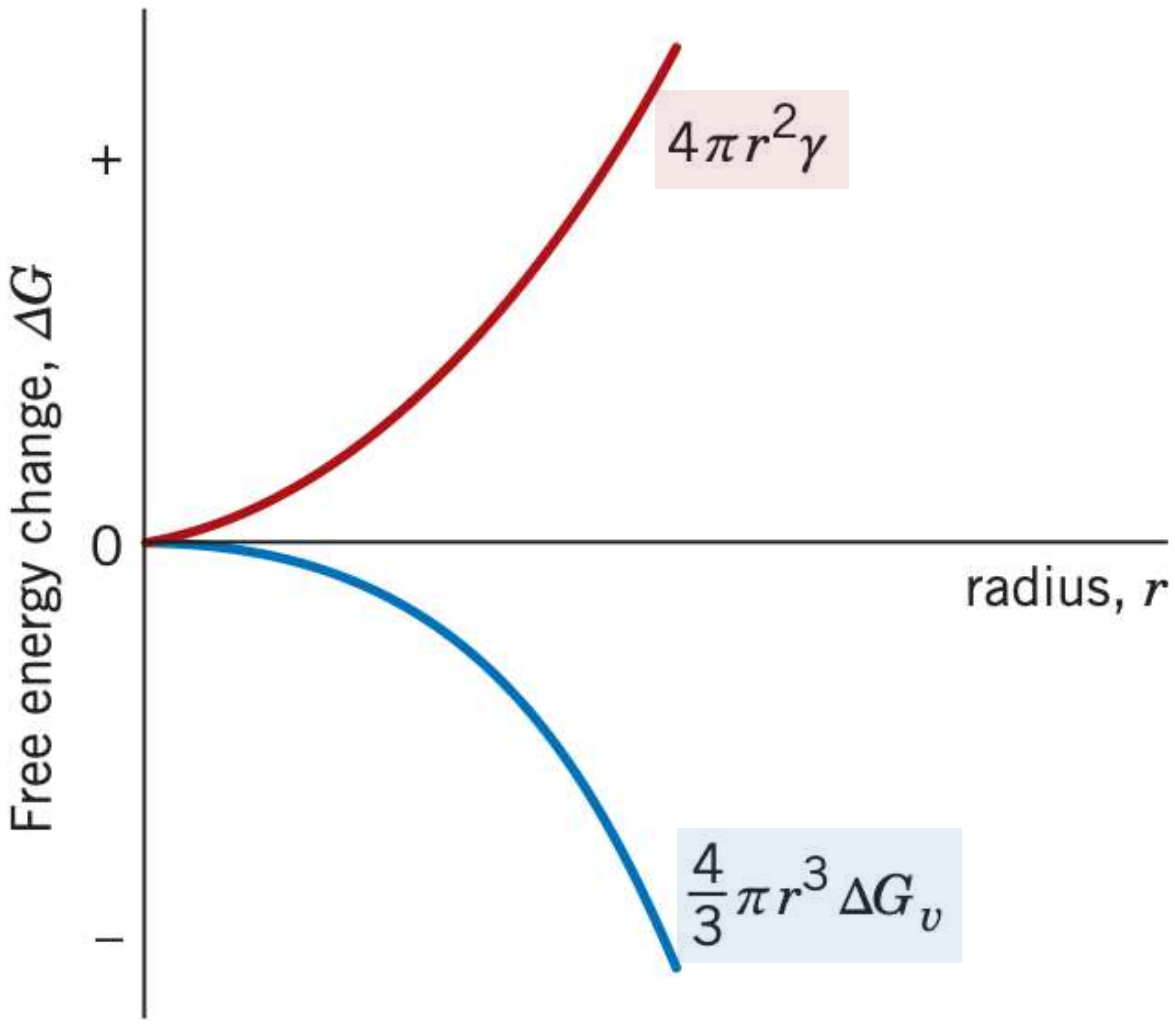
There is a **tradeoff!** But notice:

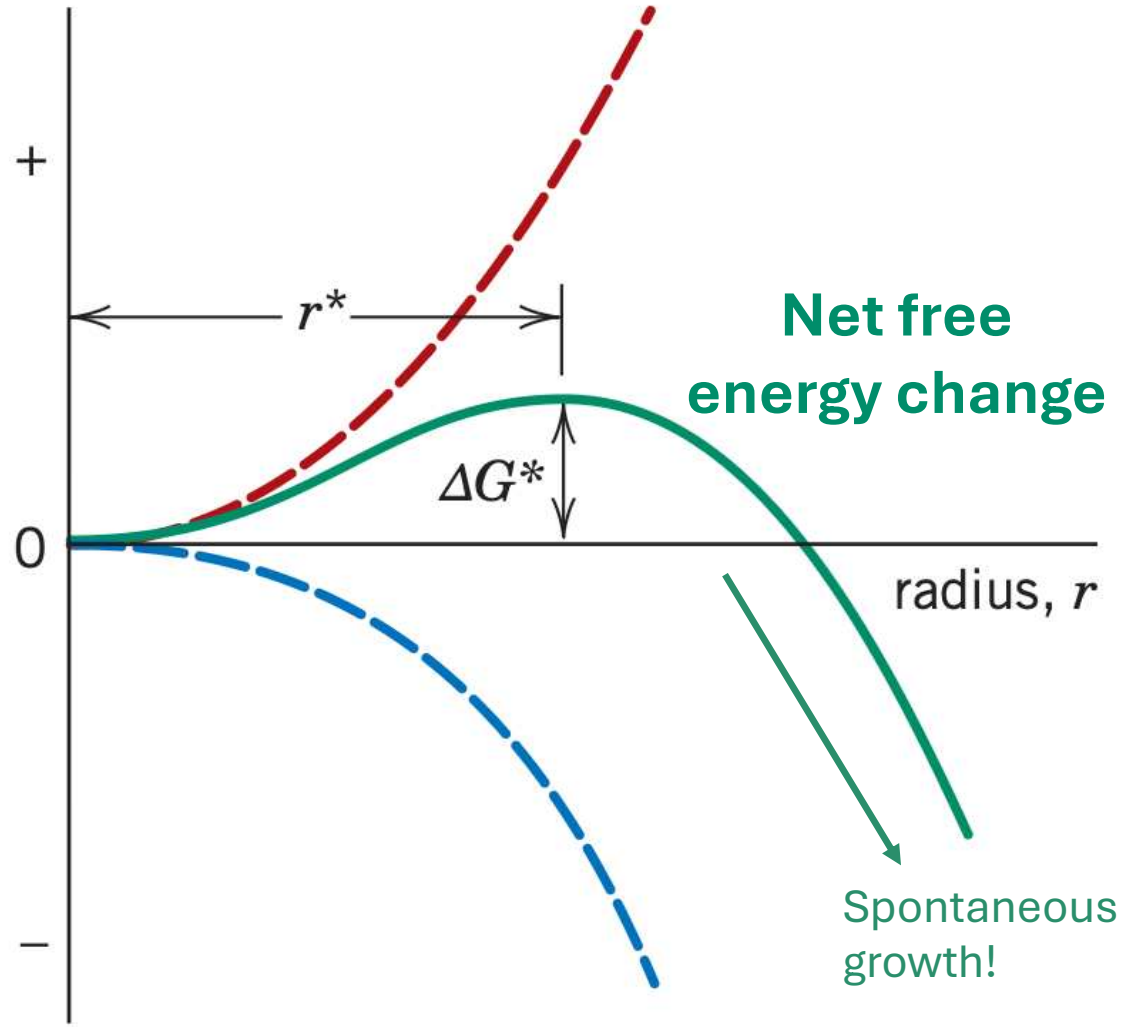
Unfavorable surface term $\propto r^2$

Favorable bulk term $\propto r^3$

The bulk term should win out at sufficiently large radius

Thermodynamics of nucleation





Thermodynamics of nucleation

The green curve is described by:

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

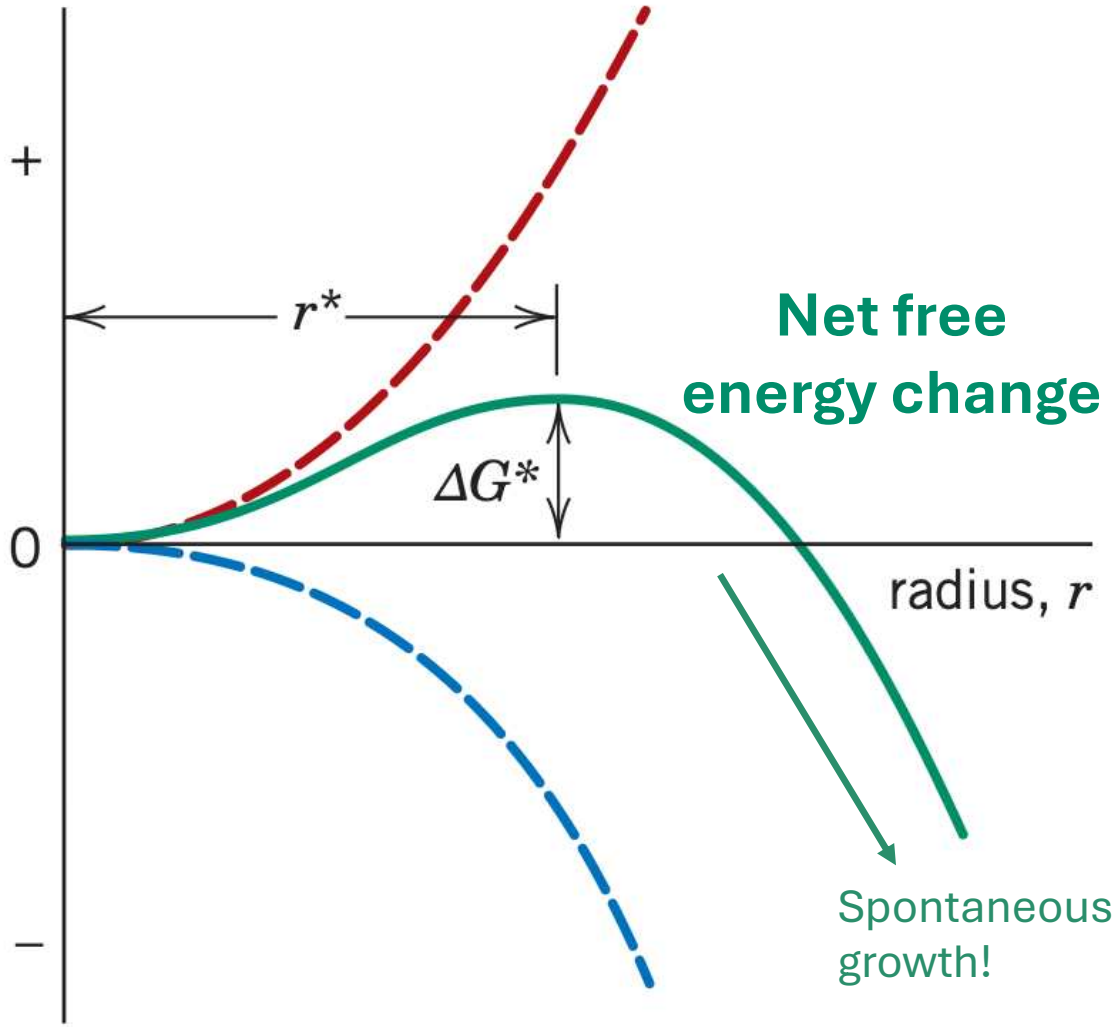
To find where the slope of $\Delta G = 0$:

$$\frac{d(\Delta G)}{dr} = \tfrac{4}{3}\pi\, \Delta G_v(3r^2) + 4\pi\gamma(2r) = 0$$

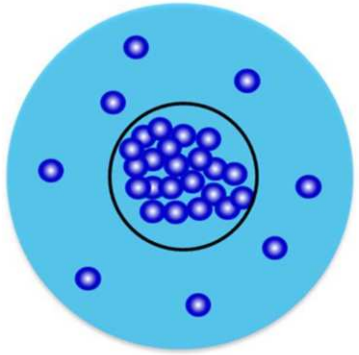
Solve for r and plug it back into ΔG:

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

There's a **critical radius (r^*)** that nuclei must reach to overcome a **barrier (ΔG^*)**



Thermodynamics of nucleation



If the surface energy (γ) is high (unfavorable),
large critical nuclei will be needed
→ unlikely to occur at high rates

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

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

There's a **critical radius (r^*)** that nuclei must reach to overcome a **barrier (ΔG^*)**

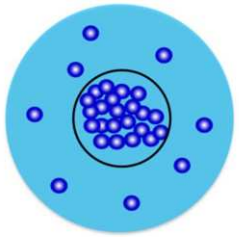
here's a critical radius (r^*) that nuclei

Net free energy change

ust reach to overcome a barrier (ΔG^*)

Spontaneous growth!

Thermodynamics of nucleation

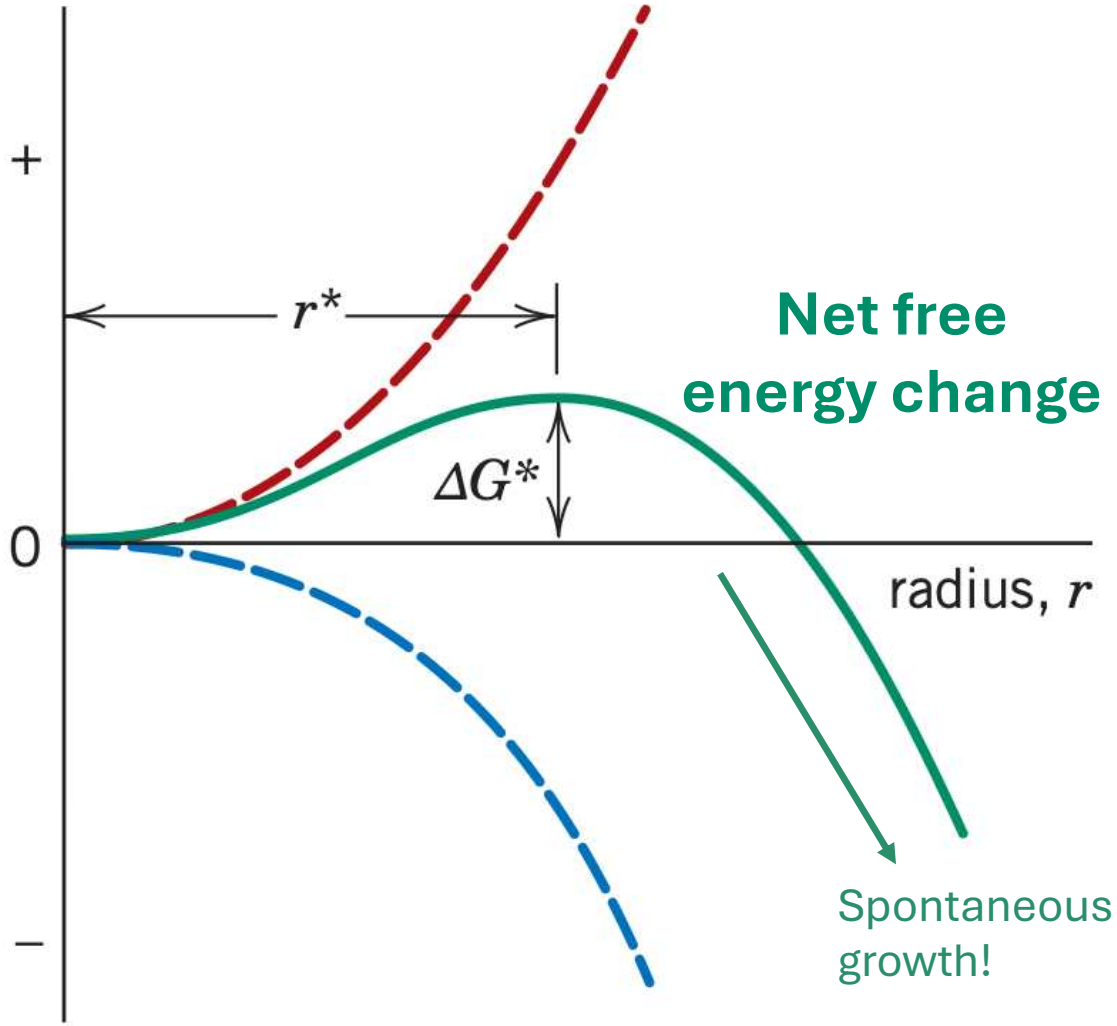


If there is a strong volumetric driving force (ΔG_v) for the phase transformation to occur, **smaller critical nuclei** will be needed
→ more likely to occur at high rates

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

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

There's a **critical radius (r^*)** that nuclei must reach to overcome a barrier (ΔG^*)



Questions on nucleation?

Next, we'll look specifically at **solidification from a liquid**

Estimating the critical radius for solidification

$$r^* = \frac{-2\gamma T_m}{\Delta H_f \Delta T}$$

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

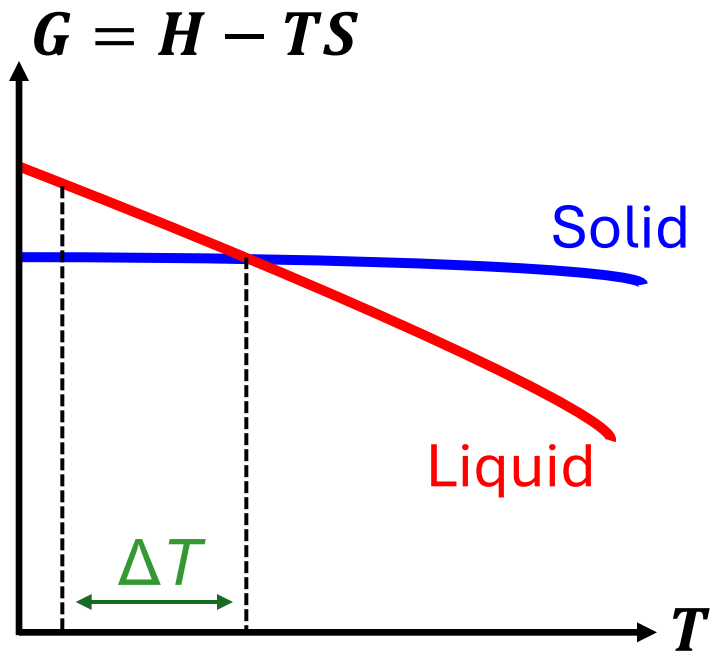
r^* = critical radius

γ = surface free energy

T_m = melting temperature

ΔH_f = latent heat of solidification

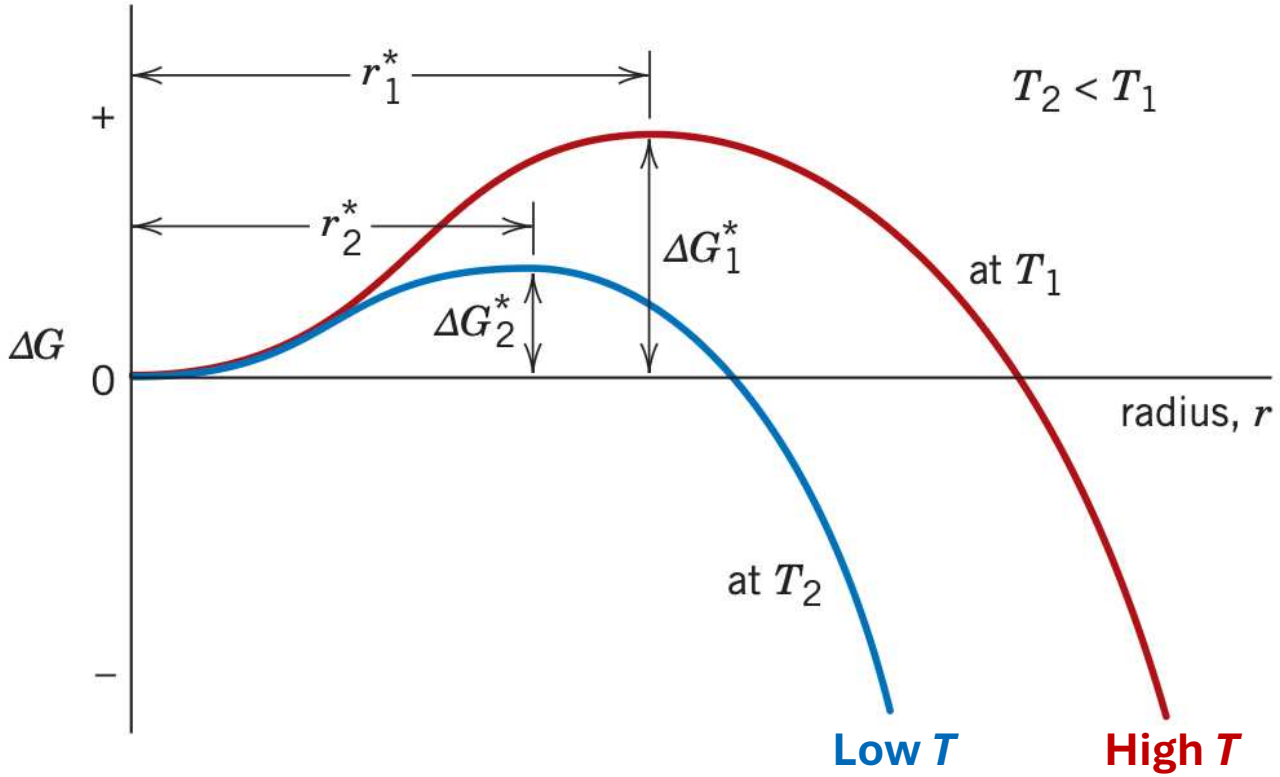
$\Delta T = T_m - T$ = supercooling



The critical radius (r^*) decreases as we cool and ΔT increases

There's a **critical radius (r^*)** that nuclei must reach to overcome a barrier (ΔG^*)

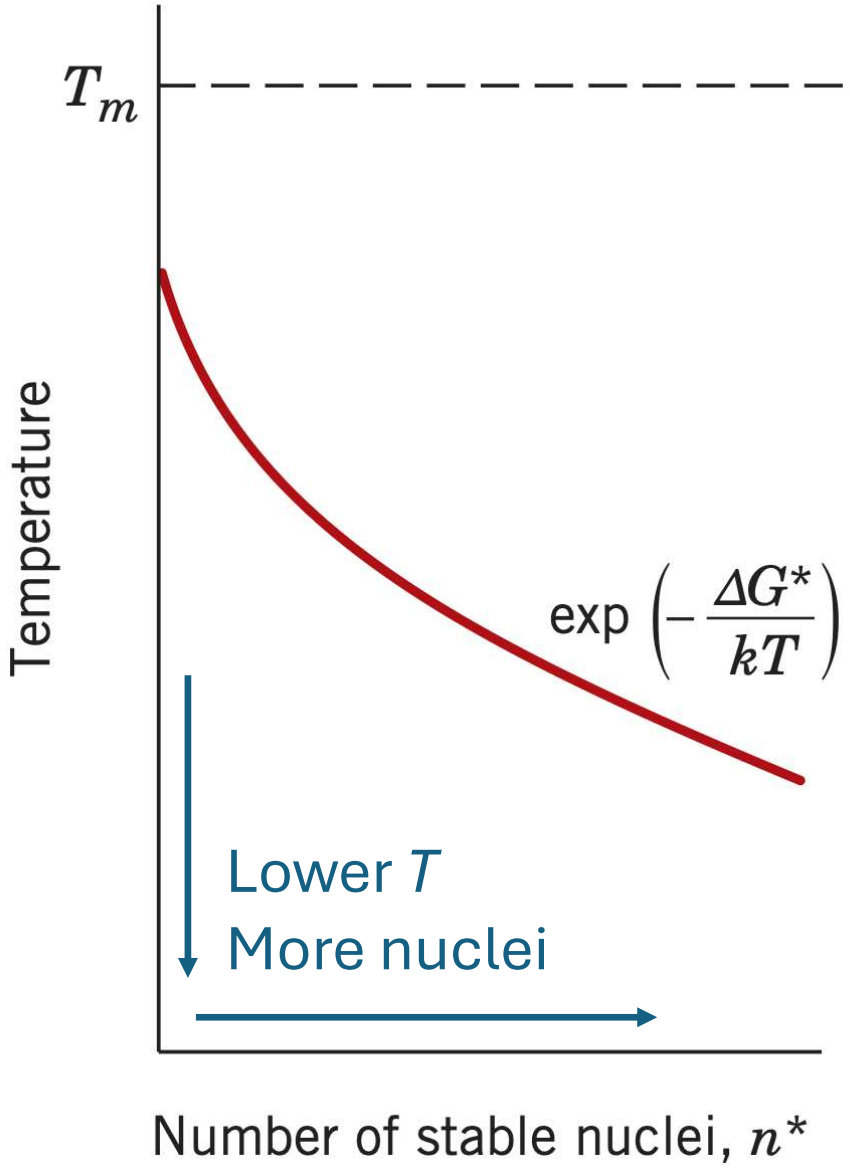
Estimating the critical radius for solidification



Kinetics – let's quantify this ⟵

Lower temperature means smaller critical radius. Does this mean nucleation occurs more rapidly as we undercool?

