

Materials Engineering I (MSE 214)

Lecture 11-12: Polymers and Metals Review

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Recap: Fracture Toughness

$$\sigma_c = \sqrt{\frac{2E\gamma}{\pi a}}$$

$$\sigma_c \sqrt{\pi a} = \boxed{\sqrt{2E\gamma}} \rightarrow \text{Material properties}$$

$$\sigma_c \sqrt{\pi a} = \boxed{K_c} \rightarrow \text{Critical stress intensity factor or Fracture Toughness}$$

More generally:

$$K_{Ic} = Y\sigma\sqrt{\pi a}$$

Y : Dimensionless geometric constant

K_c has units of $\text{MPa}\sqrt{m}$

Why is K_c important?

If you know K_c and a , you can solve for stress needed to cause fracture (σ_c)

If you know K_c and the stress in the system (σ), you can solve for the maximum crack size that can be tolerated before fracture (a_c)

Do note that this is for **brittle** fracture!

Failure occurs when

$$K > K_{Ic},$$

or

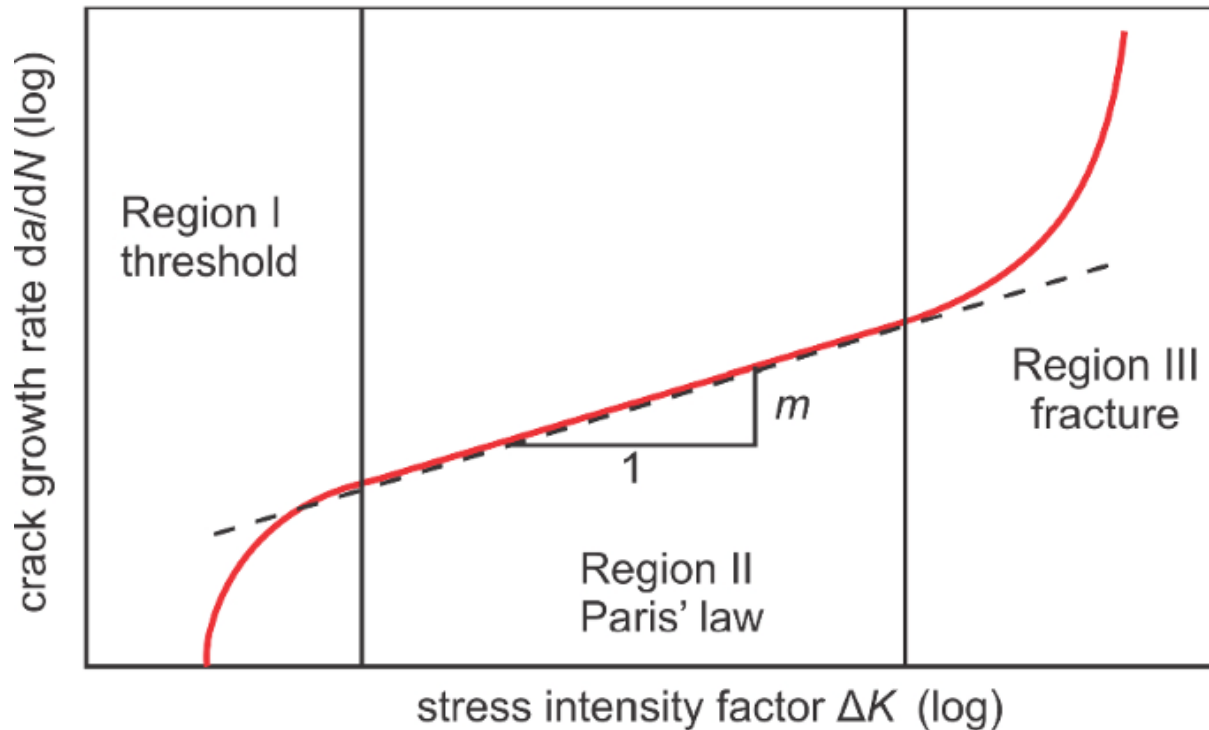
$$\sigma > \sigma_c$$

or

$$a > a_c$$

Paris' Law (Crack growth equation)

Crack growth equations are used to calculate the size of a fatigue crack growing from cyclic loads



Paris' Law

$$\frac{da}{dN} = C(\Delta K)^m$$

C and m are determined experimentally

Paris' law only holds for mid-range of crack growth.

Can be used to estimate cycles to failure

Typical plot of crack growth vs stress intensity range

$$\Delta K = K_{max} - K_{min}$$

Maximum and minimum stress intensity factors in a stress cycle

Paris' Law in action

A large plate contains a crack of length $2a_0 = 10$ mm in the center

The plate is subjected to a constant amplitude cyclic tensile stress ranging from 100 MPa to 200 MPa.

Assume the fatigue crack growth rate is given by Paris' Law with:

$$\frac{da}{dN} = 0.42 \times 10^{-11} (\Delta K)^3$$

1) What is the crack growth rate for a crack of this size?

$$2a = 10 \text{ mm}$$

$$\Delta K = K_{max} - K_{min}$$

$$K = Y\sigma\sqrt{\pi a}$$

$$\Delta K = Y\Delta\sigma\sqrt{\pi a}$$

$$\Delta K = 1(100)\sqrt{\pi \cdot 0.005}$$

$$\Delta K = 12.53 \text{ MPa}\sqrt{\text{m}}$$

$$\frac{da}{dN} = 0.42 \times 10^{-11} (12.53)^3 = 8.26 \times 10^{-9} \text{ m/cycle}$$

Paris' Law in action

A large plate contains a crack of length $2a_0 = 10$ mm in the center

The plate is subjected to a constant amplitude cyclic tensile stress ranging from 100 MPa to 200 MPa.

Assume the fatigue crack growth rate is given by Paris' Law with:

$$\frac{da}{dN} = 0.42 \times 10^{-11} (\Delta K)^3$$

2) Assuming that the fracture toughness of this material is $60 \text{ MPa}\sqrt{\text{m}}$, estimate the number of cycles to failure

$$2a = 10 \text{ mm}$$

$$K_{IC} = 60 \text{ MPa}\sqrt{\text{m}}$$

Let us first determine the critical crack size under these conditions

$$K_{IC} = Y \sigma_{max} \sqrt{\pi a_c}$$

$$a_c = 28.7 \times 10^{-3} \text{ m}$$

At these conditions, complete and rapid fracture occurs at a crack length of 28.7×10^{-3} m.

Paris' Law in action

A large plate contains a crack of length $2a_0 = 10$ mm in the center

The plate is subjected to a constant amplitude cyclic tensile stress ranging from 100 MPa to 200 MPa.

Assume the fatigue crack growth rate is given by Paris' Law with:

$$\frac{da}{dN} = 0.42 \times 10^{-11} (\Delta K)^3$$

Knowing a_c , how do we find the cycles to failure?

$$a_c = 28.7 \times 10^{-3} \text{ m}$$

$$\int_0^{N_f} dN = \int_{a_0}^{a_c} \frac{da}{0.42 \times 10^{-11} (\Delta K)^3}$$

$$N_f = \int_{5 \times 10^{-3}}^{28.7 \times 10^{-3}} \frac{da}{0.42 \times 10^{-11} (\Delta K)^3}$$

$$\Delta K = Y \Delta \sigma \sqrt{\pi a}$$

$$\Delta K = 1(100) \sqrt{(3.14)a}$$

$$\Delta K = 177.2 \sqrt{a}$$

$$N_f = \int_{5 \times 10^{-3}}^{28.7 \times 10^{-3}} \frac{da}{2.34 \times 10^{-5} \cdot a^{\frac{3}{2}}}$$

Paris' Law in action

A large plate contains a crack of length $2a_0 = 10$ mm in the center

The plate is subjected to a constant amplitude cyclic tensile stress ranging from 100 MPa to 200 MPa.

Assume the fatigue crack growth rate is given by Paris' Law with:

$$\frac{da}{dN} = 0.42 \times 10^{-11} (\Delta K)^3$$

$$N_f = \int_{5 \times 10^{-3}}^{28.7 \times 10^{-3}} \frac{da}{2.34 \times 10^{-5} \cdot a^{\frac{3}{2}}}$$

$$N_f = 42791 \int_{5 \times 10^{-3}}^{28.7 \times 10^{-3}} a^{-\frac{3}{2}} da$$

$$N_f = 42791 \left[(-2) a^{-\frac{1}{2}} \right]_{5 \times 10^{-3}}^{28.7 \times 10^{-3}}$$

$$N_f = 7.05 \times 10^5$$

REVIEW OF COURSE

Exam: 26th Jan 2026, 9am

- 40-50% multiple choice
- 50-60% open-ended
- Breakdown of topic: 50% Polymers, 35-40% Metals, 10-15% Composites
- 1 page of handwritten notes (refer to Lecture 1 for details)
- Please write legibly. No marks will be awarded if I cannot read your answer
- Technically allowed to respond in French but English is strongly suggested.

- Do the exercises. If you can do them, you will be a-ok!
- Do not waste time memorizing derivations.
- This is not a chemistry exam, think in terms of A-A and B-B and in functionalities

POLYMERS

50% of exam

What are Polymers?

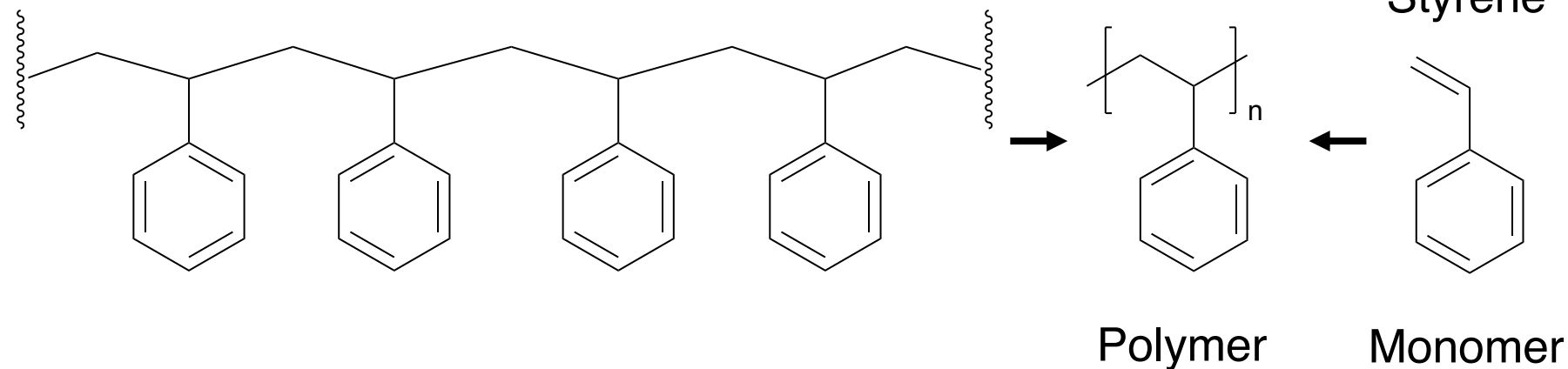
Greek: *Poly-*, “Many” + *-mer(os)*, “Part”

Polymers are large molecules that are composed of many repeating subunits

Styrofoam/Polystyrene



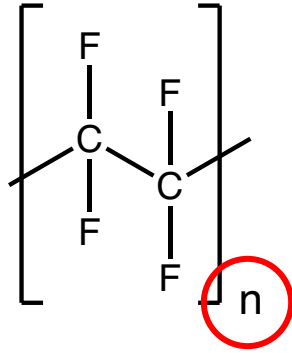
Skeletal Structural Formula



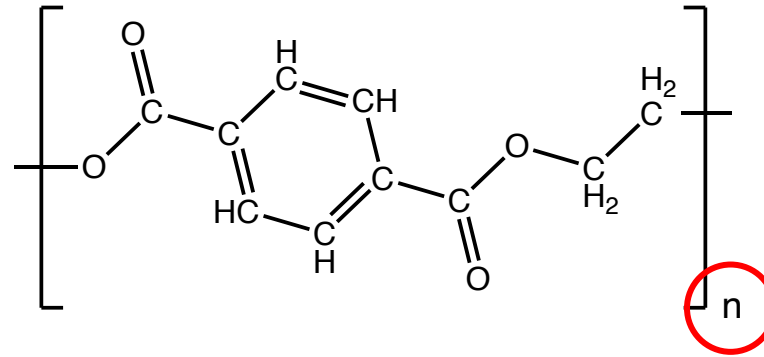
Vertices: C ; 1 line = 1 bond ; H fills up rest
Everything other than C,H needs to be written explicitly

Polymer Length and Degree of Polymerization

Teflon/PTFE
(Polytetrafluoroethylene)



PET
(Poly(ethylene terephthalate))



Polymer represented by [REPEAT UNIT]_n → n tells us the length

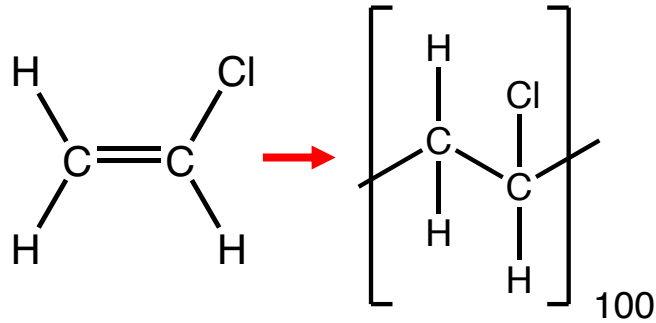
Degree of Polymerization (DP) = Average number of monomeric units in the polymer

For homopolymers (polymers made using one monomer): n = DP

For copolymers (polymers made using x different monomers): $n = \frac{DP}{x}$

Degree of Polymerization (Example)

Homopolymer ($n = DP$)



$$n = 100$$

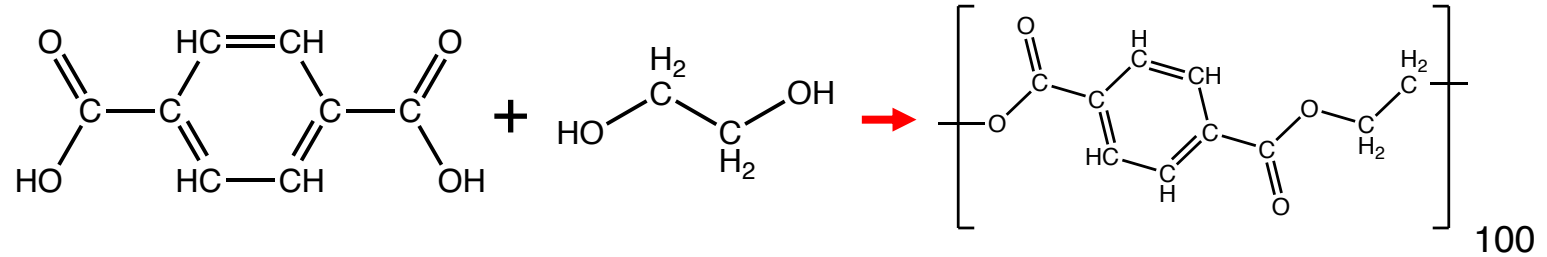
of monomers types = 1

of monomers used to make the polymer = 100

of monomeric units = 100

DP = 100

Copolymer ($n = \frac{DP}{x}$; $x = \#$ of comonomers)



$$n = 100$$

of monomers types = 2

of monomers used to make the polymer = 200

of monomeric units = 200

DP = 200

How Do We Classify Polymers?

Multiple ways of classifying polymers – Depends on the information you want to convey

1. Composition: Number of monomer types

2. Architecture: Monomer arrangement

3. Polymerization Mechanisms

4. Chemical Reaction

5. Physical Properties

.
. .
.

Polymers are complex materials

No universal classification!

The classifications are often interdependent on each other

How Do We Classify Polymers?

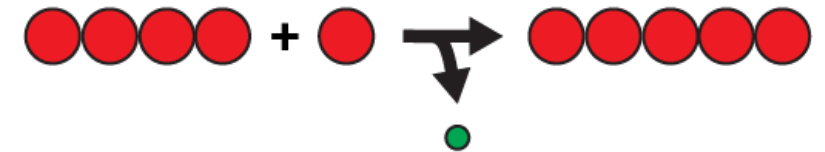
Multiple ways of classifying polymers – Depends on the information you want to convey

4. Chemical Reaction

Addition
polymerization: Polymer formed by addition reactions
No atoms lost during reaction

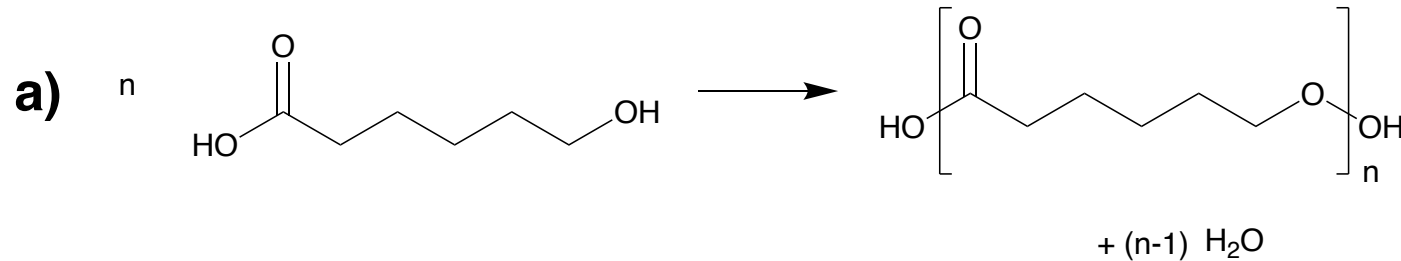


Condensation
polymerization: Polymer formed by condensation reactions
Some atoms get kicked out during the reaction
Small molecule byproduct
Polymer is *condensed* w.r.t. to the monomers

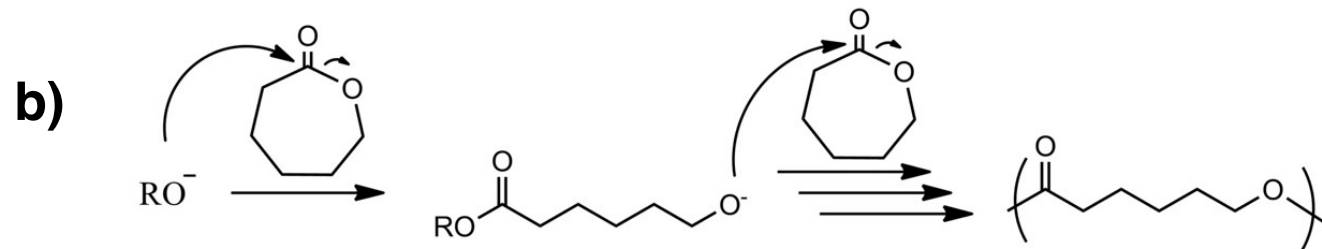


Example questions about classifications

E1 Q4: Classify the polymers that are formed from the reactions below



Ans: Homopolymer. Linear polymer. Step-growth polymer.
Condensation polymerization



Ans: Homopolymer. Linear polymer. Chain-growth polymer.
Addition polymerization

Ignoring end groups,
these are the same!

Same polymer can be made via
multiple routes!

Without specialist knowledge you
cannot tell just from looking at it /
the name of the polymer

Number Average and Weight Average Molecular Weight (M_n , M_w)

**Number Average
Molecular Weight (M_n)**

$$M_n = \frac{\sum N_x M_x}{\sum N_x}$$

N_x is the number of moles of polymer whose weight is M_x

M_n is biased towards the low molecular weight fraction

**Weight Average
Molecular Weight (M_w)**

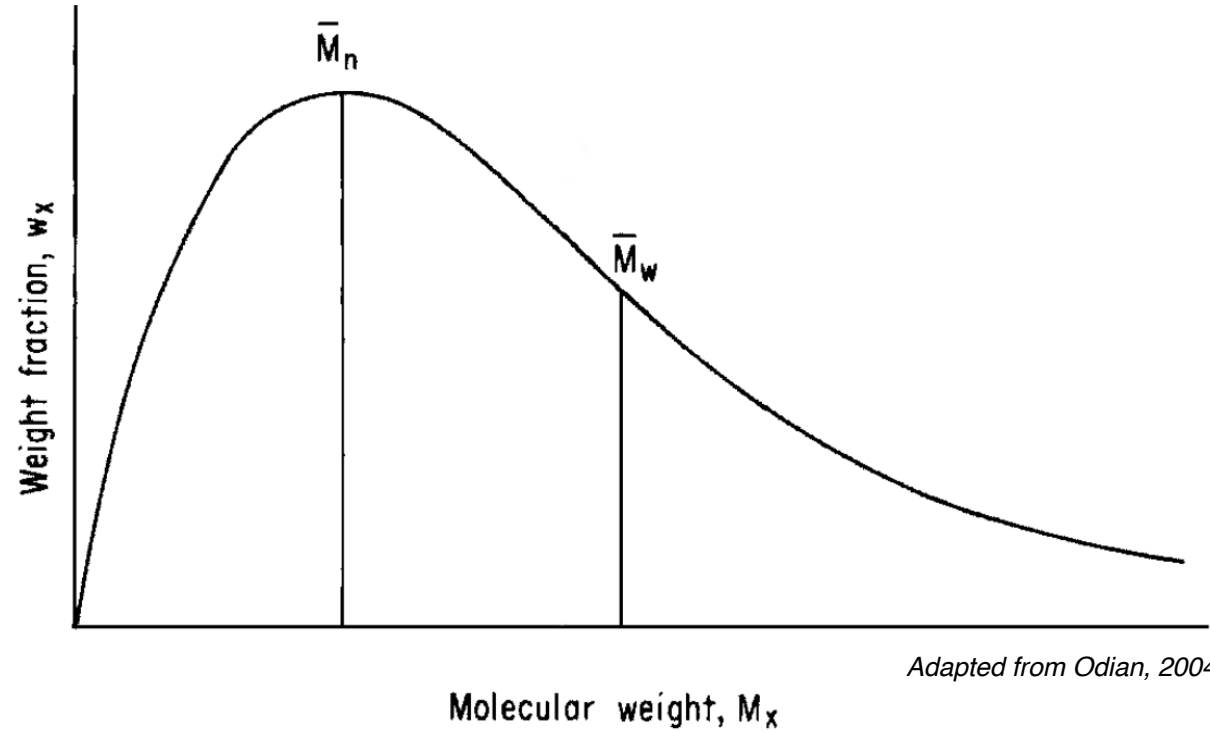
$$M_w = \frac{\sum N_x M_x^2}{\sum N_x M_x}$$

N_x is the number of moles of polymer whose weight is M_x

M_w is biased towards the high molecular weight fraction

Different characterization methods will give different types of molecular weights!

Distribution and Dispersity (\mathfrak{D})



M_n is biased towards the low molecular weight fraction

M_w is biased towards the high molecular weight fraction

Dispersity* (\mathfrak{D})

$$\mathfrak{D} = \frac{M_w}{M_n}$$

\mathfrak{D} is a parameter that measures the width of the molecular weight distribution of a polymer samples

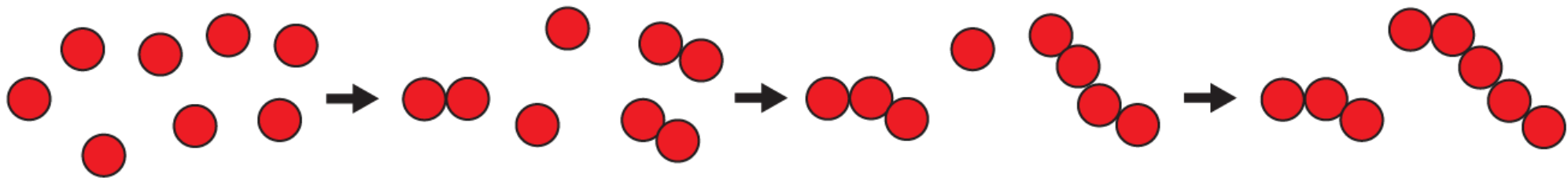
High dispersity = broad distribution
Low dispersity = narrow distribution

\mathfrak{D} cannot be smaller than 1

*Sometimes written as Polydispersity Index (PDI). This term has since been deprecated but can be found in older literature.

STEP-GROWTH POLYMERIZATION

Step-growth*: Polymer grows via the reaction between any pairs of reactive species

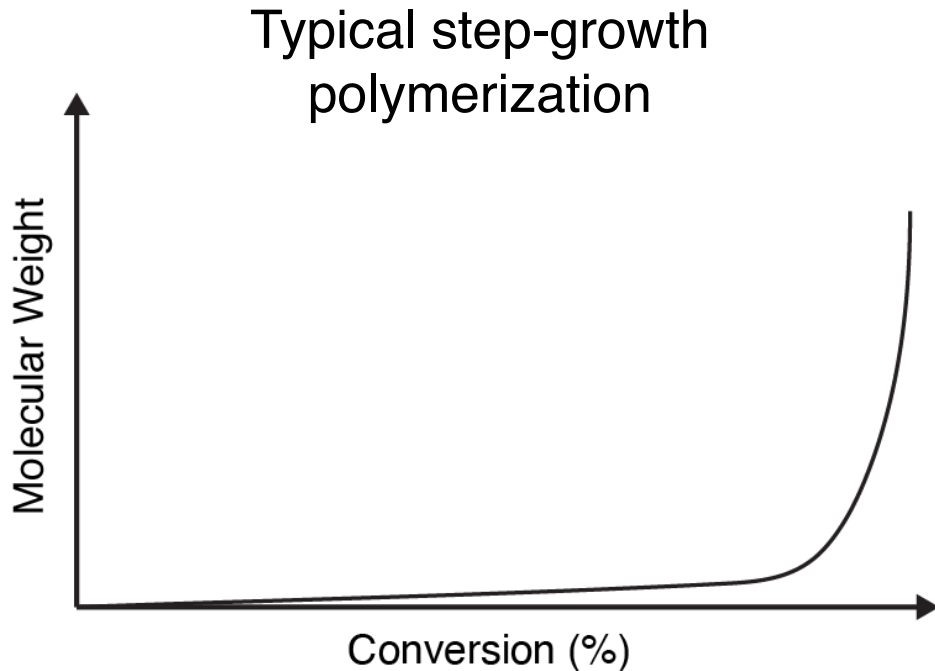


Step-growth Polymerization and Molecular Weight

Step-growth: Polymer grows via the reaction between any pairs of reactive species

Recall: Molecular weight influences polymer properties

How do we control molecular weight during step-growth polymerization?



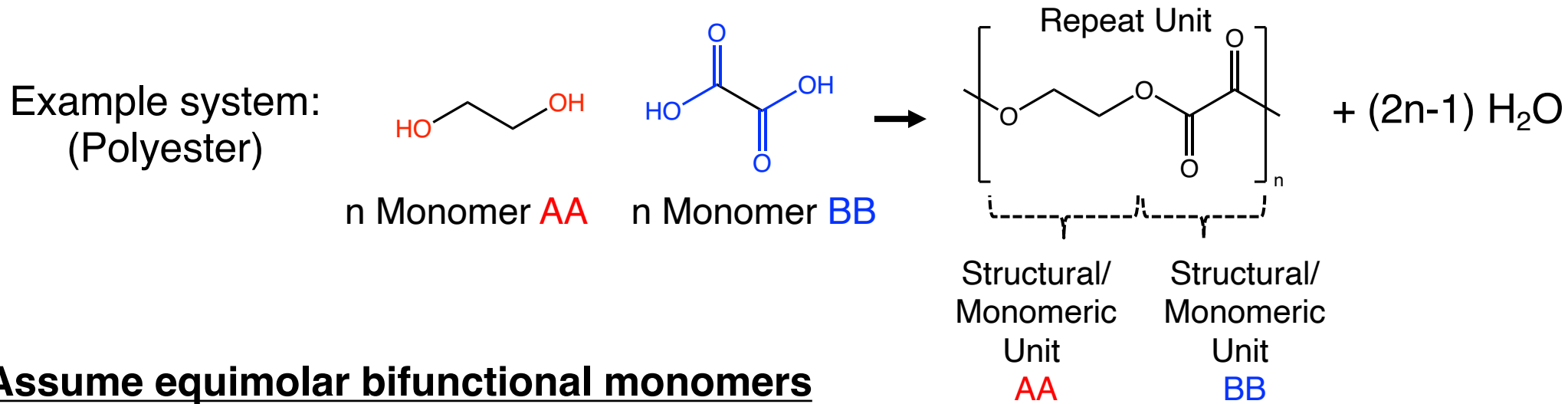
monomer + monomer	→ dimer
dimer + monomer	→ trimer
dimer + dimer	→ tetramer
trimer + monomer	→ tetramer
trimer + dimer	→ pentamer
trimer + trimer	→ hexamer
tetramer + monomer	→ pentamer
tetramer + dimer	→ hexamer
tetramer + trimer	→ heptamer
tetramer + tetramer	→ octamer
	⋮

Assume reactivity of functional groups are independent of x -mer length

Molecular weight increases slowly!