The kinetics of nucleation



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

Large (negative) exponent = small number

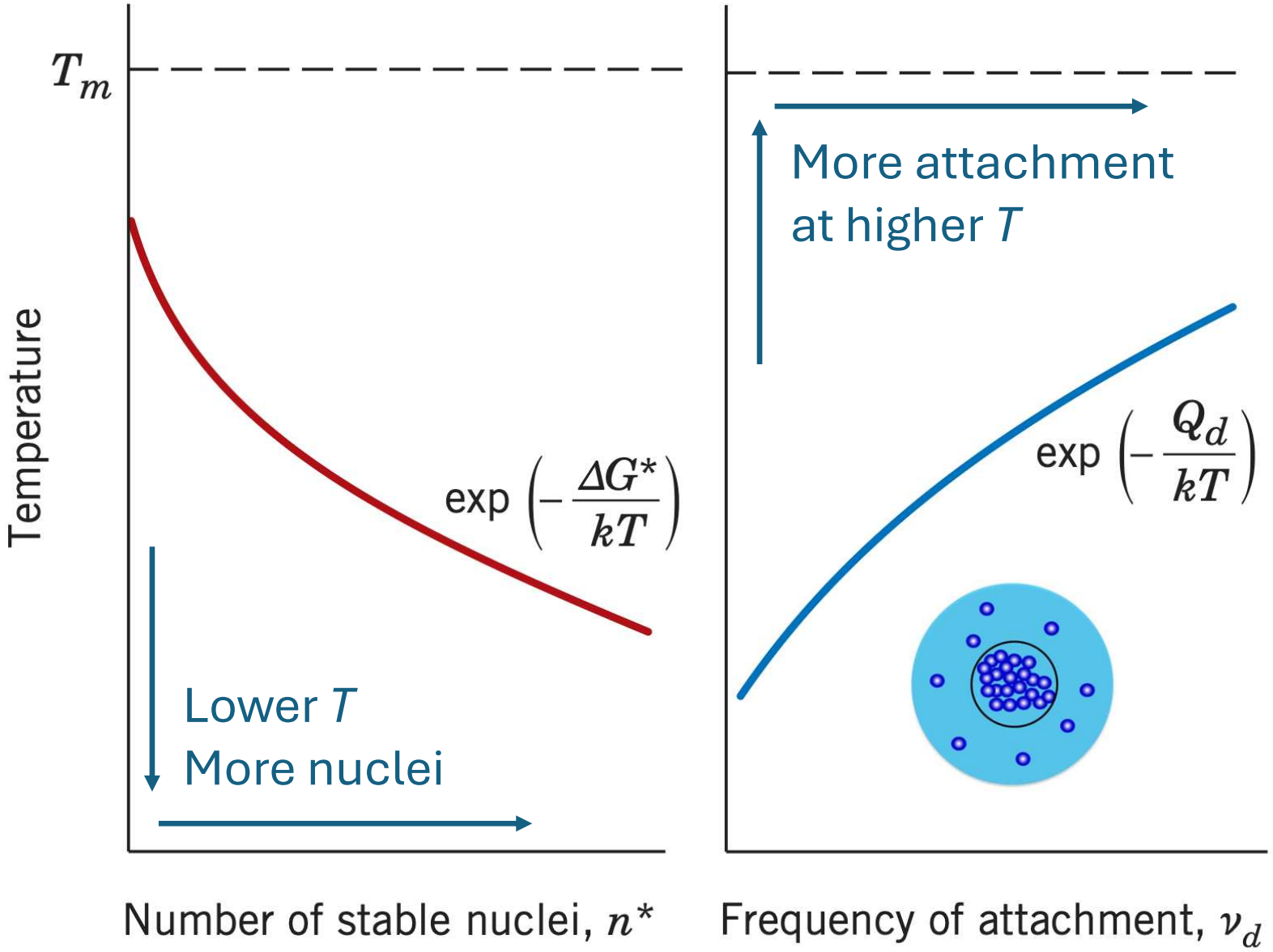
The number of nuclei that meet the critical size

The *total* number of nuclei

Because the barrier (ΔG^*) for nucleation gets much lower as temperature decreases:

Greater undercooling → more stable nuclei

The kinetics of nucleation



Activation energy

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

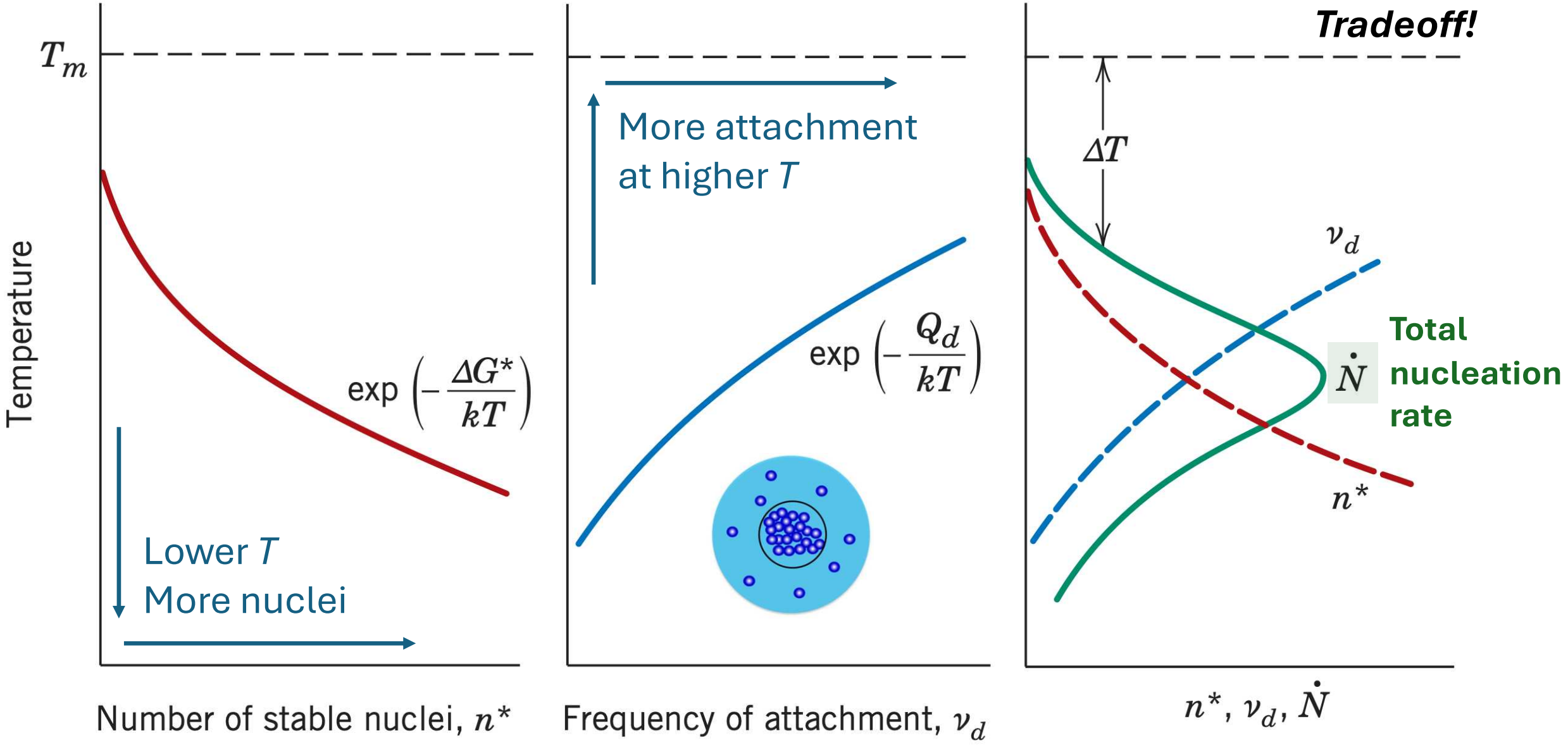
Frequency of attachment

Some constant

Greater undercooling → less frequent attachment of new atoms to the existing nuclei

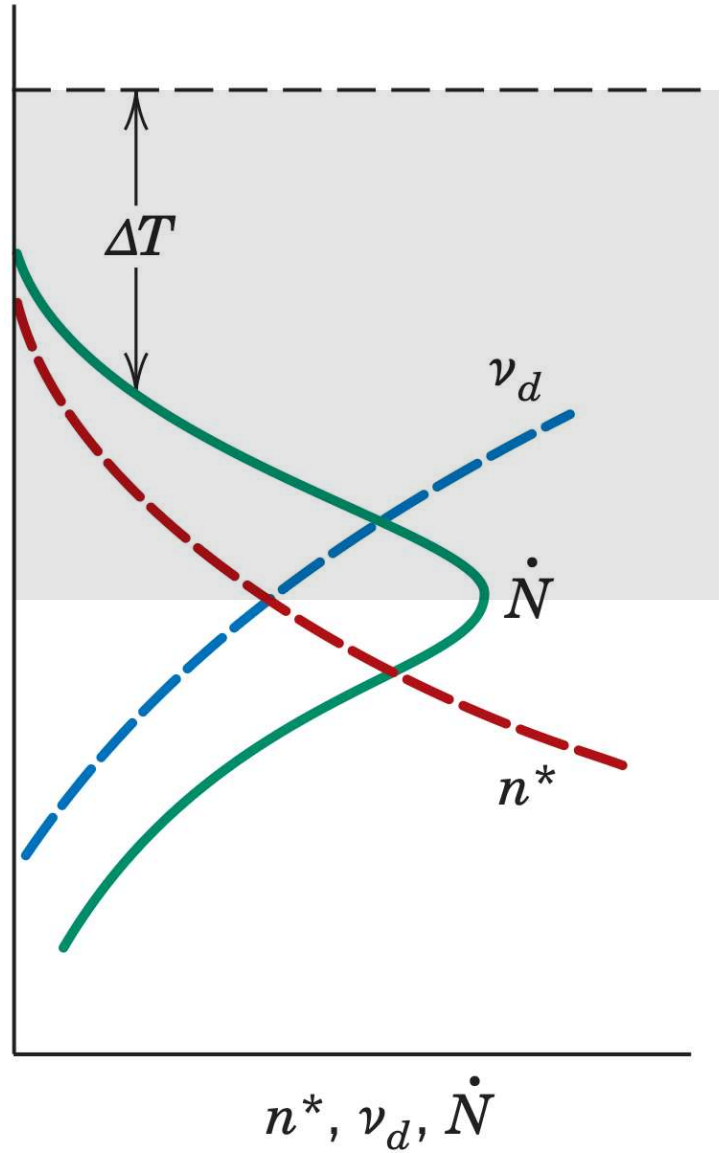
Because diffusion is much slower at low T

The kinetics of nucleation



The kinetics of nucleation

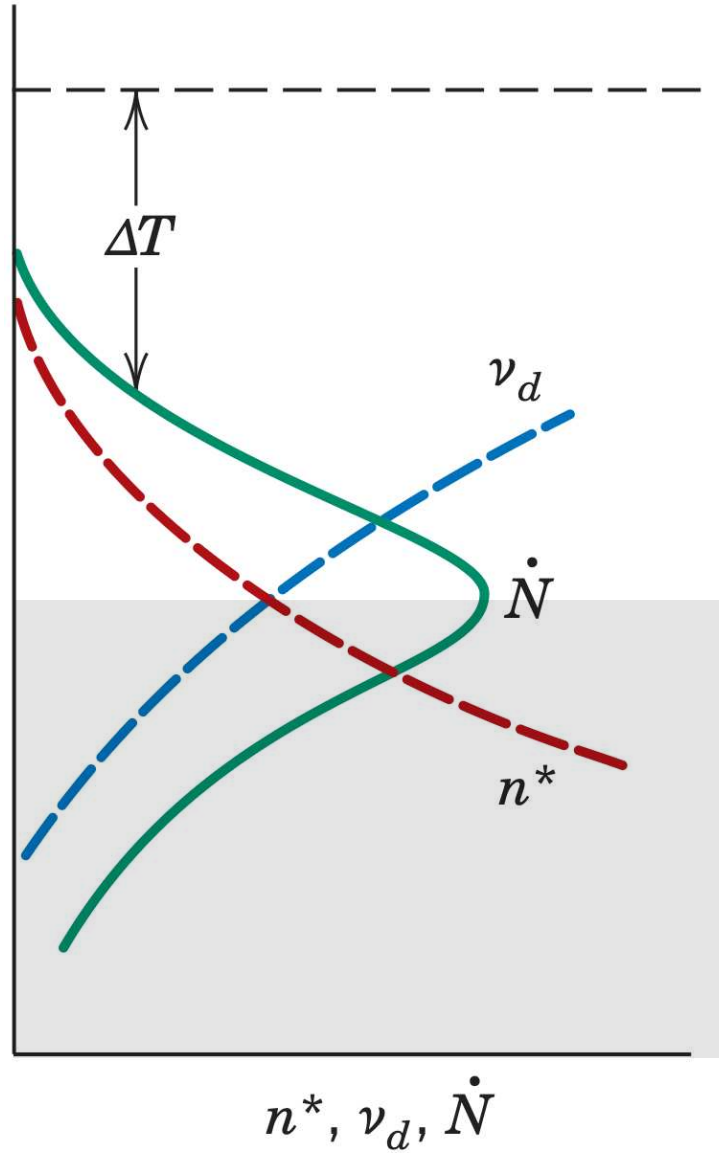
At small undercooling (just below melting point):
Diffusion is fast but there are not many stable nuclei



The kinetics of nucleation

At large undercooling (well below melting point):

There are more stable nuclei but diffusion is slow

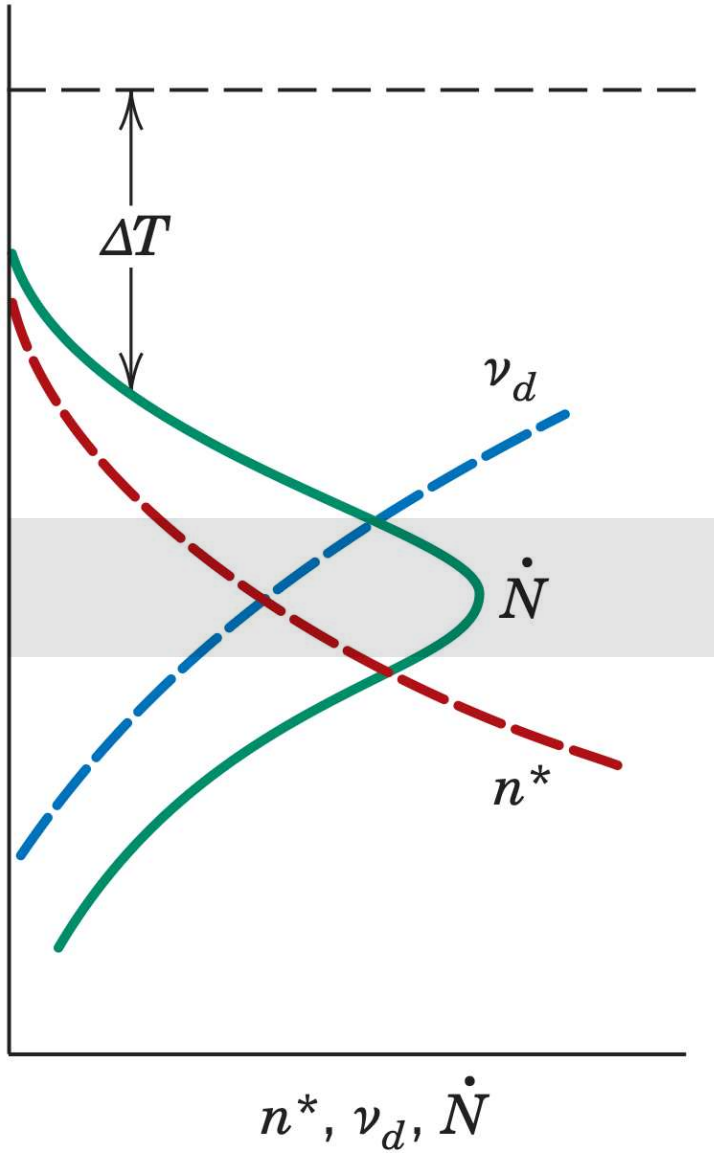


The kinetics of nucleation

There is a sweet spot to maximize the nucleation rate

Lots of stable nuclei and reasonably fast diffusion

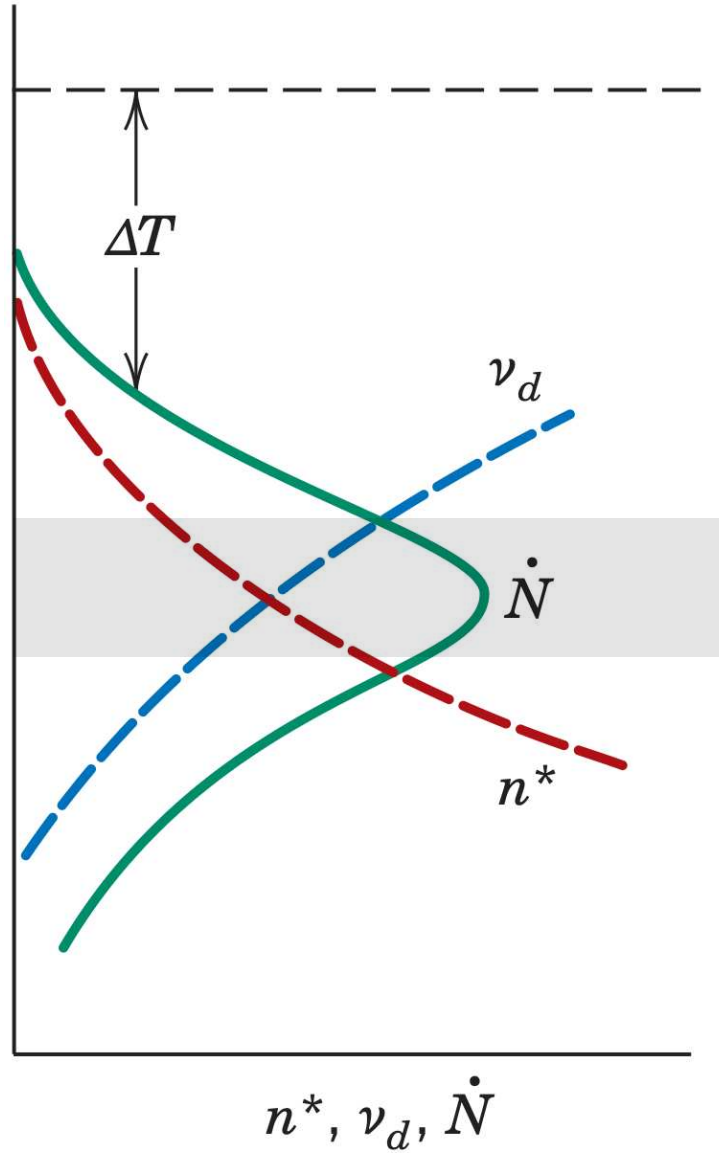
Far below the melting point…But not “too far” below it



The kinetics of nucleation

Table 10.1
Degree of Supercooling (ΔT) Values (Homogeneous Nucleation) for Several Metals

Metal	ΔT (°C)
Antimony	135
Germanium	227
Silver	227
Gold	230
Copper	236
Iron	295
Nickel	319
Cobalt	330
Palladium	332

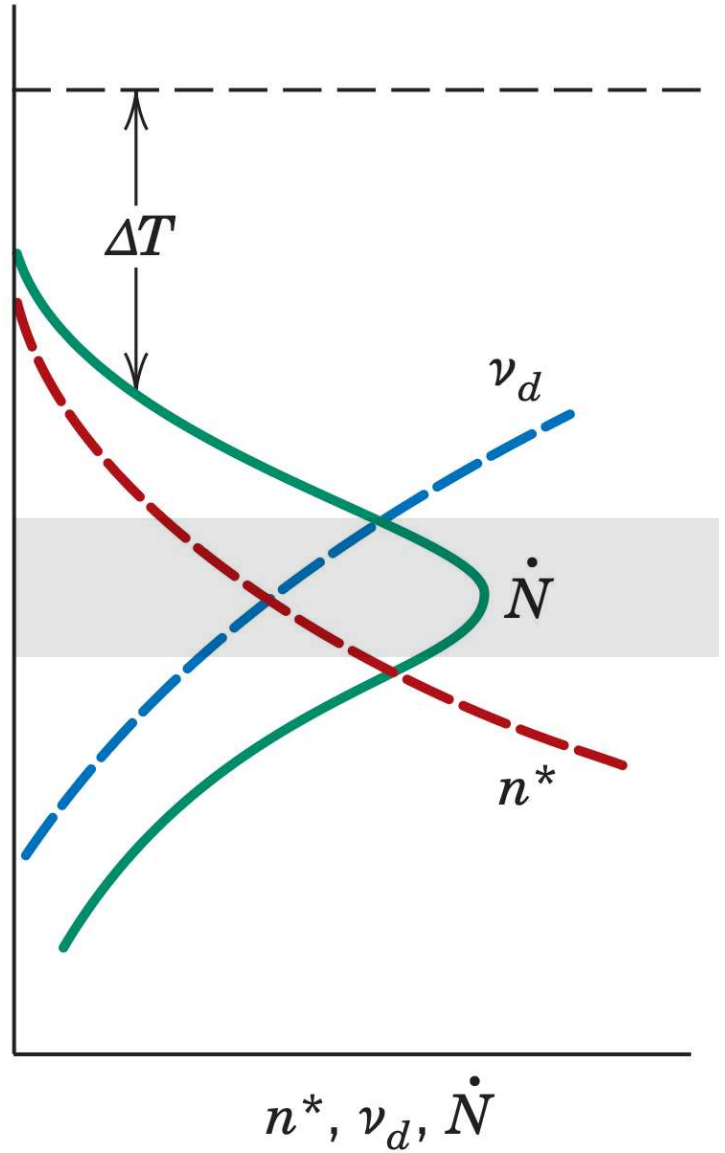


The kinetics of nucleation

Table 10.1
Degree of Supercooling (ΔT) Values (Homogeneous Nucleation) for Several Metals

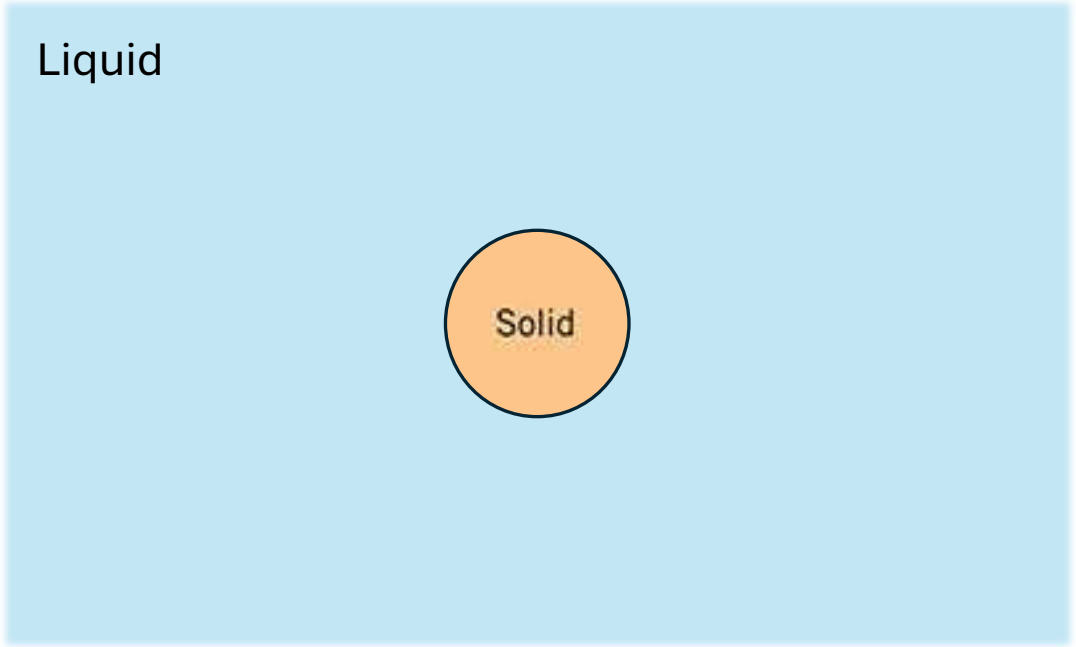
Metal	ΔT (°C)
Antimony	135
Germanium	227
Silver	227
Gold	230
Copper	236
Iron	295
Nickel	319
Cobalt	330
Palladium	332

Do these seem too large? It assumes nucleation is **homogeneous**



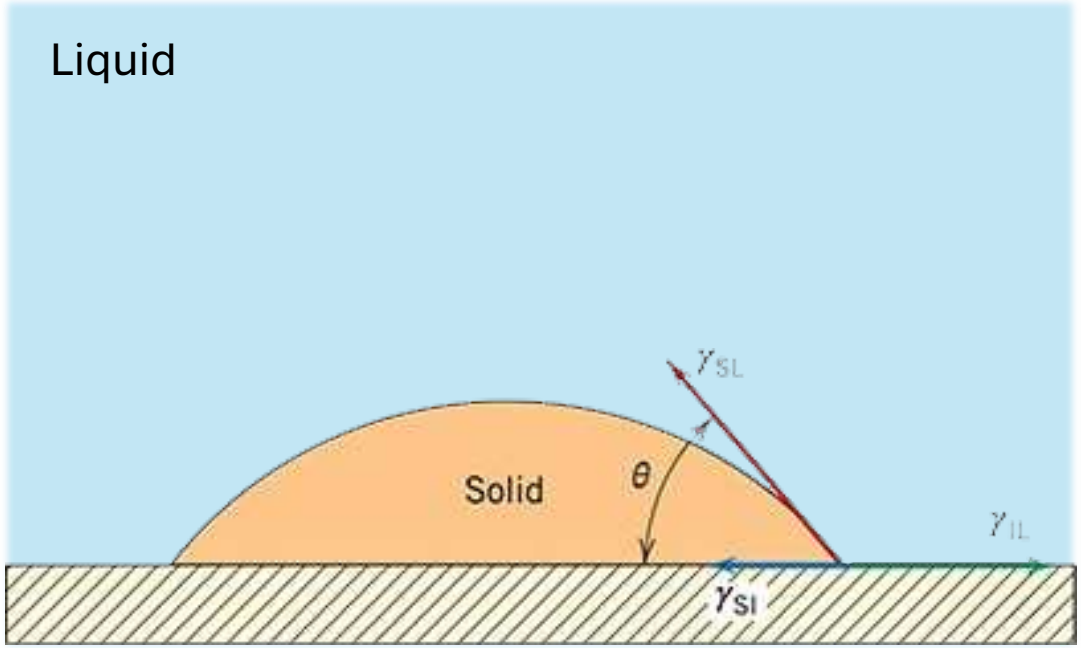
Homogenous versus heterogeneous nucleation

Homogeneous nucleation



Spherical particle with
broken bonds on all sides

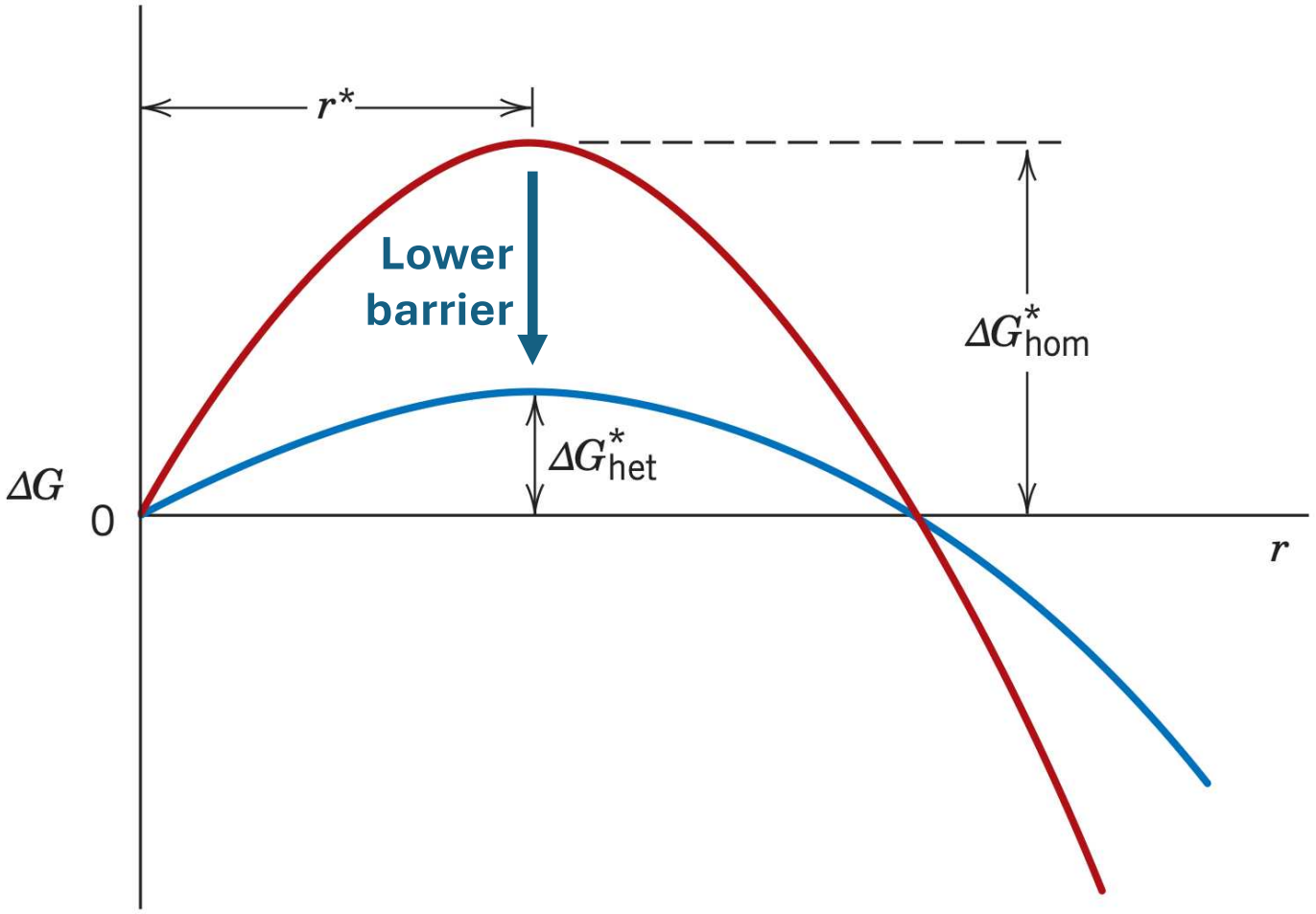
Heterogeneous nucleation

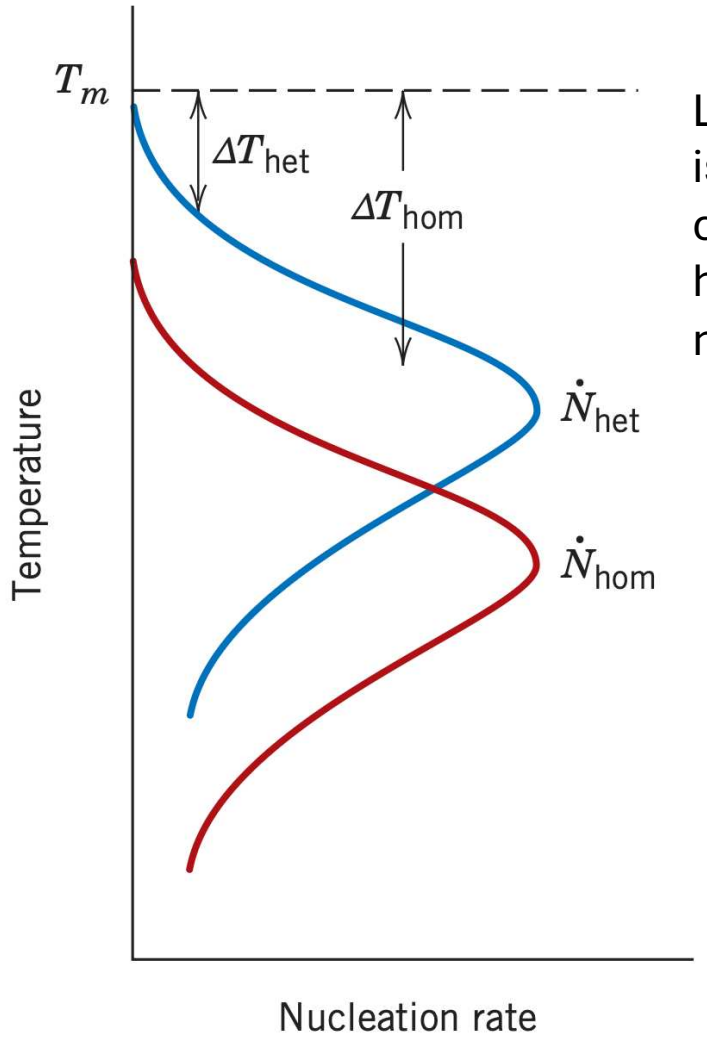


Surface or interface

The surface passivates
some of the broken bonds
→ **more favorable!**

Homogenous versus heterogeneous nucleation



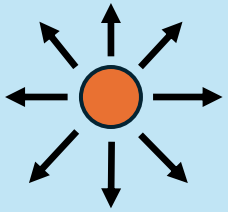


Less undercooling is needed to optimize heterogenous nucleation

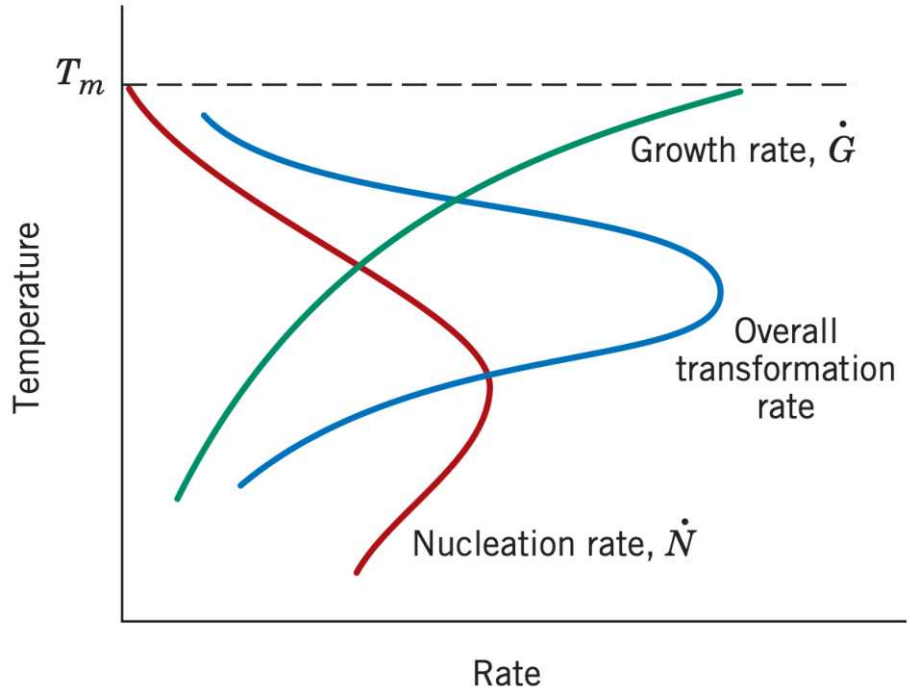


Supercooled water

How about *after* nucleation? Particles grow



After each **nucleus** reaches a critical size, it **grows spontaneously**



This is another process that depends on diffusion, so the **growth rate** expression looks familiar:

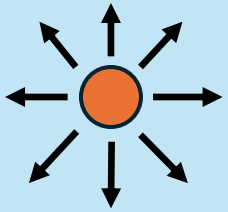
$$\dot{G} = C \exp\left(-\frac{Q}{kT}\right)$$

$\dot{G}$ is the growth rate
C is a constant
Q is an activation energy

Reduced growth rate as we cool…

Nucleation  **Growth**

How about *after* nucleation? Particles grow

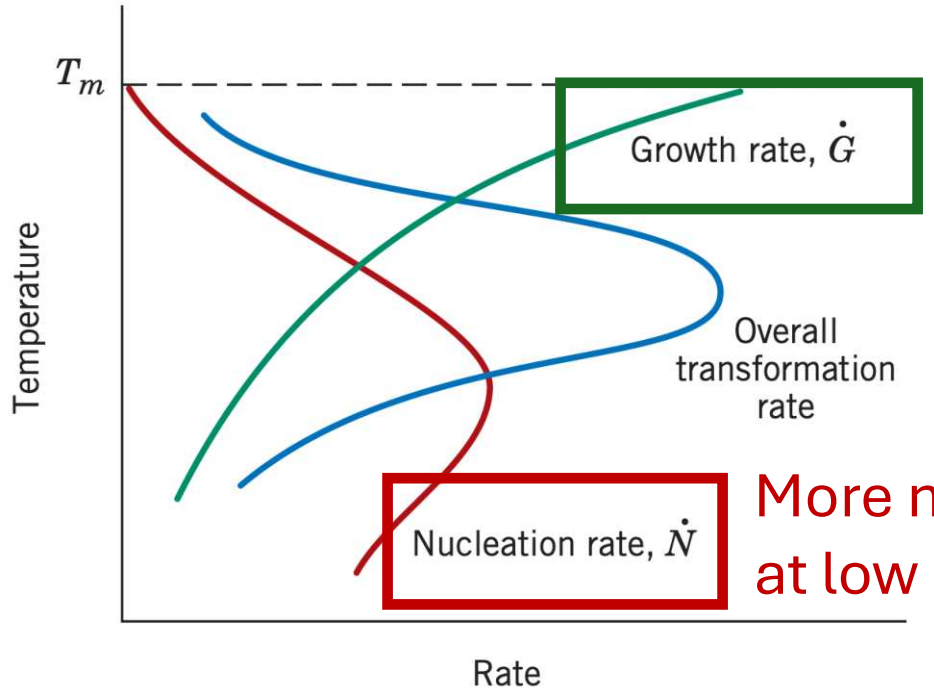


After each **nucleus** reaches a critical size, it **grows spontaneously**

This is another process that depends on diffusion, so the **growth rate** expression looks familiar:

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

$\dot{G}$ is the growth rate
C is a constant
Q is an activation energy



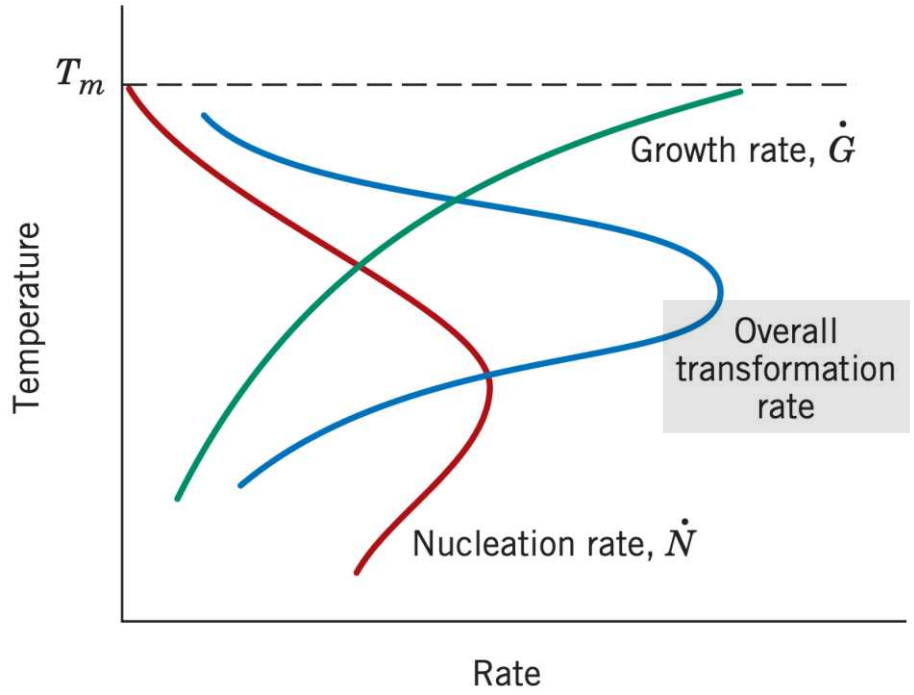
Faster growth at high T

More nuclei at low T

Reduced growth rate as we cool…

Nucleation  **Growth**

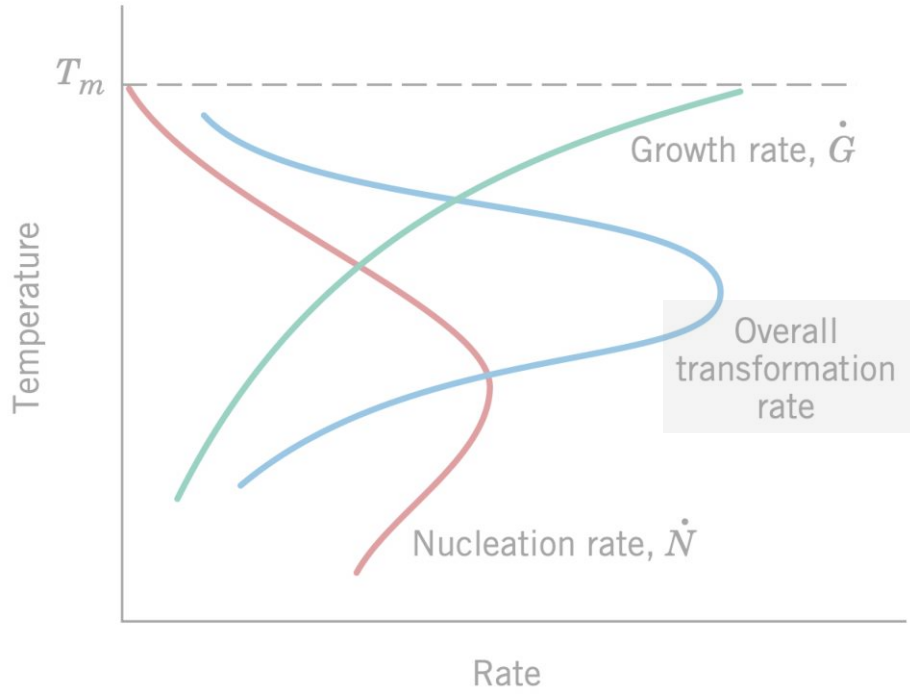
Measuring the rate of phase transformations

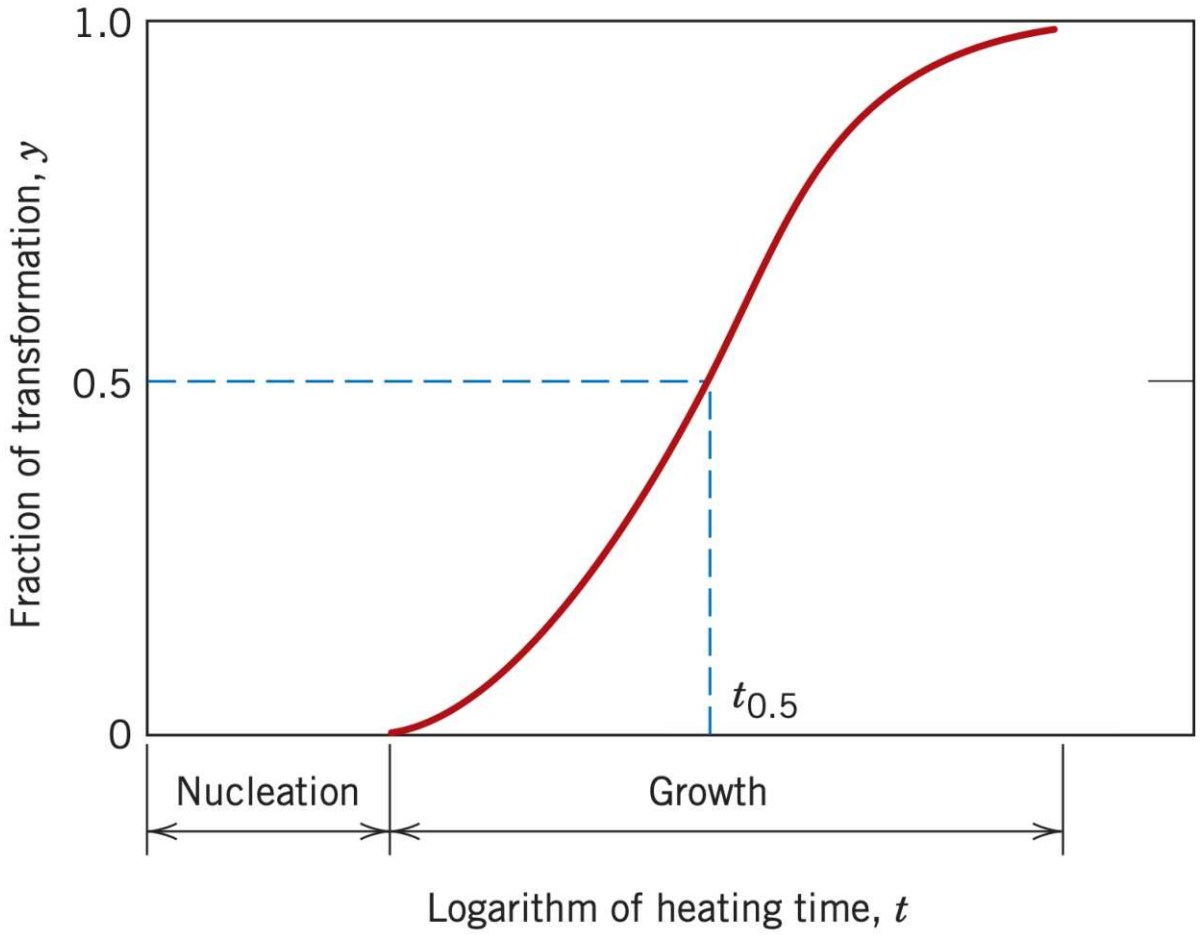


How do we determine this experimentally?

Measuring the rate of phase transformations

We can use a characterization technique (like XRD) to determine **what fraction of the sample contains the new phase as a function of time**





This generally follows an S-shape

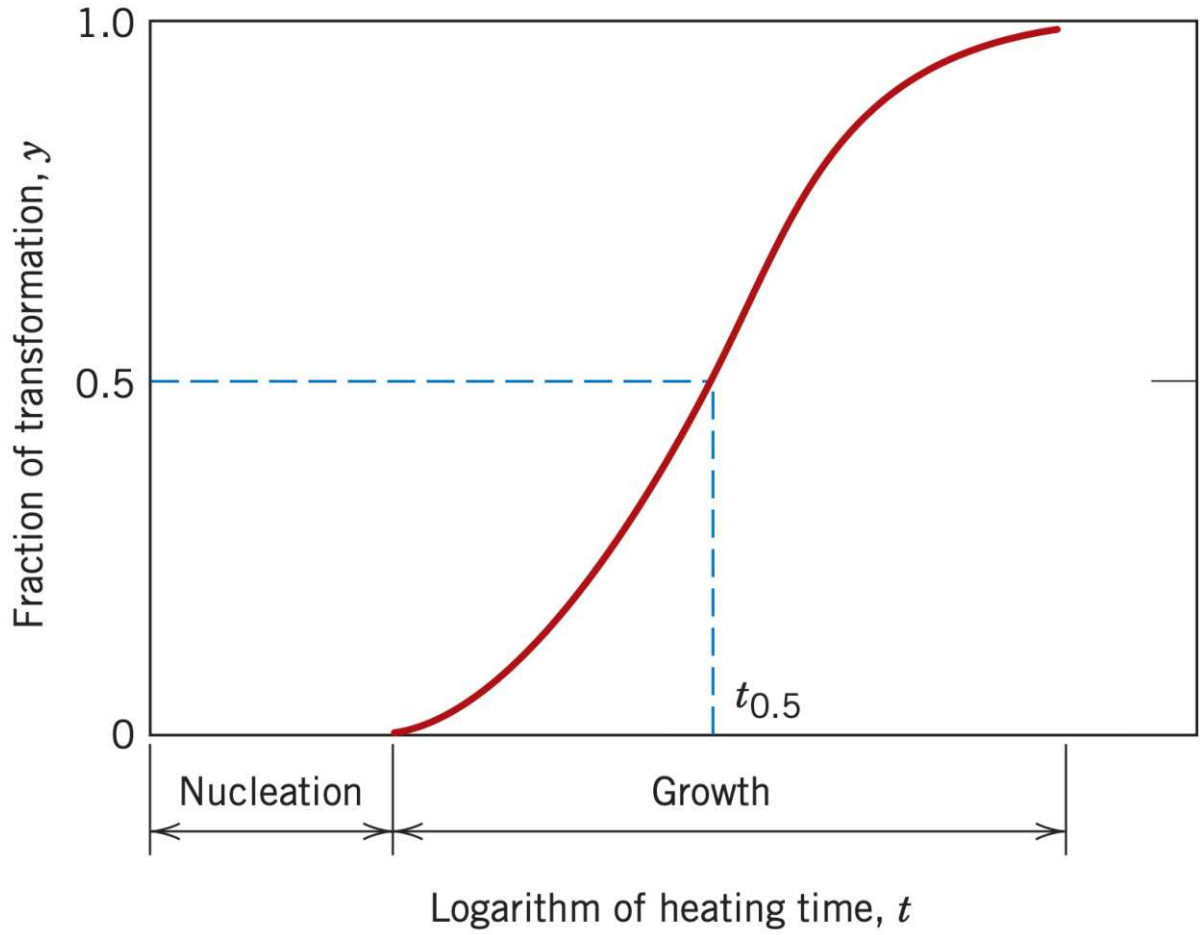
Measuring the rate of phase transformations

Avrami equation:

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

y is the fraction transformed
k and n are constants
t is time

We expect this to be highly dependent on temperature!



This generally follows an S-shape

Measuring the rate of phase transformations

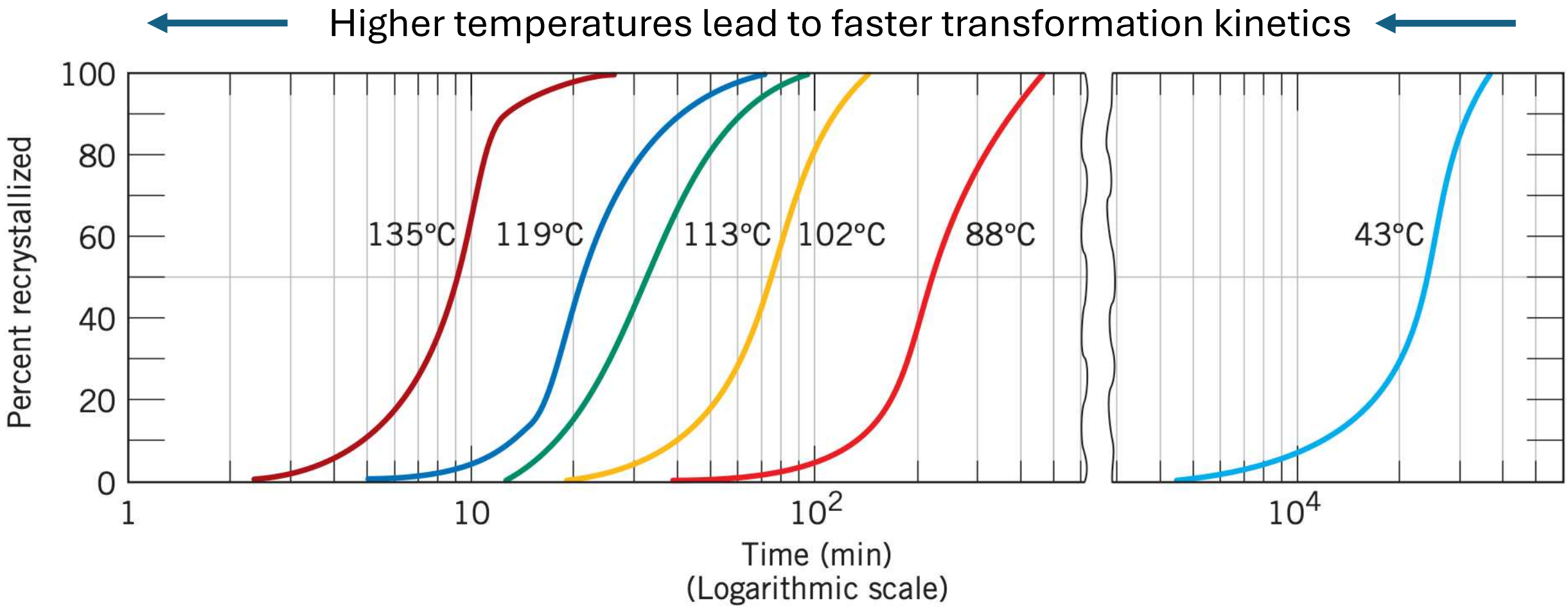
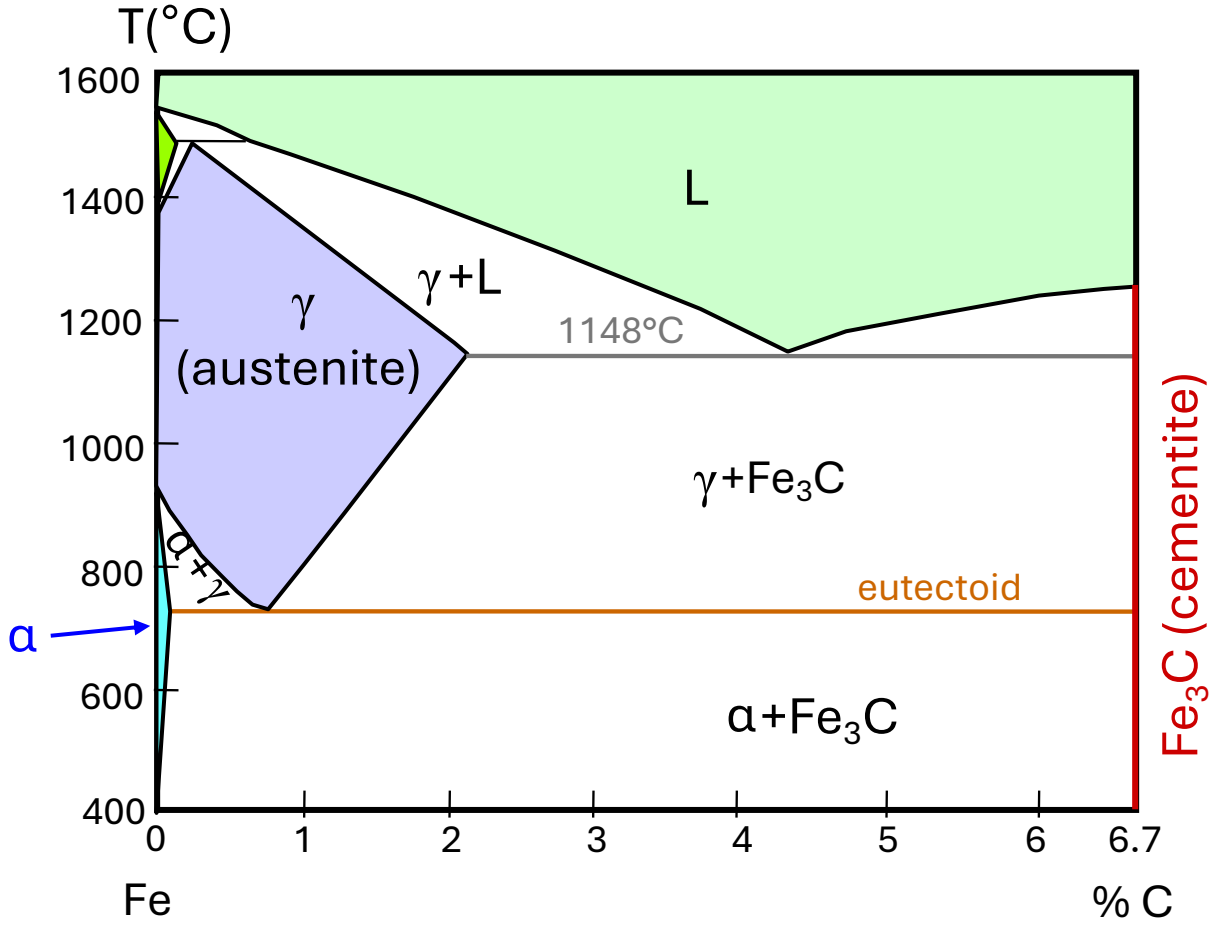


Figure 10.11 Percent recrystallization as a function of time and at constant temperature for pure copper.

Questions on transformation rates?