Step-growth Polymerization and Molecular Weight

For a desired polymer length, how much monomer do we need to react?



Assume equimolar bifunctional monomers

Conversion (p):

$$p = \frac{[M]_0 - [M]}{[M]_0}$$

Fraction of reactant that has reacted at time t

$[M]_0$ = Concentration of unreacted **groups OH or COOH** at $t = 0$

$[M]$ = Concentration of unreacted **groups OH or COOH** at t

Number average degree of polymerization (\bar{X}_n)

$$\bar{X}_n = \frac{[M]_0}{[M]} = \frac{1}{1-p}$$

Carothers Equation

$$\frac{\text{Total number of molecules initially present}}{\text{Total number of molecules at time } t}$$

Average number of **monomeric units** per chain

Step-growth Polymerization and Molecular Weight

Number average degree of polymerization (\bar{X}_n): $\bar{X}_n = \frac{[M]_0}{[M]} = \frac{1}{1-p}$

Carothers Equation

Total number of molecules initially present
Total number of molecules at time t

Average number of **monomeric units** per chain



Number average molecular weight $\bar{M}_n = \frac{\text{total weight of polymers}}{\text{total number of polymers}}$

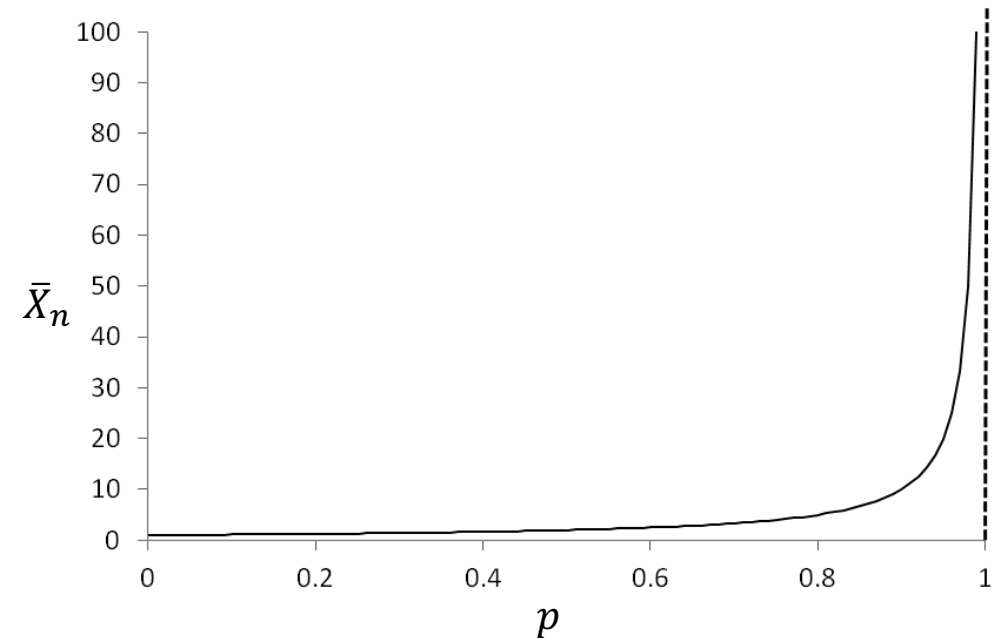
$$= M_0 \bar{X}_n + M_{eg} \approx M_0 \bar{X}_n, \text{ i.e. } M_{eg} \text{ is small}$$

$$= \frac{M_0}{1-p}$$

M_0 = Mean of the molecular weights of the two monomeric units

M_{eg} = Molecular weight of the end groups

p = Conversion



Assuming equimolar reagents:

To achieve high molecular weight polymers, the reaction needs to be very near completion!

At $p = 0.9$, $\bar{X}_n = 10$

At $p = 0.98$, $\bar{X}_n = 50$

At $p = 0.999$, $\bar{X}_n = 1000$

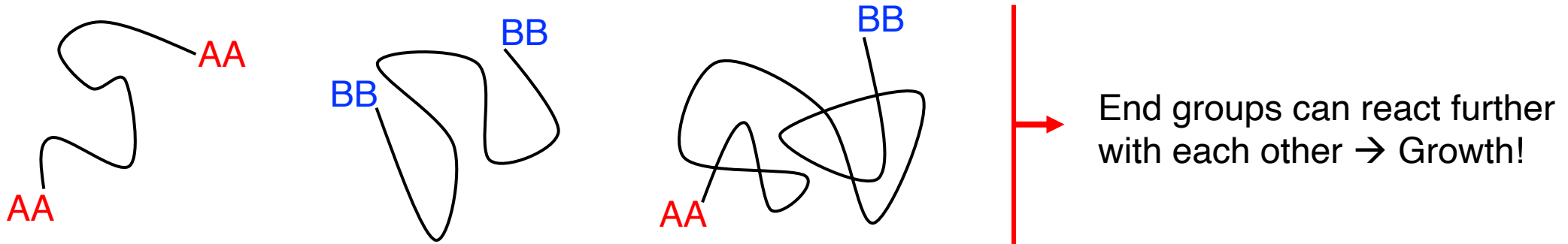
High Temperatures
 Long reaction times

Controlling Molecular Weight in Step-Growth Polymerization

At $p = 0.98$, $\bar{X}_n = 50$
At $p = 0.99$, $\bar{X}_n = 100$
At $p = 0.999$, $\bar{X}_n = 1000$

At large p , small changes in p leads to large changes in \bar{X}_n .
Not practical to control \bar{X}_n solely using p

Even if you could stop the reaction perfectly, what happens if the polymers are heated again?



Nonstoichiometric reaction → Polymerization stops when one reagent is completely used up

1. Adjust relative concentration of bifunctional reagents
2. Introduce monofunctional monomer (chain stopper)

Controlling Molecular Weight in Step-Growth Polymerization

Case 1. **AA** and **BB**, with **BB** in excess

$$\bar{X}_n = \frac{1+r}{1+r-2rp}, \quad r = \frac{N_A}{N_B} \leq 1$$

$$\text{If } N_A = N_B \rightarrow r = 1 \rightarrow \bar{X}_n = \frac{1}{1-p}$$

If $p = 1 \rightarrow \bar{X}_n = \frac{1+r}{1-r}$ Growth is now limited!
(Realistically, p is never 1)

Some perspective:

At $p = 1, r = 0.99, \bar{X}_n = 201$

At $p = 1, r = 0.999, \bar{X}_n = 2001$

At $p = 0.99, r = 0.99, \bar{X}_n = 67$

At $p = 0.99, r = 1, \bar{X}_n = 100$

Stoichiometric control is important!

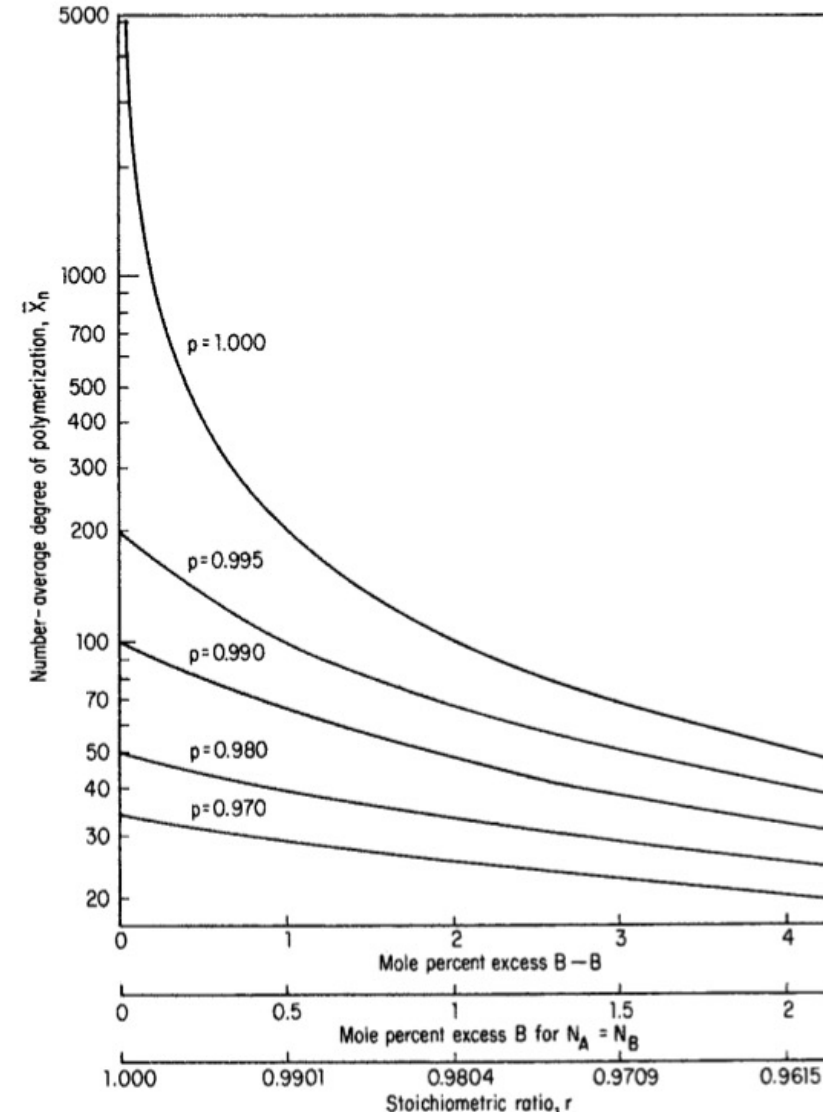


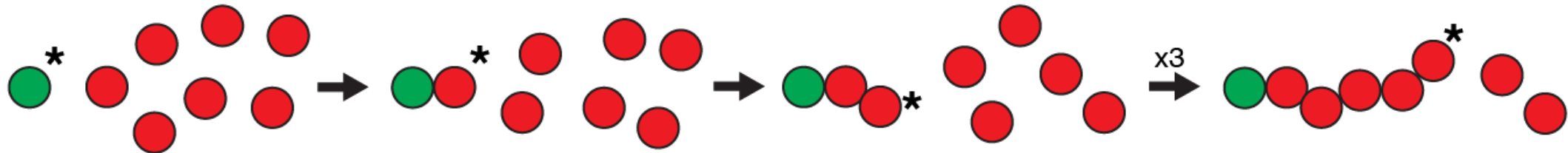
Fig. 2-8 Dependence of the number-average degree of polymerization \bar{X}_n on the stoichiometric ratio r for different extents of reaction p in the polymerization of A-A with B-B.

*Case 2 will be described in an exercise

Adapted from Odian 2004

CHAIN-GROWTH POLYMERIZATION

Chain-growth*: Polymer grows via the reaction of monomer(s) onto **active site(s)** on the polymer chain
Active site(s) regenerated at the end of each growth step



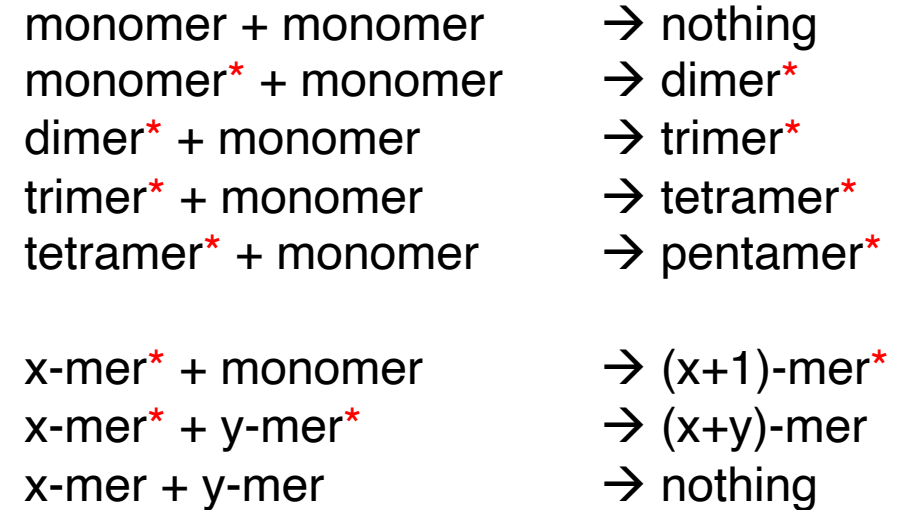
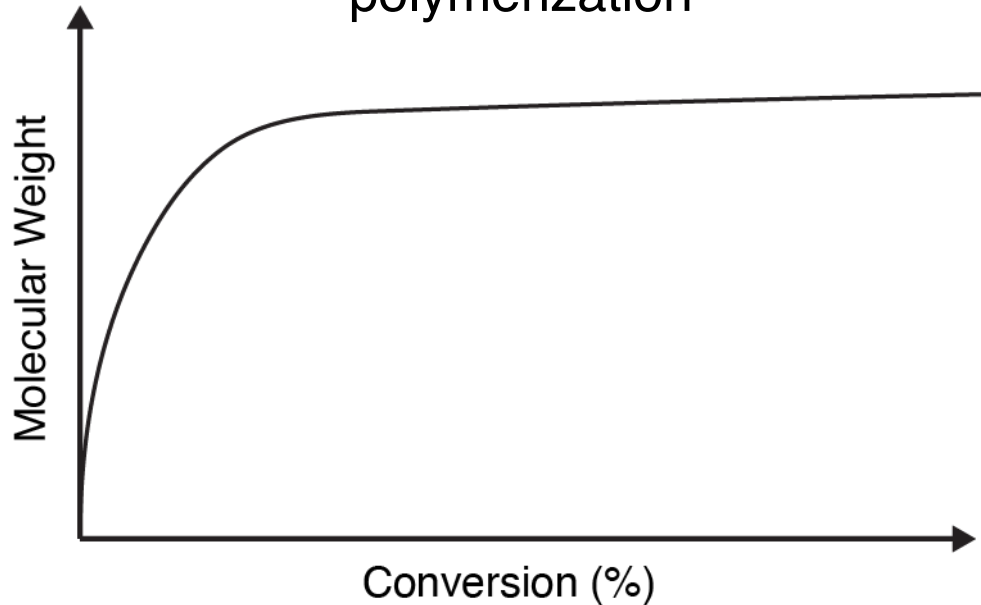
Chain-growth Polymerization and Molecular Weight

Chain-growth: Polymer grows via the reaction of monomer(s) onto **active site(s)** on the polymer chain

Recall: Molecular weight influences polymer properties

How do we control molecular weight during chain-growth polymerization?

Typical chain-growth polymerization



Only molecules with * can react!

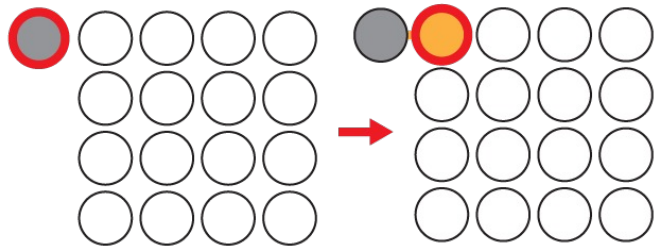
Only a limited number of * in system

But molecules with * grow quickly!

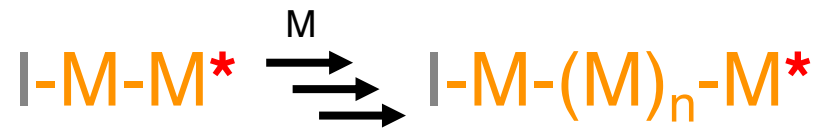
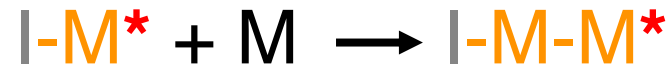
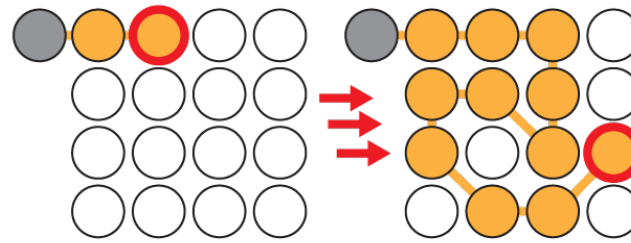
The other monomers are not doing anything

Chain-growth Polymerization: The Three Phases

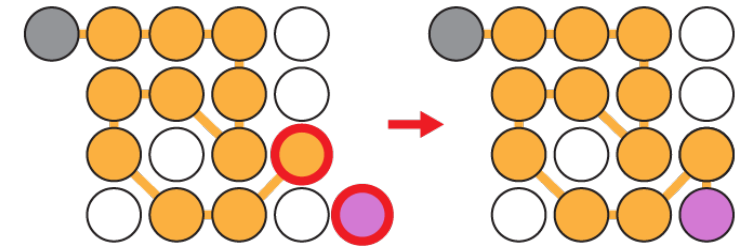
Initiation



Propagation

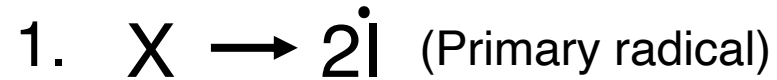


Termination



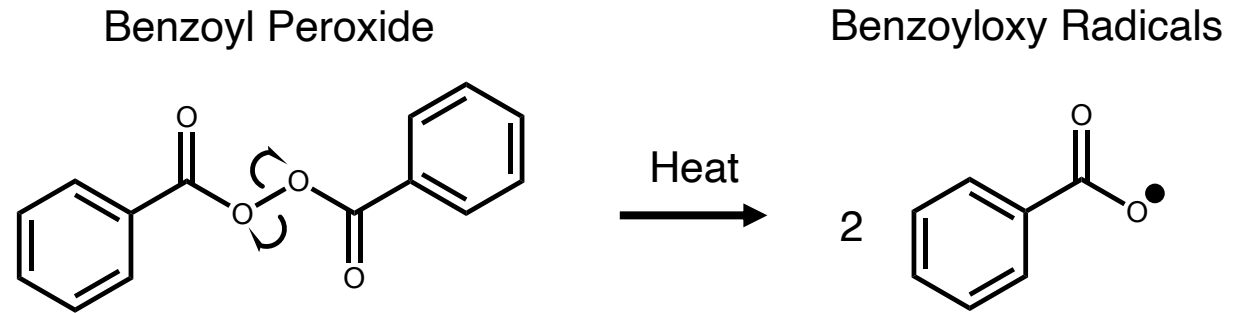
Chain-growth Polymerization: Initiation

Initiation → Two reactions

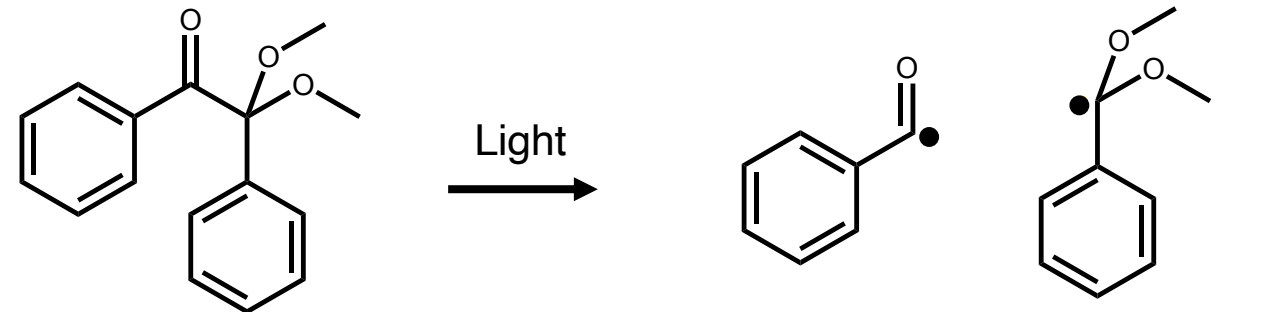


Depending on the initiator, primary radicals can be formed via heat, redox reactions, radiation, and electricity.

One of the reasons why some polymers are cured with heat or light!



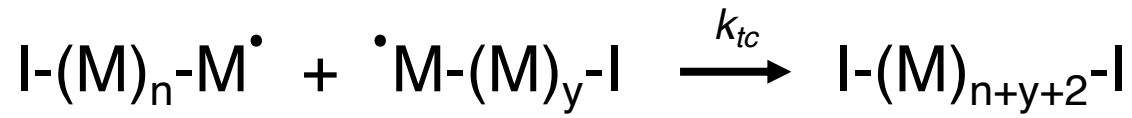
2,2-Dimethoxy-2-phenylacetophenone



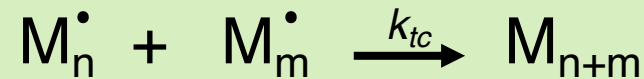
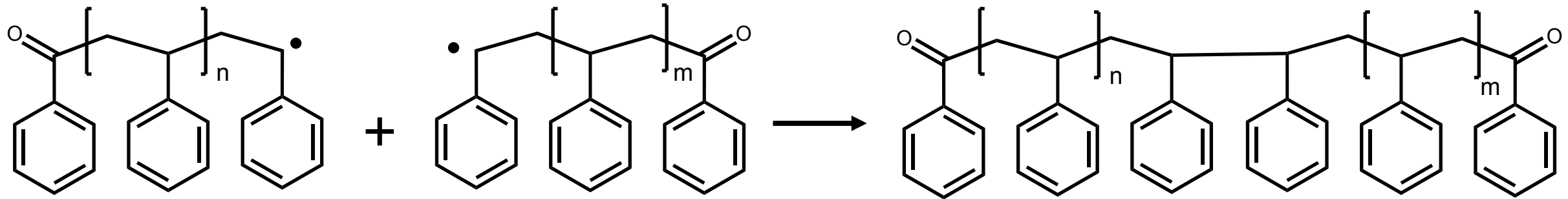
Chain-growth Polymerization: Termination

Termination → 2 types

Coupling



k_{tc} = rate constant for termination coupling



2 polymer chains → 1 polymer chain

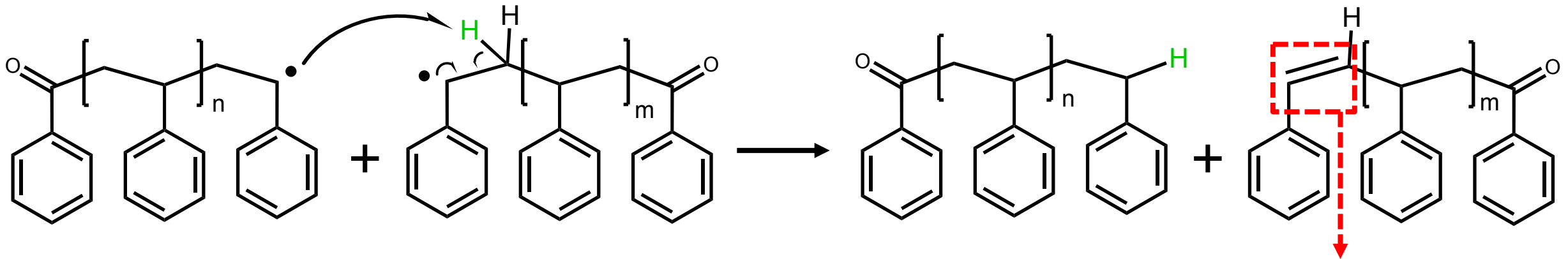
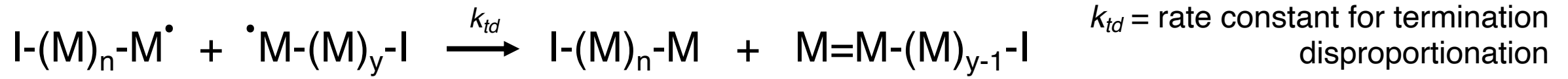
“Dead” polymer → No more radical / active site

→ How does this impact molecular weight?

Chain-growth Polymerization: Termination

Termination → 2 types

Disproportionation



$M_n^\bullet + M_m^\bullet \xrightarrow{k_{td}} M_n + M_m$
2 polymer chains → 2 polymer chains
“Dead” polymer → No more radical / active site



How does this impact molecular weight?

Chain-growth Polymerization: Molecular Weight

How many monomers are added to each radical chain before termination?

Kinetic chain length ν : Average number of monomers consumed per radical which initiates a polymer chain

$$\nu = \frac{\text{Rate of monomer addition to chain}}{\text{Rate of new chain formation}}$$

$$\nu = \frac{R_p}{R_i} = \frac{R_p}{R_t} \quad \text{Steady state approximation: initiation = termination rate}$$

$$R_p = k_p [M] \left(\frac{f k_d [I]}{k_t} \right)^{\frac{1}{2}}$$

$$R_i = 2 f k_d [I]$$

(For thermal initiation)

$$\nu = \frac{k_p [M] \left(\frac{f k_d [I]}{k_t} \right)^{\frac{1}{2}}}{2 f k_d [I]} = \frac{k_p [M]}{2 (f k_d k_t [I])^{\frac{1}{2}}}$$

Changing $[M]$ or $[I]$ to change kinetic chain length will also change the rate of polymerization

Chain-growth Polymerization: Molecular Weight

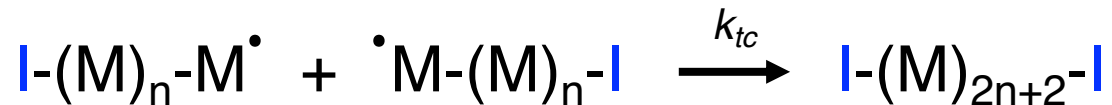
Number average degree of polymerization \bar{X}_n is related to ν

Termination by coupling: $\bar{X}_n = 2\nu$

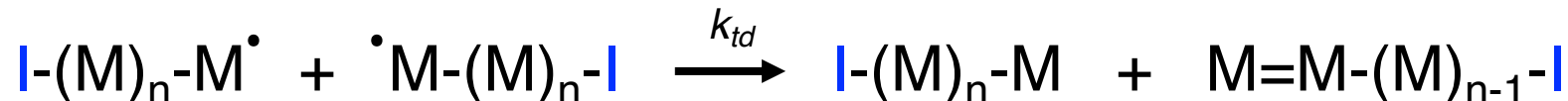
Termination by disproportionation: $\bar{X}_n = \nu$

Number average molecular weight: $M_n = M_o \bar{X}_n$
(M_o is the molecular weight of the monomer)

Terminate by coupling



Terminate by disproportionation



We can use the number of initiator fragments per chain to determine the mode of termination

Chain-growth Polymerization: Molecular Weight

Number average degree of polymerization \bar{X}_n is related to ν

Let a be the fraction of chains that terminate by coupling

→ $(1 - a)$ is the fraction of chains that terminate by disproportionation

Let b be the average number of initiator fragments per polymer → $b = \frac{\text{Total number of initiator fragments}}{\text{Total number of polymer molecules}}$

b is a value between 1 and 2 and represents the extent of mixed mode termination

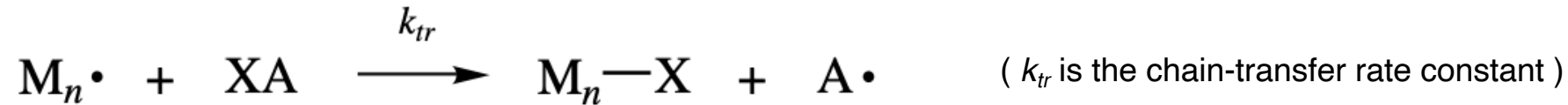
$$\bar{X}_n = b\nu = \frac{2\nu}{2-a} = \frac{2R_p}{(2-a)R_t} = \frac{2k_p[M]}{4-2a(fk_d k_t [I])^{\frac{1}{2}}} \quad R_p = k_p[M] \left(\frac{fk_d[I]}{k_t} \right)^{\frac{1}{2}}$$

Two Problems:

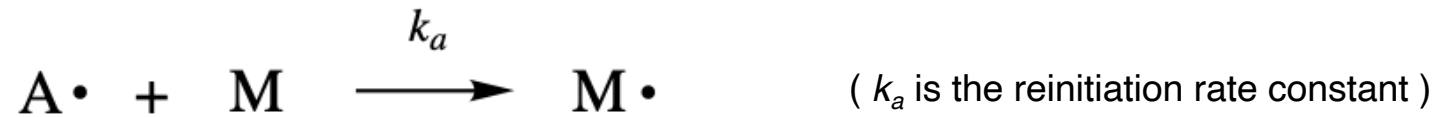
1. Degree of polymerization and rate of polymerization are coupled
2. Experimental degree of polymerization observed to be lower than predicted

Chain-growth Polymerization: Chain Transfer

Premature termination via transfer of radical to another species



XA could be monomer, initiator, solvent, polymer, or other substance.
X is the atom or species transferred to the chain



Chain transfer results in the production of a new radical $\text{A}\cdot$, which reinitiates polymerization

Chain transfer \neq termination of radical

Chain transfer just causes a premature decrease in the size of the propagating polymer chain

Important: Chain Growth \neq Step Growth

Step Growth

$$\bar{X}_n = \frac{[M]_0}{[M]} = \frac{1}{1 - p}$$

Chain Growth

$$\bar{X}_n = \frac{2 k_p [M]}{4 - 2a (f k_d k_t [I])^{\frac{1}{2}}}$$

\bar{X}_n = Average number of monomeric units in the polymer

Step Growth: All monomers reacting at the same time.