Phase transformations in steel



Ferrite (α) is weak and soft, often used in magnets





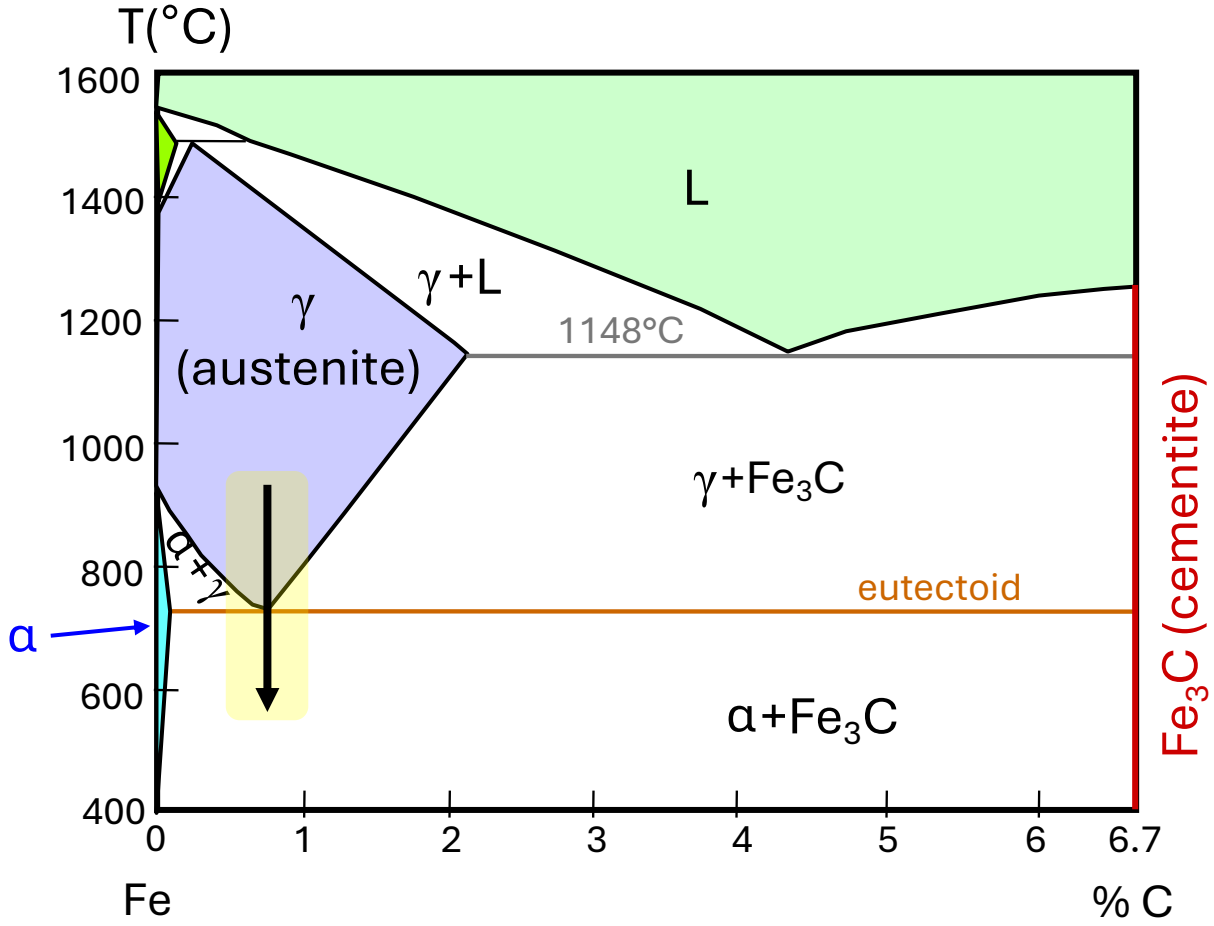
Austenite (γ) is moderately hard and ductile

Cementite (Fe_3C) is hard but very brittle – not used on its own



But is used in two-phase mixtures ←

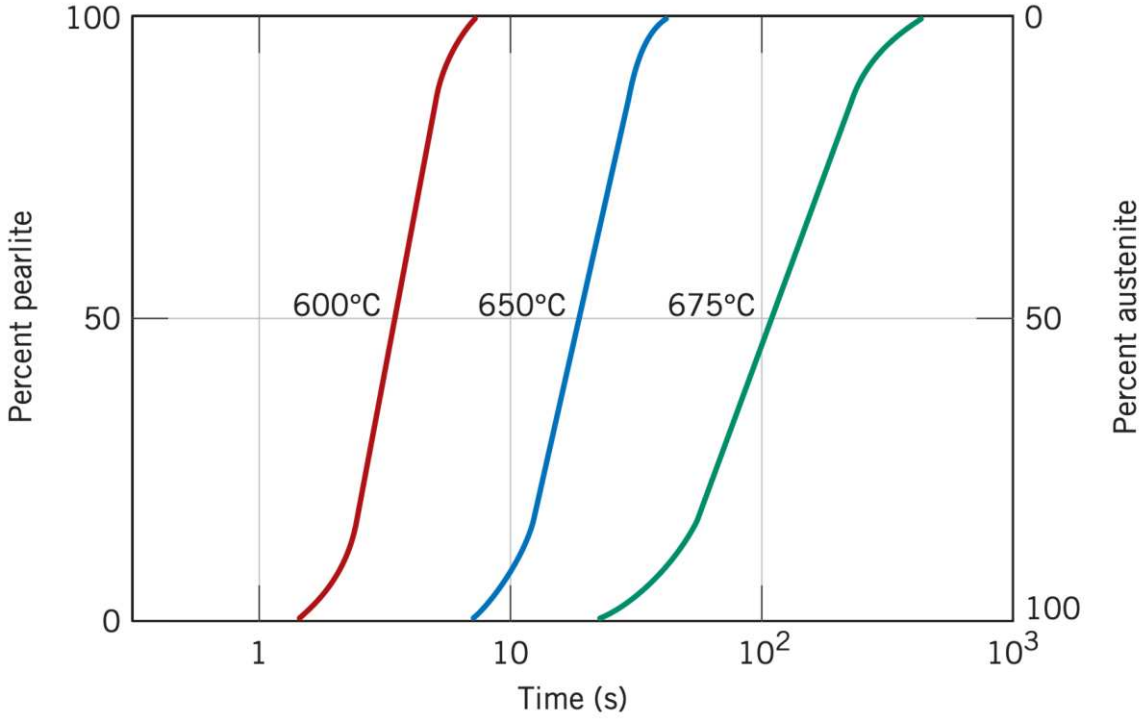
Phase transformations in steel



Consider the **eutectoid reaction:**

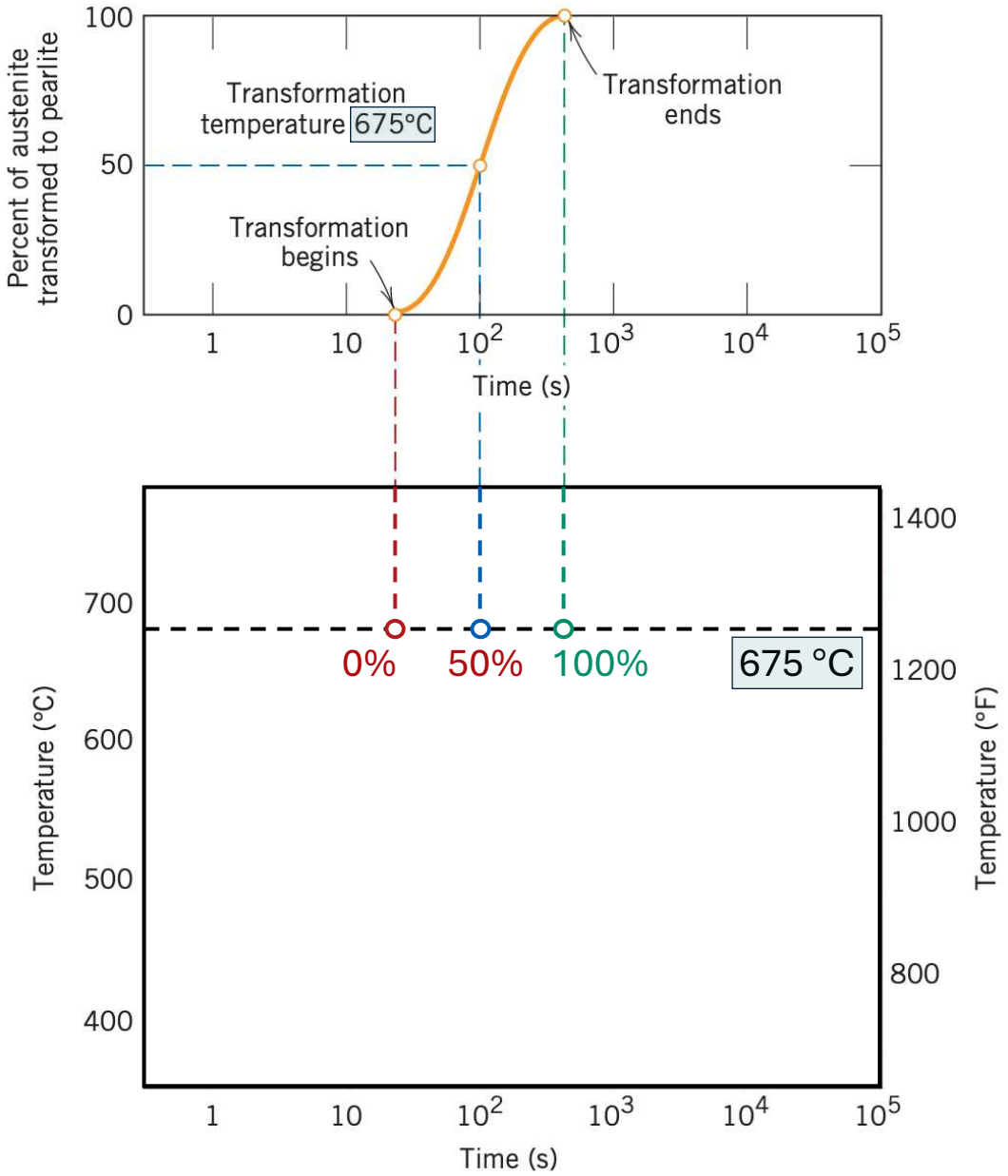
Austenite (γ) → Ferrite (α) + Cementite (Fe_3C)

Pearlite



Is there a better way to plot this?

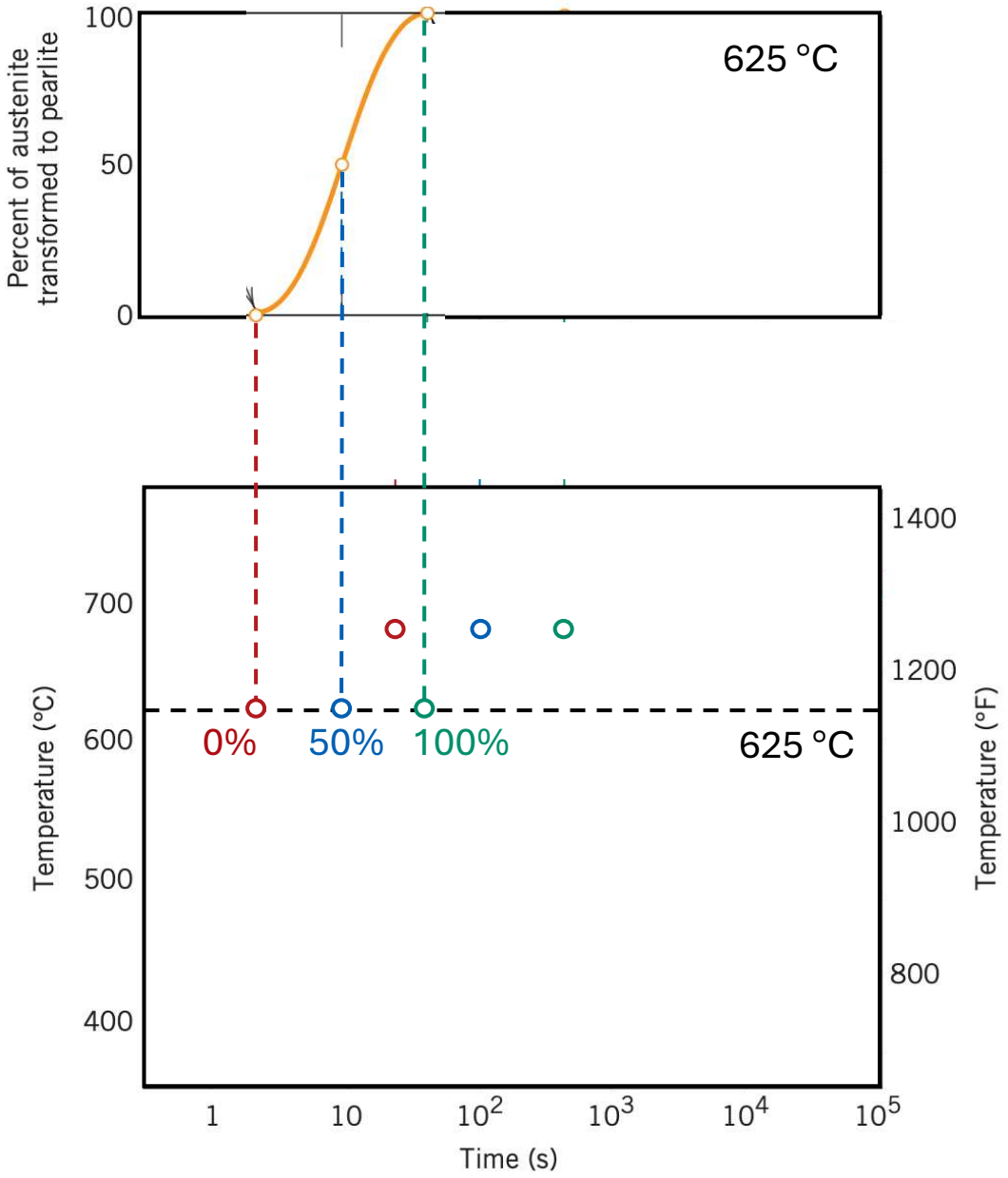
Time-Temperature-Transformation (TTT) Diagrams



TTT diagrams succinctly show us **how the rate of phase transformation varies with temperature and time**

Each point represents the time and temperature at which $X\%$ of the material has transformed (usually we plot $X = 0, 50, 100\%$)

Time-Temperature-Transformation (TTT) Diagrams

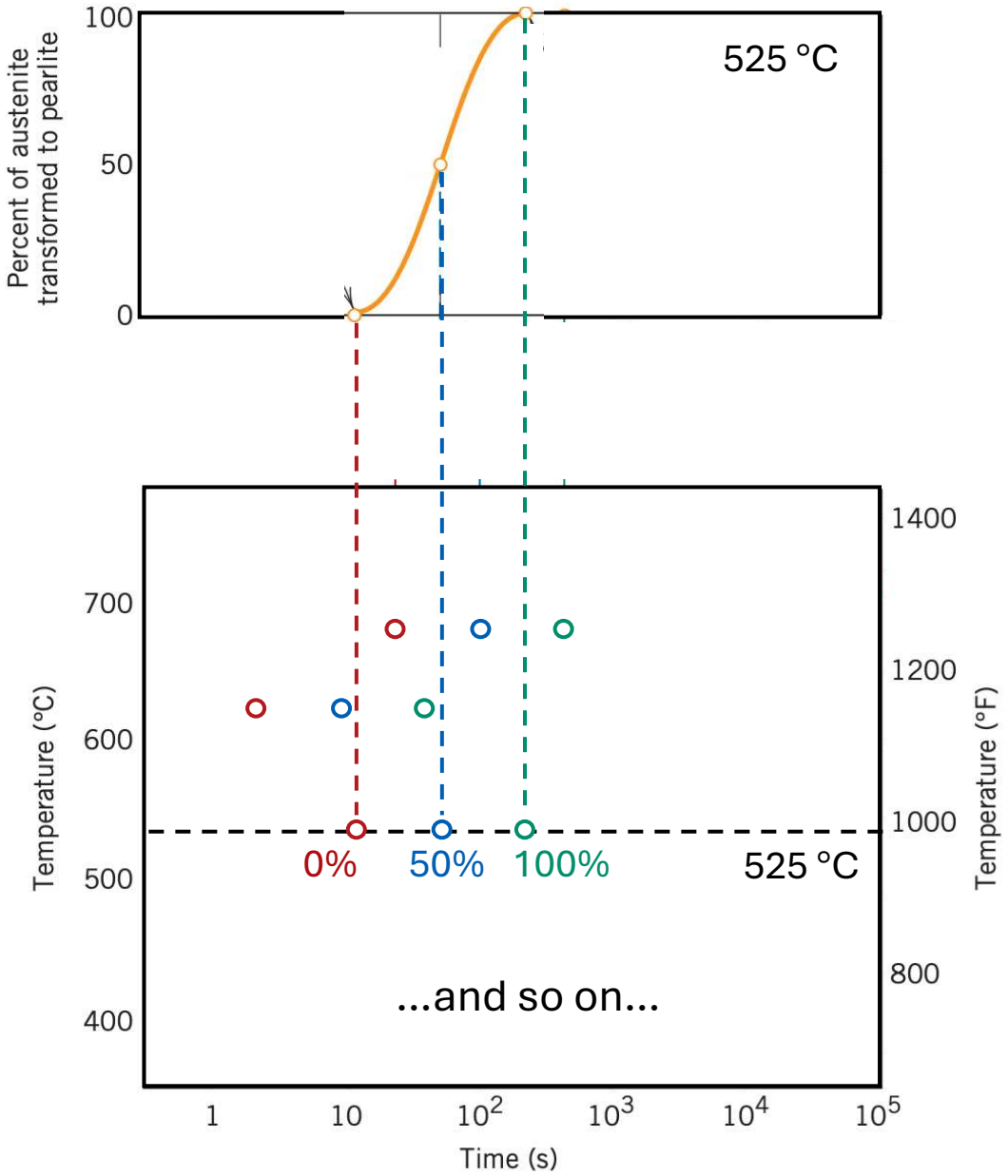


TTT diagrams succinctly show us **how the rate of phase transformation varies with temperature and time**

Each point represents the time and temperature at which $X\%$ of the material has transformed (usually we plot $X = 0, 50, 100\%$)

Do this at **varied temperatures**

Time-Temperature-Transformation (TTT) Diagrams



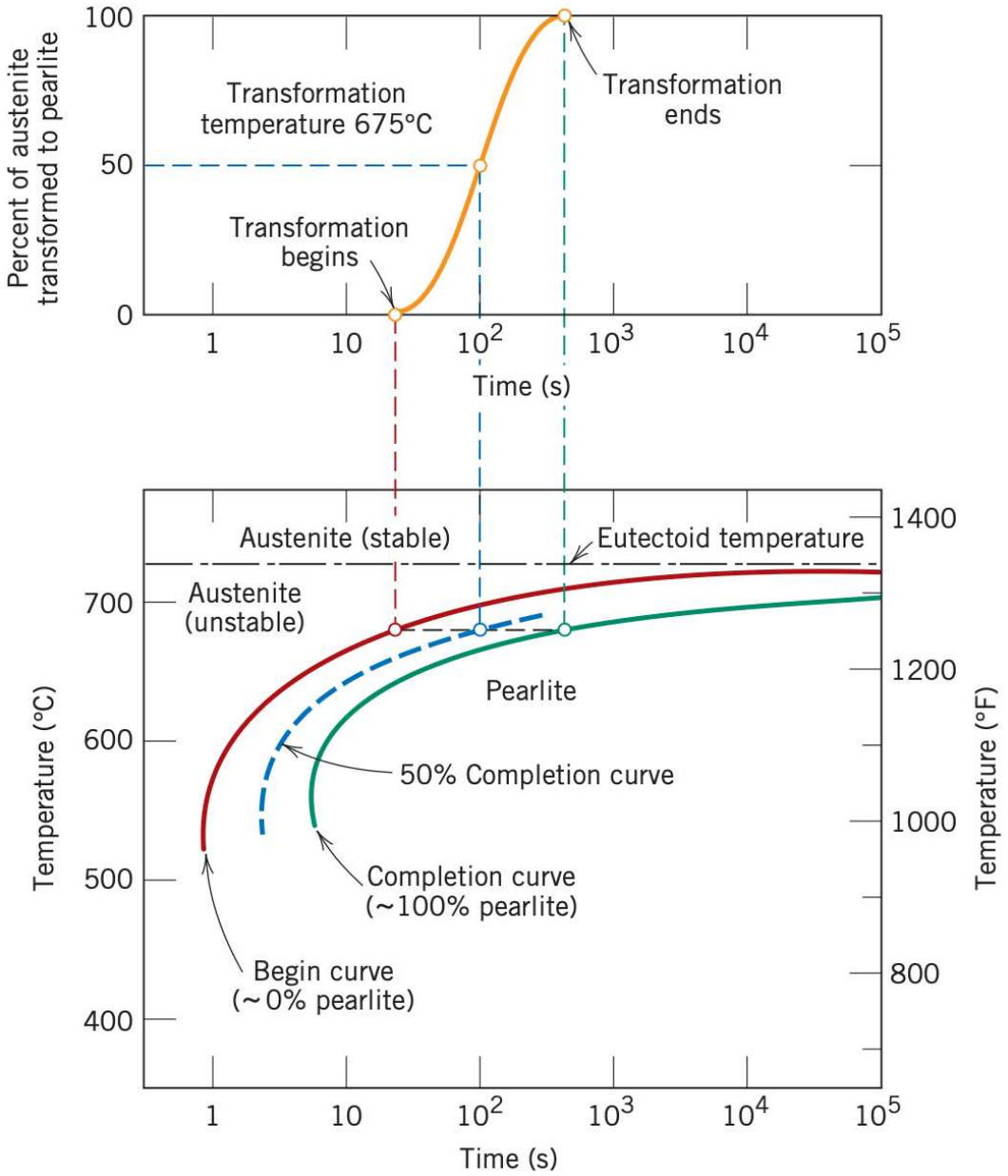
TTT diagrams succinctly show us **how the rate of phase transformation varies with temperature and time**

Each point represents the time and temperature at which $X\%$ of the material has transformed (usually we plot $X = 0, 50, 100\%$)

Do this at **varied temperatures**

Then connect the dots

Time-Temperature-Transformation (TTT) Diagrams



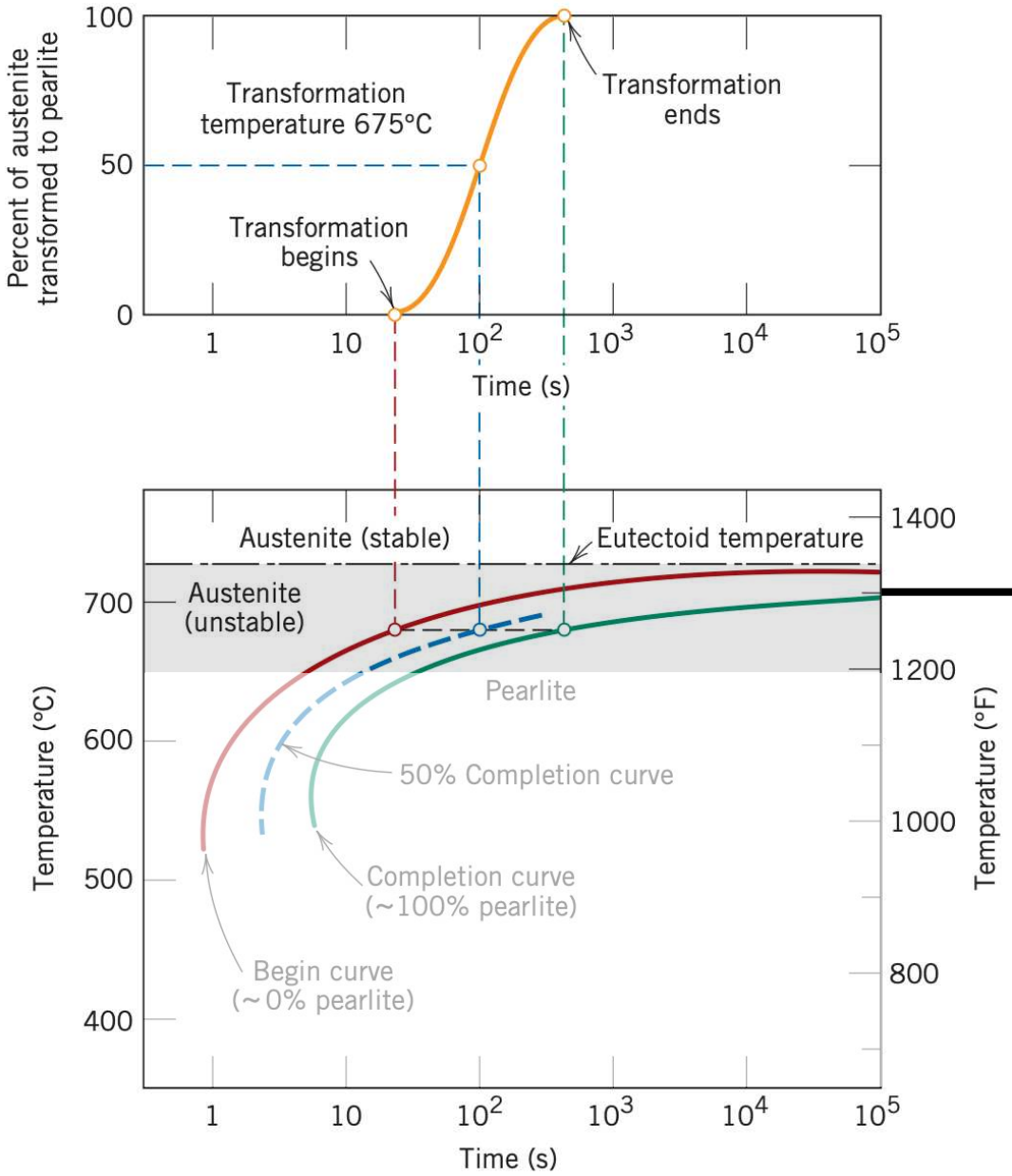
TTT diagrams succinctly show us **how the rate of phase transformation varies with temperature and time**

Each point represents the time and temperature at which $X\%$ of the material has transformed (usually we plot $X = 0, 50, 100\%$)

Do this at **varied temperatures**

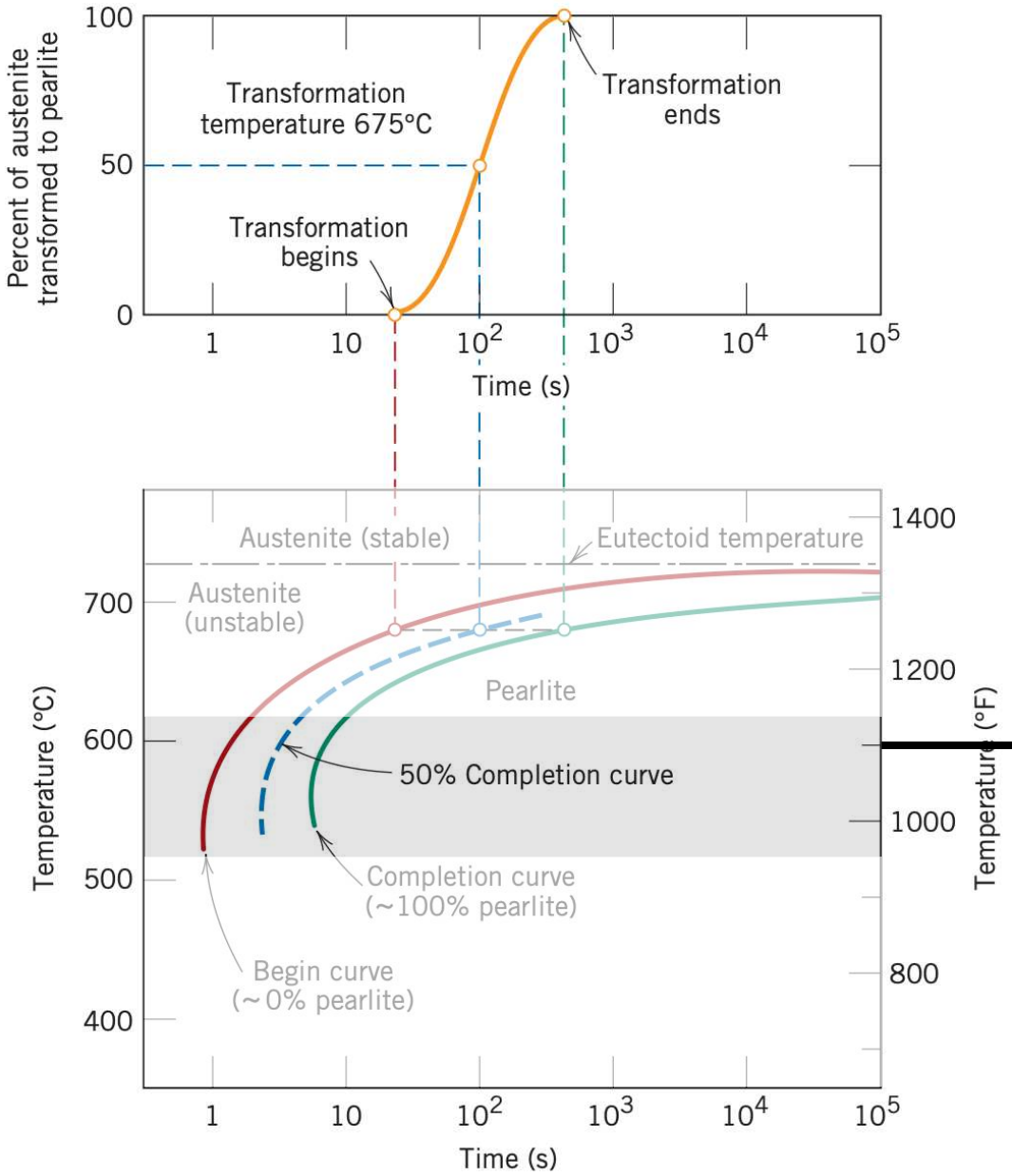
Then connect the dots

Time-Temperature-Transformation (TTT) Diagrams



At small undercooling, it takes a long time to complete the transformation

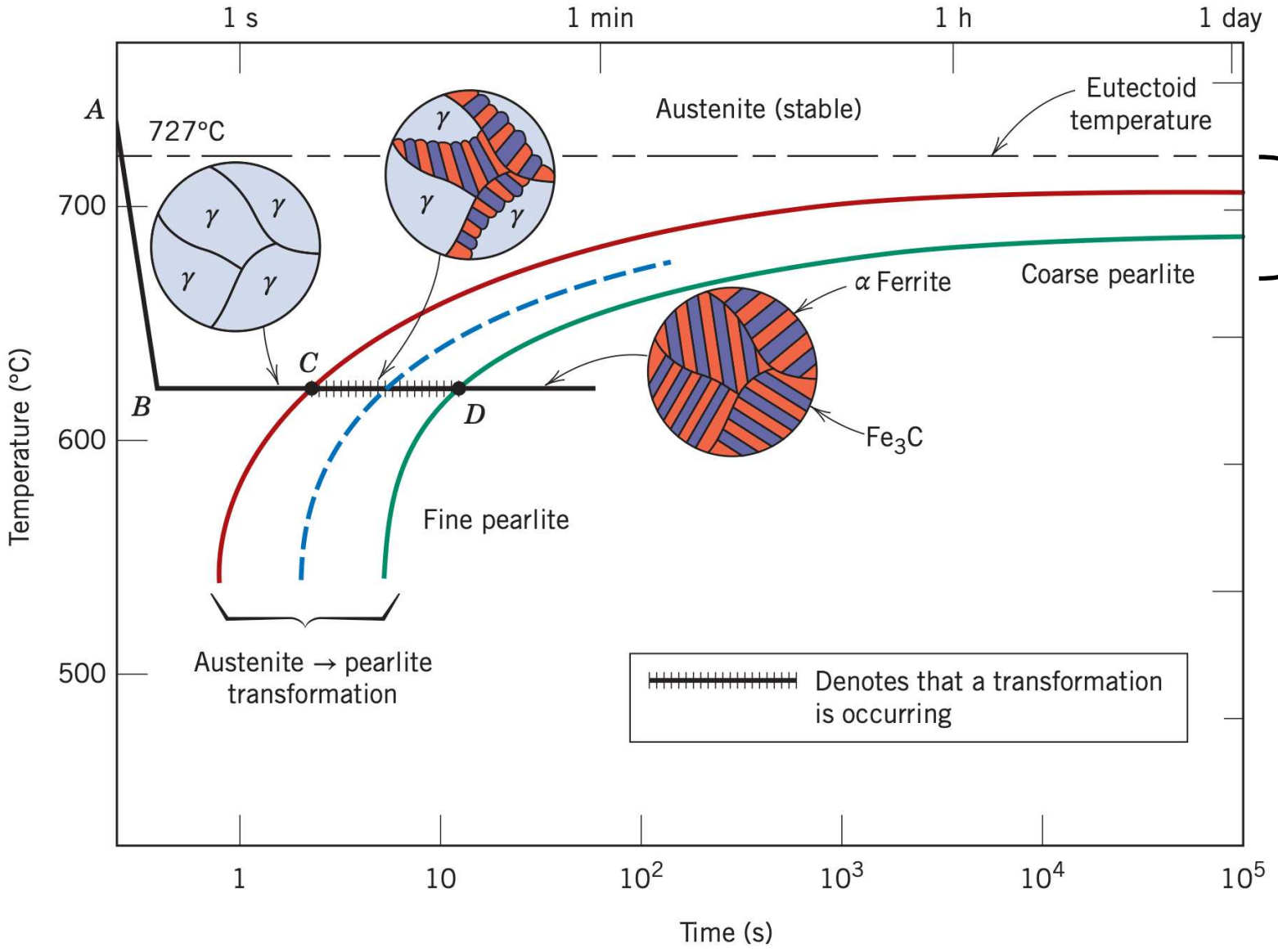
Time-Temperature-Transformation (TTT) Diagrams



Shortest transformation times occur at moderate undercooling

Questions on TTT diagrams?
Before we discuss microstructure?

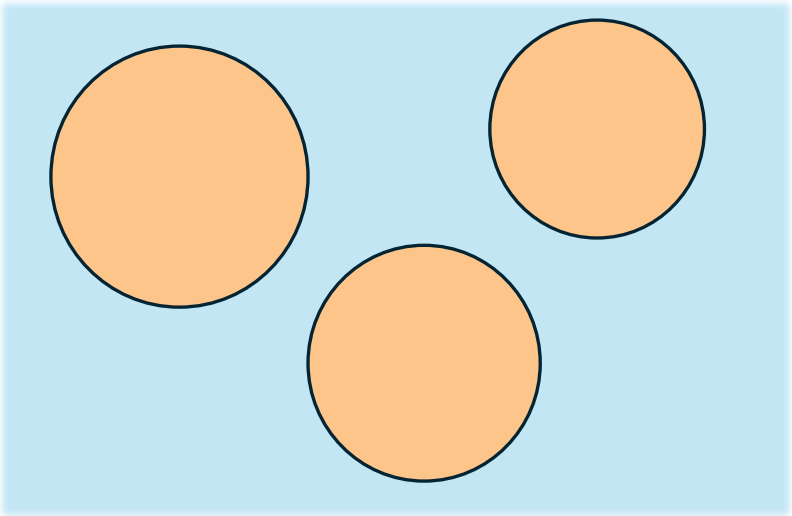
TTT Diagrams and Microstructure



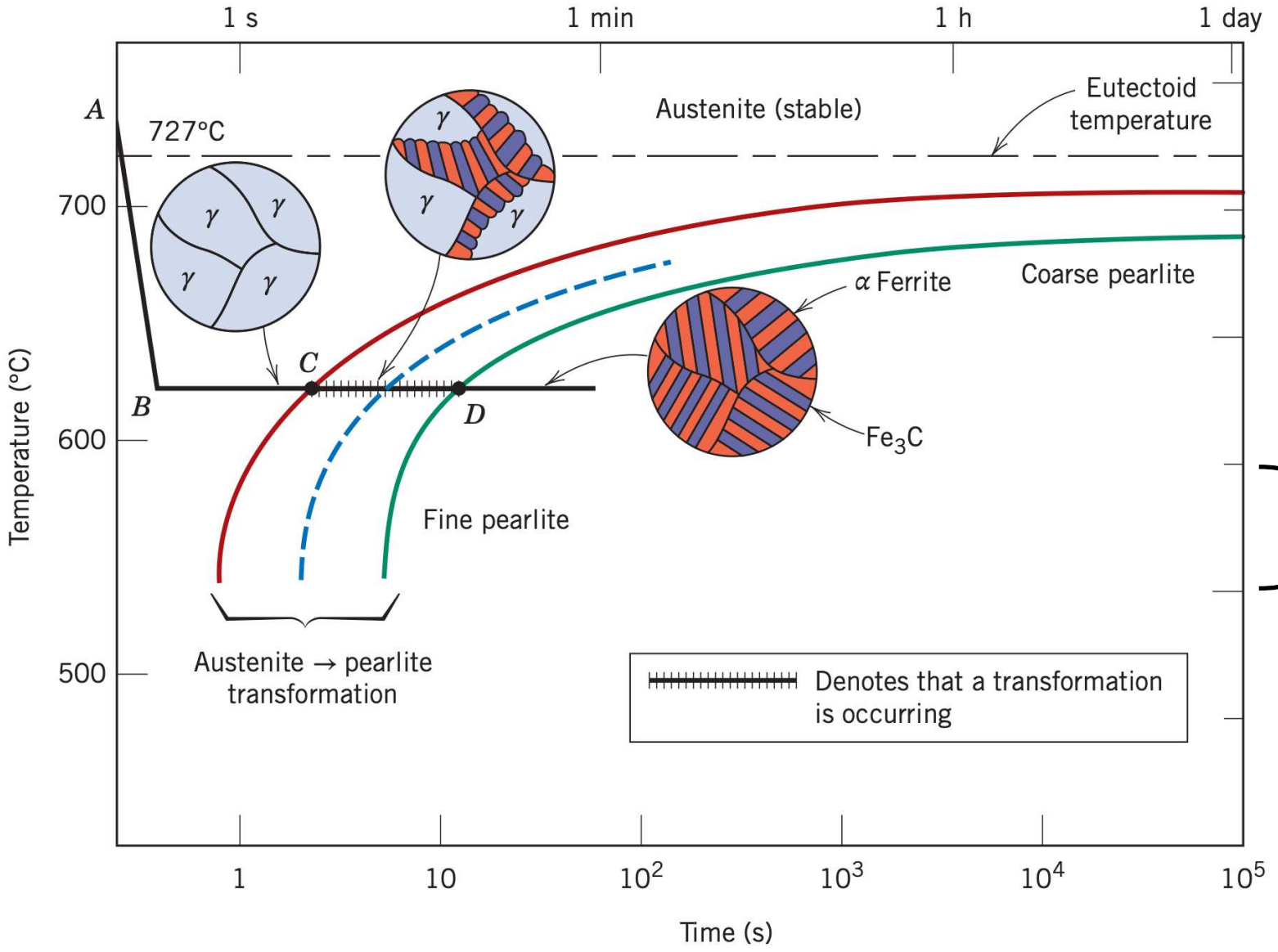
At small undercooling:

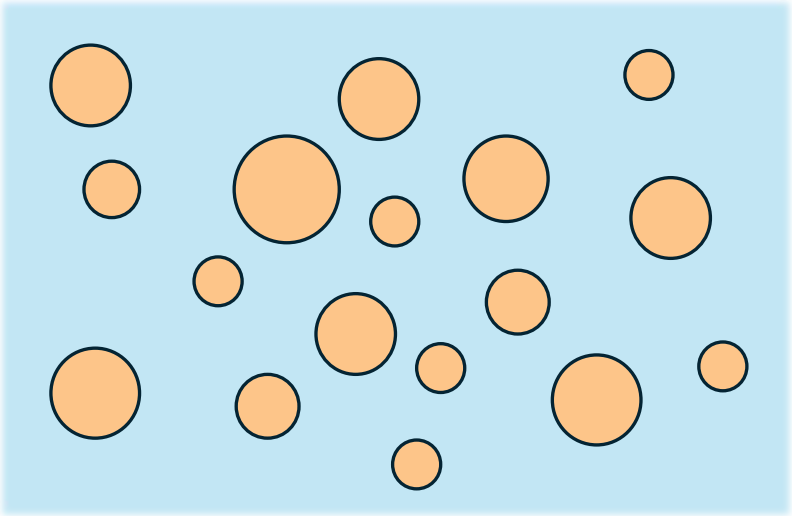
- Few stable nuclei
- But they grow fast

→ **Large grains (coarse pearlite)**



TTT Diagrams and Microstructure



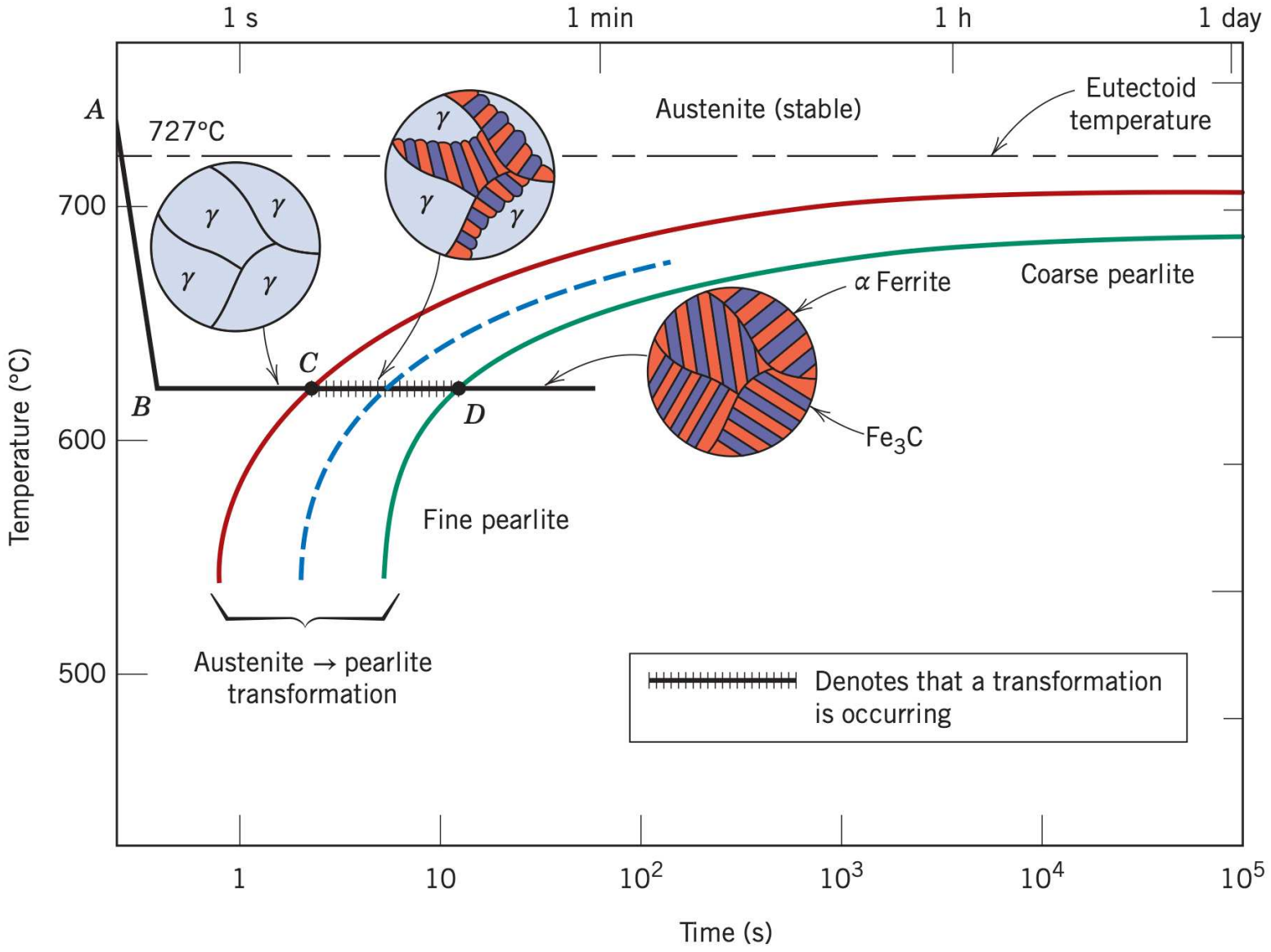


At large undercooling:

- Many stable nuclei
- They have limited growth

→ **Small grains (fine pearlite)**

TTT Diagrams and Microstructure



Coarse

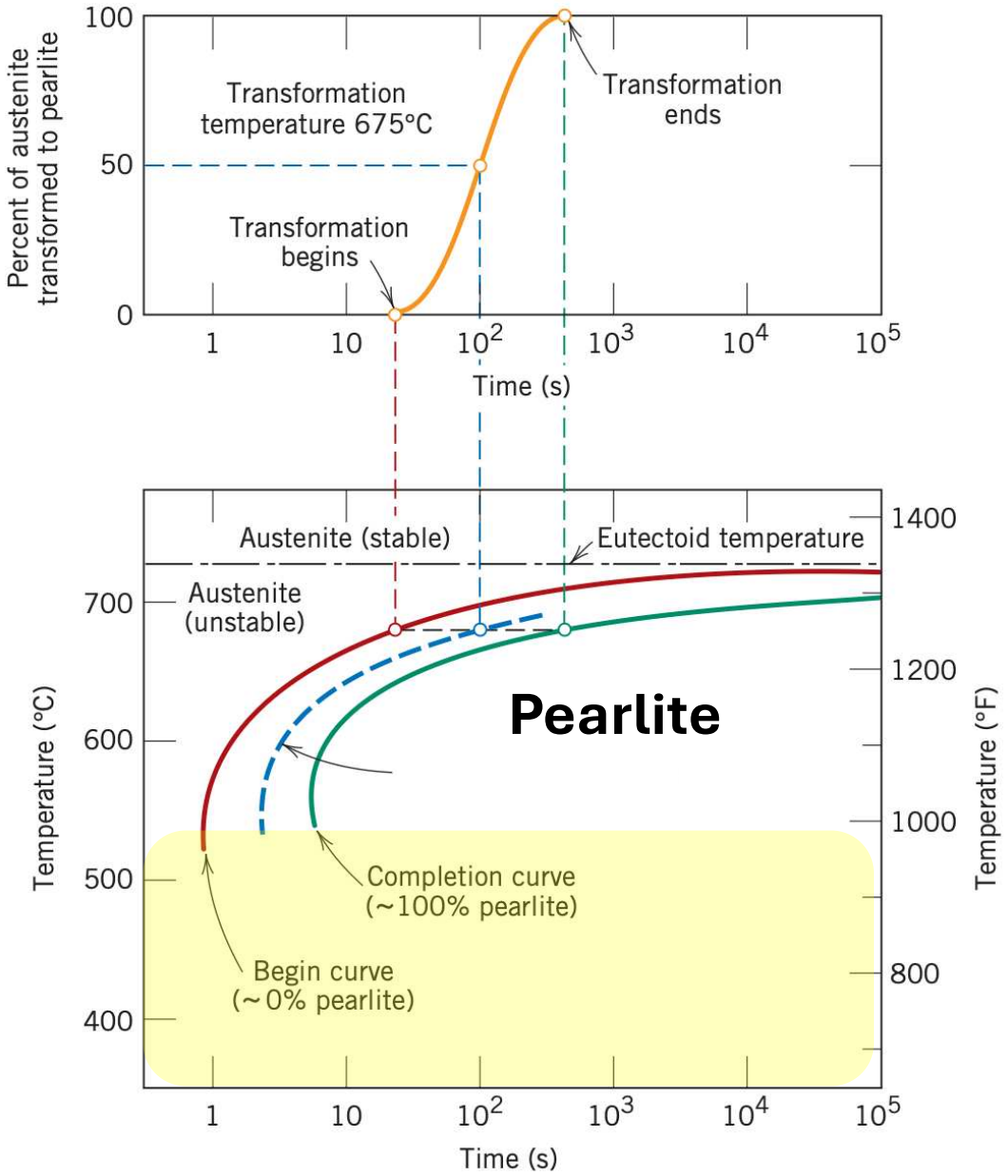


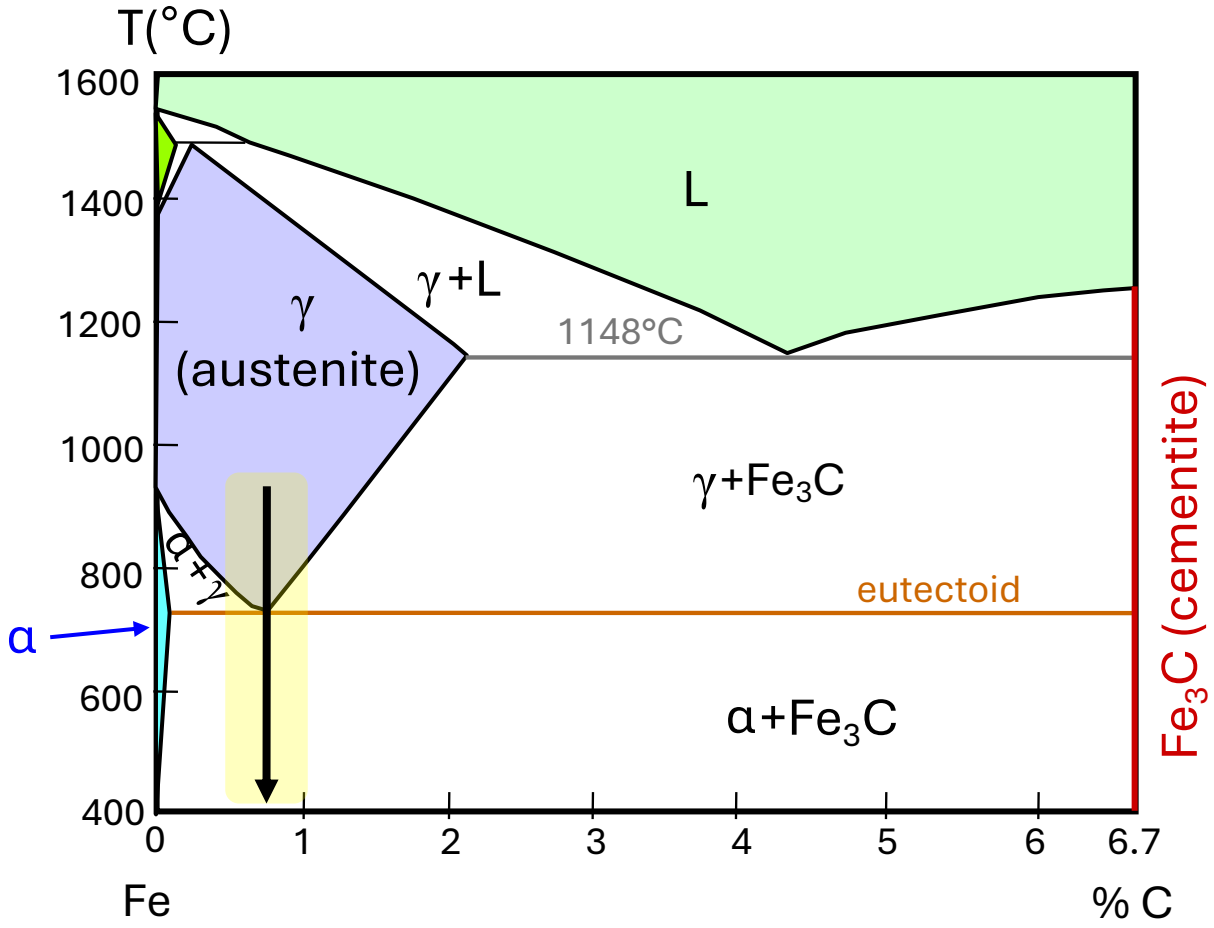
Fine



These differ only in their cooling process!

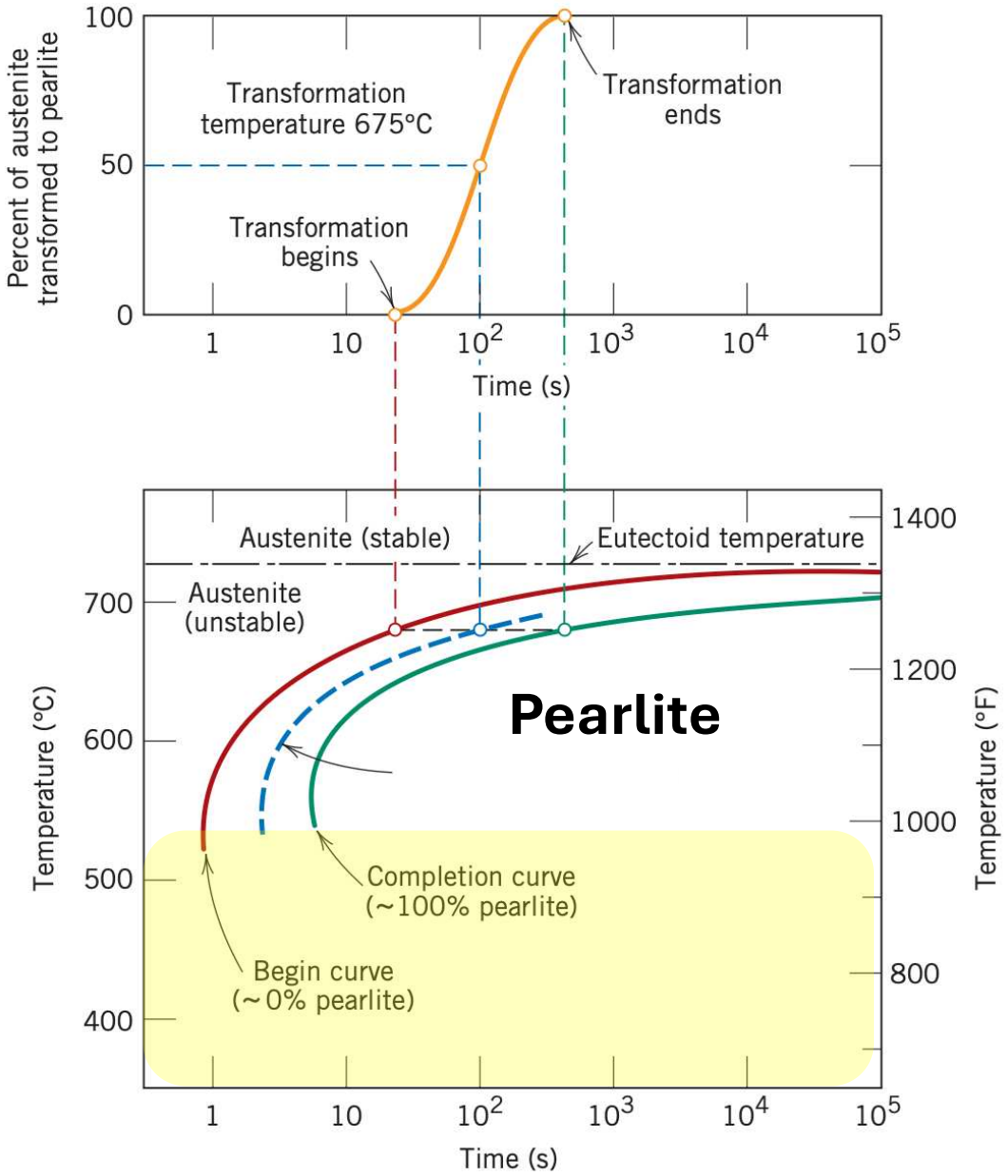
What if we supercool further?