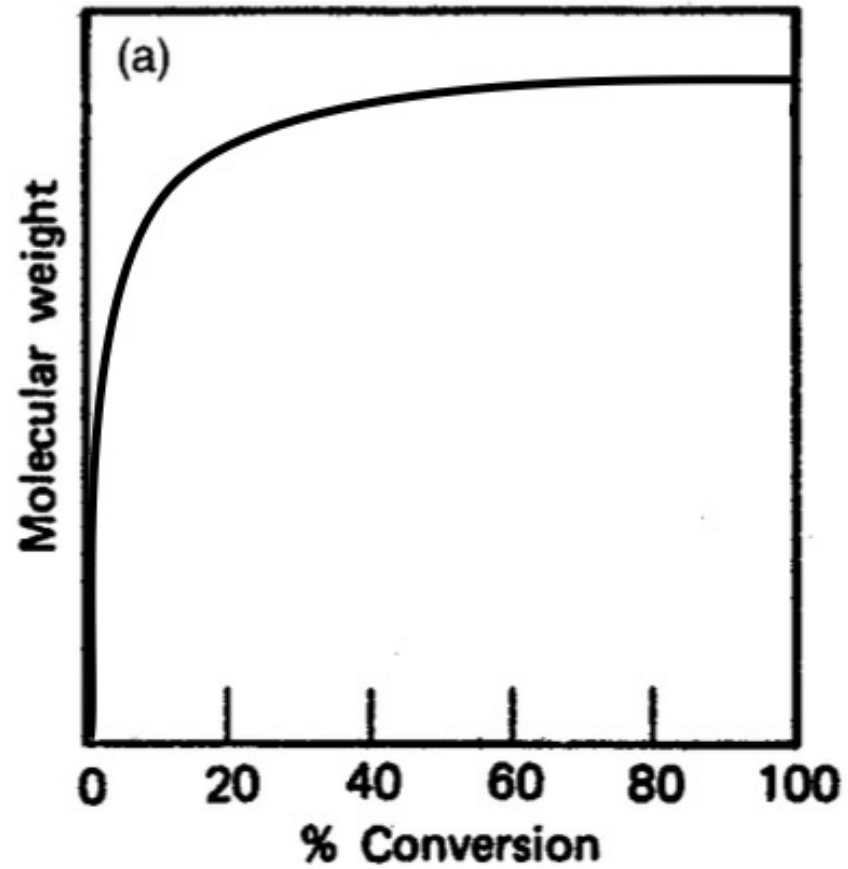
Can assume average length of each chain = total number of initial monomers divided by total number of current chains.

Chain Growth: Only some monomers reacted

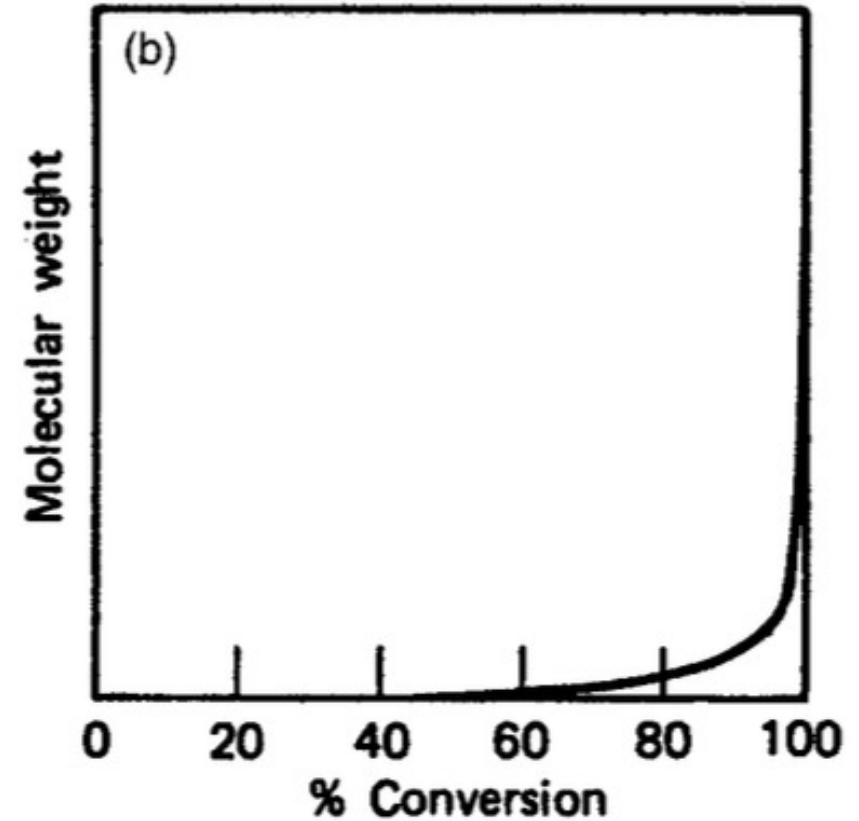
$\frac{[M]_0}{[M]}$ provides no meaningful information

Molecular Weight Evolution: Step vs Chain

Chain-growth Polymerization

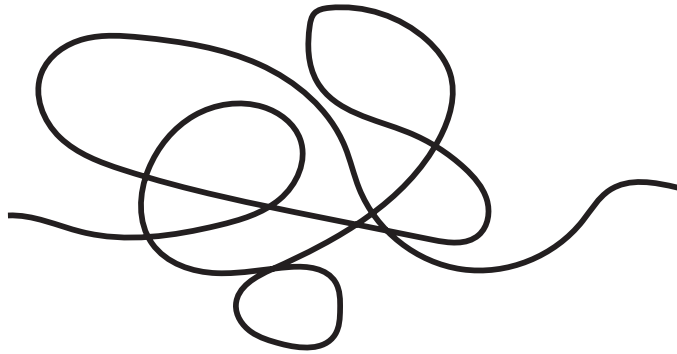


Step-growth Polymerization

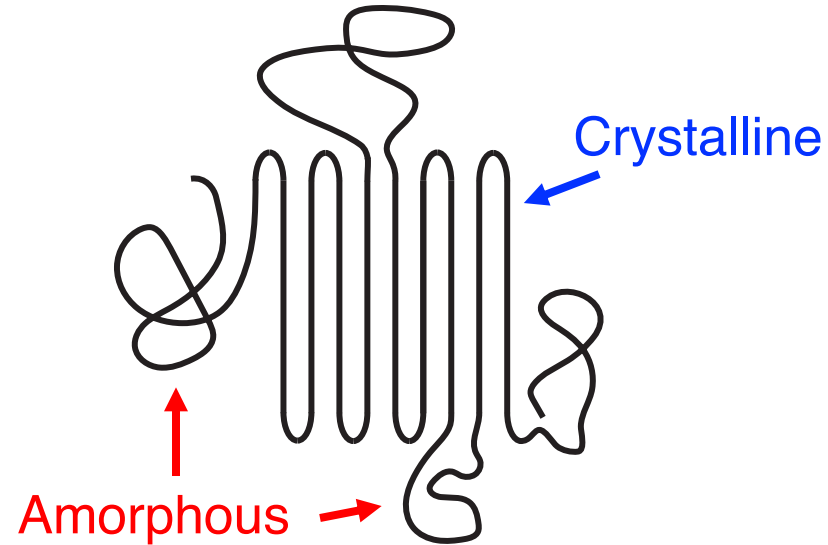


How do polymers crystallize?

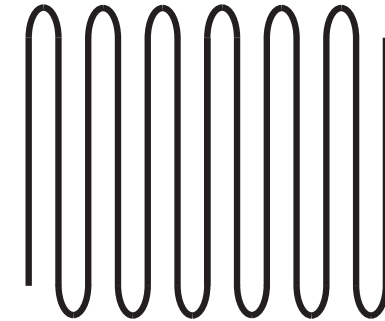
Amorphous



Semi-crystalline



Crystalline



Crystallization is thermodynamically favorable!

Lowers energy state of the polymer

Polymers states:

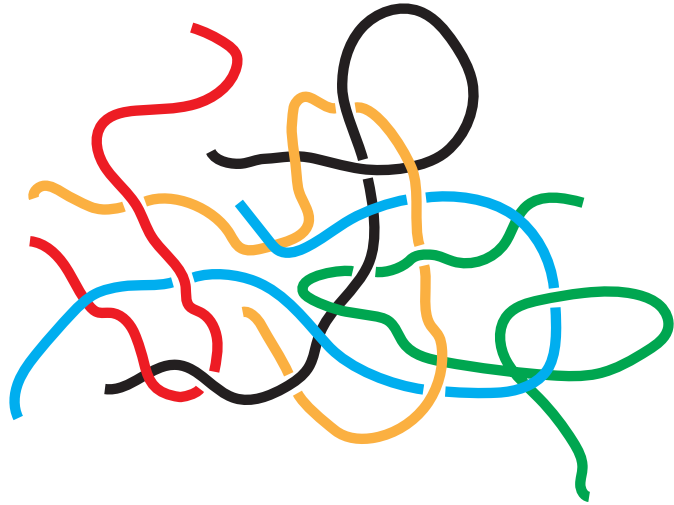
Can be completely amorphous

Can be semi-crystalline

Can never be 100% crystalline

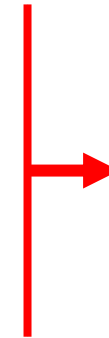
How do polymers crystallize?

For a system with multiple chains, how does crystallization happen?



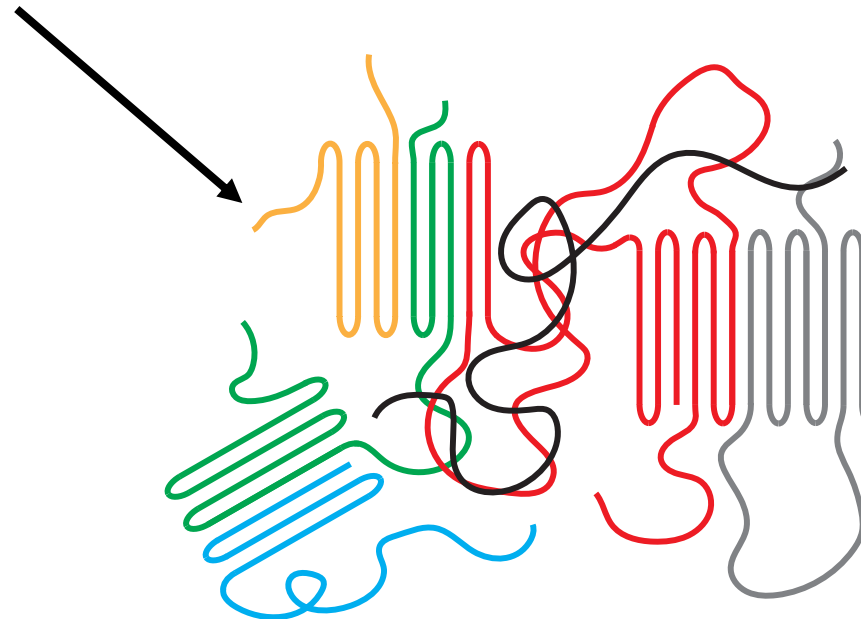
Long chains tend to get entangled and make crystallization difficult

Entanglements prevent 100% crystallinity and result in semi-crystallinity



Interactions between polymer chains prevent 100% crystallinity

Polymers that *can* crystallize only forms semi-crystalline polymers

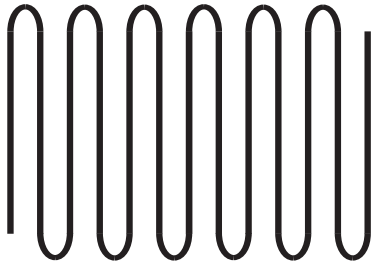


Polymer crystals surrounded by an amorphous matrix

A single chain can be involved in zero/one/multiple crystals

What favors crystallization of polymers?

Polymer Crystallite

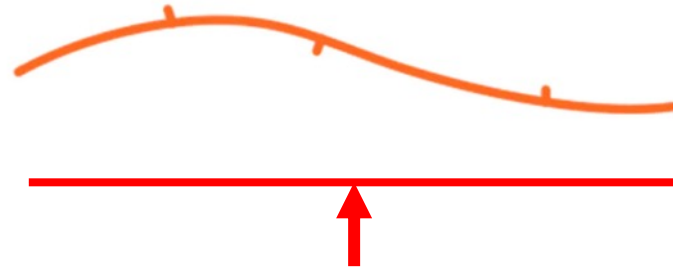


Chain needs to pack together

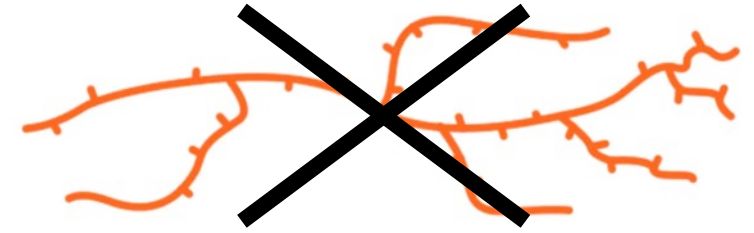


Regularity of polymer structure
+
Processing

Degree of branching



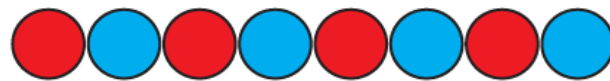
Low or no branching favors crystallization



Regularity of polymer composition



Statistical copolymers are usually amorphous

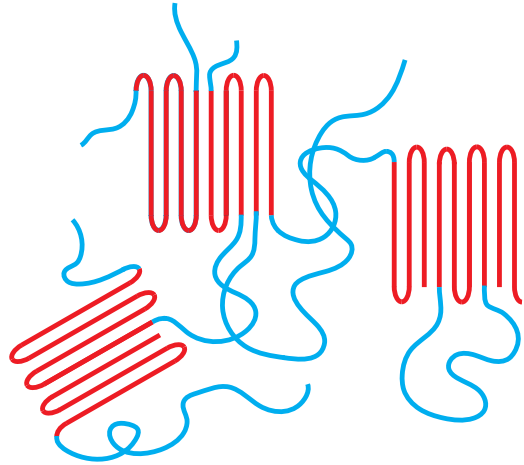


Block and alternating copolymers can crystallize



Temperature Transitions in Polymers

Two key temperature transitions



Glass transition temperature (T_g)

→ Temperature range where amorphous regions starts to move

Melting temperature (T_m)

→ Temperature range where crystalline regions starts to move

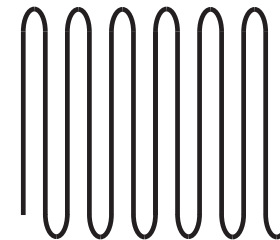
$T < T_g$
Glassy state

- Polymer behaves like a stiff and brittle solid
- Polymer chains are effectively rigid

$T > T_g$
Rubbery state

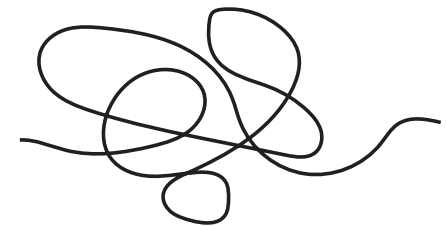
- Polymer behaves like a soft and easily deformed solid
- Polymer chains are mobile

Crystallite



Heat
 $T > T_m$
→

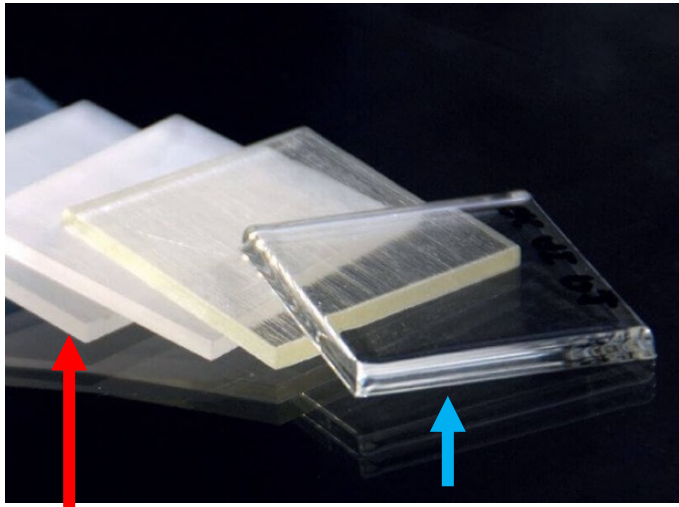
Amorphous



$T_m > T_g$

T_g and T_m impact polymer properties

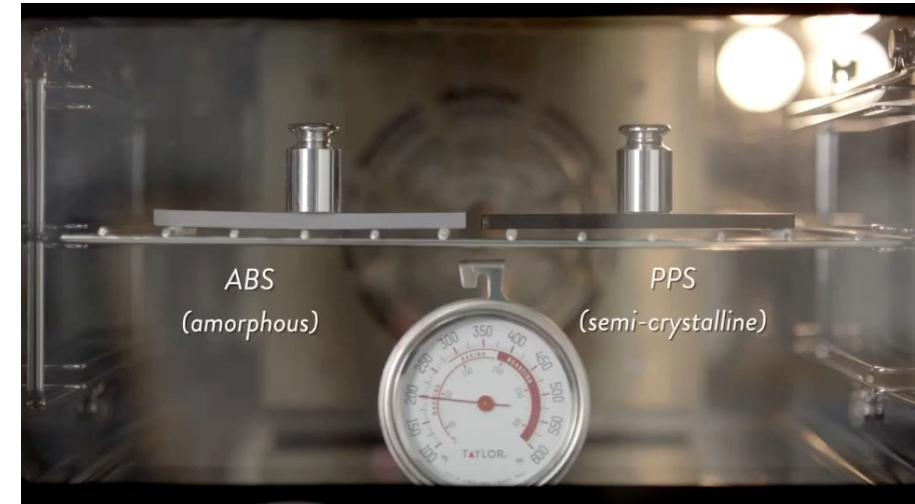
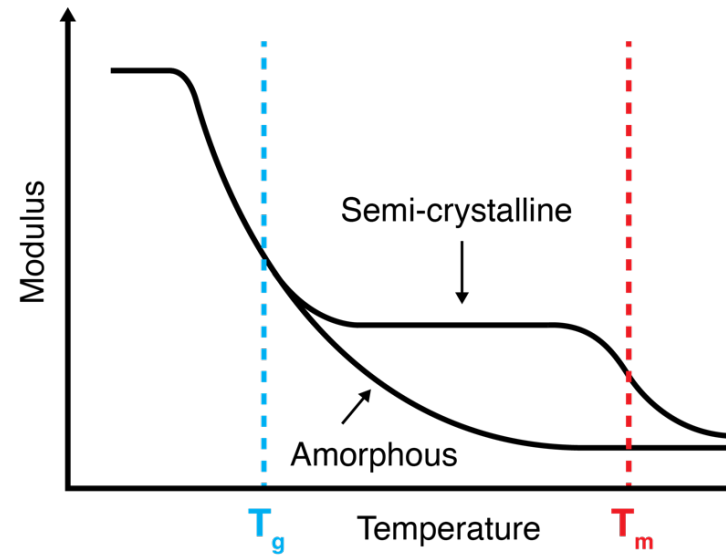
Optical



Semicrystalline Amorphous

Degree of crystallinity is inversely proportionate to light transmission

Mechanical



The T_g and T_m impact the mechanical properties of the polymer at the operating temperature

T_g of Polymer Blends

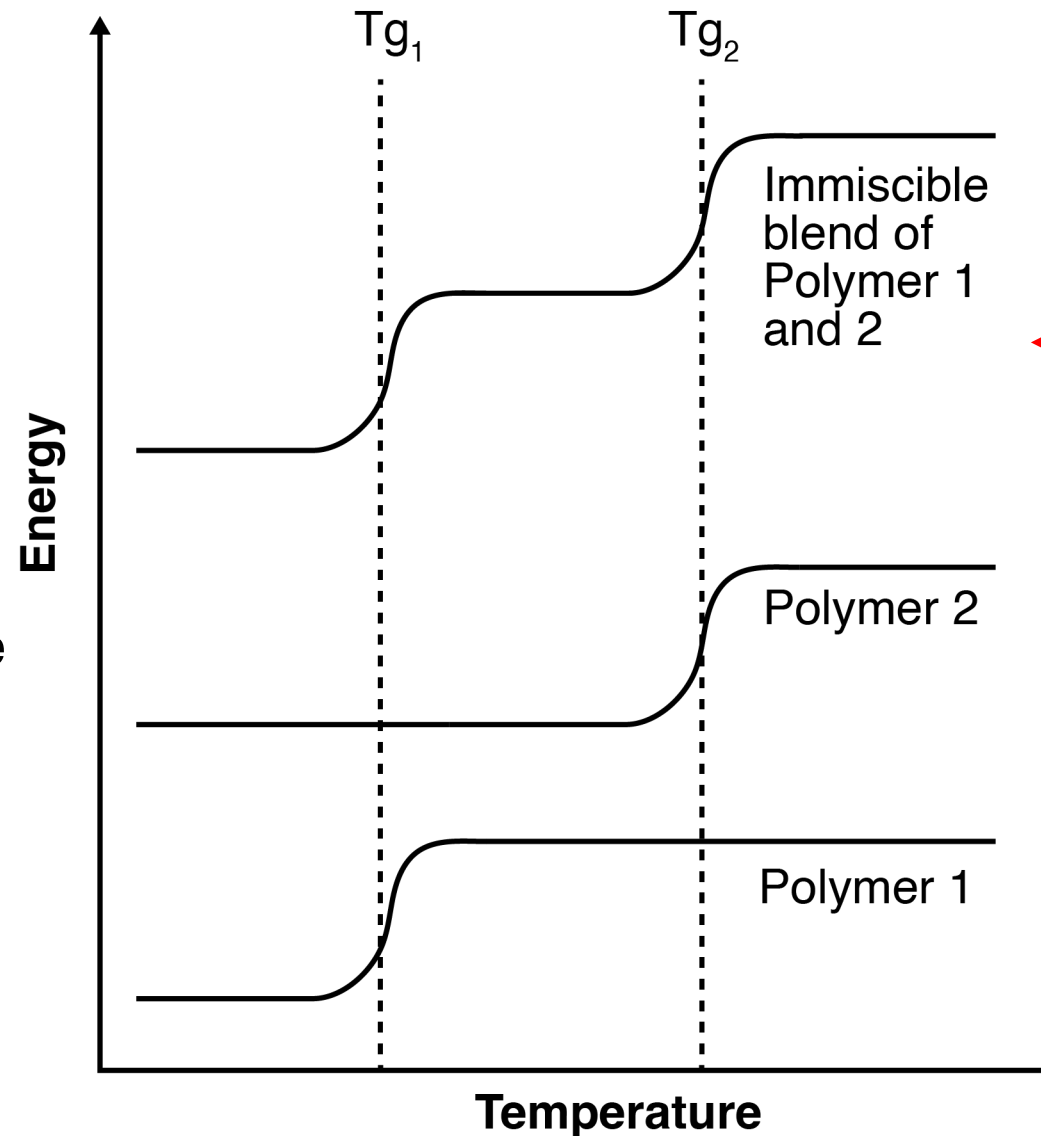
Immiscible blends

Two T_g values

Each T_g value is associated with one polymer in the immiscible blend

T_g(s) can be used to determine if a blend is miscible or not

(If these were semi-crystalline polymers, you would expect 2 T_ms as well!)

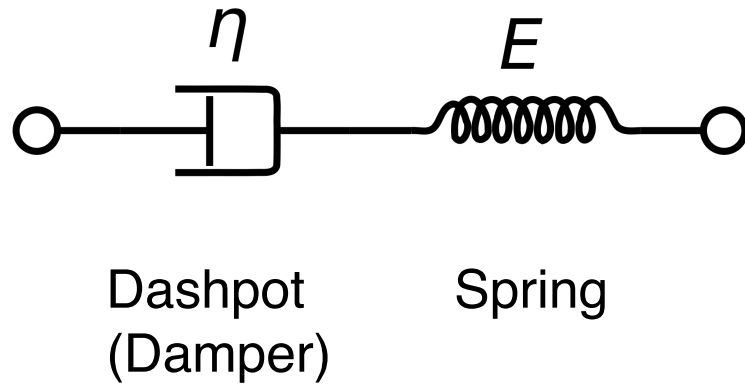


← We won't cover this but **Differential Scanning Calorimetry** is one technique used to determine T_g

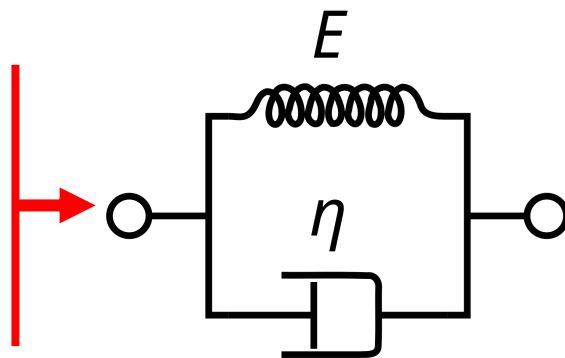
Mechanical Properties of Polymers

Polymers are viscoelastic* materials → Time and temperature-dependent mechanical properties

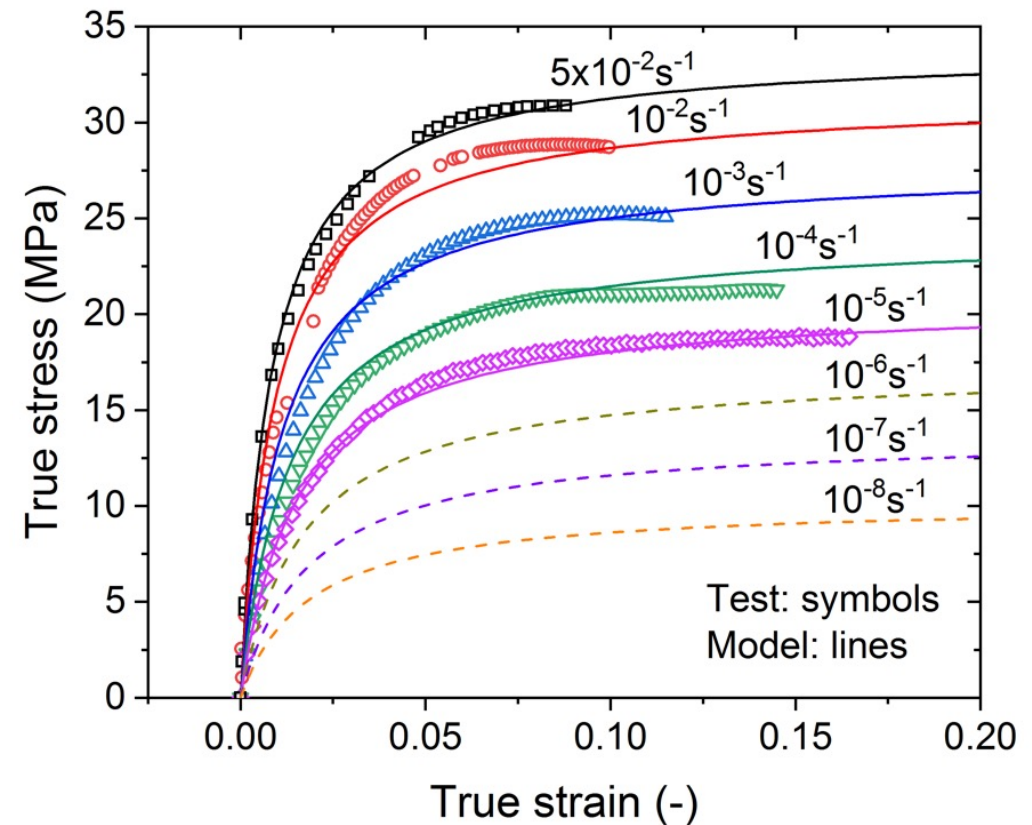
A very simplified model to describe this: **Maxwell model**



Kelvin-Voigt model



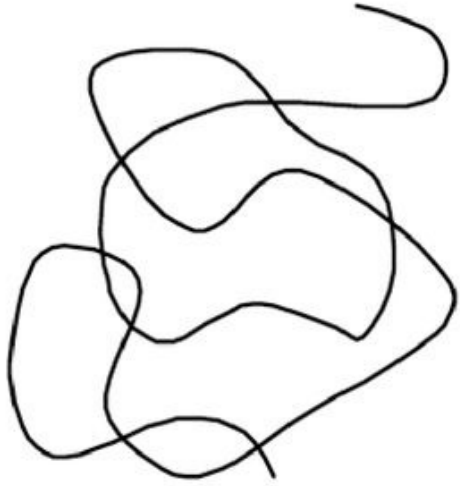
Strain rate dependence on mechanical properties



*viscoelasticity can be an entire course in itself!

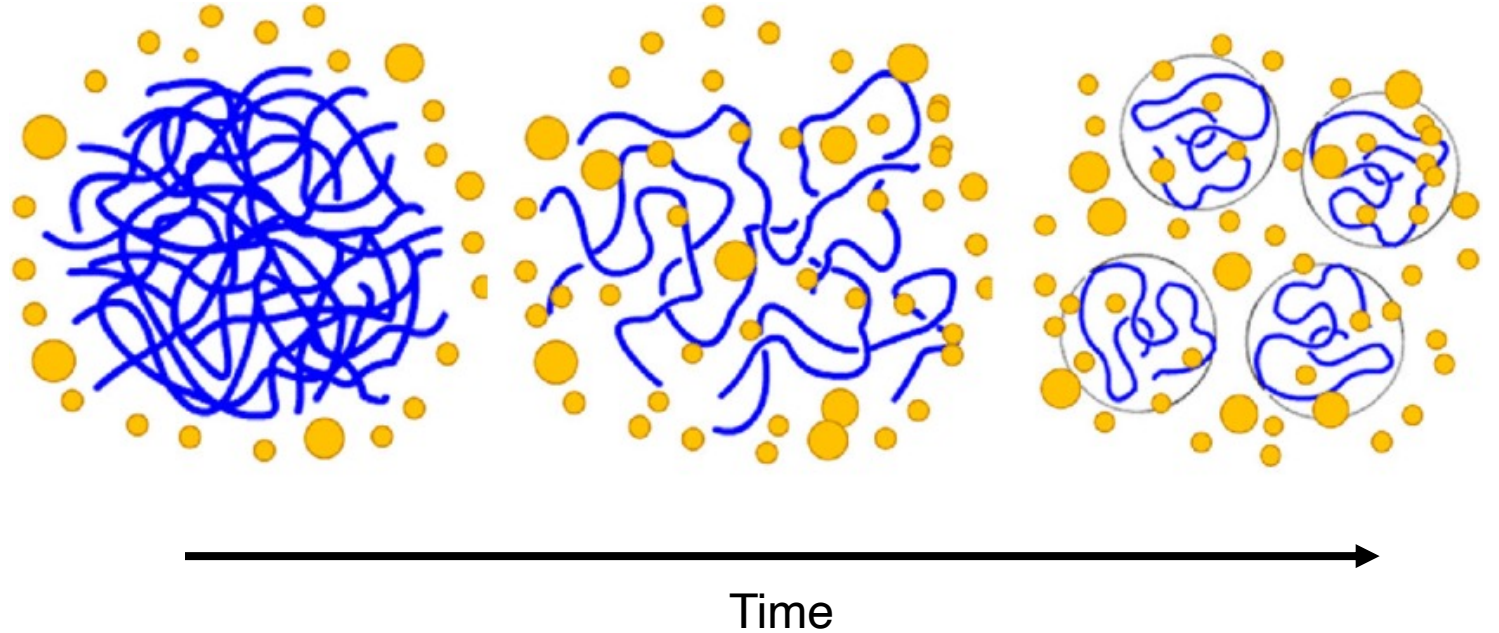
Polymers and Solvents

Good solvent



Monomer-solvent interactions
more favorable than monomer-
monomer interactions

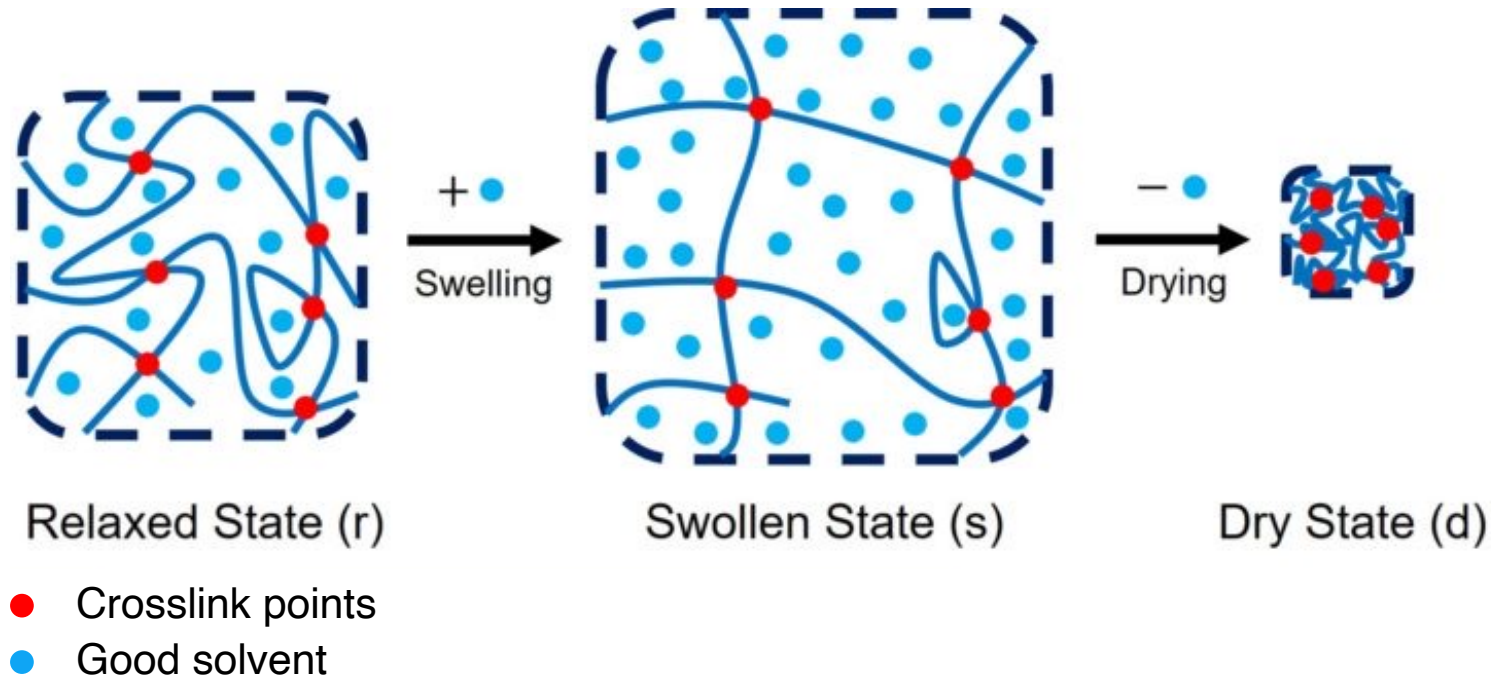
**Schematic of polymer dissolution in
good solvent**



Note 1: Polymer does not degrade, it dissolves. No loss of monomer!
Note 2: Polymer chains remain coiled even when dissolved. Why?

Solvation and Swelling

The presence of crosslinks prevents dissolution in a good solvent and results in swelling

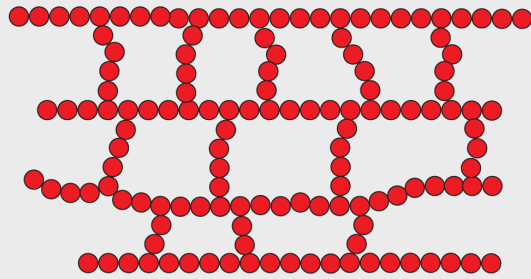


Crosslink: A bond or short sequence of bonds that links one polymer chain to another

Note: An uncrosslinked polymer in a bad solvent will not dissolve

Chemical and physical crosslinks

Chemical crosslinks

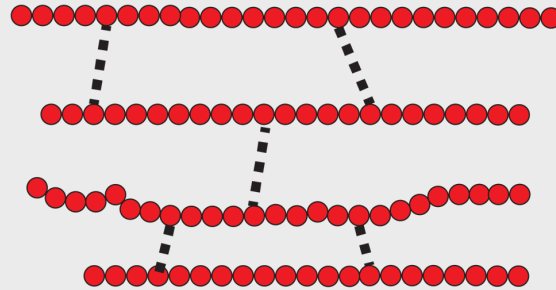


Covalent chemical bonds
between polymer chains

Strength of covalent
bonds are strong!

Covalent bonds are
permanent. Not transient

Physical crosslinks



Non-covalent bonds
between polymer chains

Strength of noncovalent
bonds are weak!

Noncovalent bonds are
transient. Often time-
dependent

**Chemically crosslinked
polymers are often stronger**

**Common to have both
chemical and physical
crosslinks!**

**Physically crosslinked
polymers are stimuli-
responsive**

Classic Polymer Manufacturing Processes

- Extrusion
- Injection Molding
- Thermoforming
- Blow Molding
- Compression Molding
- Transfer Molding
- Vacuum Casting
- Rotational Molding



Typically used for large-volume production

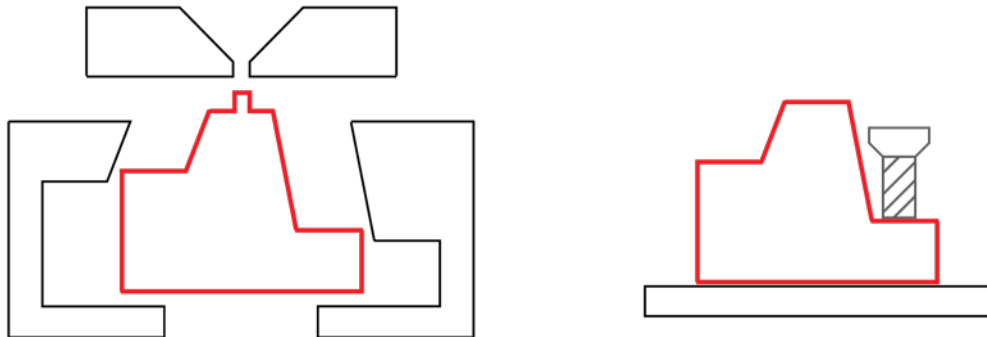
General concept for many of these processes:

1. Heat up polymer feedstock to a liquid state or to a softened state
2. Deform softened polymer or fill mold with liquid polymer
3. Cool polymer down to solidify it.

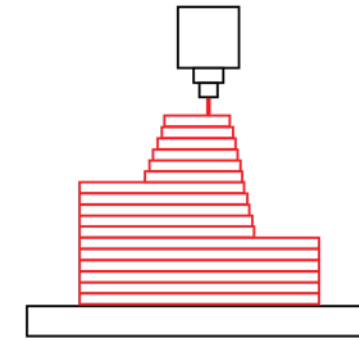
Additive Manufacturing (AM)

Some challenges with "traditional" polymer manufacturing approaches:

- Limited part complexity
- Difficult to pivot between part designs
- Optimized for scale — start up cost is very high
- Subtractive approaches* can be wasteful



Additive Manufacturing



Part is built in a layer-by-layer[^] manner

- "Complexity for free"
- Easy to pivot between multiple designs
- Can be more material efficient
- Small-scale

Polymers are stable, too stable...



Polymers are designed to last a long time
→ Great product!

Breakdown of polymers are hard

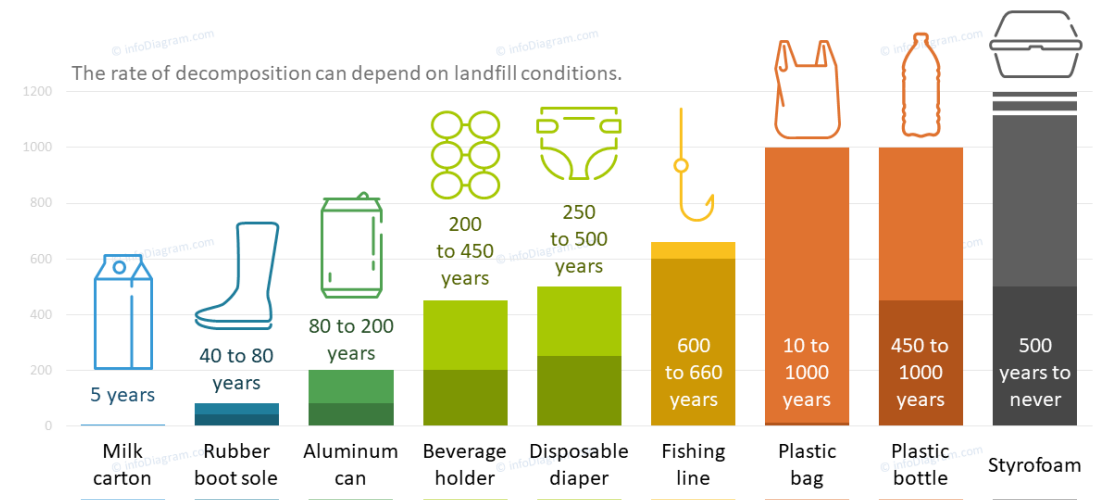
- Microorganisms do not recognize polymers so they cannot break it down easily
- Breaking down polymers result in the release of toxic small-molecules and microplastics

Flipside → We can't get rid of it!



Time to Decompose Plastics

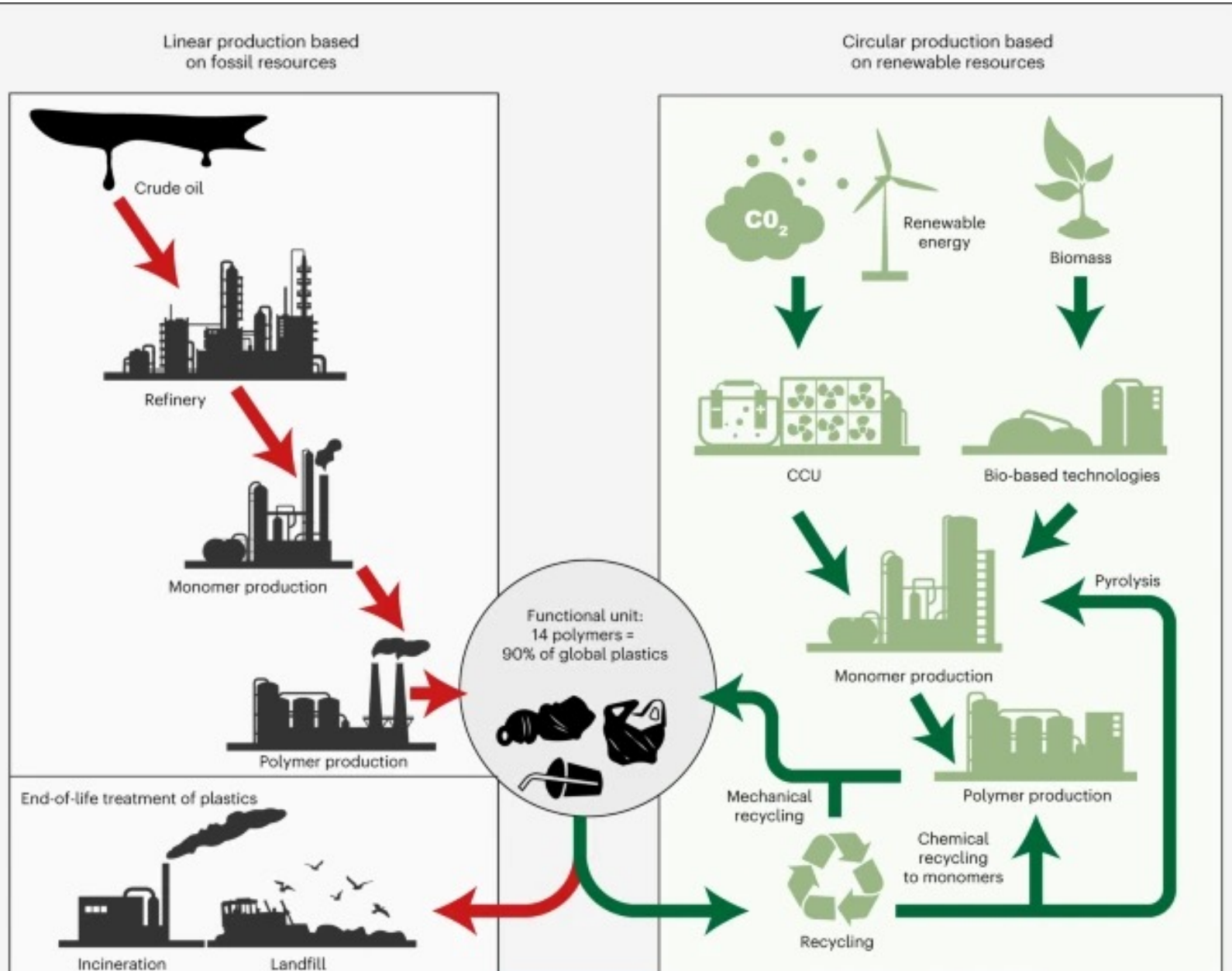
Estimated Minimum and Maximum Chart by Waste Type



Get these slides & icons at www.infoDiagram.com

Data source: NOAA.gov

Polymer Sustainability

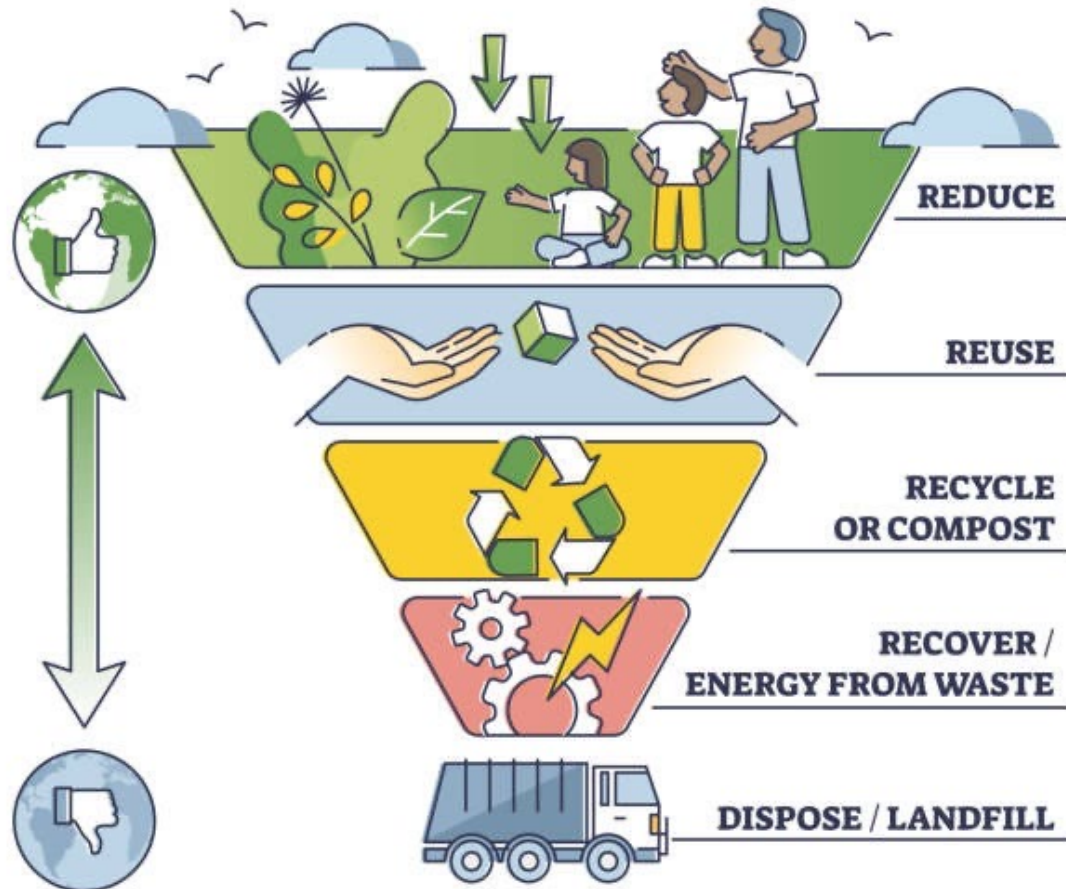


Polymers are not inherently bad, but the way we produce and use them are not sustainable!

Complex challenge that encompasses science, manufacturing, policy, and politics

Some ways to tackle Polymer Sustainability

Recycling is not that effective.
Reduce and reuse!



Policy can be a powerful tool to enact
broad changes in society

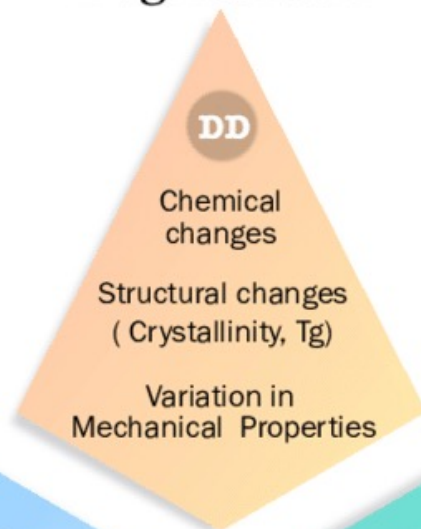
Timeline

Key dates related to the Directive on single-use plastics

- 4 February 2022 **Commission adopts Implementing Decision 2022/162**
[Implementing Decision 2022/162](#) lays down rules for the calculation, verification and reporting on the reduction in the consumption of single-use plastic food containers and beverage cups
 - 1 October 2021 **Commission adopts Implementing Decision 2021/1752**
[Implementing Decision 2021/1752](#) lays down rules for the calculation, verification and reporting of data on the separate collection of waste single-use plastic beverage bottles
 - 3 July 2021 **The EU no longer allows certain single-use plastic items to be placed on the Member States market; and marking requirements enter into force**
[Find out more about the marking specifications and download the pictograms](#)
 - 31 May 2021 **Commission adopts guidelines on single-use plastics products, and implementing decision on reporting on fishing gear**
[View the guidelines in all EU languages](#)
[View the implementing decision on reporting on fishing gear](#)
 - 2 July 2019 **Directive on single-use plastics enters into force**
 - 16 January 2018 **Publication of the EU plastics strategy - outlining the need for a legislative proposal on single-use plastics**
- [Hide 2 Items ^](#)

Unintended Consequences

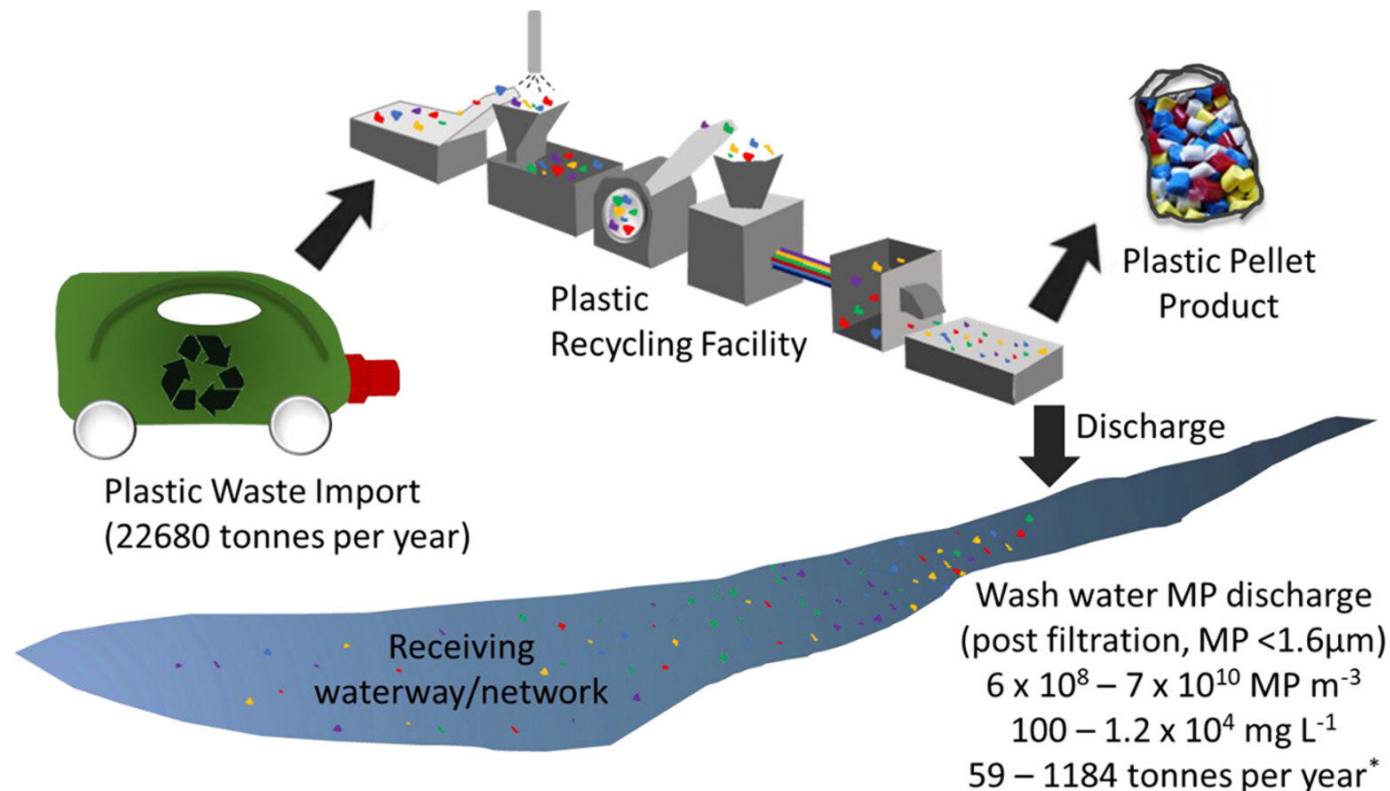
Degree of Degradation



Degree of Mixing (Composition)



Presence of Low Molecular Weight Compounds

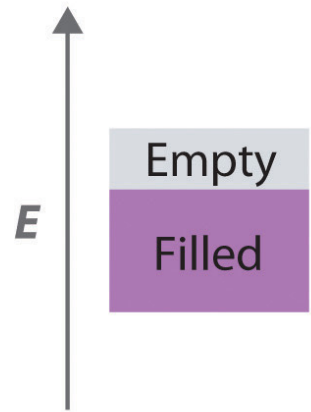


METALS

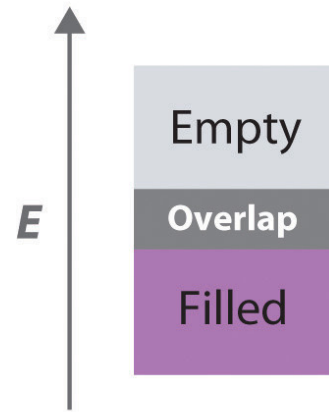
35-40% of exam

What are Metals?

Metals (2 types of band structure)



Partially filled valence band

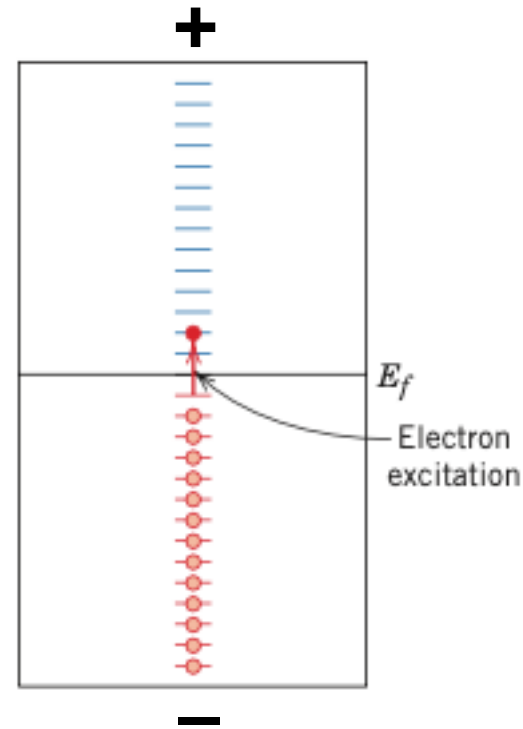


Filled valence band

Conduction band overlaps with valence band

Very little energy needed to promote electron into next available energy state

Electric field can cause electrons to flow



Key defining property of metals

No band gap between valence and conduction band

Electric field sufficient to promote electrons across gap

Conductivity **decreases** with temperature

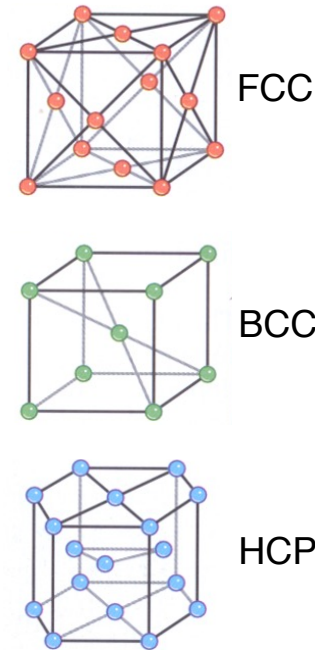
Conductive even at absolute zero (0 K)

How Do We Classify Metals?