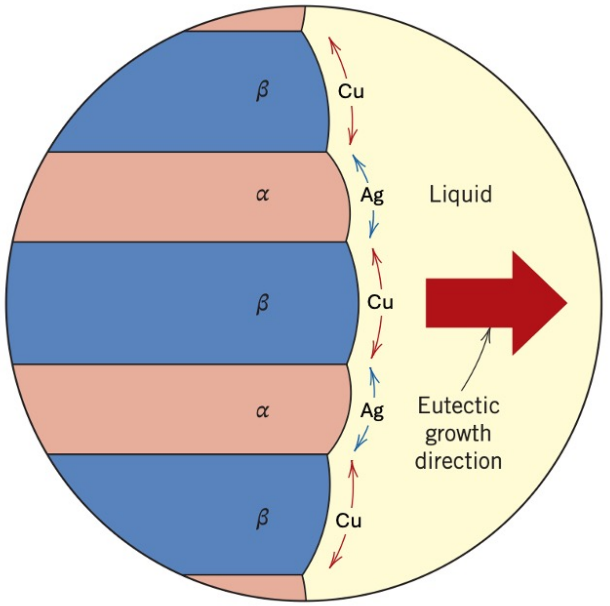




The same phases (α + Fe_3C) are expected, but what about their **microstructure?**

What if we supercool further?

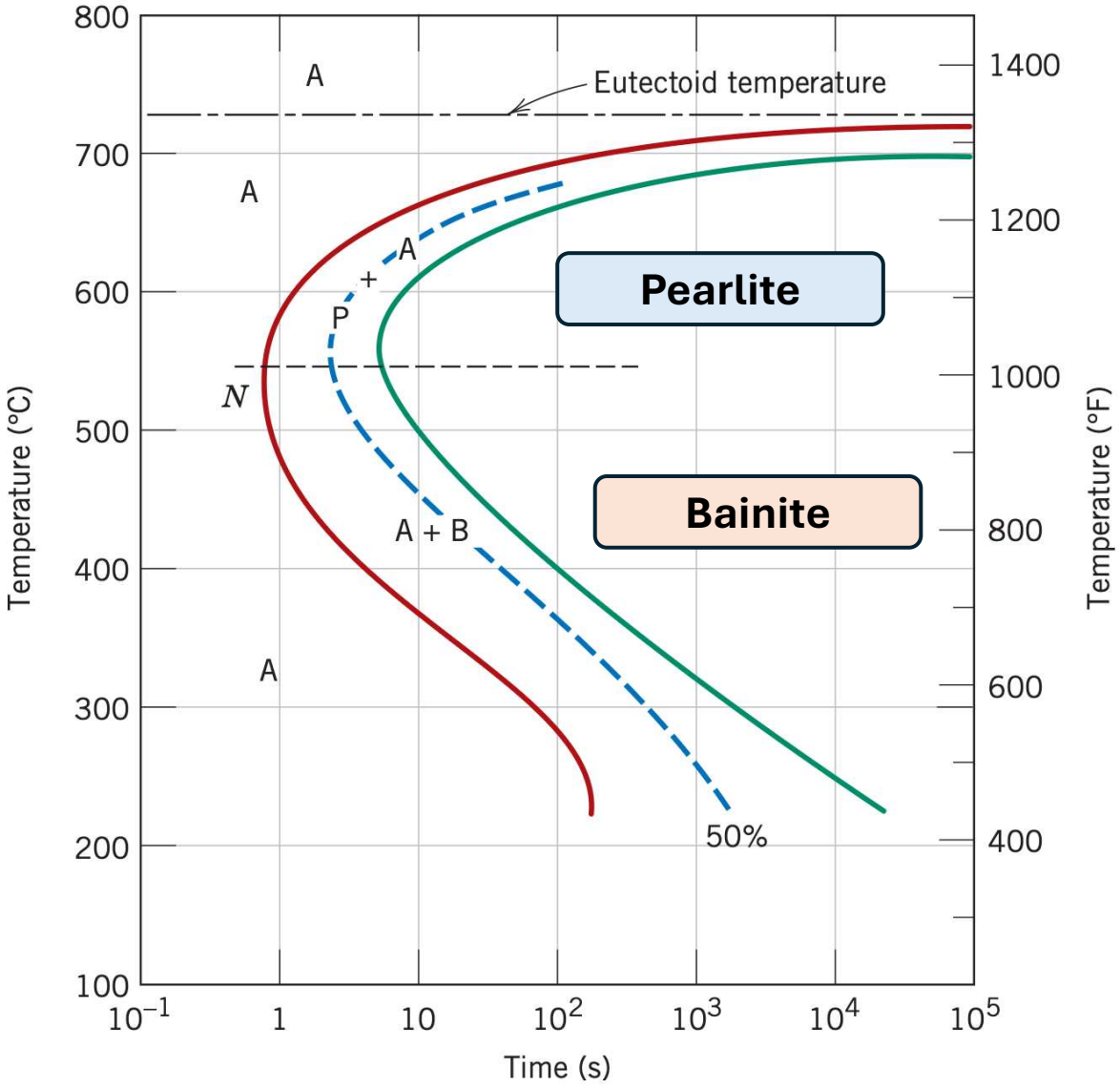


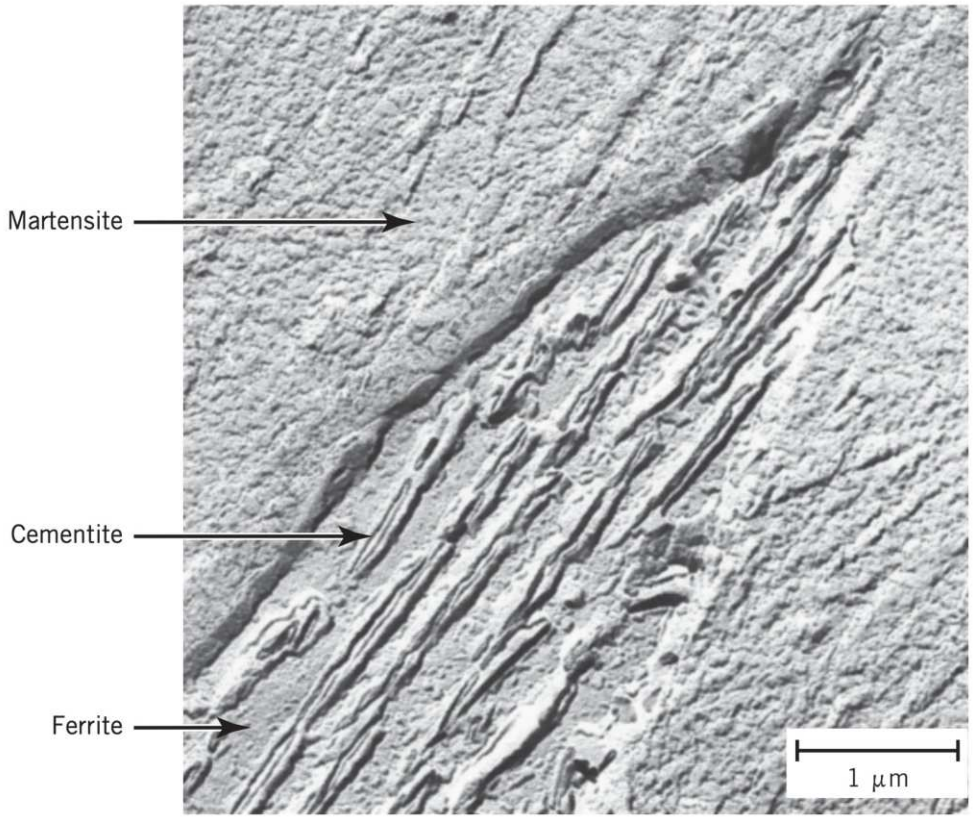


Recall that eutectoid transformations require **diffusion**

But what if we cool to such low temperature that **diffusion is severely restricted?**

Answer: the bainite microstructure

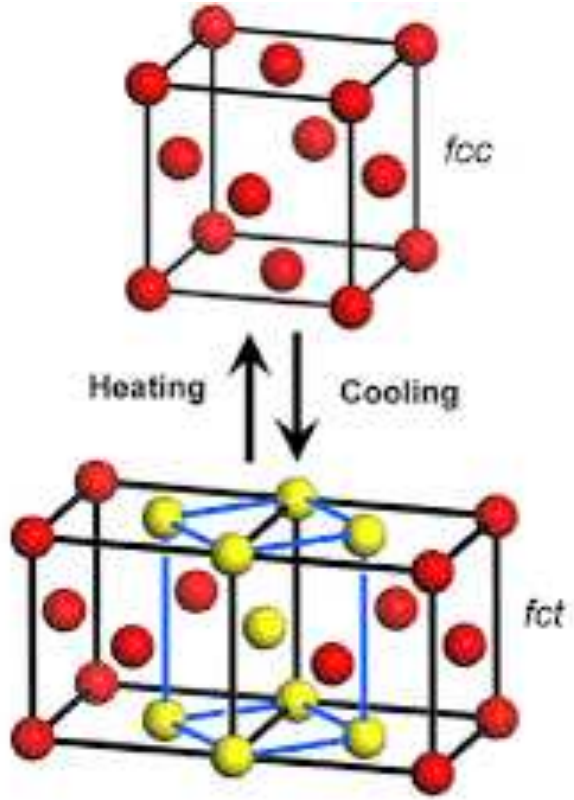


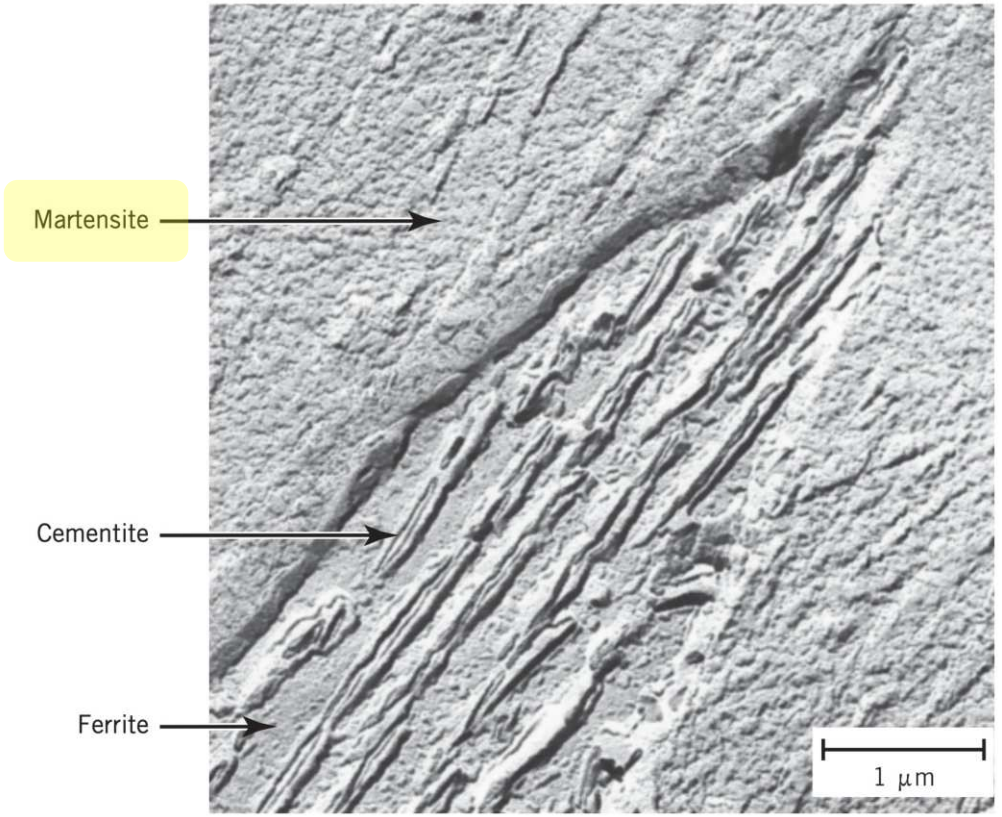


Think of bainite as having very fine “needles” of cementite embedded in a ferrite matrix

If we cool fast enough, we can form martensite

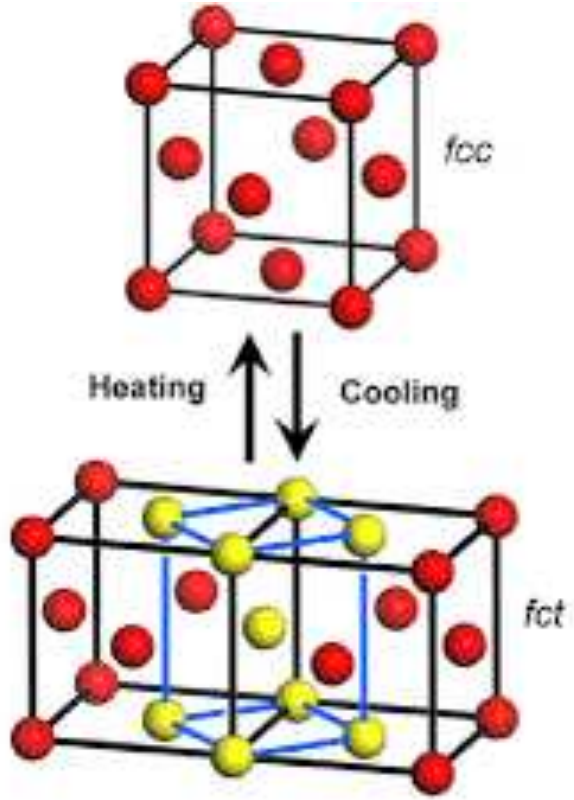
Martensite formation involves a ***diffusionless* transformation** from austenite – no change in composition, just a tetragonal distortion of the unit cell!

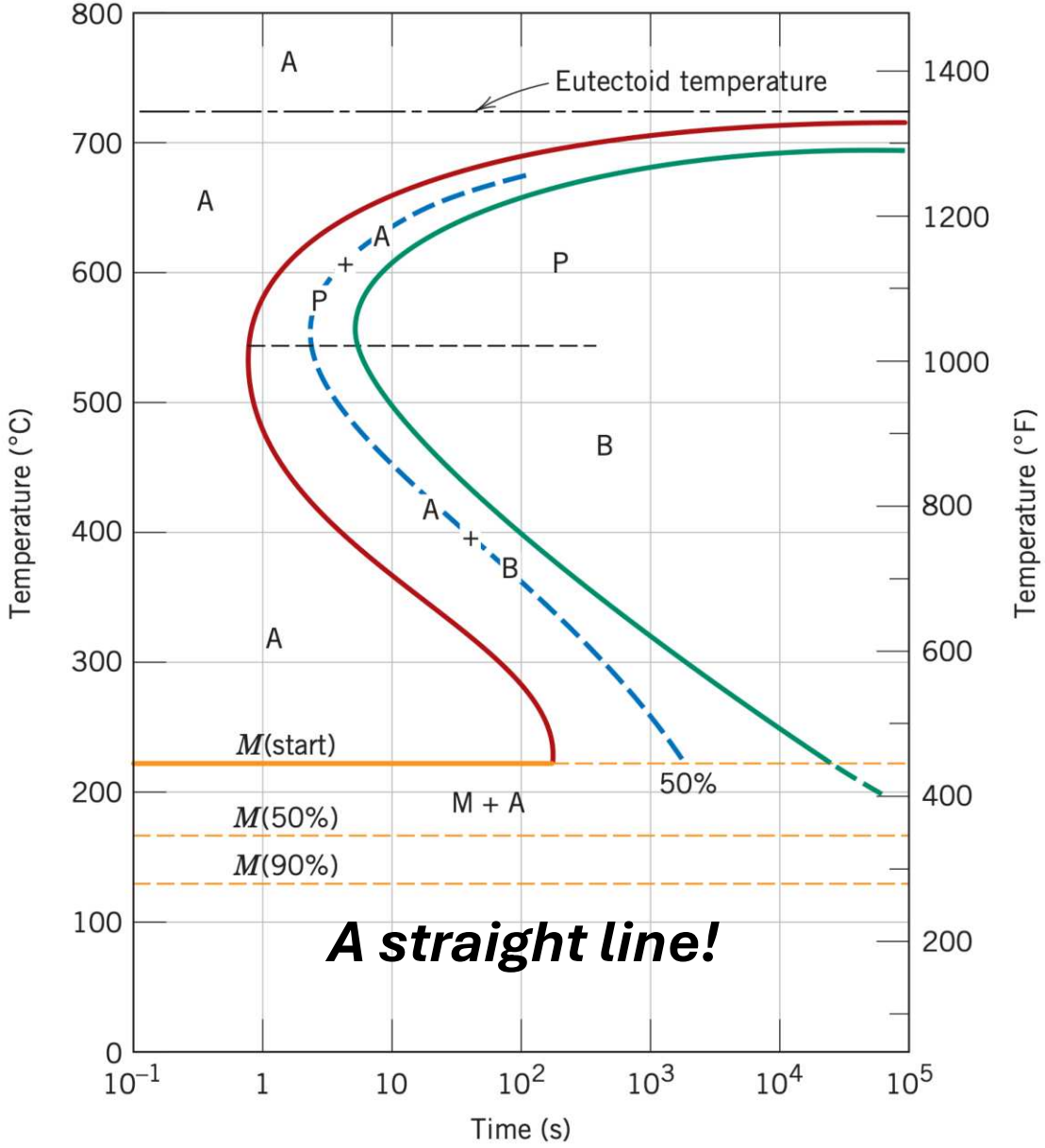




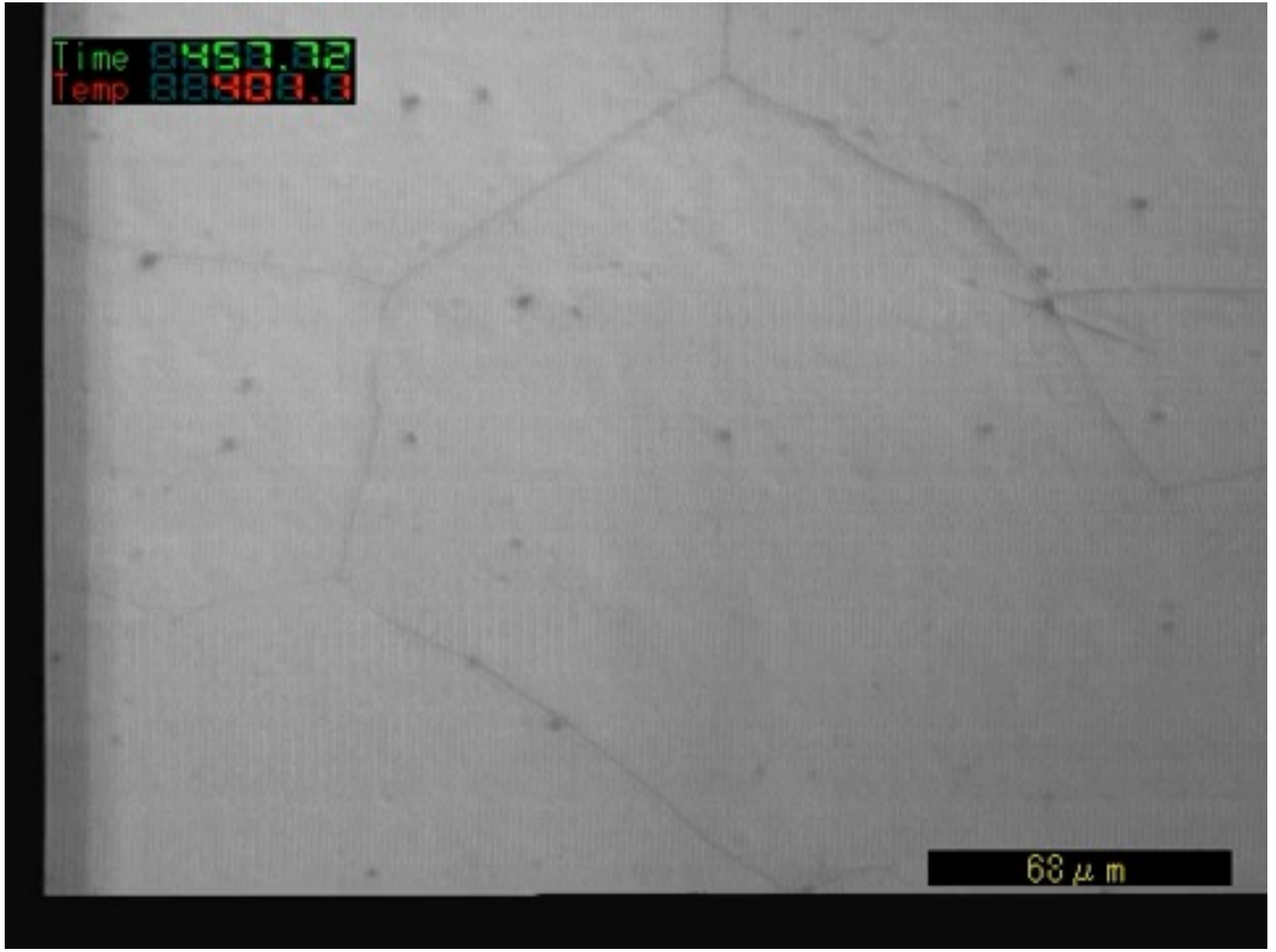
The martensitic transformation is *fast*

Martensite formation involves a ***diffusionless* transformation** from austenite – no change in composition, just a tetragonal distortion of the unit cell!

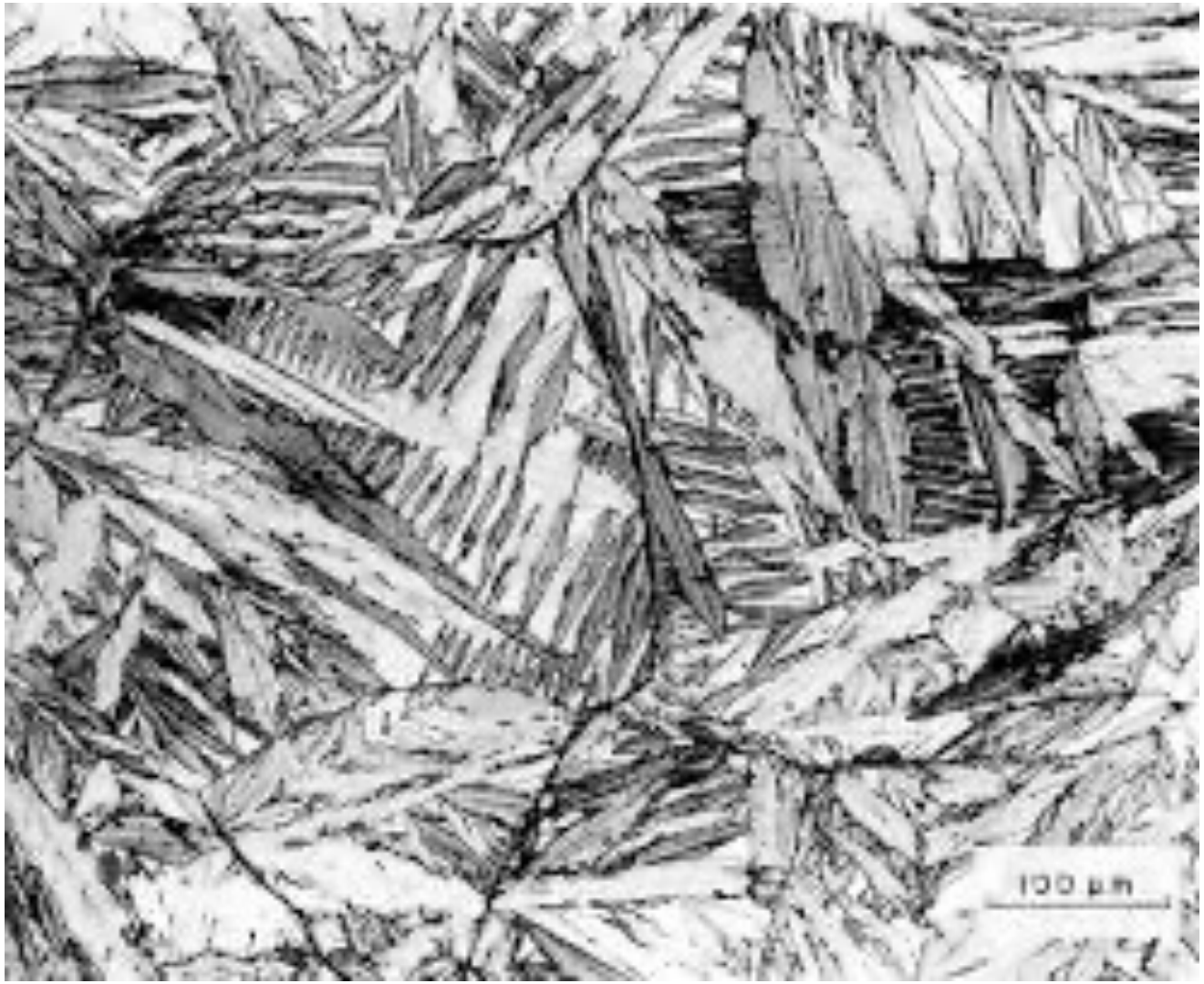




The martensitic transformation is *fast*



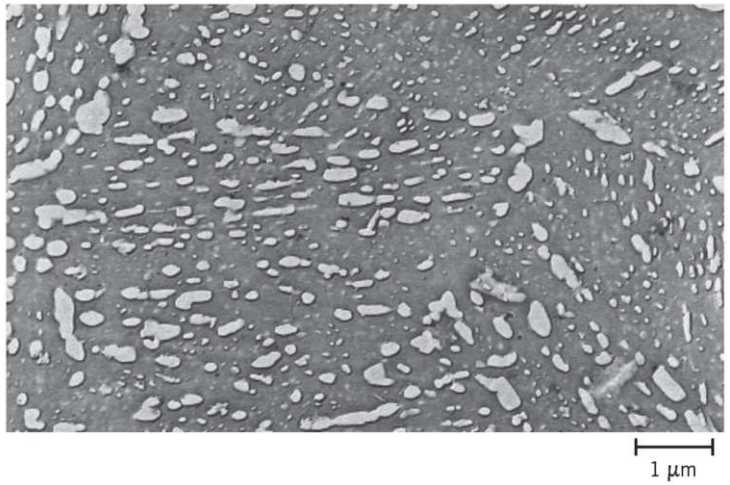
Martensite has unique properties



Very hard and strong but also **brittle…**

Can we alleviate this by tempering?