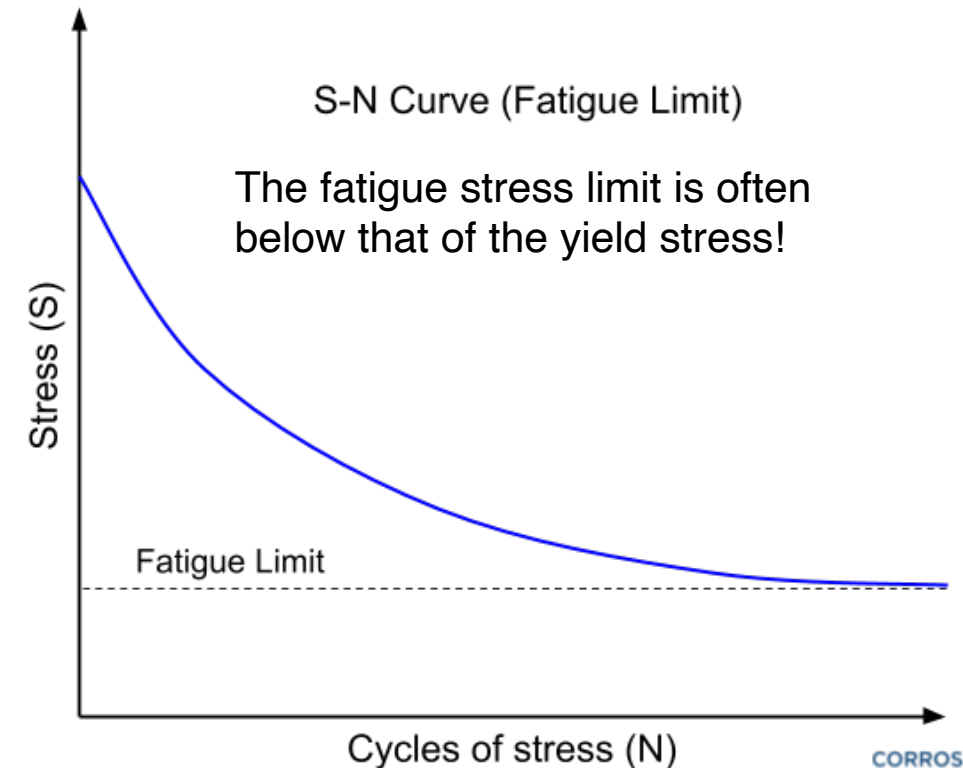
Multiple ways of classifying metals – Depends on the information you want to convey

1. Composition: Ferrous or Non-ferrous
2. Composition: Alloy or Pure metals
3. Crystal structure
4. Refractory or not?
5. Base metal vs. Precious metal
6. Corrosion resistance
7. Mechanical Properties
8. Microstructure

Crystal Structure



Mechanical Properties



How Do We Classify Metals?

Multiple ways of classifying metals — Depends on the information you want to convey

6. Corrosion resistance

Another way to introduce corrosion resistance: **Cathodic protection**

Idea: Protect a metal (the cathode) by sacrificing another one (the anode)

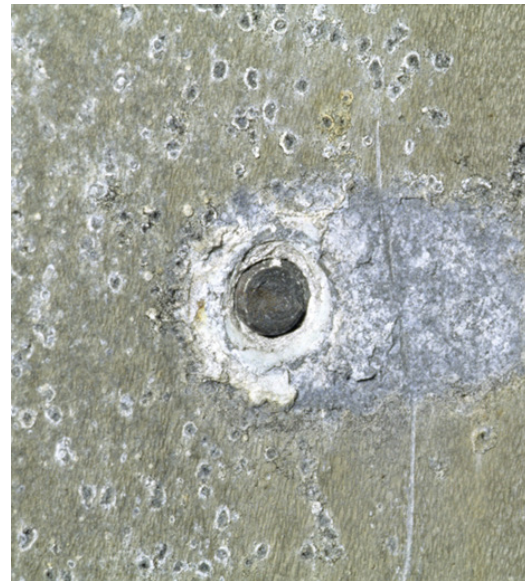
Since it's an electrochemical system (think battery), need to have a "circuit".

Metals in electrical contact with an electrolyte

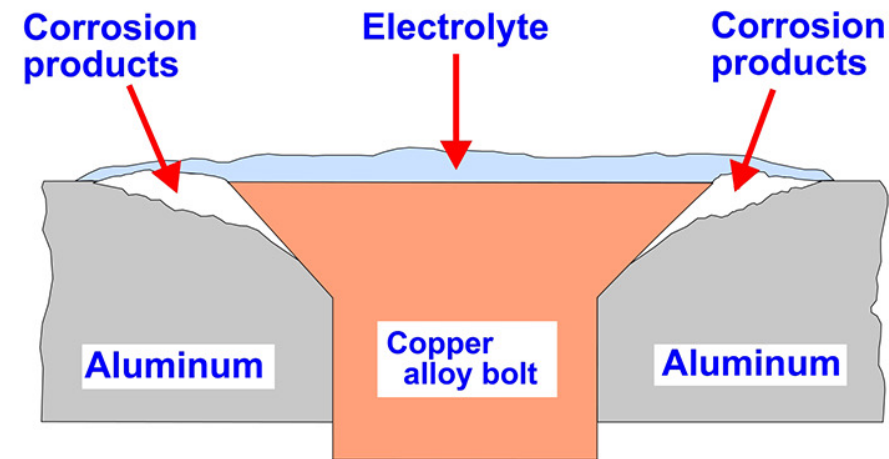
Galvanic corrosion

If unintentional → Sacrifice the wrong metal!

Corrode something that is corrosion resistant



Copper bolt in aluminum



Aluminum protected the copper
Aluminum corroded

How Do We Classify Metals?

Multiple ways of classifying metals — Depends on the information you want to convey

2. Composition: Alloy or Pure metals

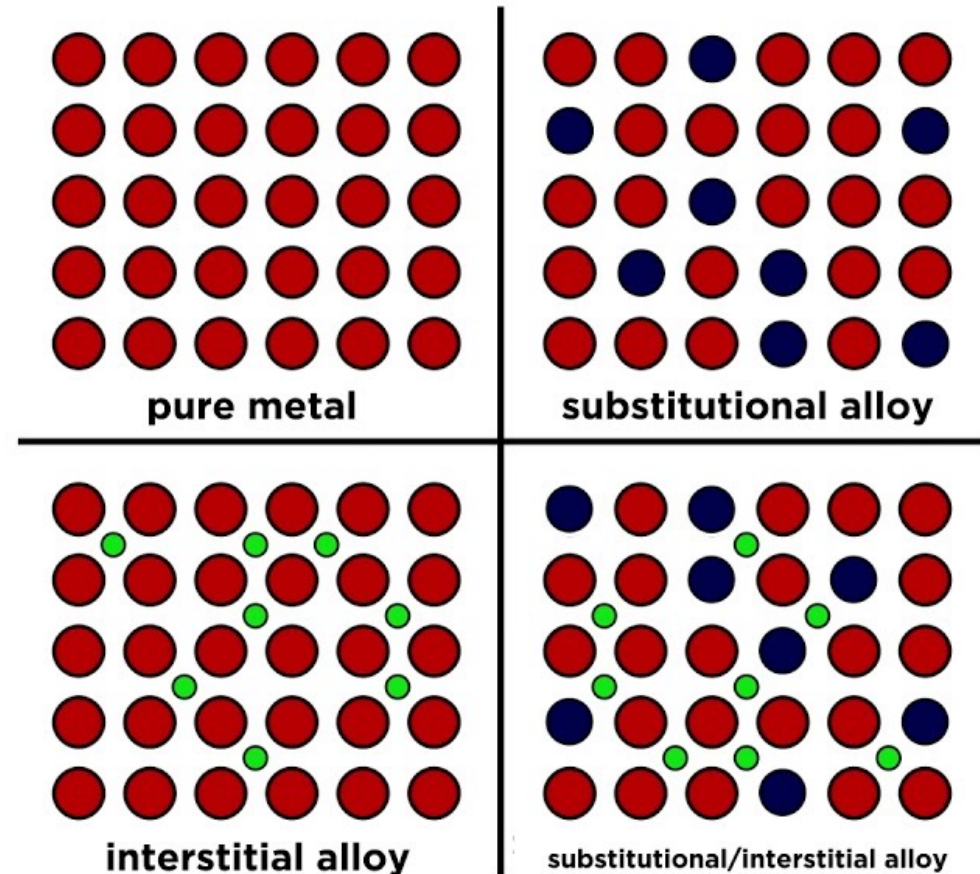
An alloy is a mixture of chemical elements, in which at least one is a metallic element.

The majority of elements should be metallic elements

Most metals used today are alloys!

Very few pure metals are used:
Cu, Ag, Au, Pt

Atomic representation of alloying



Hume-Rothery Rules for Binary Solid Solutions

For substitutional solid solutions

1. Difference in atomic radii is $< 15\%$
2. Crystal structures have to be the same
3. Similar electronegativity
4. Similar valency

For interstitial solid solutions

1. Solute atom has to fit within "pore" space of the unit cell
2. Similar electronegativity
3. Similar valency

If Hume-Rothery rules are not fulfilled \rightarrow Low to no solubility of element in the metal

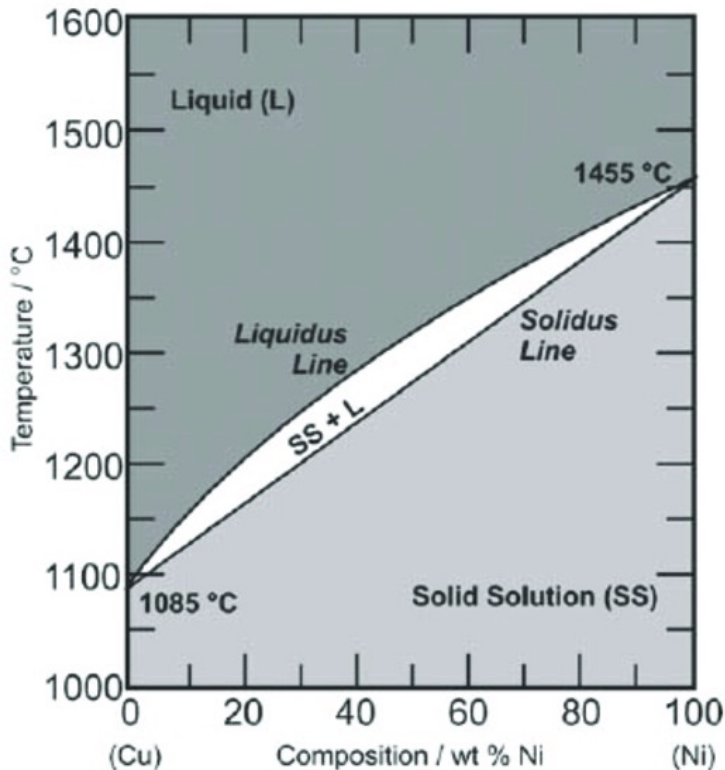
Hume-Rothery rules only tell you if elements mix, not how much they mix

Hume-Rothery Rules for Binary Solid Solutions (Examples)

Copper and Nickel

Will they form a solid solution?

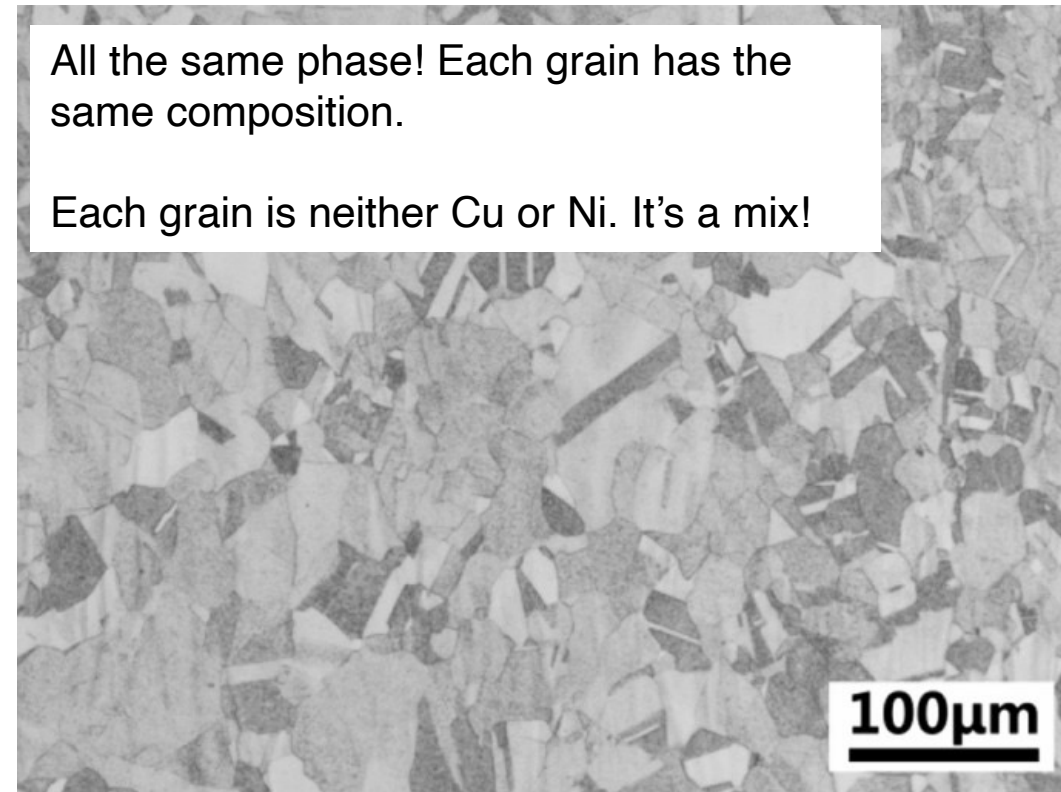
Element	Atomic Radius (nm)	Crystal Structure	Electronegativity	Valency
Ni	0.125	FCC	1.80	2
Cu	0.128	FCC	1.90	2



Cu and Ni are completely soluble with each other and just form a single phase prior to melting

All the same phase! Each grain has the same composition.

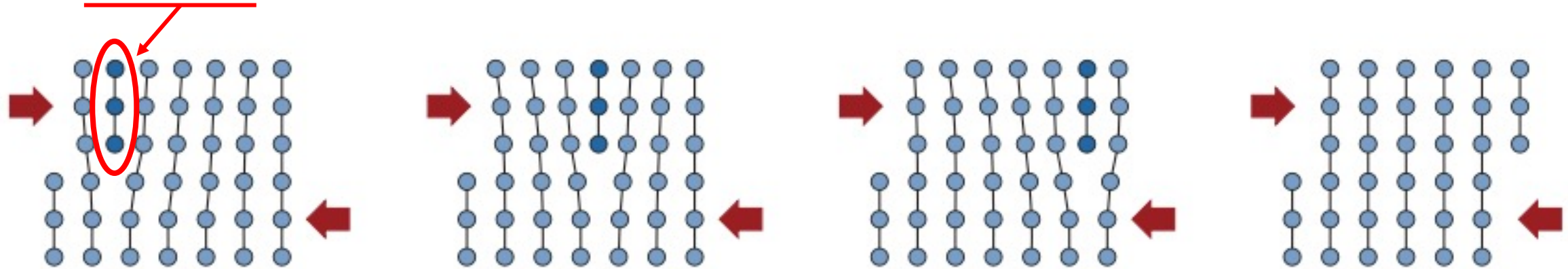
Each grain is neither Cu or Ni. It's a mix!



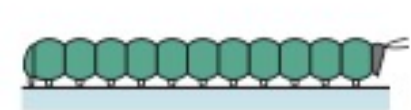
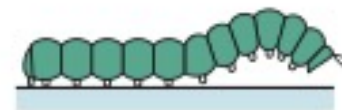
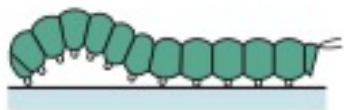
Metals and Dislocations

The strength of a metal depends on the ability of its **dislocations** to move.

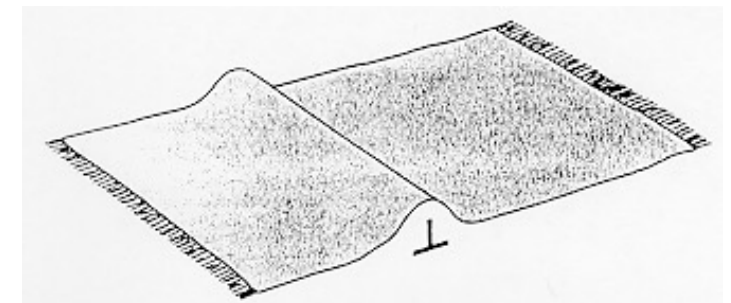
A dislocation is a line defect in the crystal where the atoms are arranged anomalously



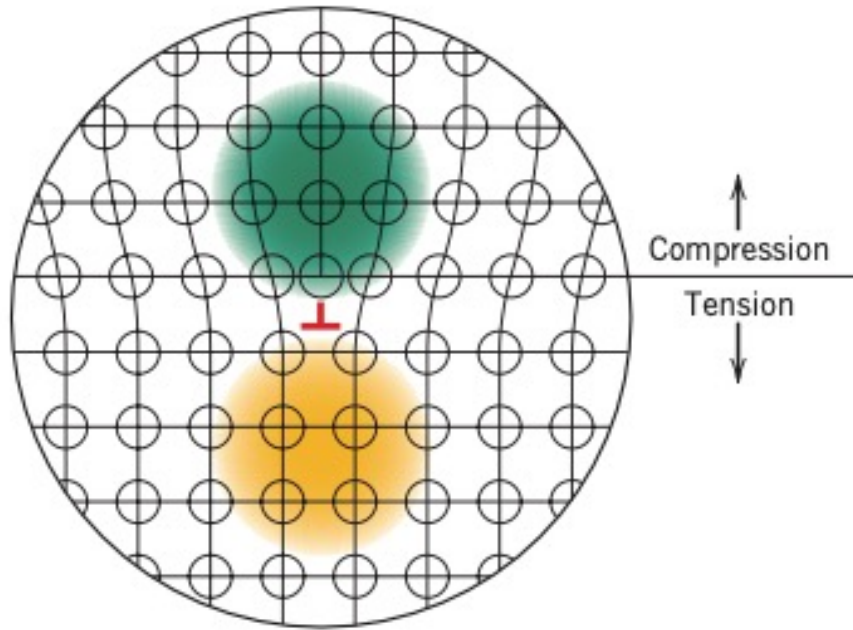
With a dislocation, only one bond needs to be broken at a time!



If you don't like bugs, it's like a ruck in a carpet →



Dislocations and strain fields



Dislocations have a strain field around them

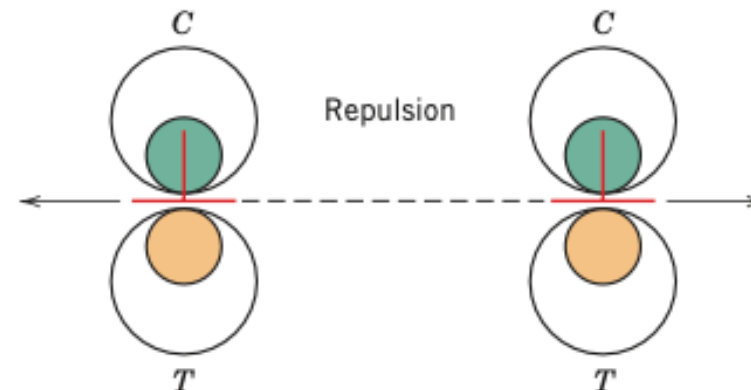
The extra half-plane of atoms distorts the surrounding lattice

Atoms directly **above** the dislocation line are being squeezed together by the additional plane (2→3)

Atoms directly **below** the dislocation line are being pulled together by the missing plane (3→2)

Implication:

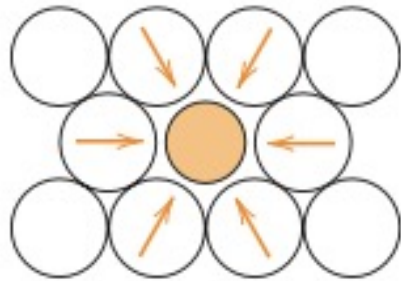
Dislocation mobility is impacted by its surrounding strain field



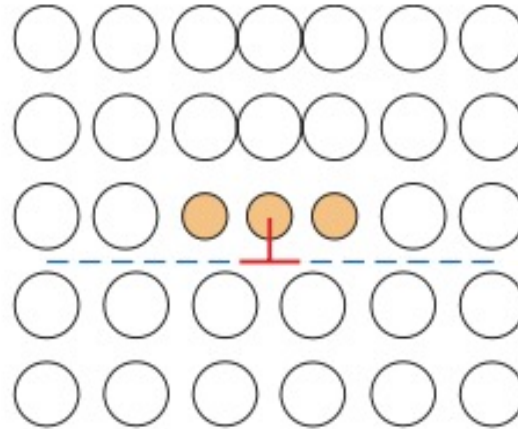
Alloying impedes dislocation movement

Size mismatch of atoms strains the lattice

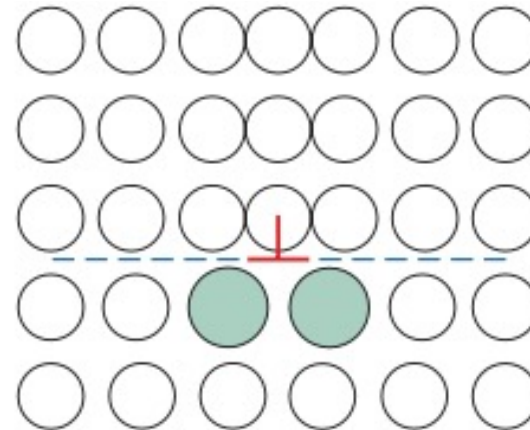
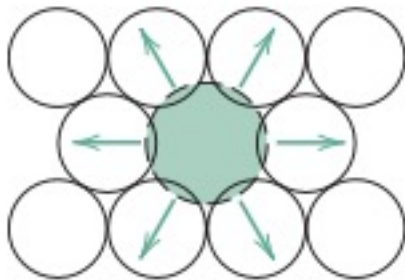
Smaller substitutional atom imposes **tensile** strains on the host lattice



Strain field between dislocation and substitutional atoms can interact



Larger substitutional atom imposes **compressive** strains on the host lattice



Effect 1

Pins the dislocation



Harder to start moving

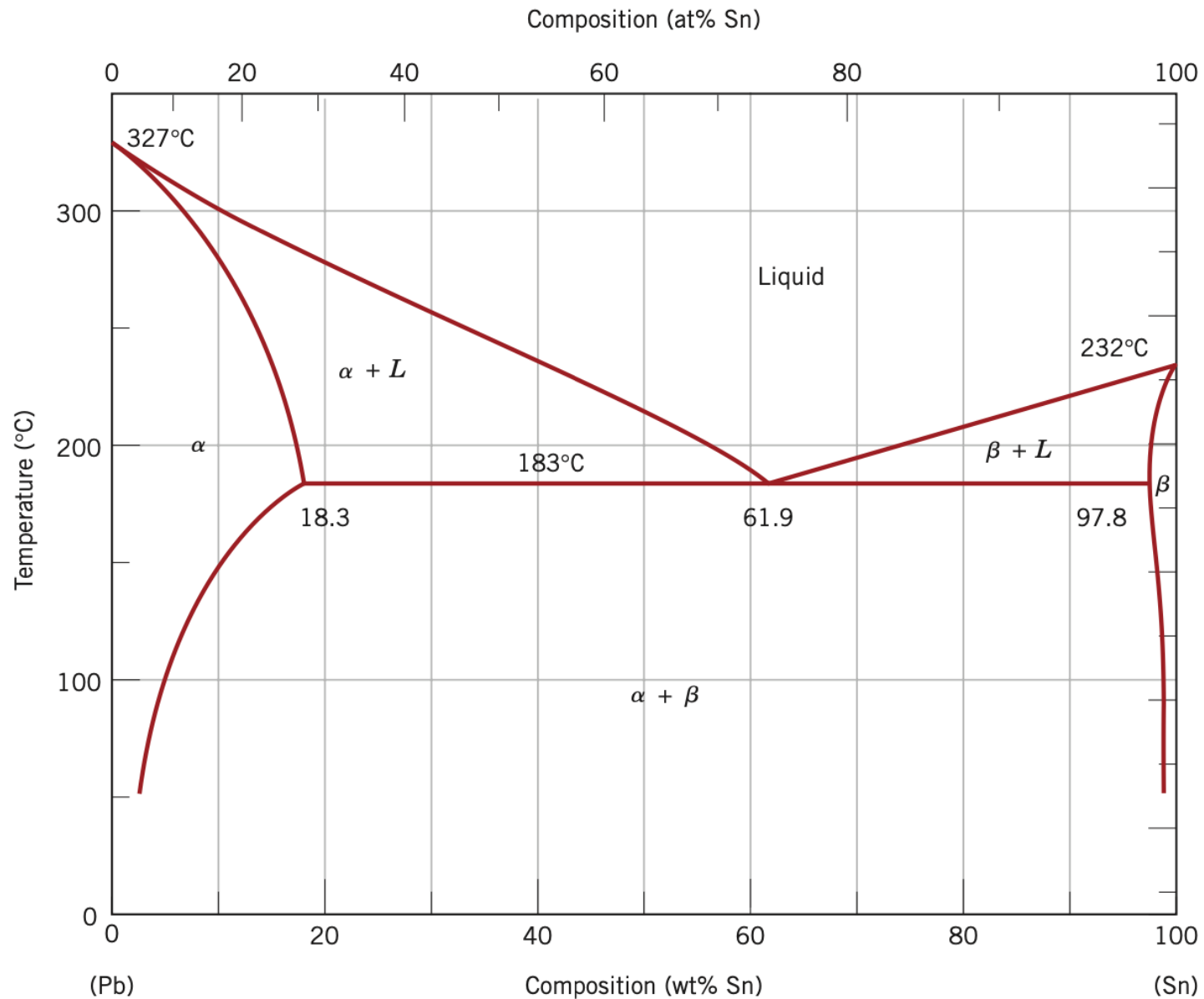
Effect 2

Strain field impedes dislocation movement

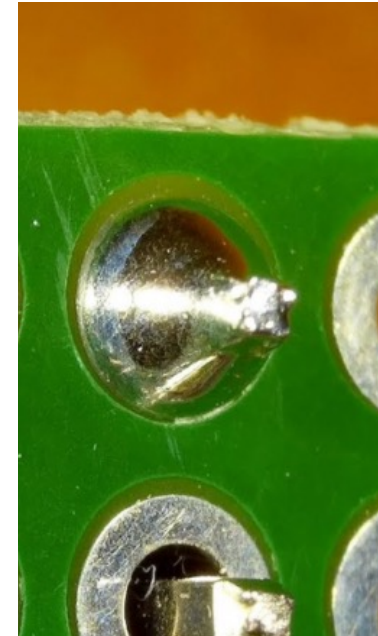


Harder to keep moving

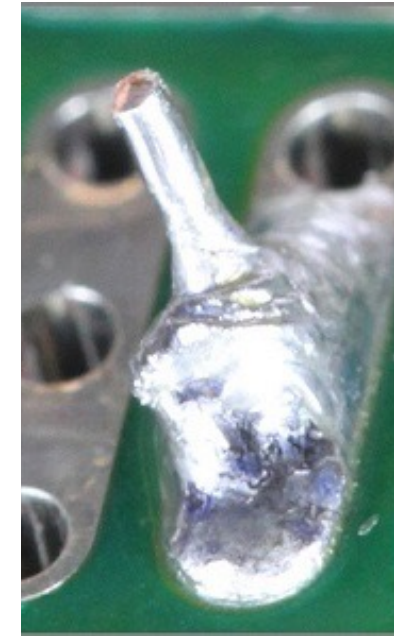
Phase diagrams explains the thermal behavior of metals



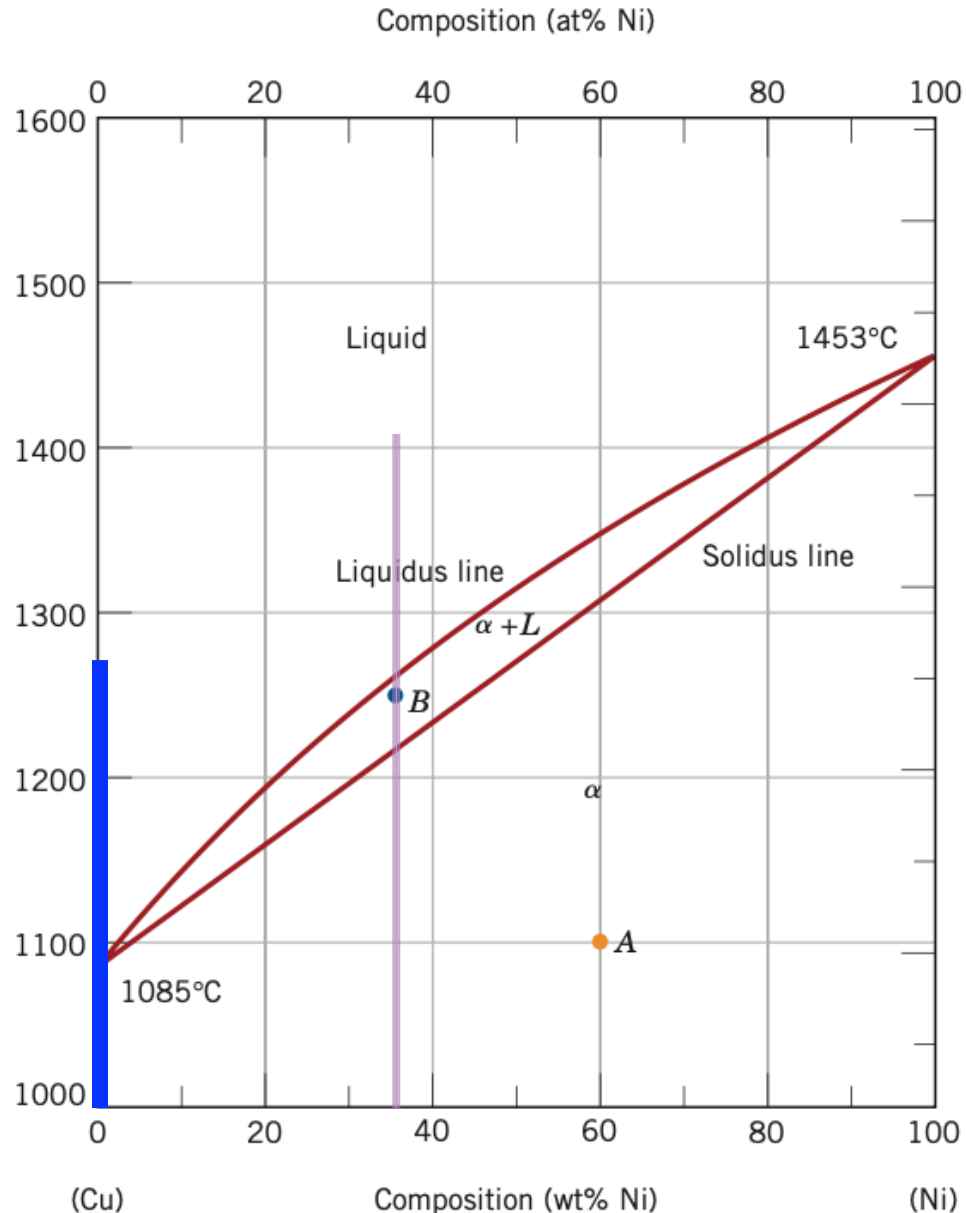
Good solder joint



Cold solder joint





How do we read a phase diagram?