Tempering martensite to improve its ductility

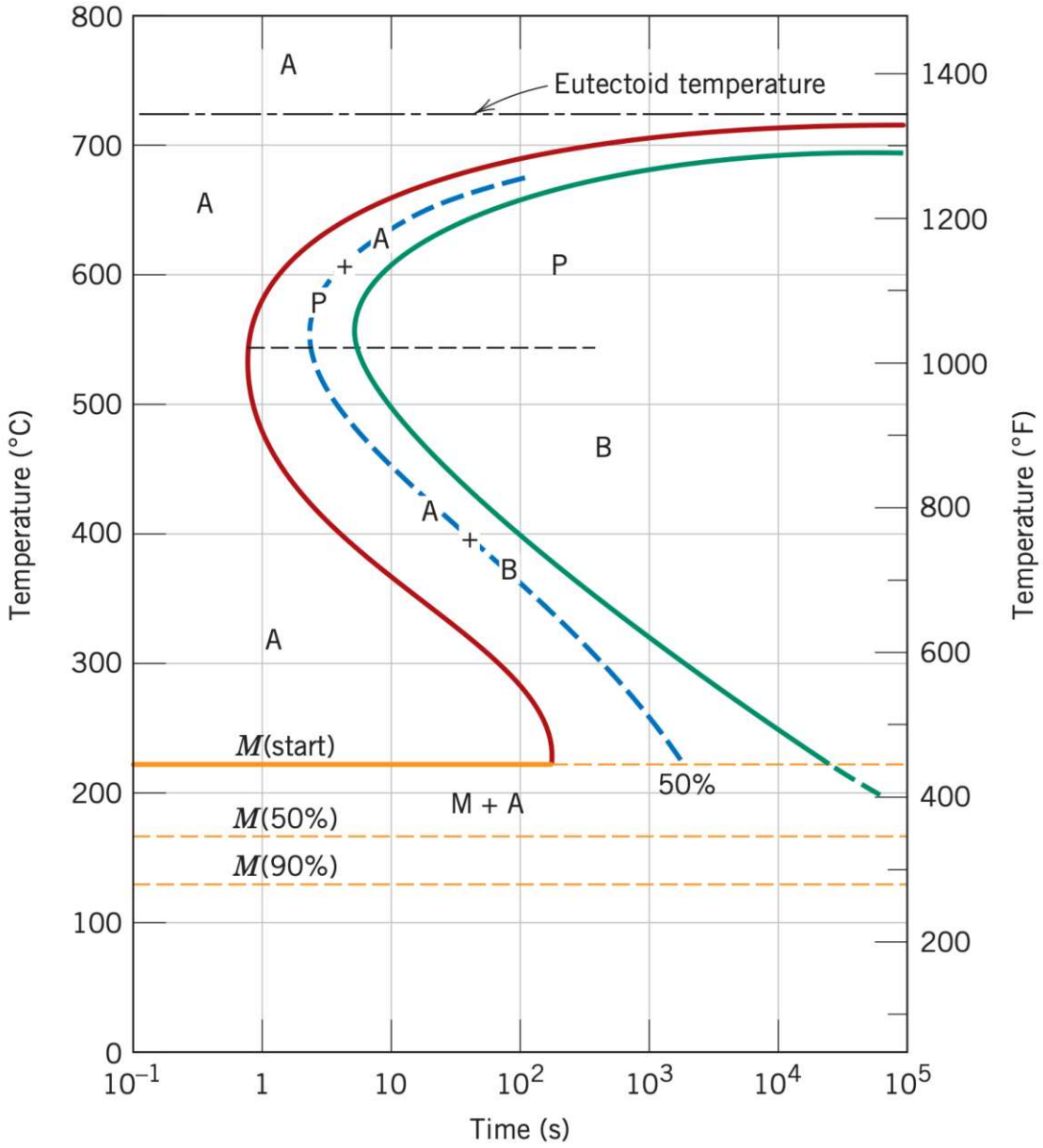


Martensite $\rightarrow \alpha + \mathbf{Fe_3C}$

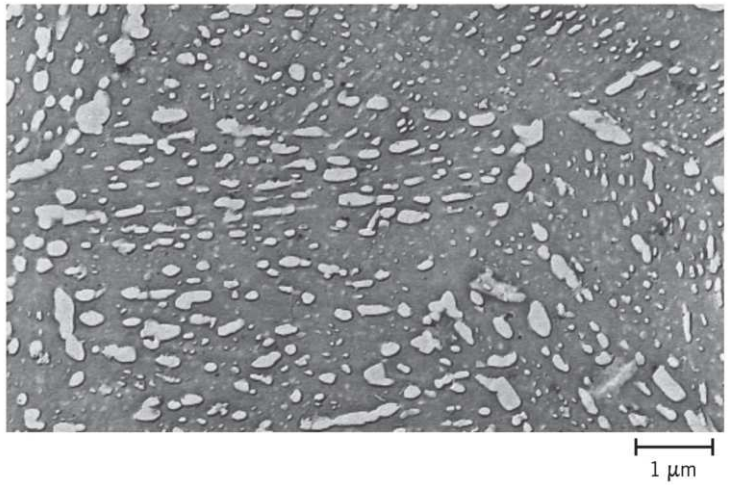
The extent of this phase transformation can be controlled by how long we hold at moderate temp.

Rapidly cool

Heat back up to moderate temp.

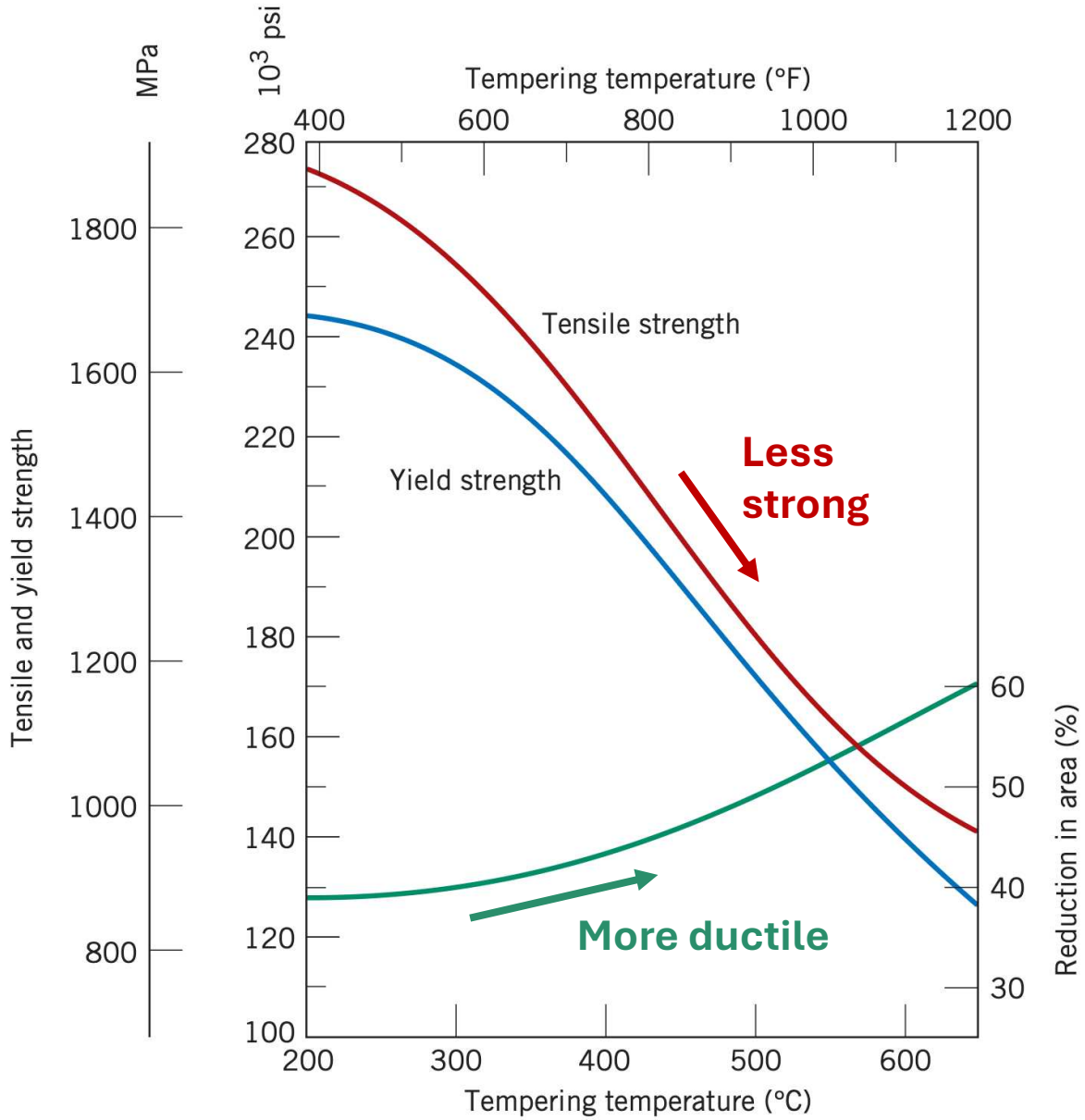


Tempering martensite to improve its ductility

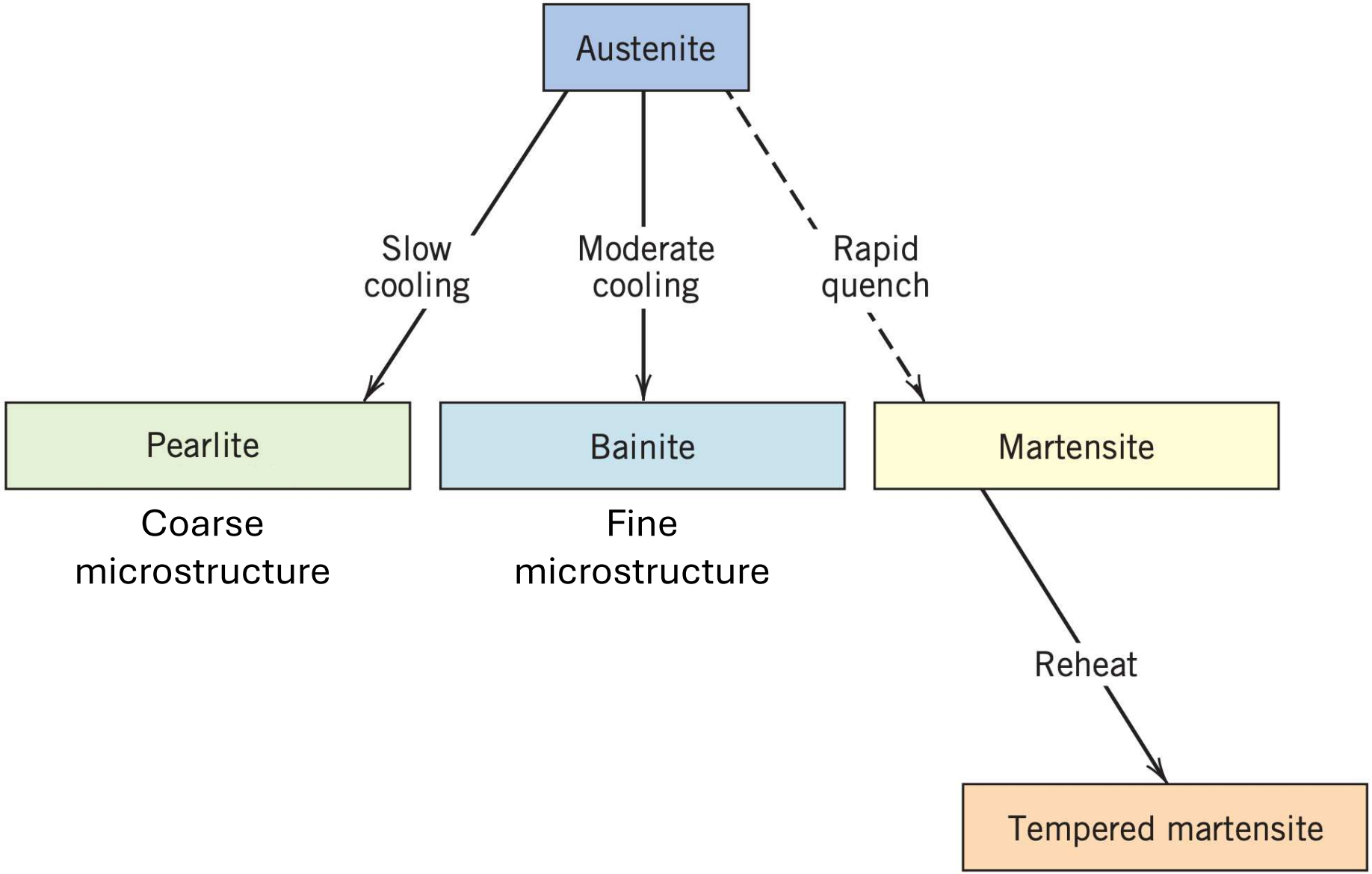


Martensite $\rightarrow \alpha +$ **Fe_3C**

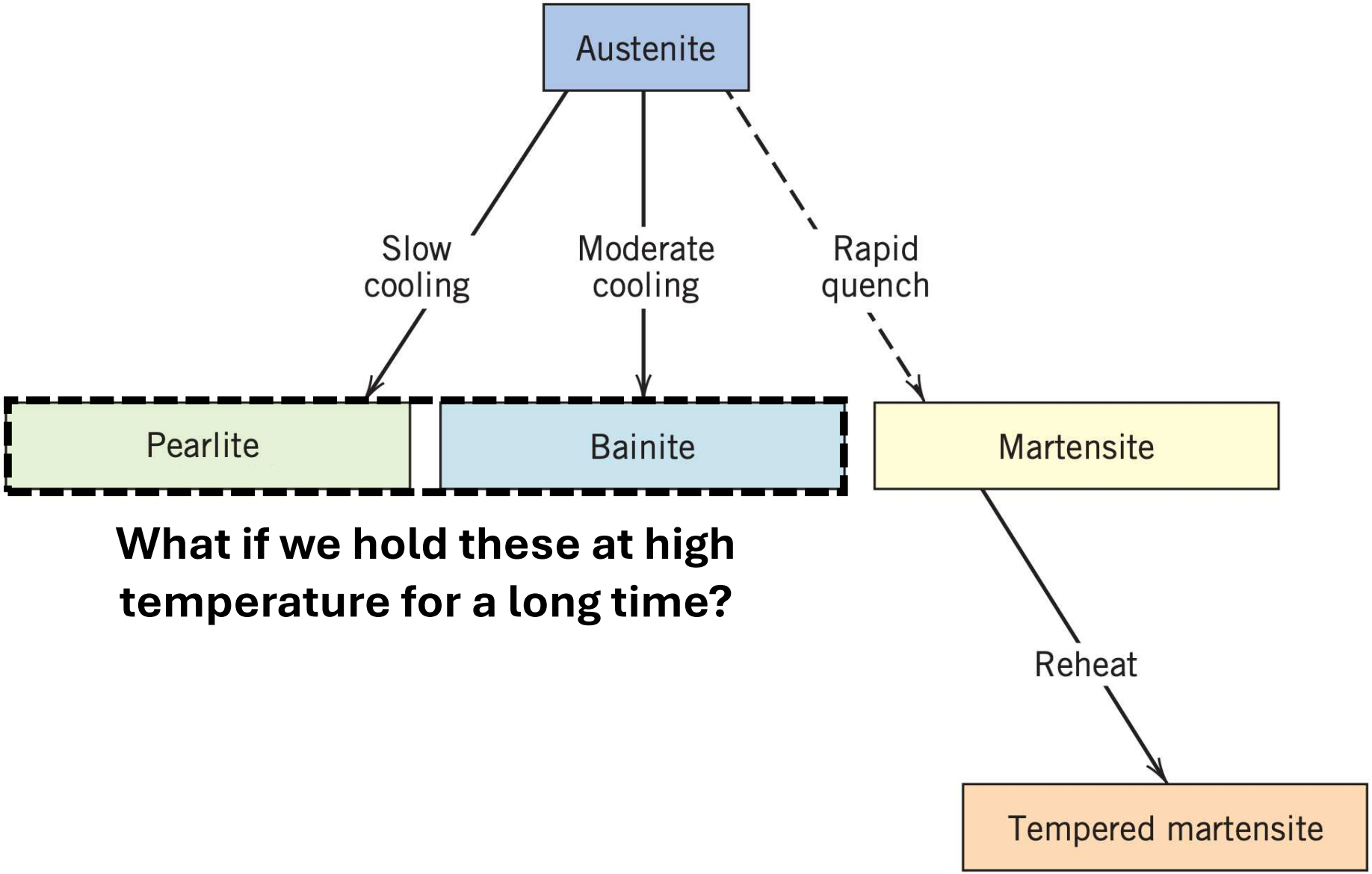
The extent of this phase transformation can be controlled by how long we hold at moderate temp.



A summary of common steel microstructures



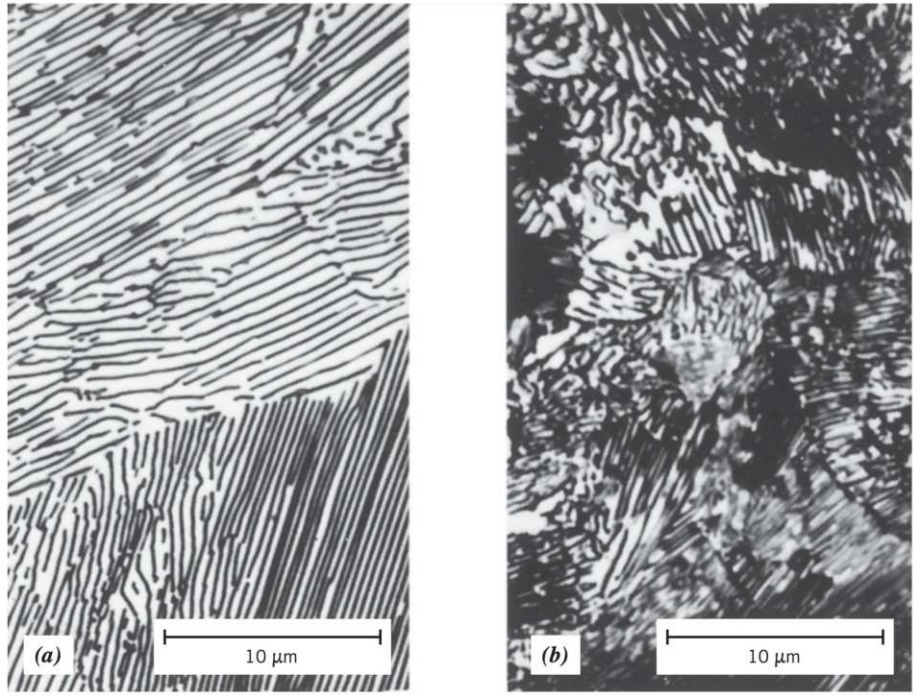
A summary of common steel microstructures



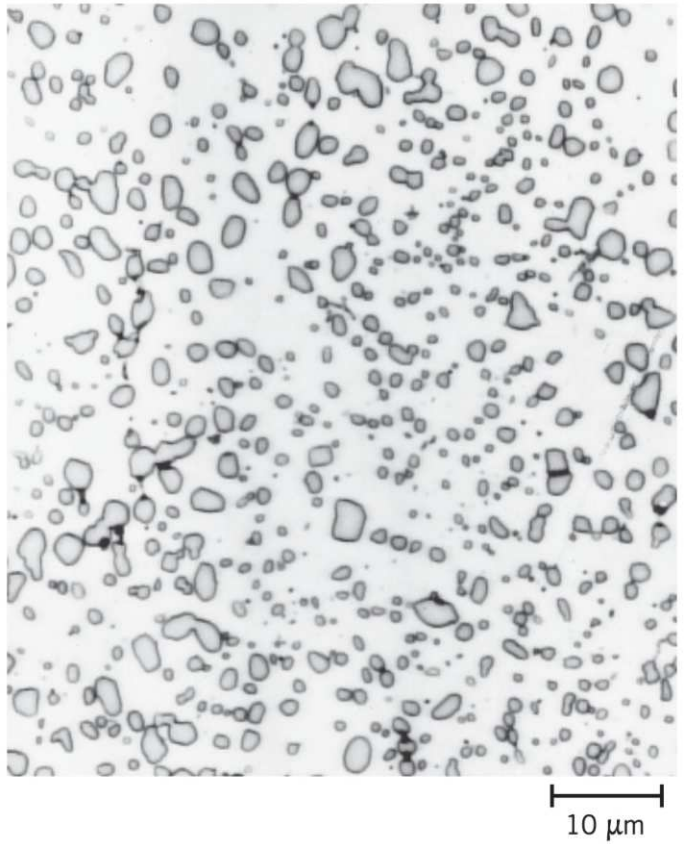
What if we hold these at high temperature for a long time?

Another microstructure: spheroidite

Coarse **Fine**



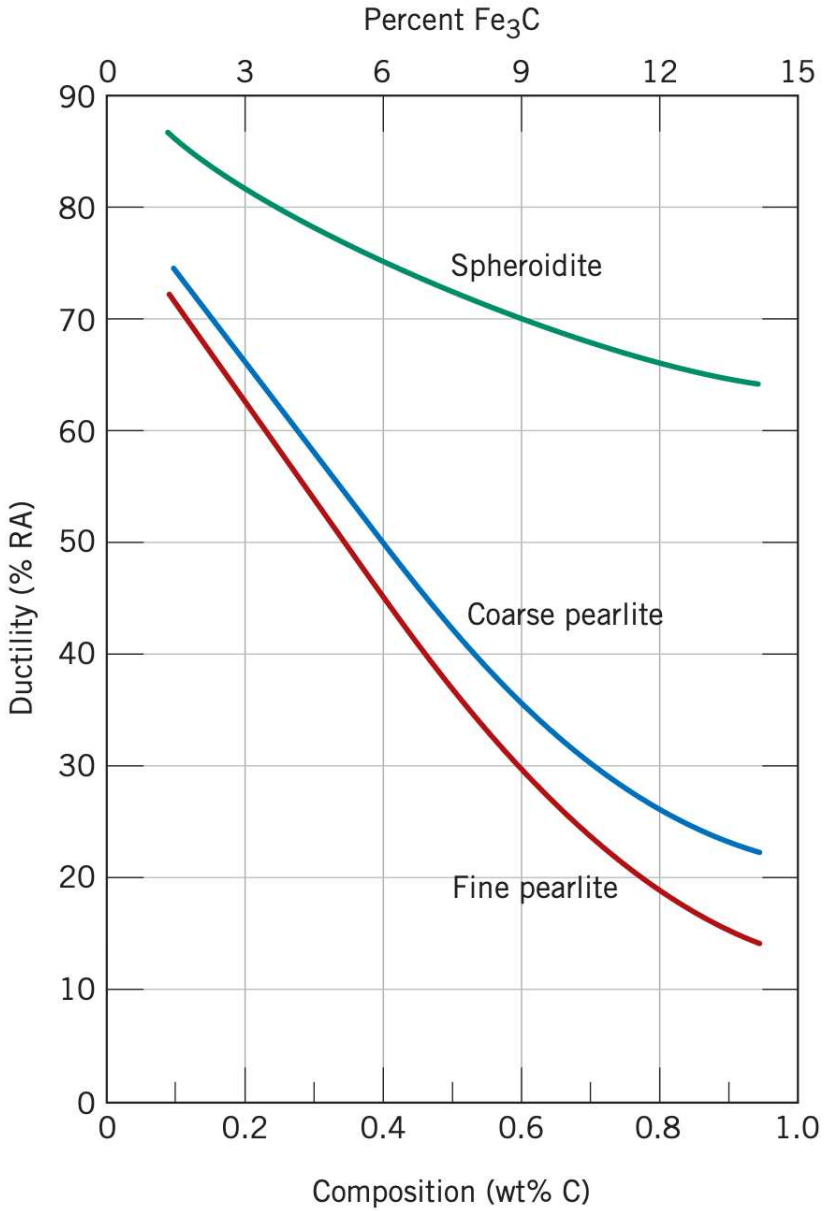




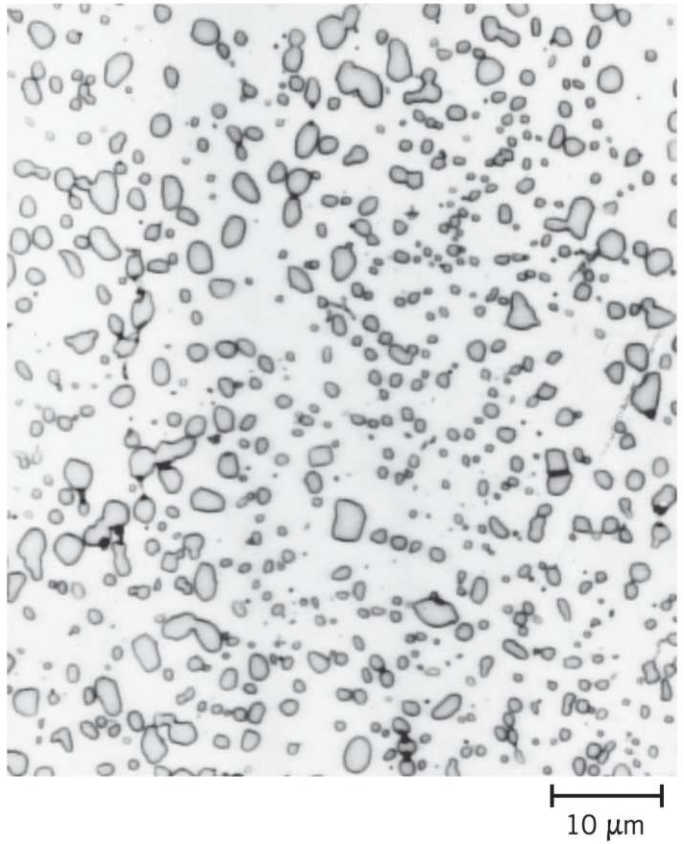
Notice the eutectic microstructure has a lot of grain boundaries…These are not very favorable

Given enough time, these grains will ***coarsen*** to form **spheroidite:** Spherical cementite (Fe_3C) particles embedded in a ferrite (α) matrix.

Microstructure and mechanical properties



Less grain boundaries = less barriers for dislocation motion = much **softer material**



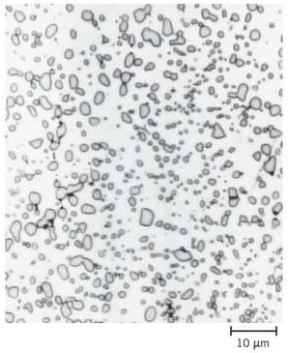
Given enough time, these grains will ***coarsen*** to form **spheroidite:** Spherical cementite (Fe_3C) particles embedded in a ferrite (α) matrix.