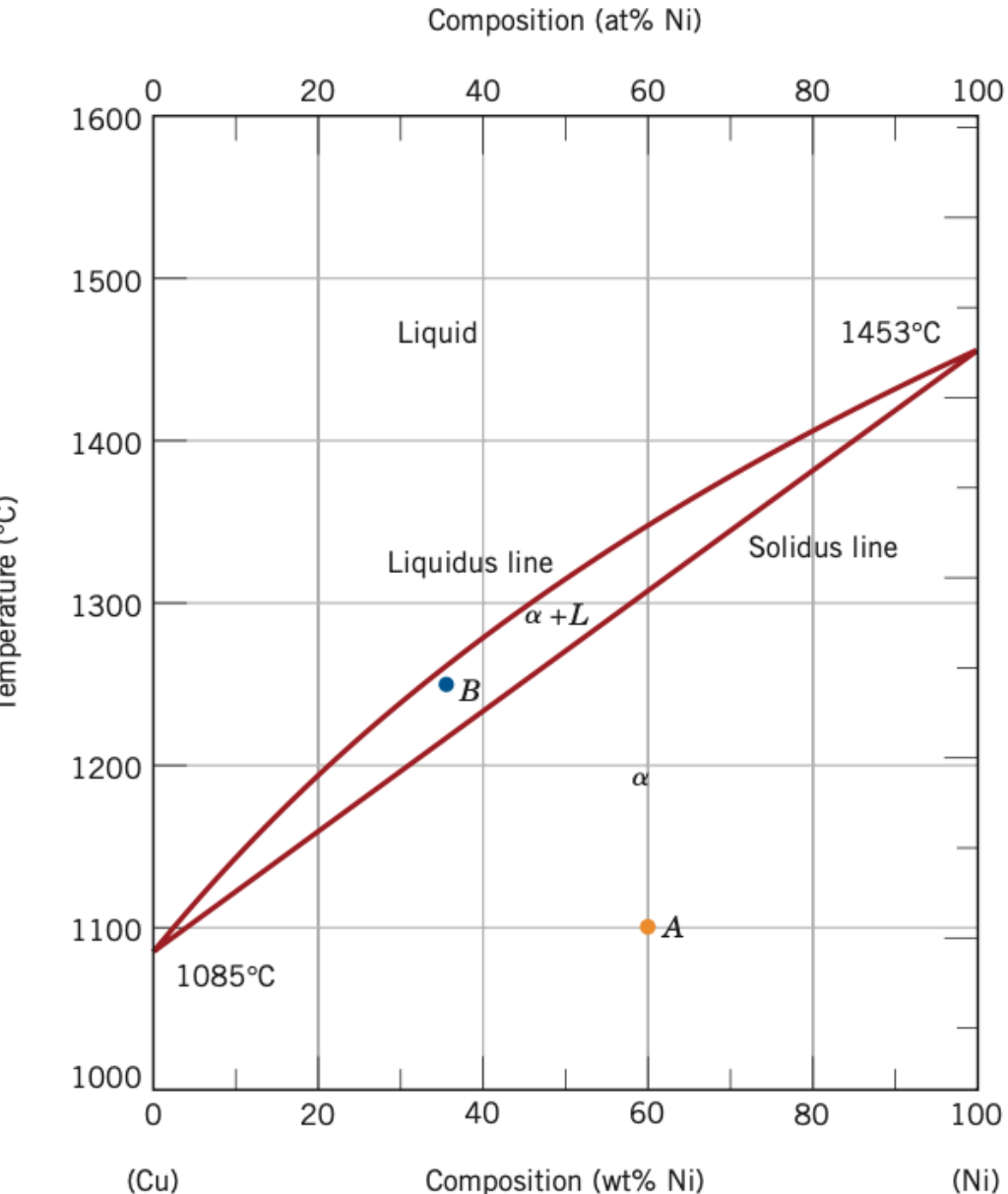
How to read a phase diagram:

1. For a specific composition, draw a vertical line through the temperatures of interest
2. Note the regions it passes through
3. Note the transition temperatures

Example 1:  Solid Cu below 1085°C
Pure Cu Liquid above 1085°C

Example 4:  Solid α below ~1220°C
Cu₆₅Ni₃₅ $\alpha + L$ between 1220°C and 1270°C
L above 1270°C

How do we use a phase diagram to determine compositions?



Single phase region:

Amount of phase: 100%

Composition of phase: Same as that of the alloy

Point A: $\text{Cu}_{40}\text{Ni}_{60}$, 100% of the alloy is the α phase

Two phase region:

Amount of each phase: Determine via lever rule

Composition of each phase: Determine via tie line

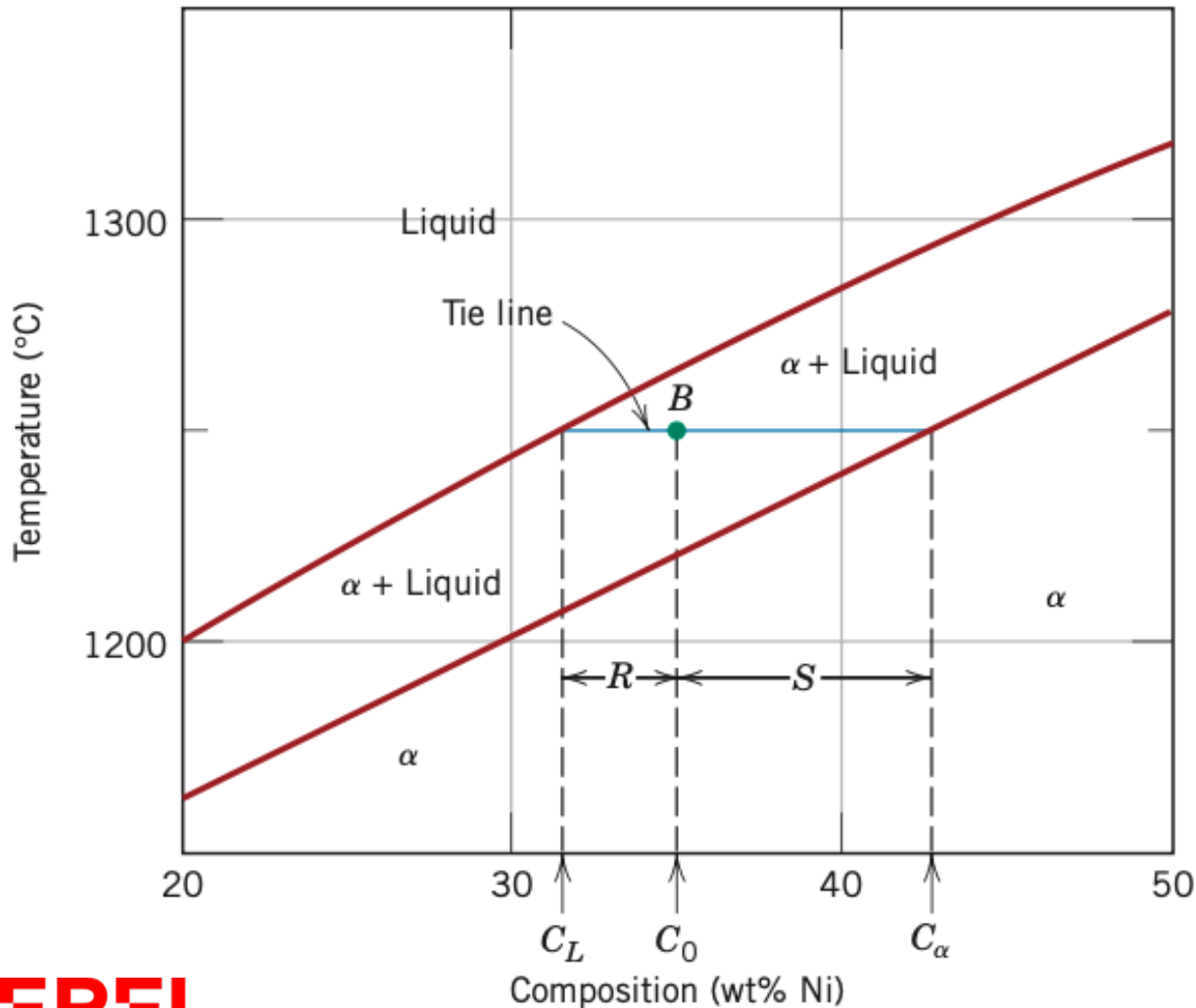
Point B: Some percent is α phase of some composition

Some percent is the liquid phase of some composition

Why do they need to have different compositions?

Tie lines: Method to determine phase compositions

Let's zoom in to the region around **Point B**



Step 1: Identify the composition and temperature of interest (Eg. **Point B**: $\text{Cu}_{65}\text{Ni}_{35}$ at 1250°C)

Step 2: Draw a horizontal line through the point until it intersects the phase boundaries

Note: This horizontal line is called a tie line

Step 3: From these intersection points, draw vertical lines down to the composition axis

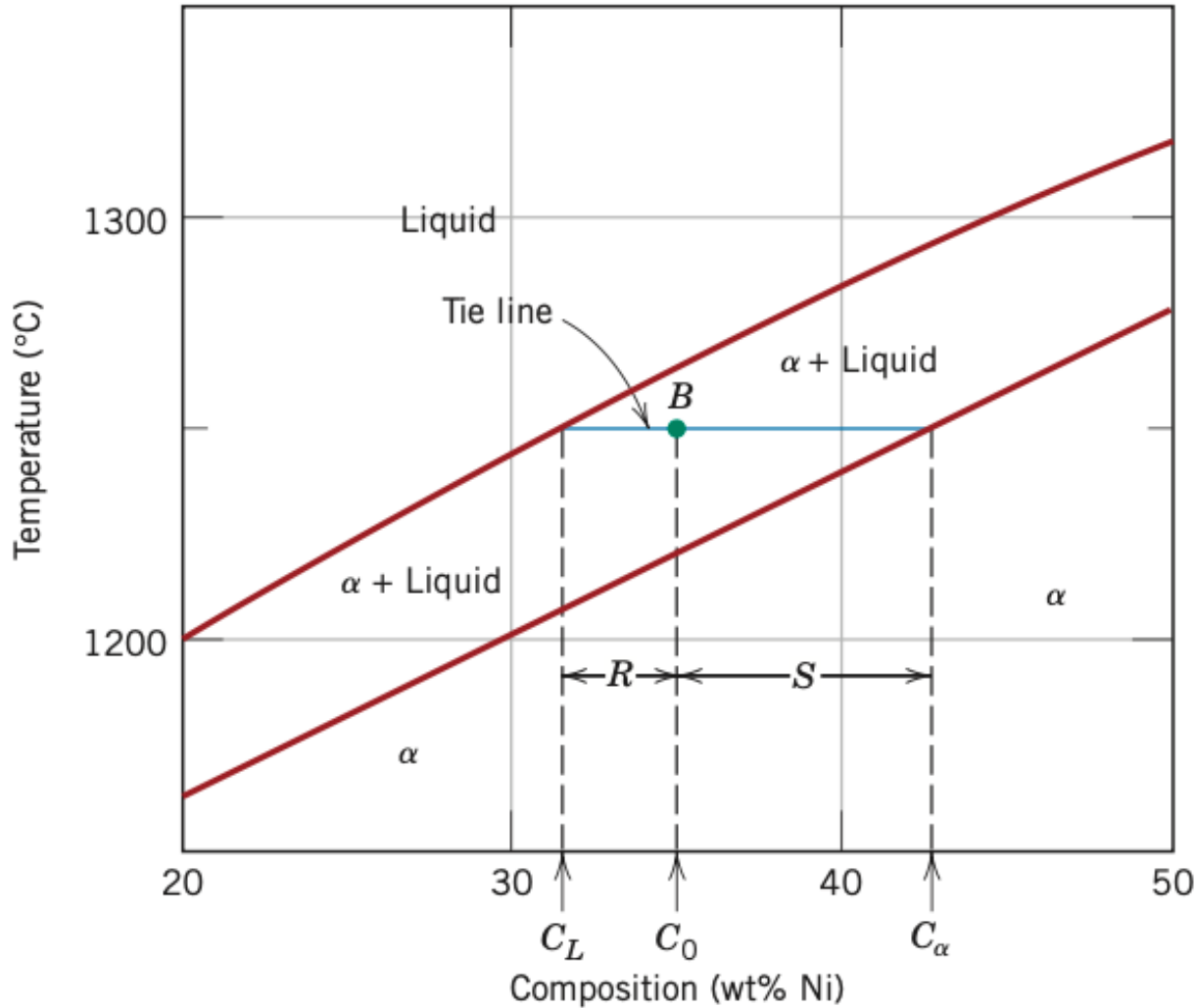
Step 4: Read composition values for each phase

For **Point B**: $\text{Cu}_{65}\text{Ni}_{35}$ at 1250°C

Composition of liquid (C_L) = $\text{Cu}_{68.5}\text{Ni}_{31.5}$

Composition of α phase (C_α) = $\text{Cu}_{57.5}\text{Ni}_{42.5}$

Lever rule to determine phase amounts



$$W_L = \frac{S}{R + S} \quad \text{or} \quad W_L = \frac{C_\alpha - C_0}{C_\alpha - C_L}$$

Old school: If no axis, use a ruler! (It is a ratio afterall)

Precise: Use the compositions on the x axis

Only need to use one of the element values to calculate the composition

For **Point B**:

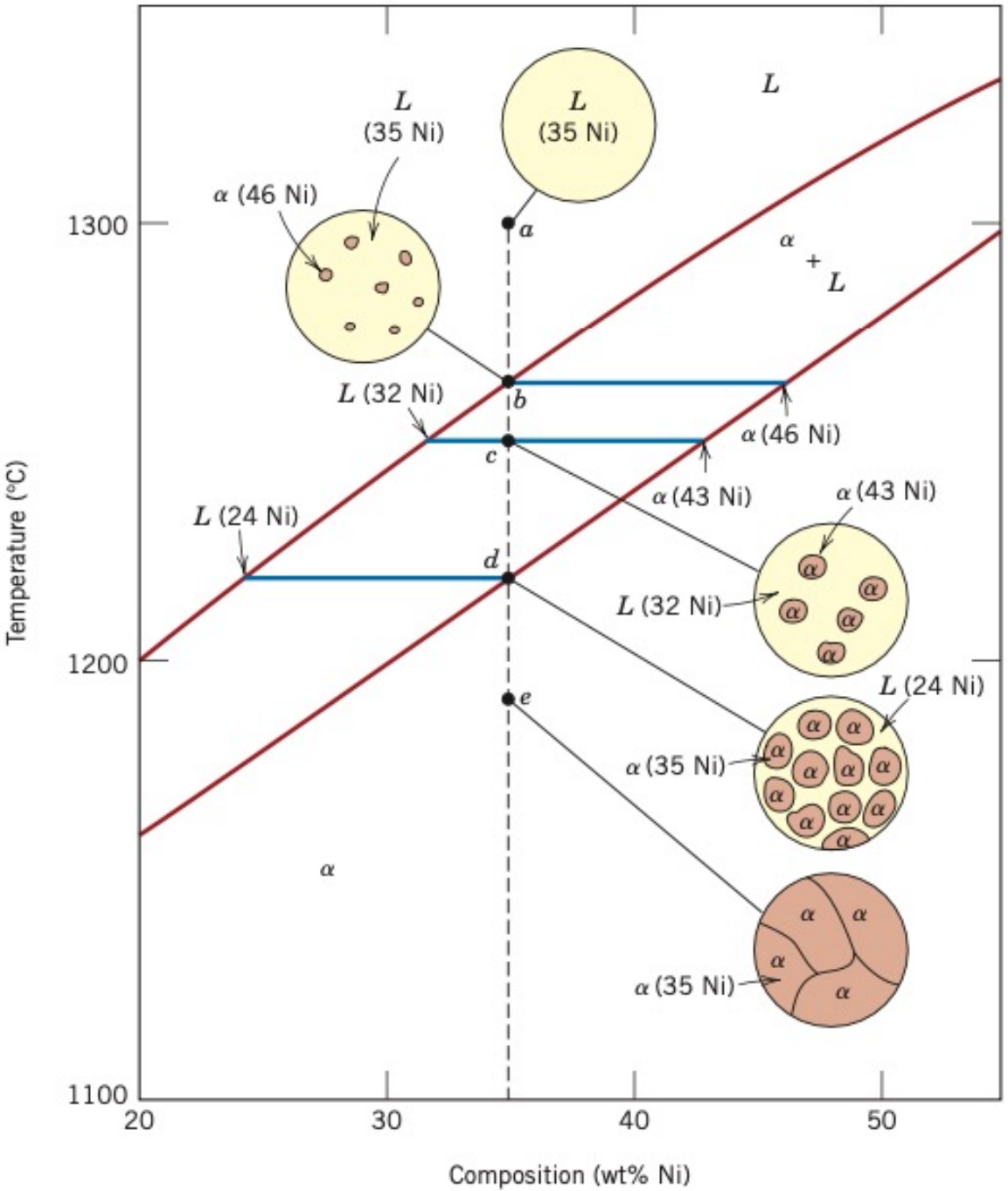
$$C_0 = 35.0 \text{ wt\% Ni}$$

$$C_L = 31.5 \text{ wt\% Ni}$$

$$C_\alpha = 42.5 \text{ wt\% Ni}$$

$$W_L = \frac{42.5 - 35}{42.5 - 31.5} = 0.68$$

At **Point B**, 68% of the alloy is liquid by mass



Important: Phase Diagrams reflect the compositions and fractions at equilibrium

Equilibrium is almost never achieved in real life solidification processes!

Even in non-equilibrium conditions, the phase diagram can still provide insights about solidification

The original solidus line (solid) tells you the composition of the α phase that forms at that temperature

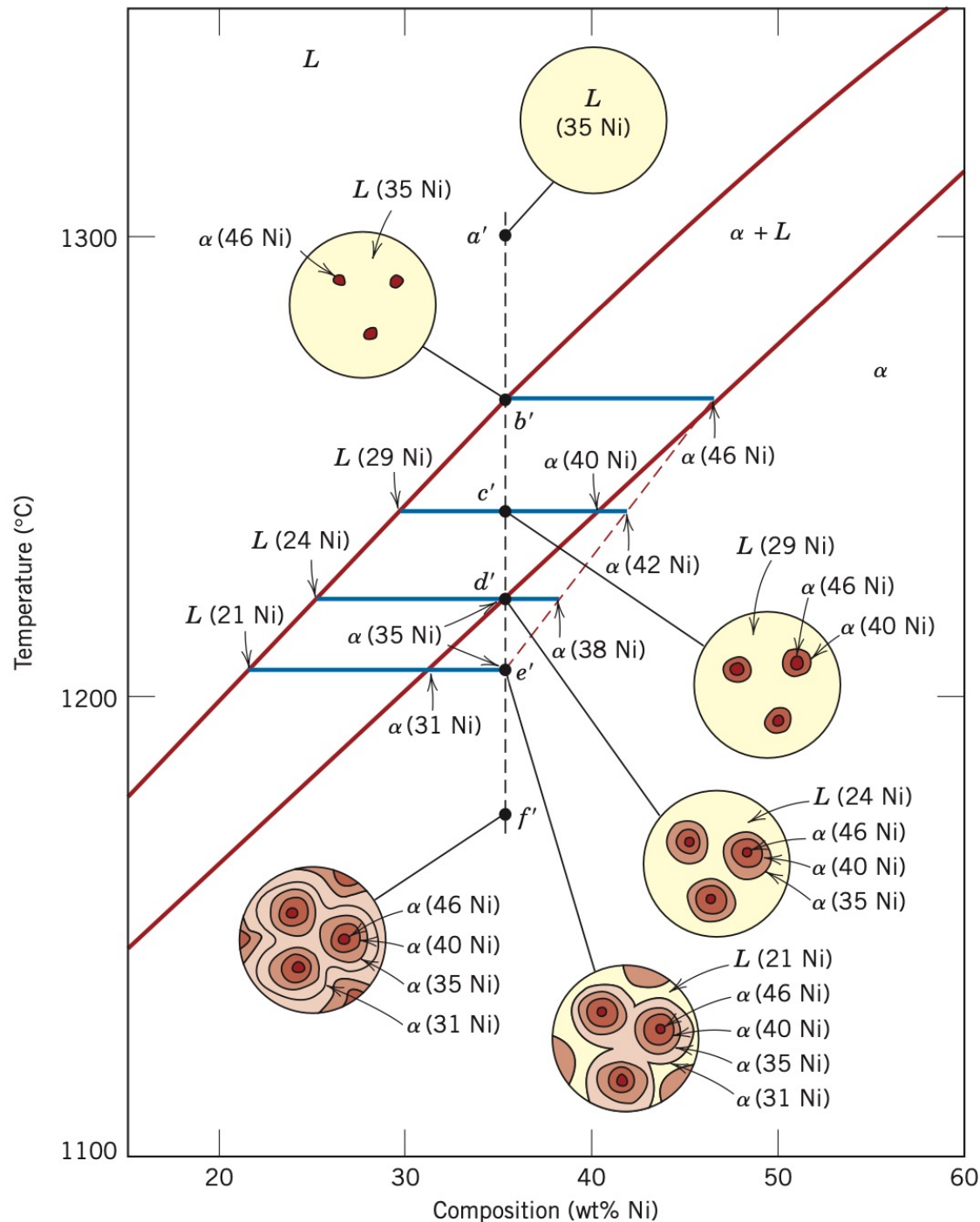
The shifted solidus line (dashed) tells you the average composition of all the α phase at that temperature

Outcome of rapid cooling = Inhomogeneous grain

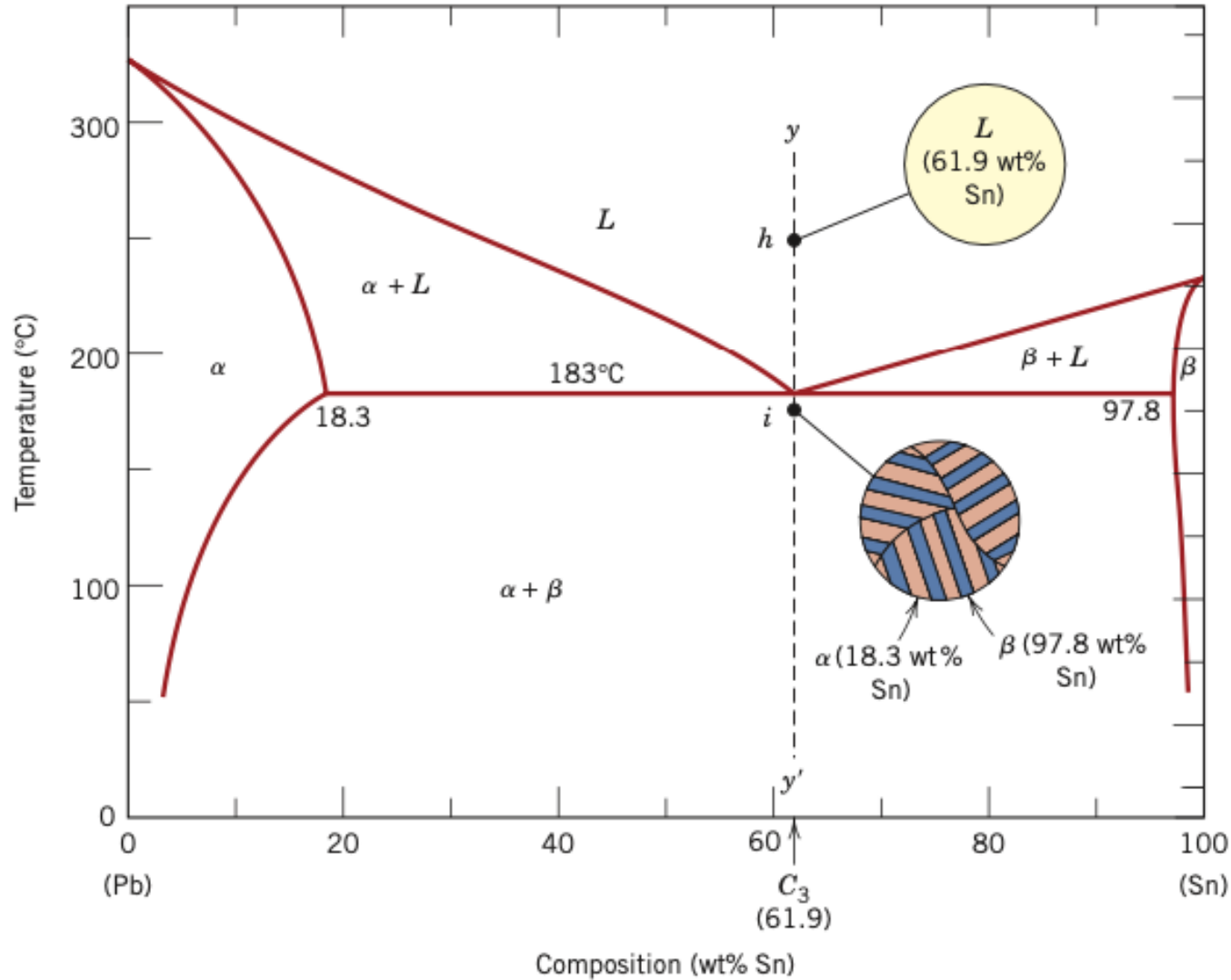
Cored structure

Implication 1: Changes to mechanical properties

Implication 2: Reduced temperature stability



Eutectic are alloys with the lowest melting points

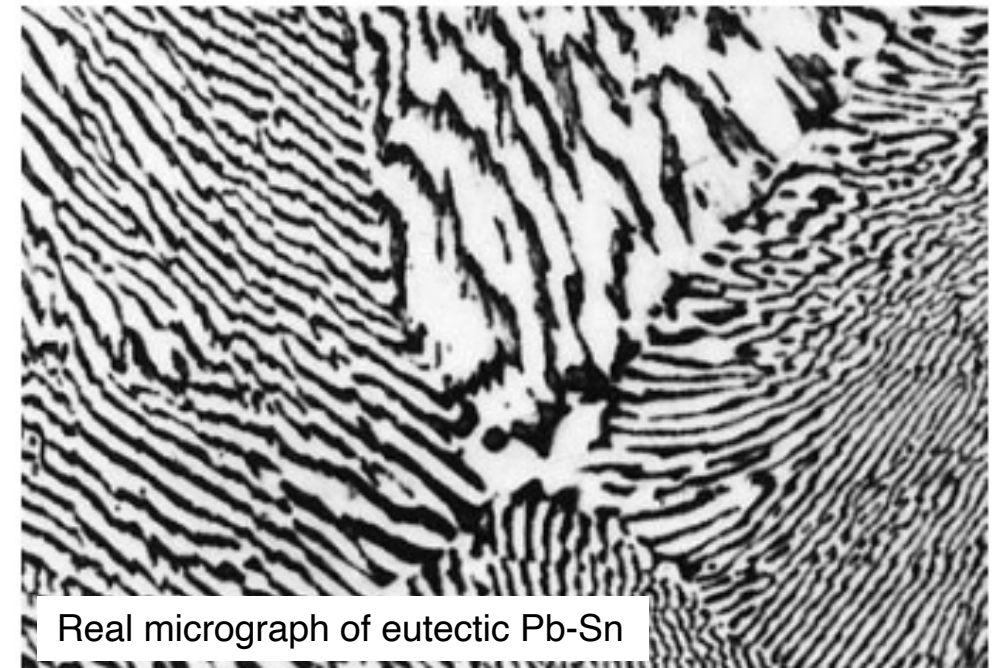


Important things about eutectics:

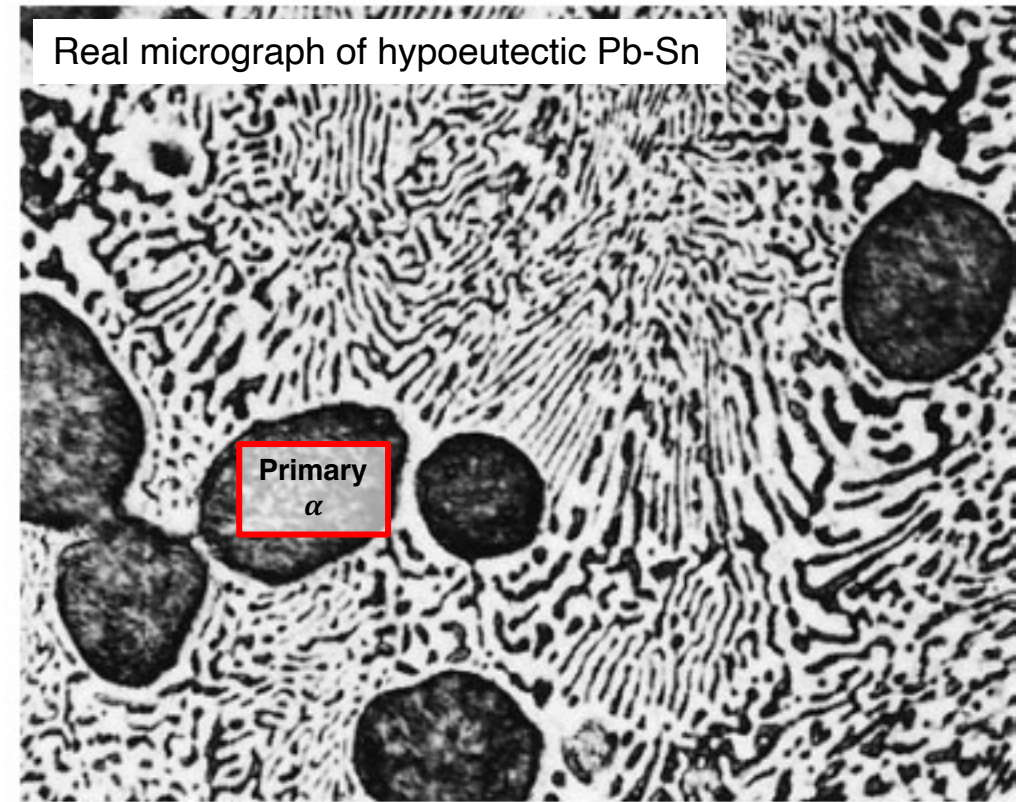
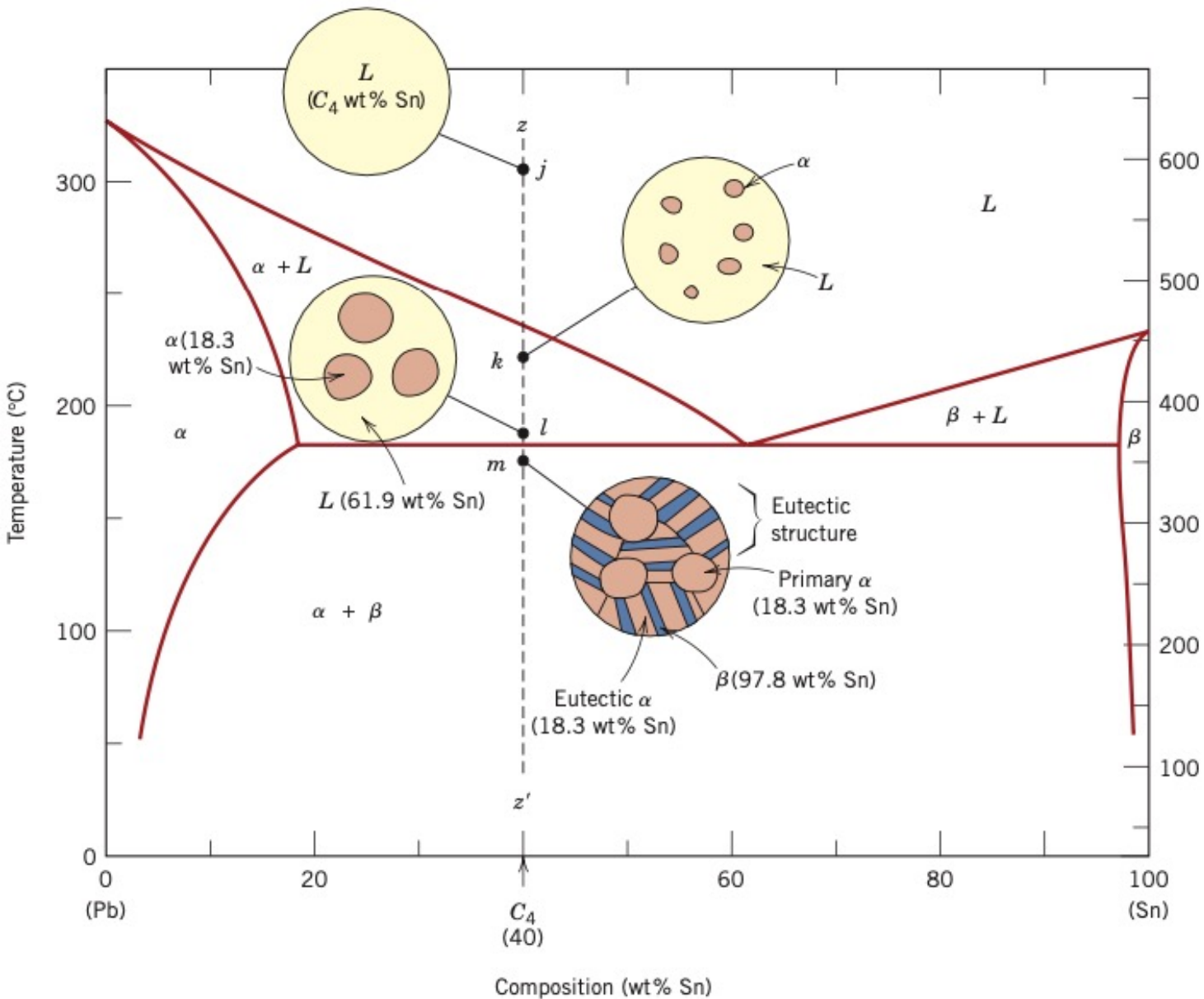
Lowest melting temperature

No L + solid region

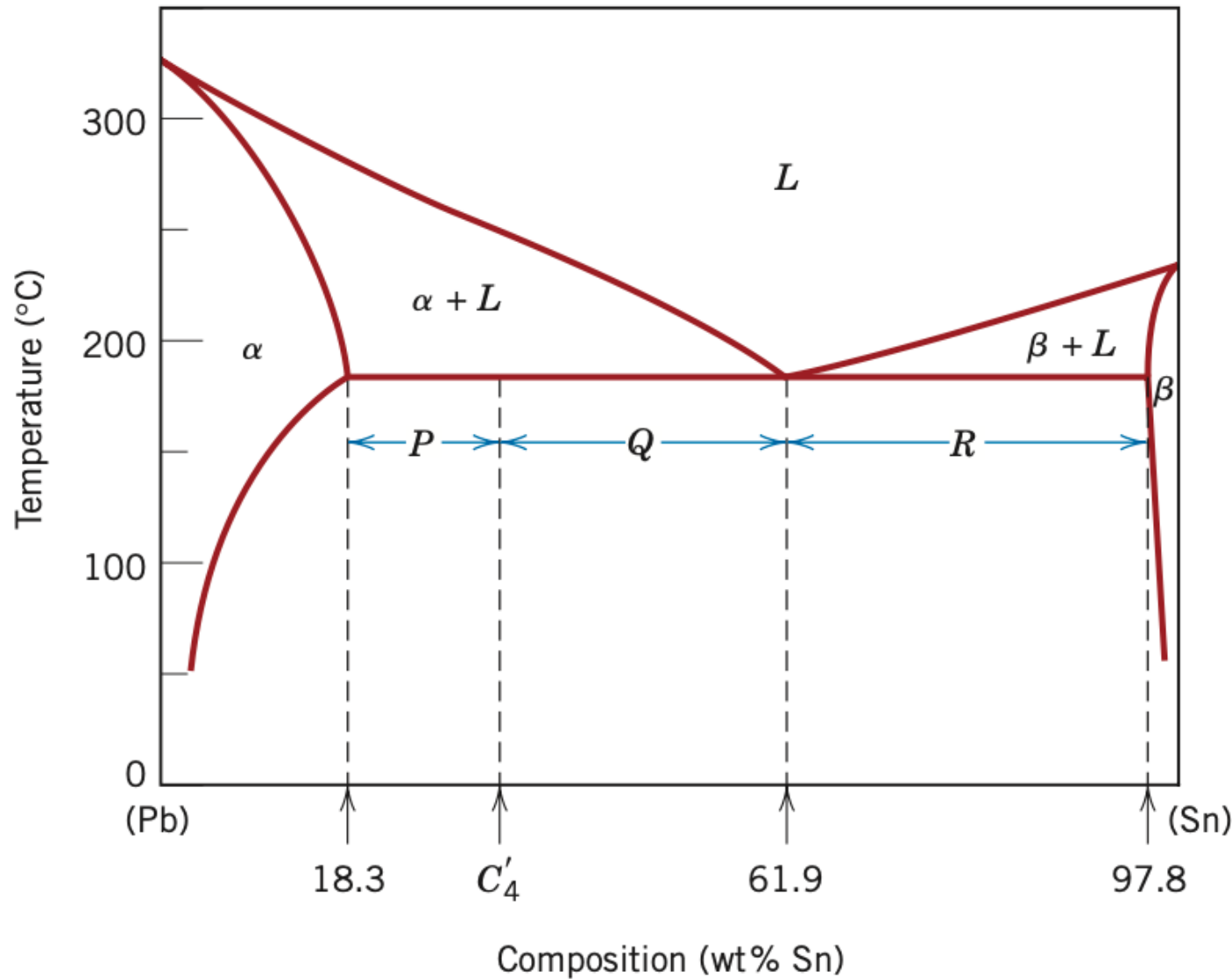
Alternating α and β layers are adopted to facilitate rapid atomic diffusion



Phase diagrams let you predict equilibrium microstructure



Calculating phase fractions in hypo/hypereutectics



Let us consider an alloy of composition C'_4 :

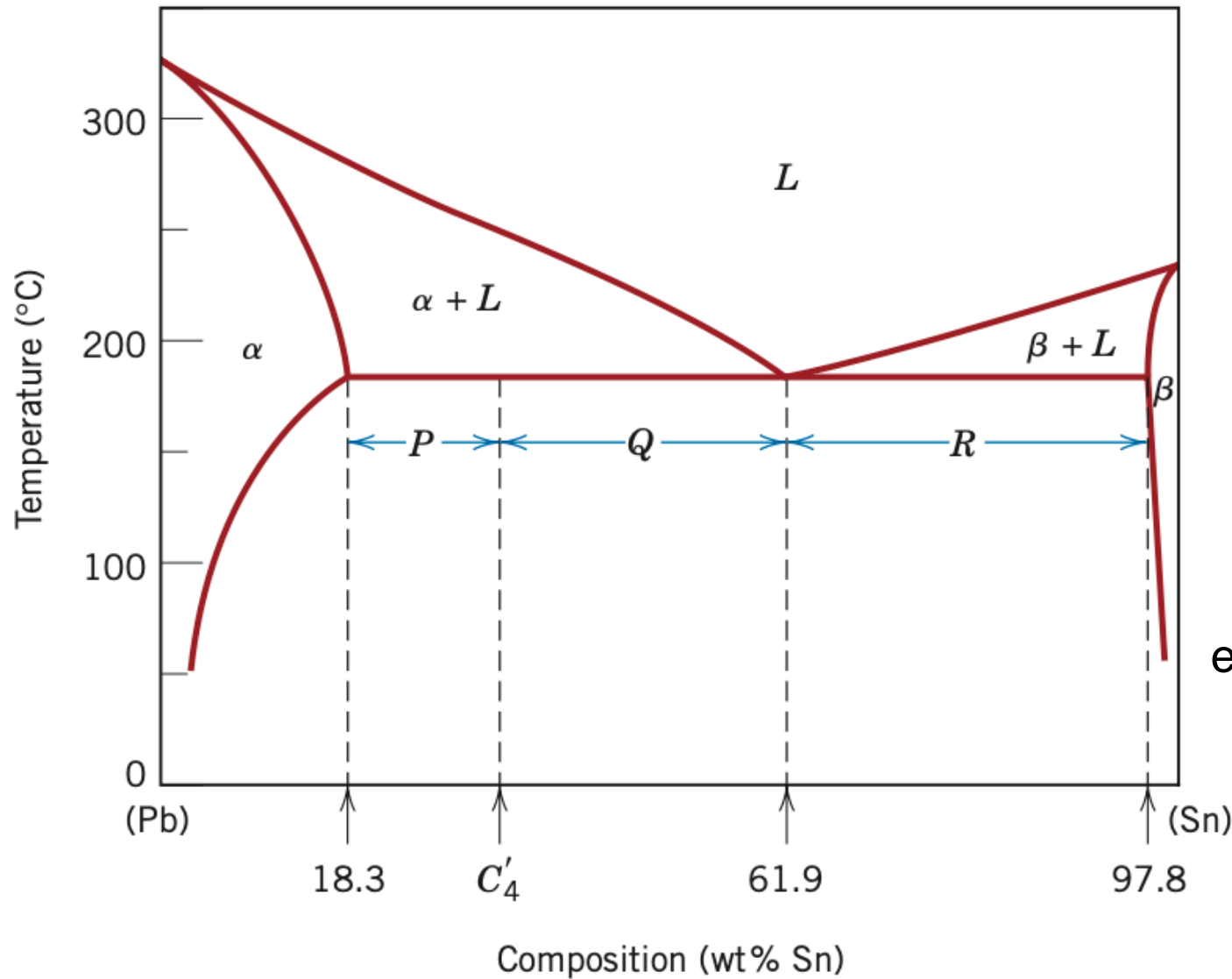
The fraction of the eutectic microconstituent W_e is the same as the fraction of liquid W_L from which it transforms

$$W_e = W_L = \frac{P}{P + Q}$$

The fraction of primary α , $W_{\alpha'}$, is just the fraction of the α phase that existed prior to the eutectic transformation

$$W_{\alpha'} = \frac{Q}{P + Q}$$

Calculating phase fractions in hypo/hypereutectics



Let us consider an alloy of composition C'_4 :

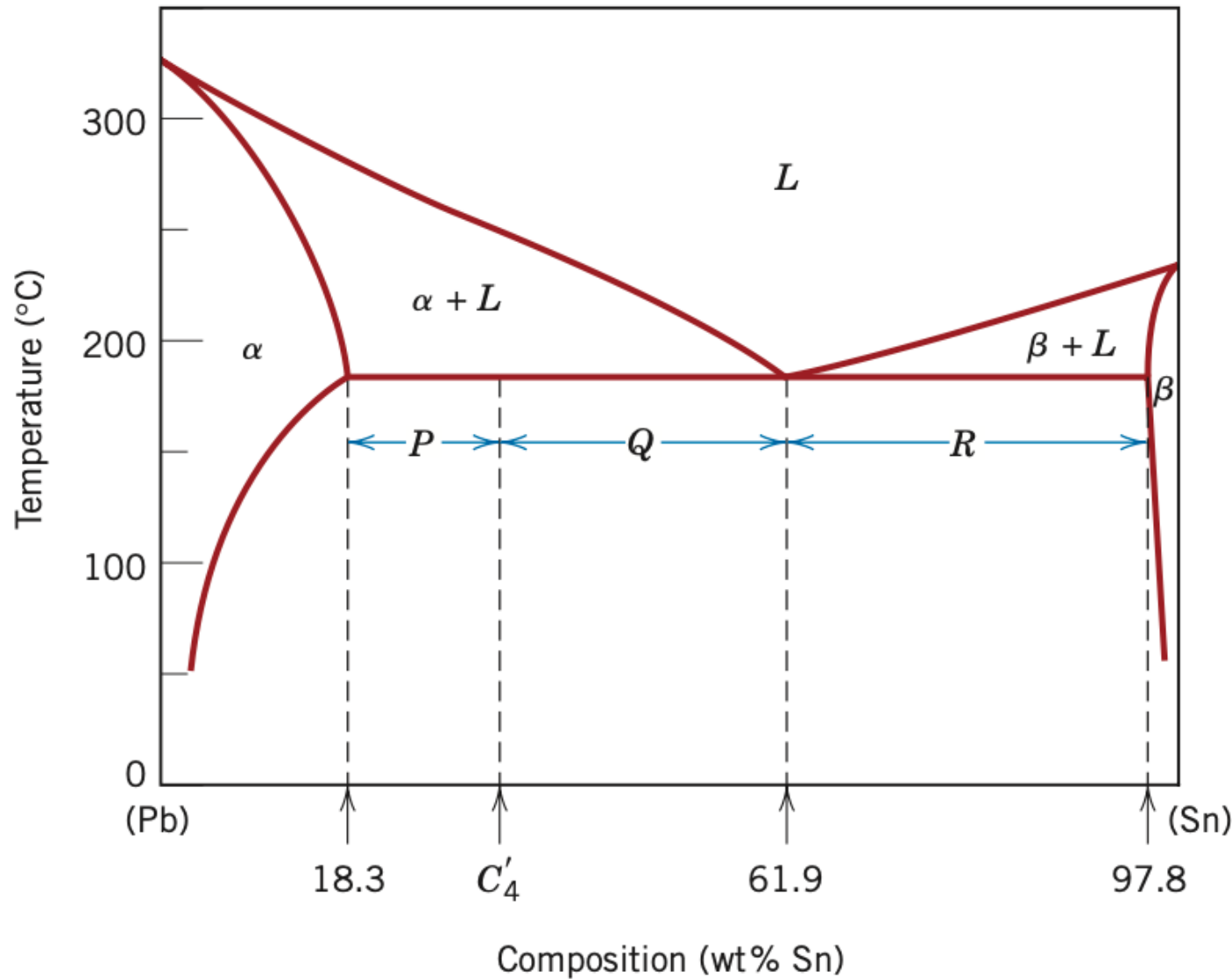
The fraction of α in the eutectic, $W_{\alpha,e}$ is determined by a tie line that extends across the entire $\alpha + \beta$ phase field from C_{eutectic}

$$W_{\alpha,e} = \frac{R}{P + Q + R}$$

Important: This is the fraction of α in the eutectic phase. Not the fraction of α in the alloy

The fraction of α from the eutectic in the alloy as a whole is $W_{\alpha,e} \times W_e$

Calculating phase fractions in hypo/hypereutectics



Let us consider an alloy of composition C'_4 :

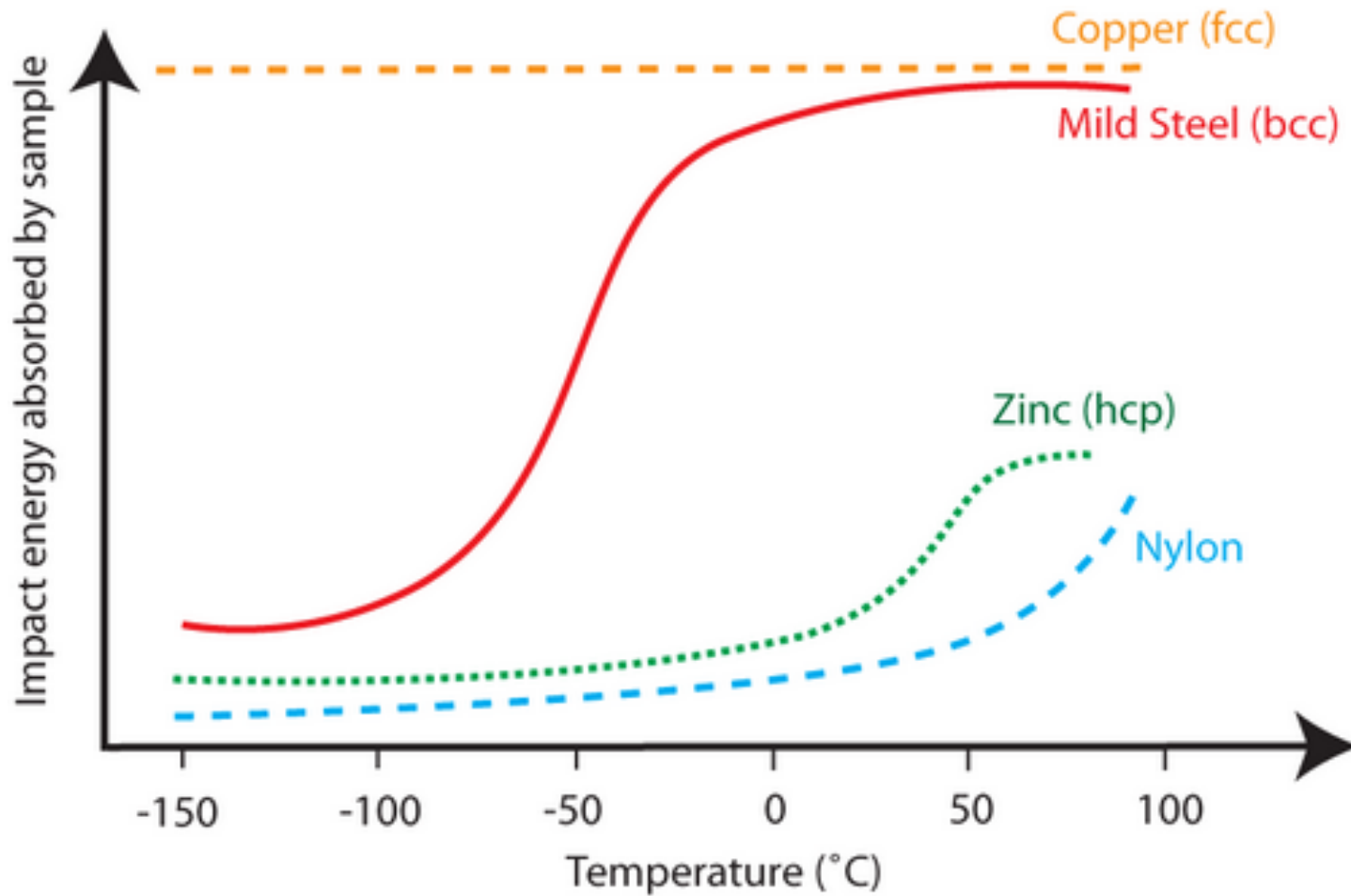
The fraction of the total α , W_α is determined by the a tie line that extends across the entire $\alpha + \beta$ phase field

$$W_\alpha = \frac{Q + R}{P + Q + R}$$

Same goes for total β , W_β

$$W_\beta = \frac{P}{P + Q + R}$$

Ductile-to-Brittle Transition Temperature (DBTT)



Can think of energy absorbed as area under the stress-strain plot

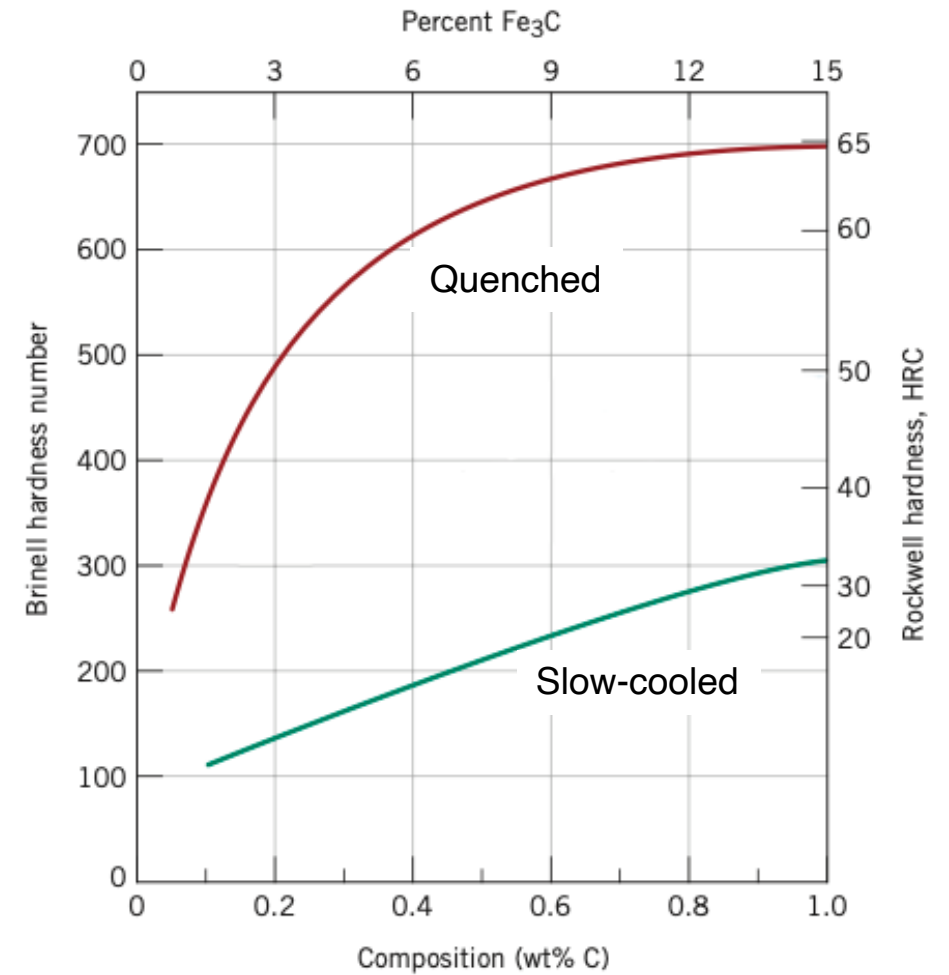
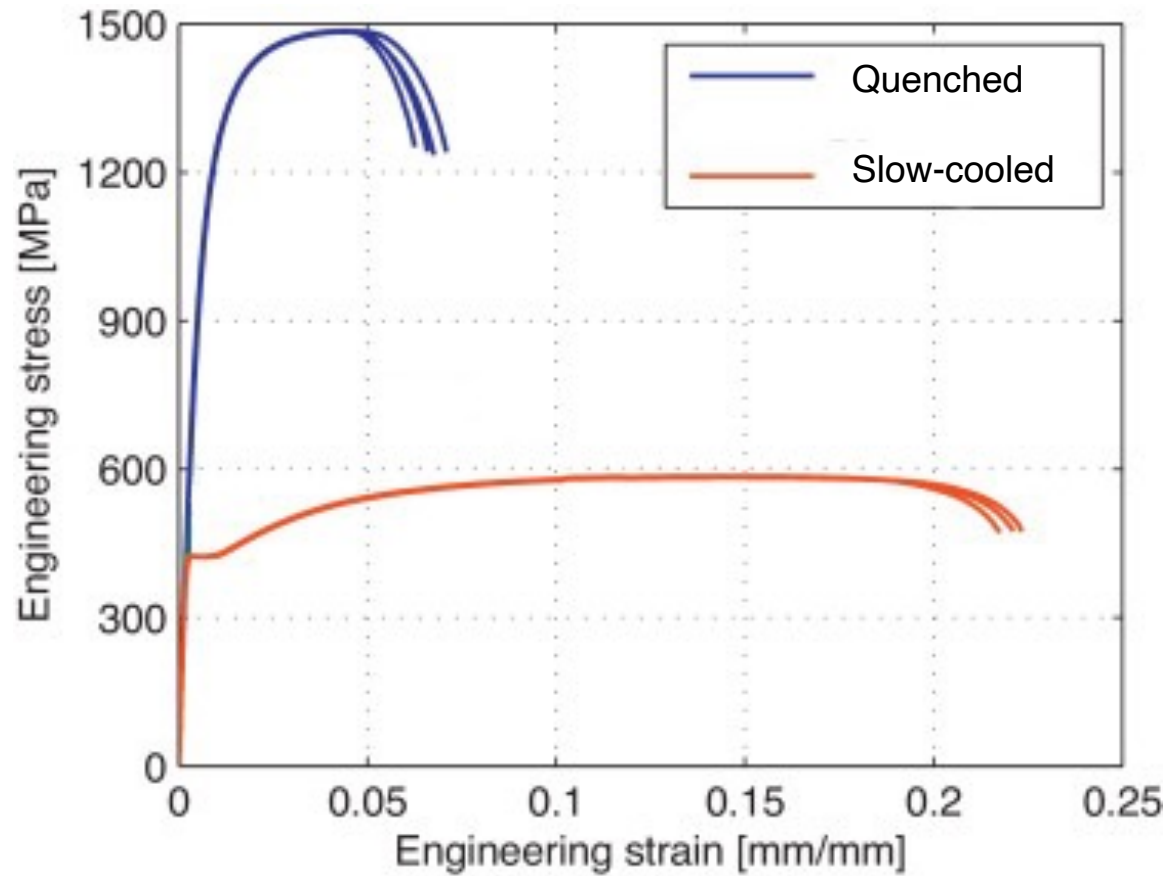


More energy absorbed = more ductile

Temperature does not affect FCC slip systems much

BCC and HCP have slip systems that have temperature-dependent behavior!