Microstructure and mechanical properties

Table 10.2 Microstructures and Mechanical Properties for Iron–Carbon Alloys

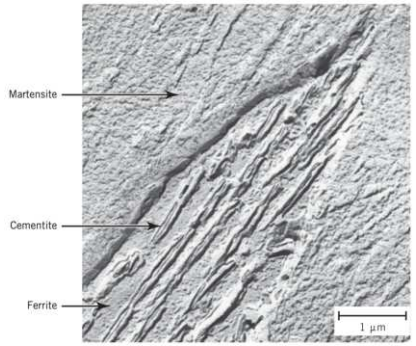
Microconstituent	*Phases Present*	*Arrangement of Phases*	*Mechanical Properties (Relative)*
Spheroidite	α-Ferrite + Fe_3C	Relatively small Fe_3C spherelike particles in an α-ferrite matrix	Soft and ductile
Coarse pearlite	α-Ferrite + Fe_3C	Alternating layers of α-ferrite and Fe_3C that are relatively thick	Harder and stronger than spheroidite, but not as ductile as spheroidite
Fine pearlite	α-Ferrite + Fe_3C	Alternating layers of α-ferrite and Fe_3C that are relatively thin	Harder and stronger than coarse pearlite, but not as ductile as coarse pearlite
Bainite	α-Ferrite + Fe_3C	Very fine and elongated particles of Fe_3C in an α-ferrite matrix	Harder and stronger than fine pearlite; less hard than martensite; more ductile than martensite

More grain boundaries = stronger but less ductile







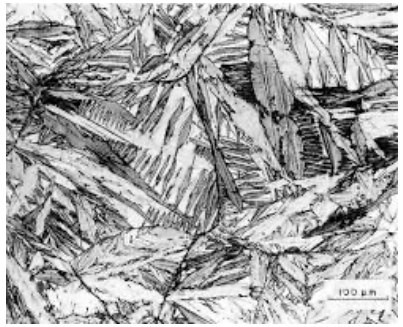


Microstructure and mechanical properties

Table 10.2 Microstructures and Mechanical Properties for Iron–Carbon Alloys

Microconstituent	*Phases Present*	*Arrangement of Phases*	*Mechanical Properties (Relative)*
Spheroidite	α-Ferrite + Fe_3C	Relatively small Fe_3C spherelike particles in an α-ferrite matrix	Soft and ductile
Coarse pearlite	α-Ferrite + Fe_3C	Alternating layers of α-ferrite and Fe_3C that are relatively thick	Harder and stronger than spheroidite, but not as ductile as spheroidite
Fine pearlite	α-Ferrite + Fe_3C	Alternating layers of α-ferrite and Fe_3C that are relatively thin	Harder and stronger than coarse pearlite, but not as ductile as coarse pearlite
Bainite	α-Ferrite + Fe_3C	Very fine and elongated particles of Fe_3C in an α-ferrite matrix	Harder and stronger than fine pearlite; less hard than martensite; more ductile than martensite
Martensite	Body-centered, tetragonal, single phase	Needle-shaped grains	Very hard and very brittle

Martensite



Questions on steel microstructures?

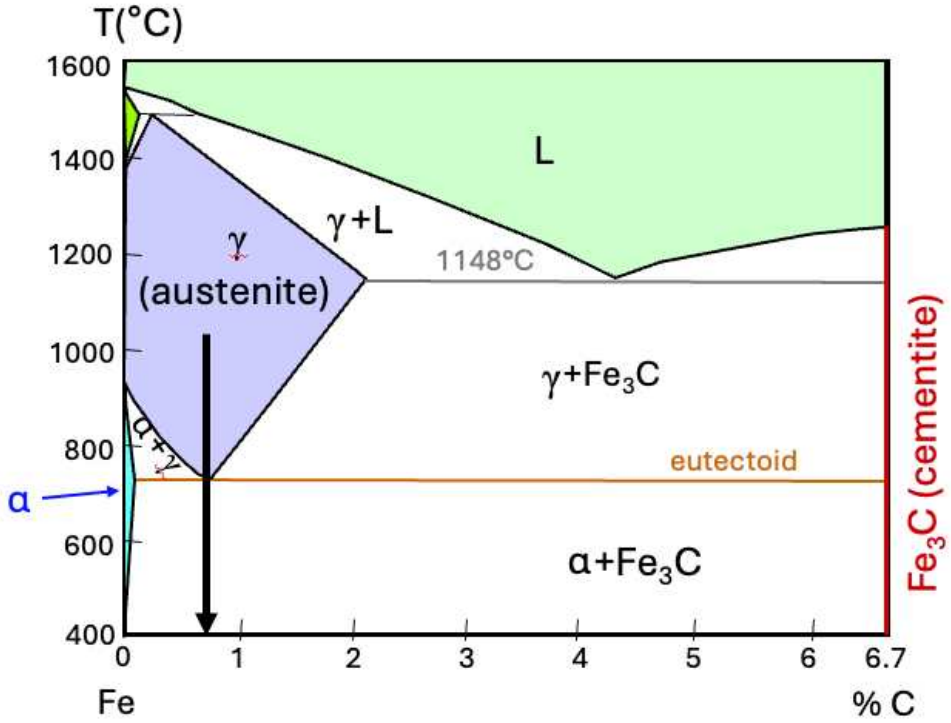
An example

Using the TTT diagram: sketch a heating profile you might use to produce the below microstructures, starting from austenite with **0.7 wt% C**:

a) 100% coarse pearlite

b) 50% fine pearlite and 50% fine bainite

c) 100% martensite



An example

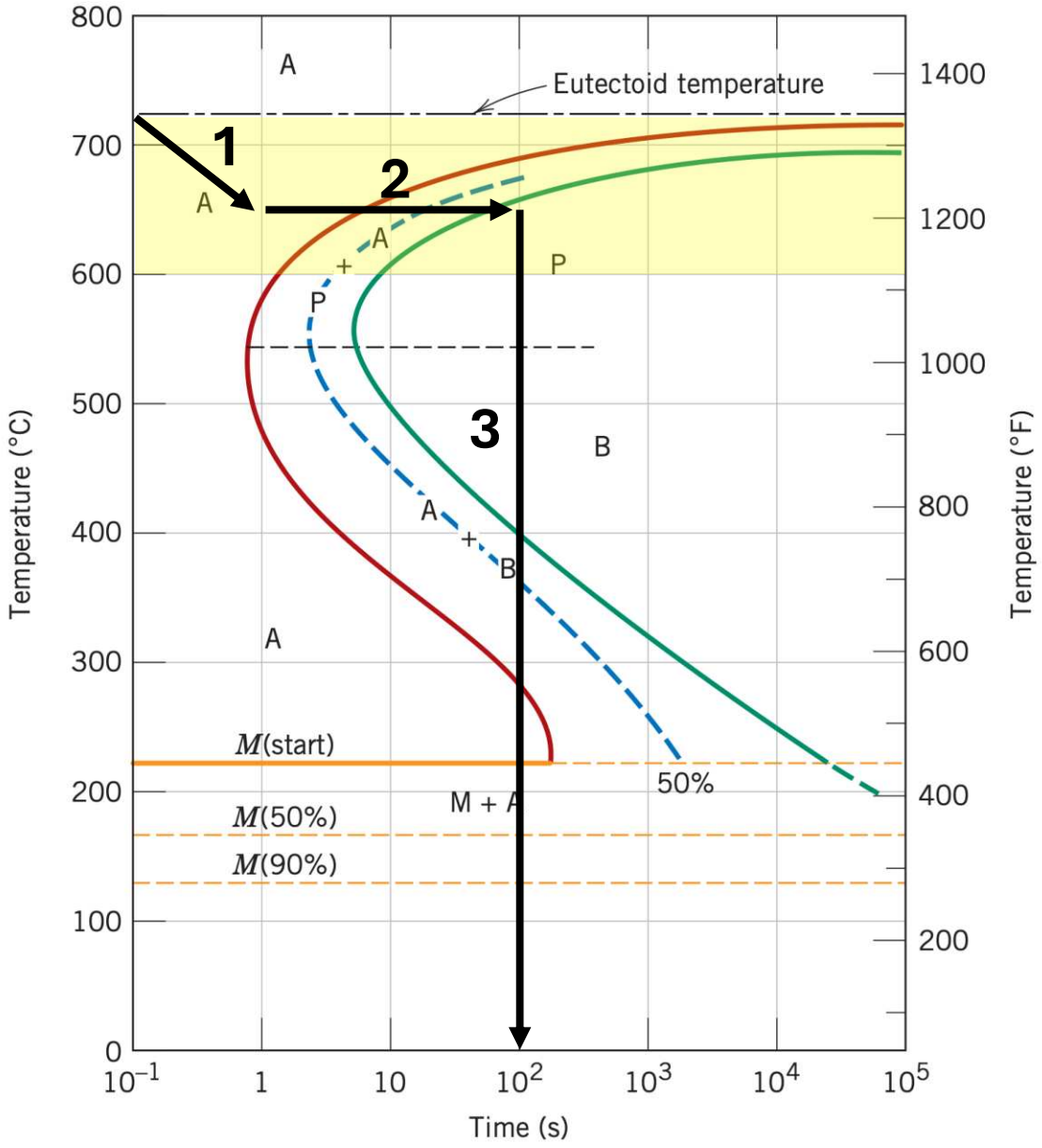
a) 100% coarse pearlite

Remember: coarse pearlite occurs at small undercooling (high temperature)

Step 1: cool to 650 °C

Step 2: hold at 650 °C for ~10^2 sec

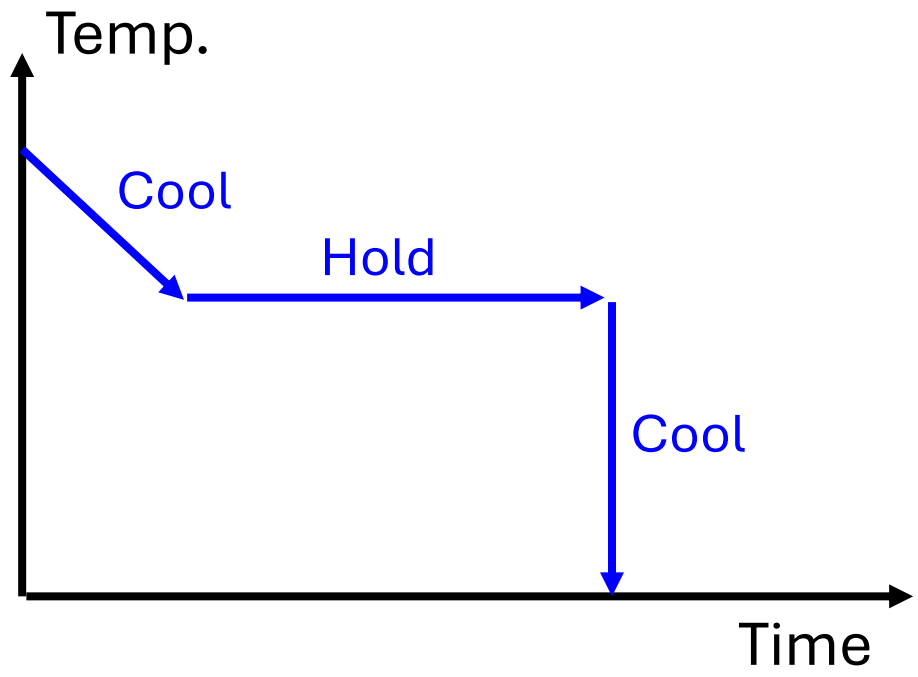
Step 3: fast cool to room temp.

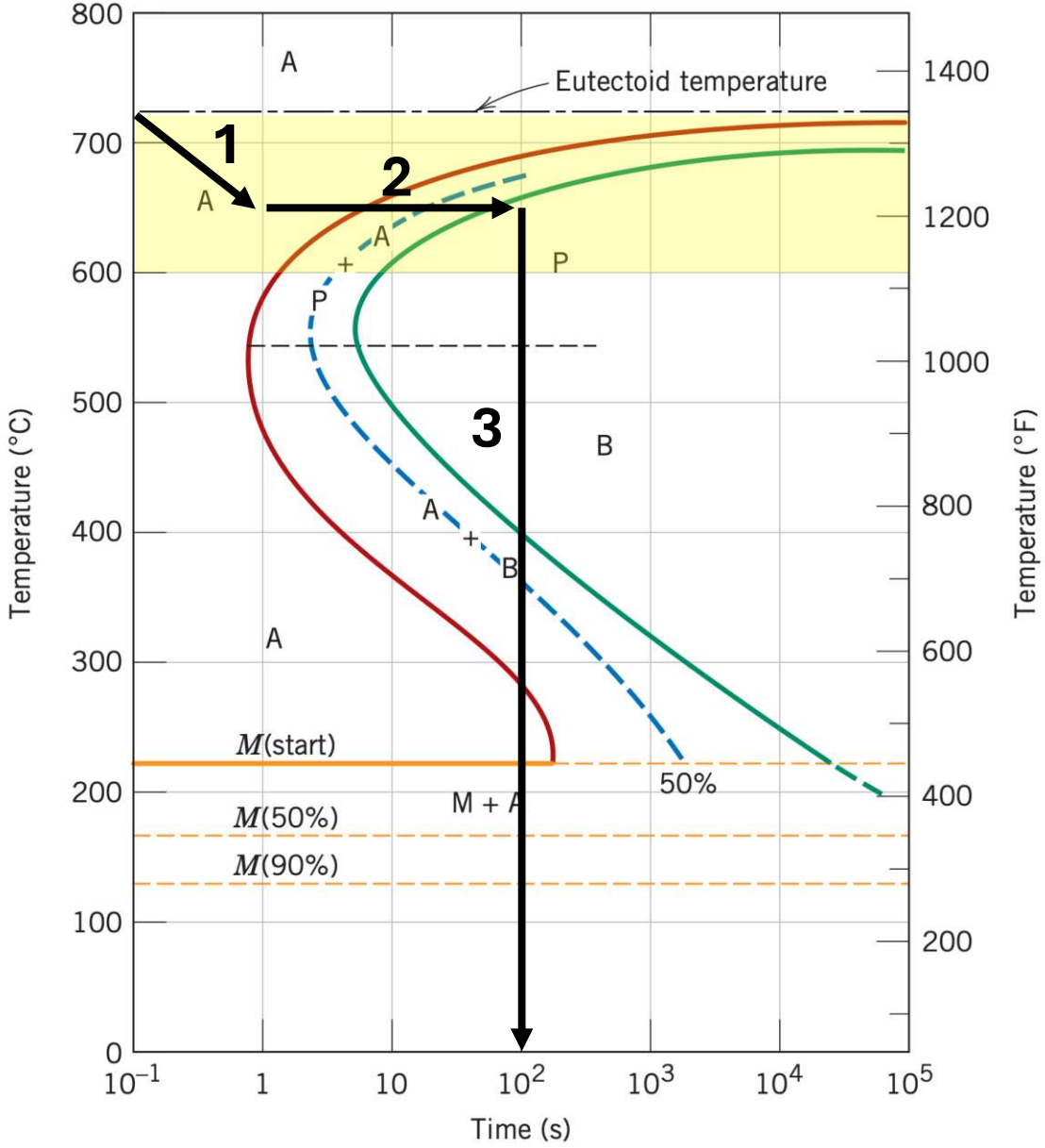


An example

a) 100% coarse pearlite

Remember: coarse pearlite occurs at small undercooling (high temperature)





An example

b) 50% fine pearlite and 50% fine bainite

Remember: fine pearlite occurs at moderate undercooling, whereas bainite occurs at large undercooling

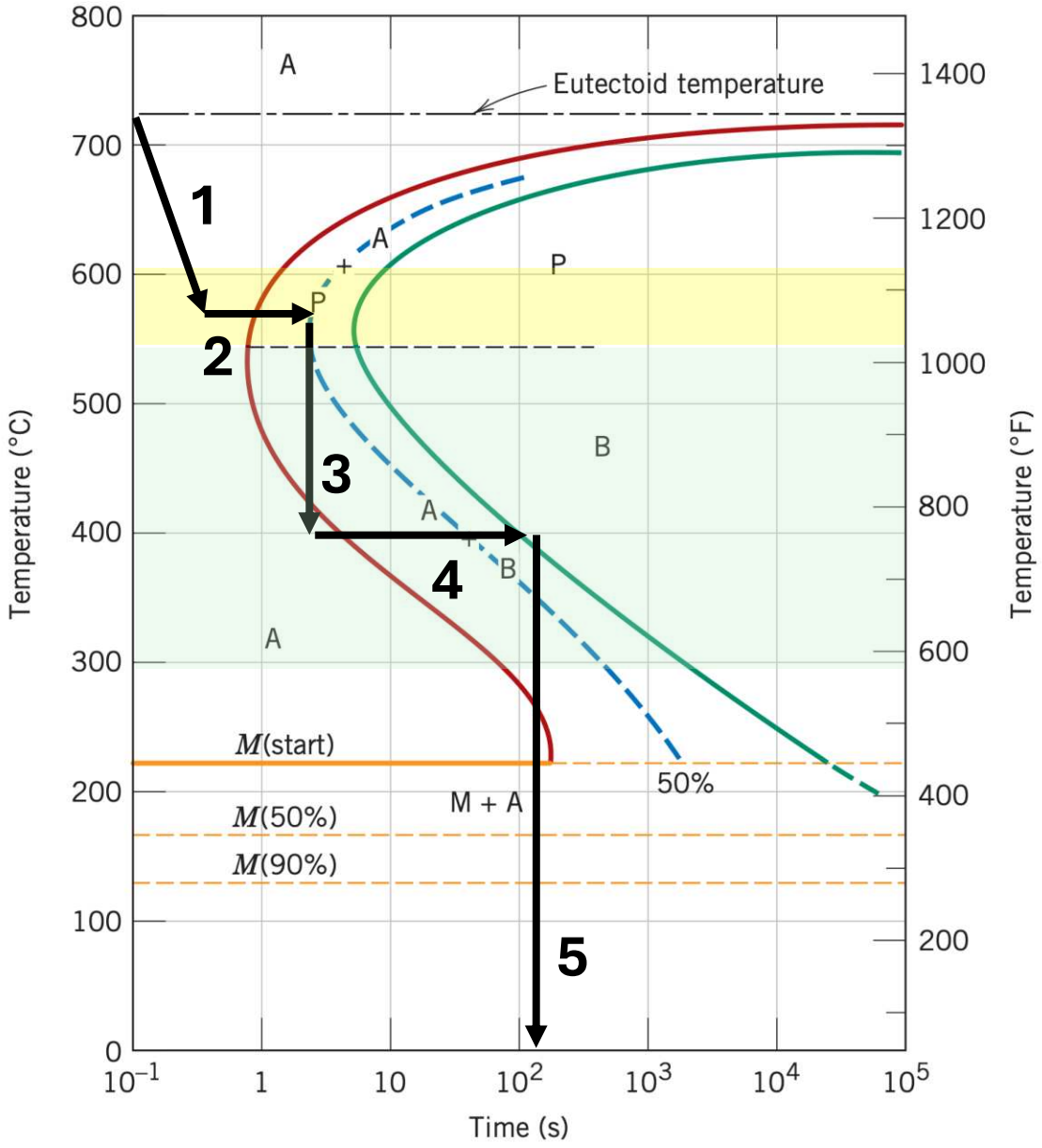
Step 1: cool to 550 °C

Step 2: hold at 550 °C until 50% transf.

Step 3: fast cool to 400 °C

Step 4: hold at 400 °C

Step 5: fast cool to room temp.

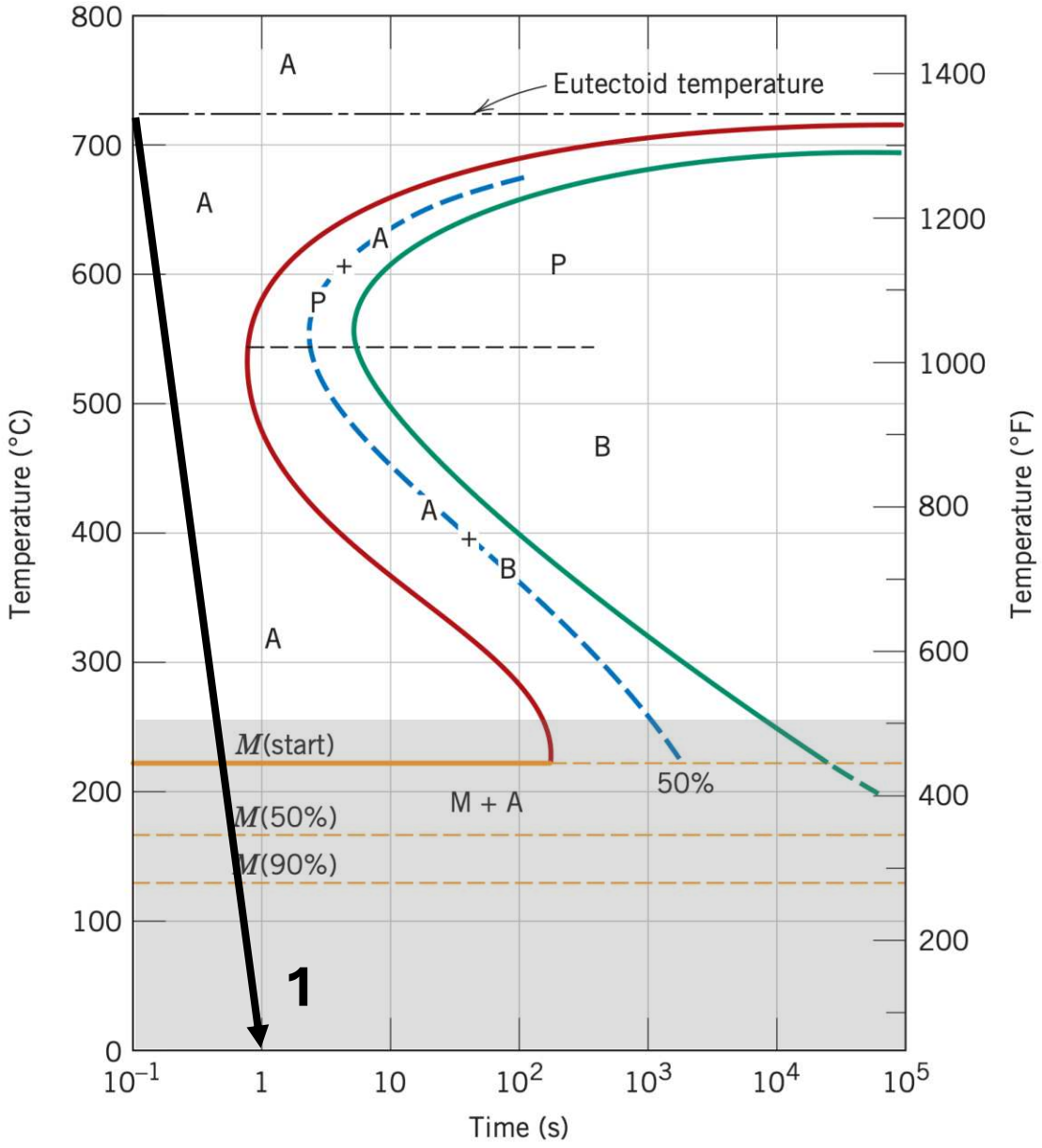


An example

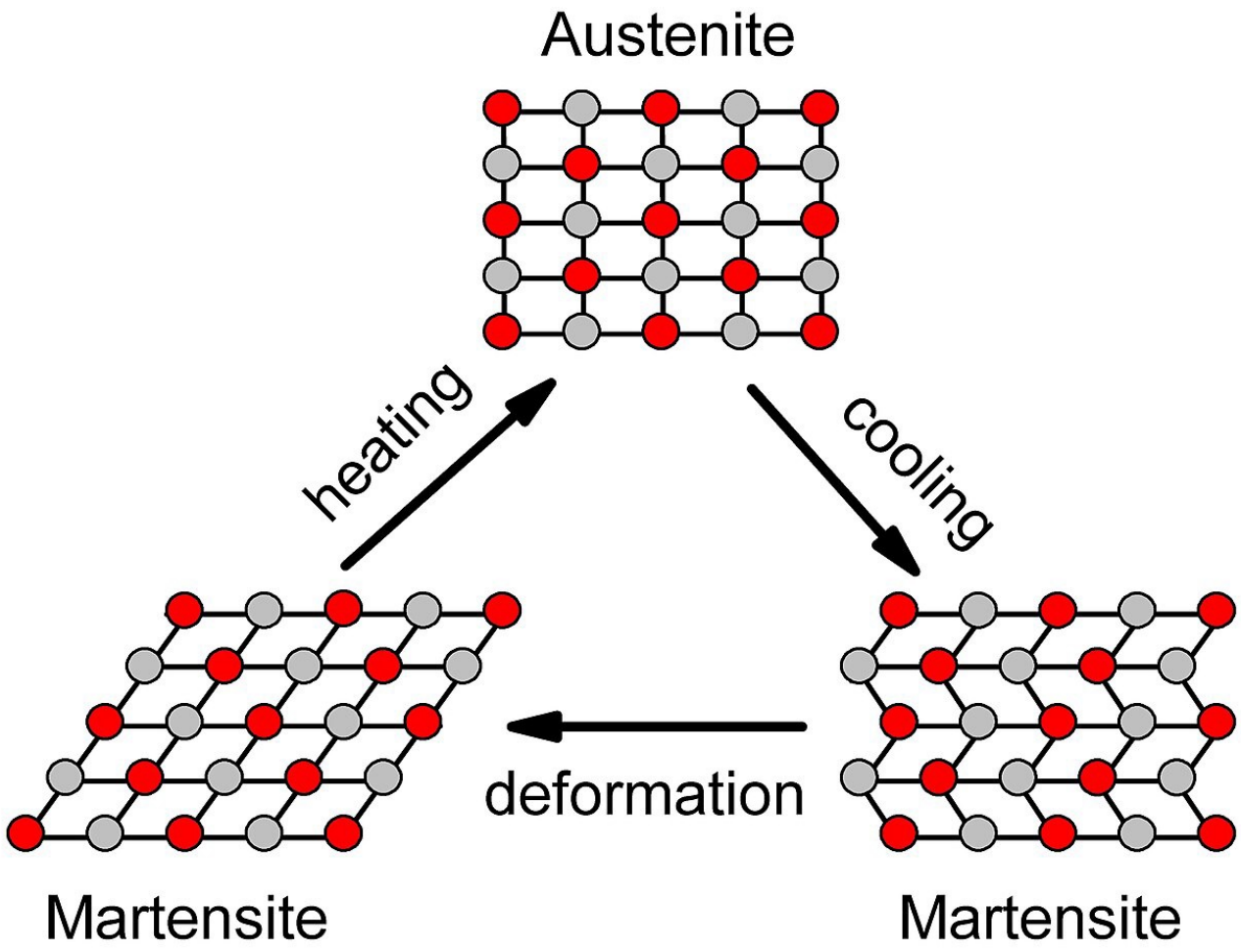
c) 100% martensite

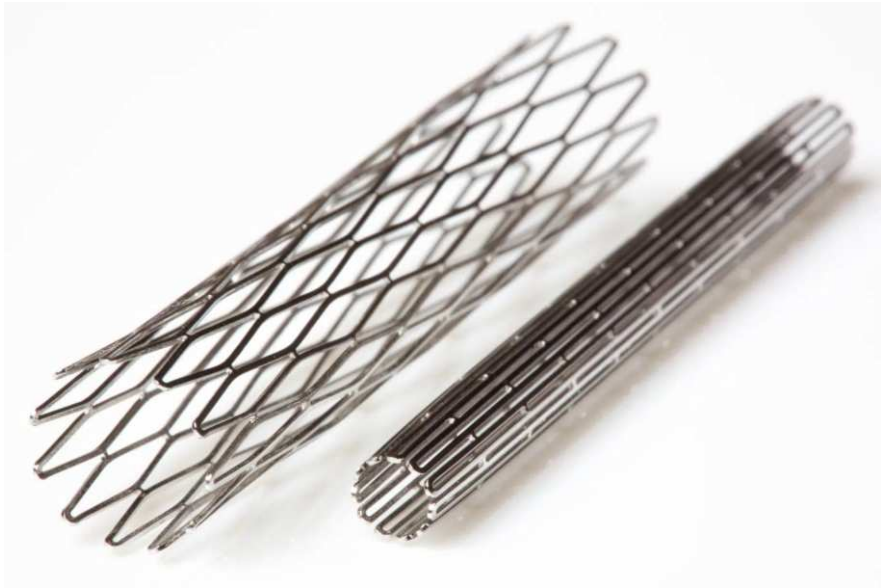
Remember: martensite occurs at very large undercooling

Single step: fast cool to room temp.



If we have time: a demo with Ni-Ti alloys (Nitinol)







"Shape memory"