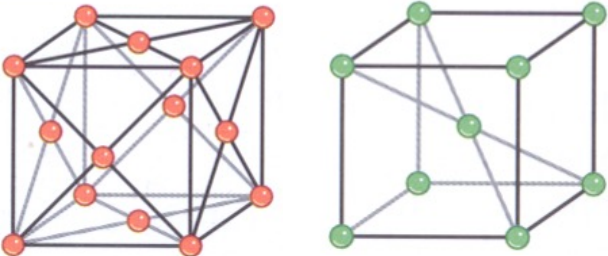
Rapid cooling of steel makes it stronger but brittle



Rapid cooling makes martensite

Rapid cooling → Quench

Austenite (γ) is FCC
 Ferrite (α) is BCC

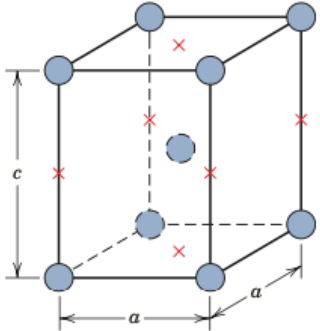


How do we rapidly transform from FCC to BCC?

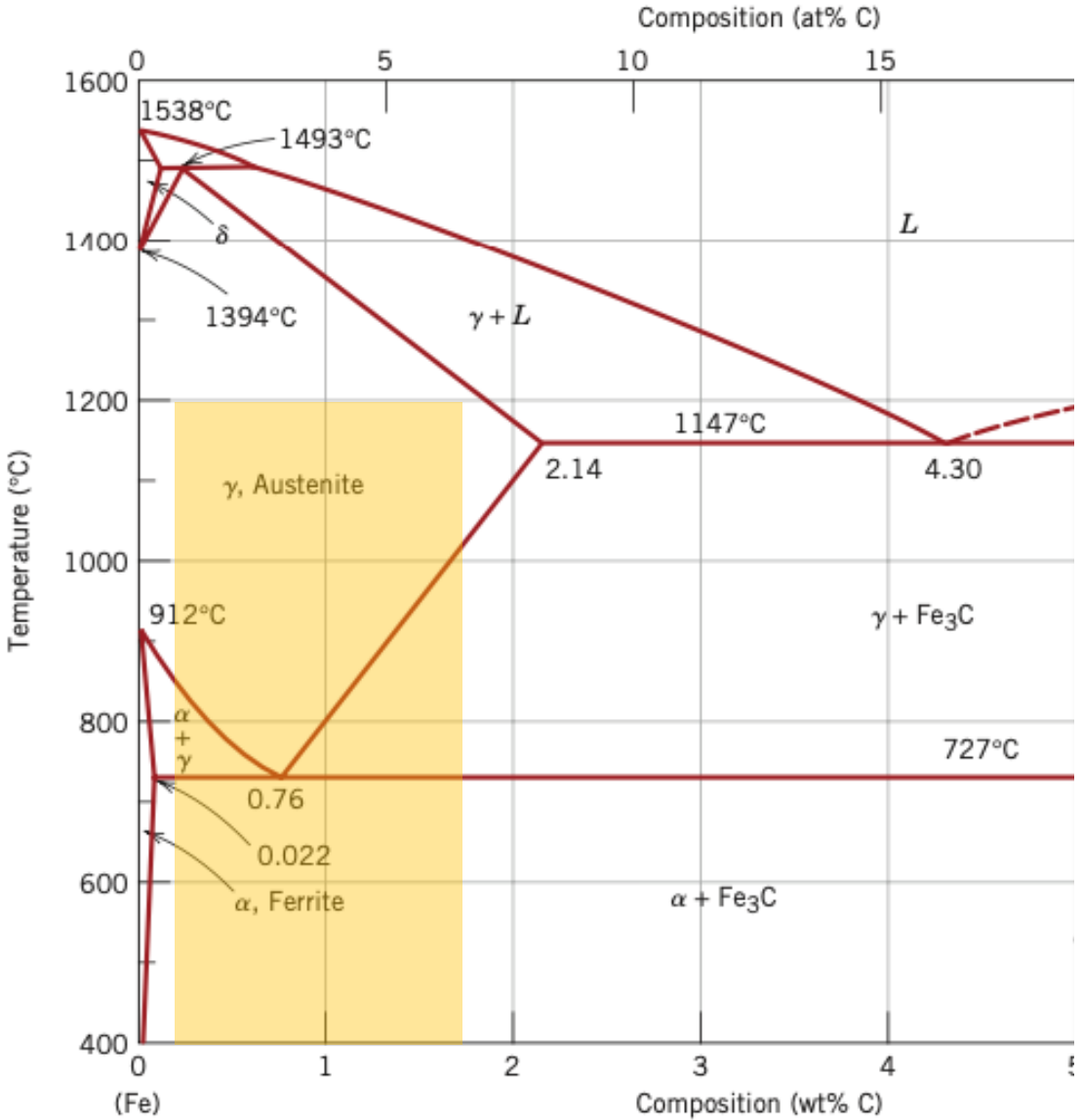
You can't → New non-equilibrium phase emerges

Martensite

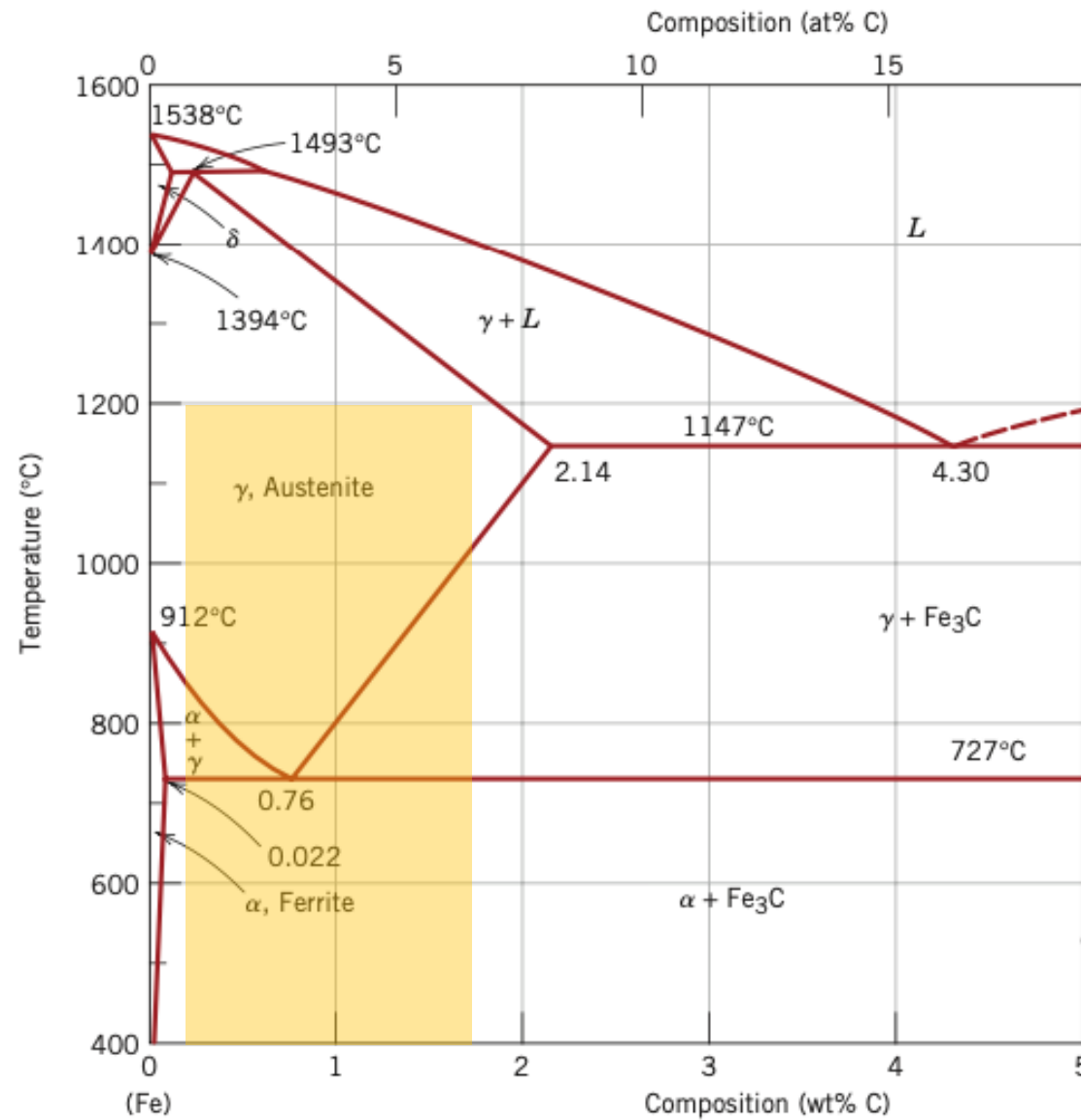
(Body Centered Tetragonal, BCT)



Not on phase diagram because not equilibrium phase!



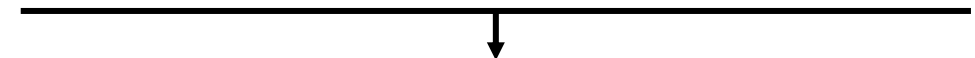
Why is martensite so hard?



Supersaturated with carbon since carbon cannot diffuse away in time. Lattice is strained / distorted due to excess carbon

Martensite formation causes volume expansion (different densities) and shape change \rightarrow Internal stresses

BCT structure has fewer active slip systems than FCC and BCC



Impede dislocation movement!

Solid-state transformations are critical in metal processing

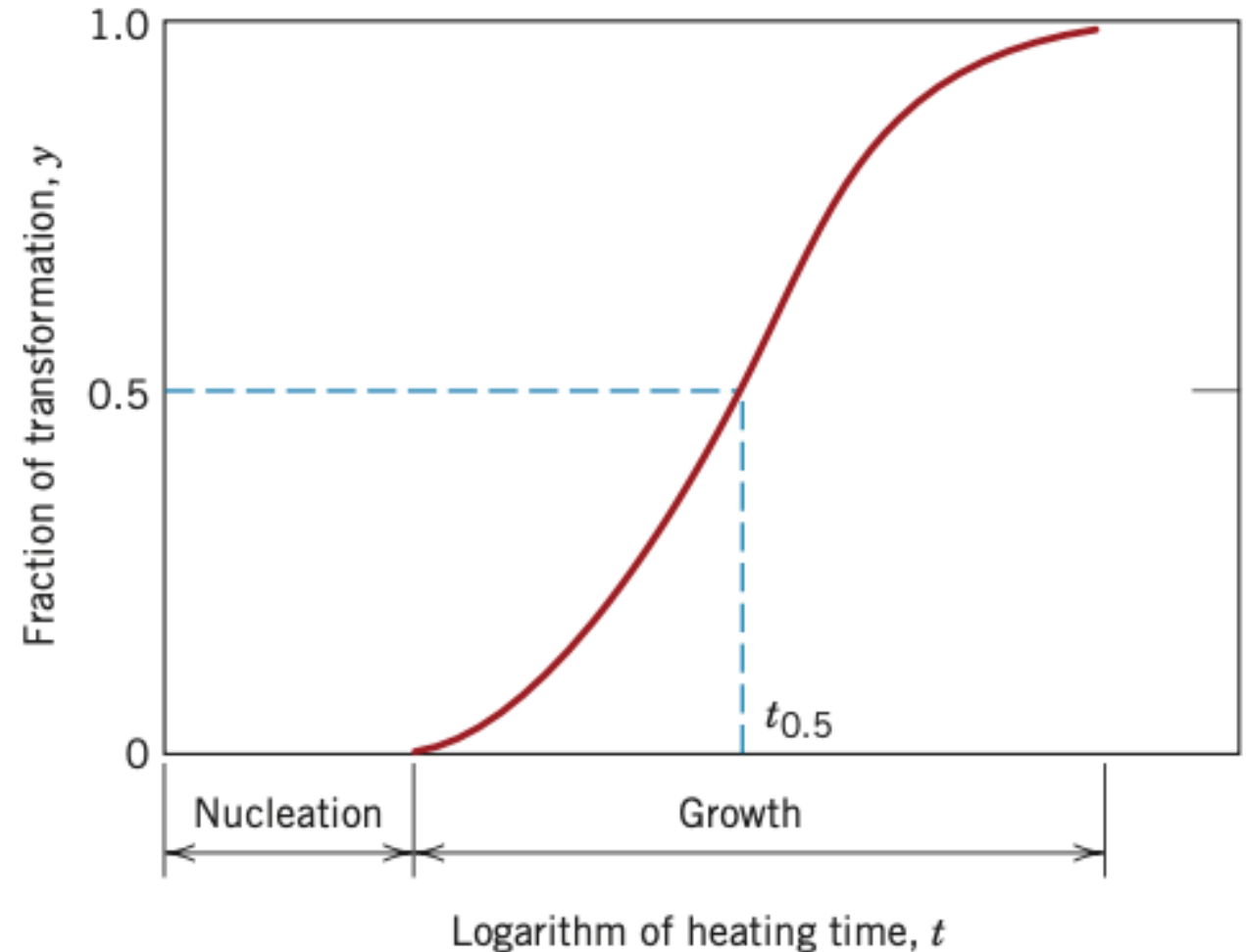
Solid-state transformation can be described by the Avrami equation:

$$y = 1 - e^{-kt^n}$$

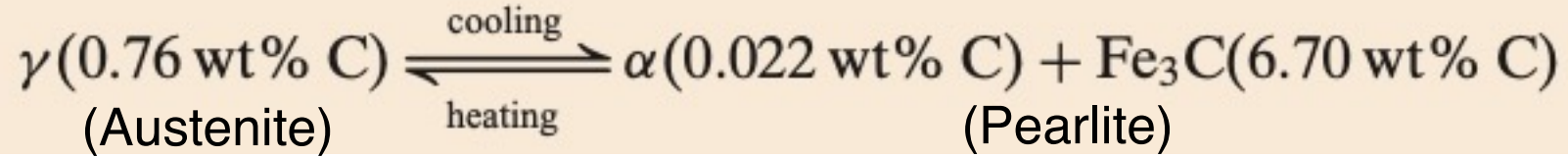
y = fraction of transformation
 k, n = time independent constants for the transformation

By convention, the rate of a transformation is taken as the reciprocal of time requires for 50% transformation

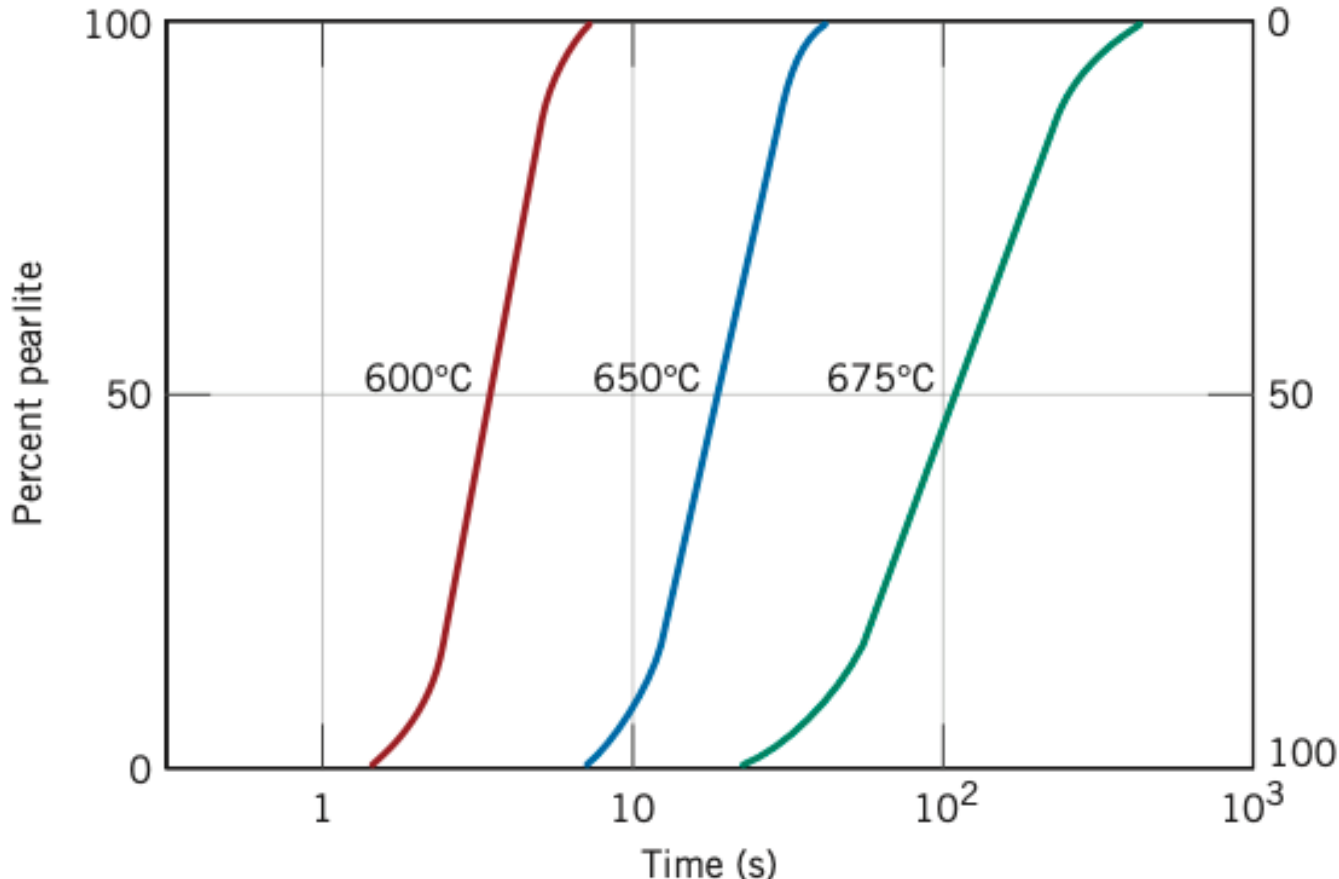
$$Rate = \frac{1}{t_{0.5}}$$



Example: How long does the iron eutectoid take to form?



Equilibrium eutectoid temperature is at 727°C



← Austenite at high temperature cooled to the temperature indicated and then maintained

Supercooling: Difference between the equilibrium transformation temperature and the hold temperature

The larger the supercooling, the larger the driving force for transformation, the faster the transformation

Time-Temperature-Transformation (TTT) diagrams*

Let's walk through this diagram:

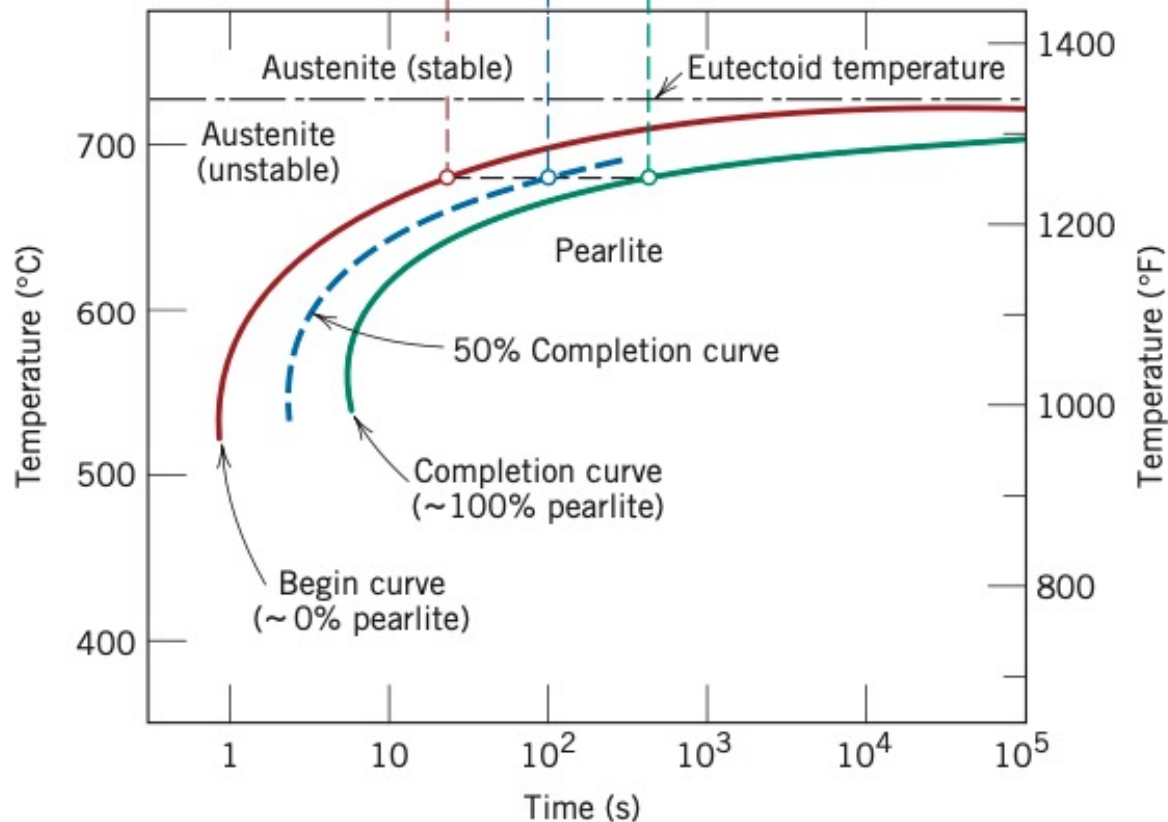
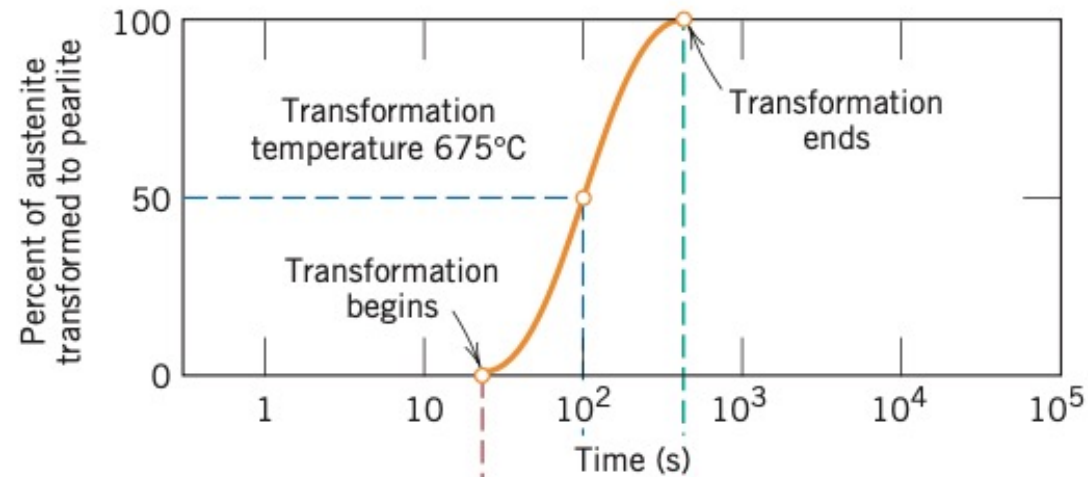
At temperatures just below the eutectoid (low supercooling) → Long times to transform (10^5 s)

The larger the supercooling, the faster the transformation rate.

At 540°C , ~ 3 s needed to go to 50% completion

Constraint 1: A TTT diagram is only valid for a particular composition.

Constraint 2: Plots are only accurate if the temperature is held constant throughout the transformation



Let's try to use a TTT diagram to predict metastable microstructure

Starting from 760°C:

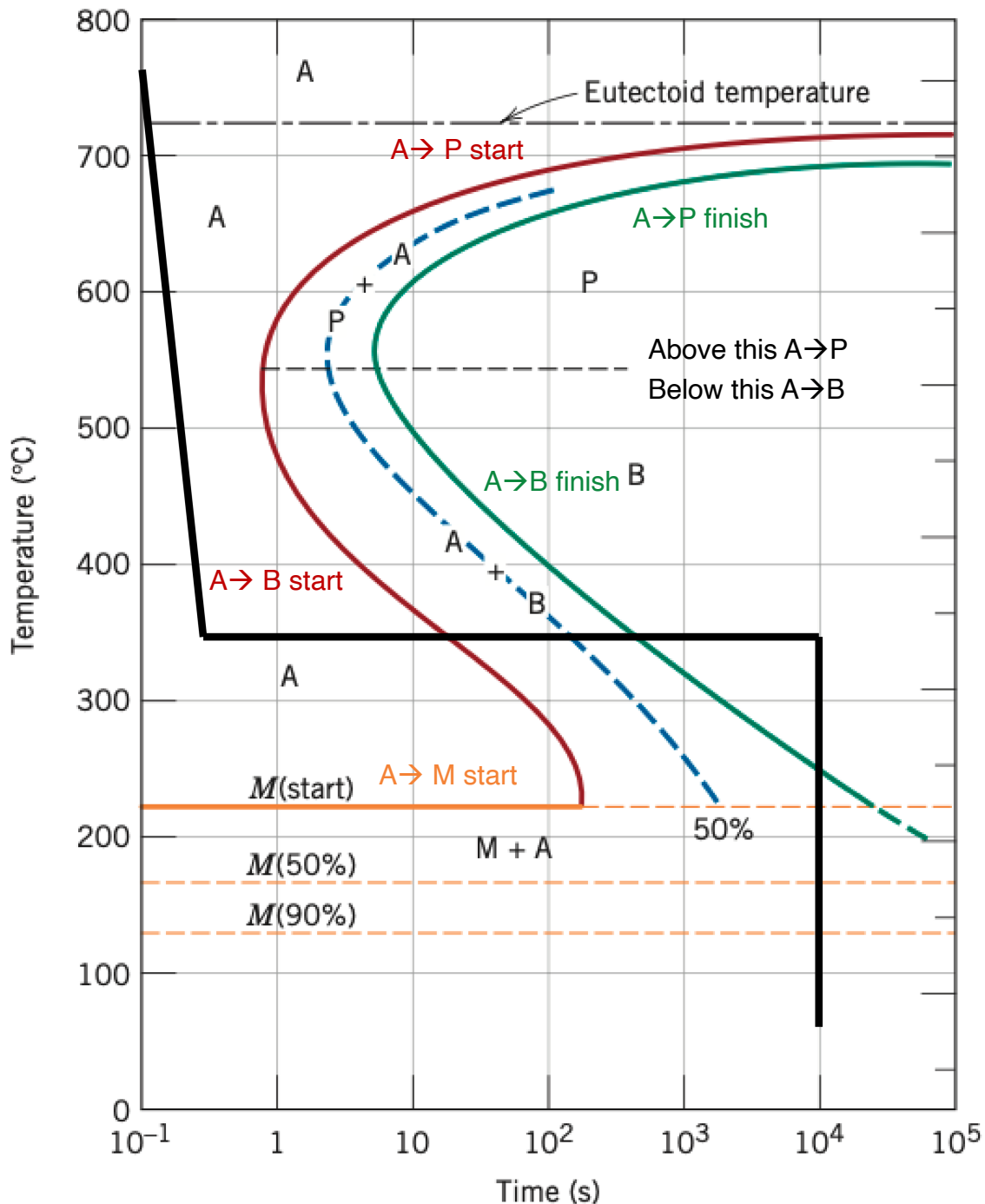
a) Rapidly cool to 350°C, hold for 10^4 s, quench to RT

Assume initial cooling is rapid enough to prevent any transformations from happening

Austenite (A) \rightarrow Bainite (B) starts ~ 10 s and is completed after ~ 600 s. After 10^4 s, it's 100% B

Quenching to RT does not produce any martensite even though it passes through the martensite region.

No austenite left to transform!



Let's try to use a TTT diagram to predict metastable microstructure

Starting from 760°C:

c) Rapidly cool to 600°C, hold for 4s, rapidly cool to 450°C, hold for 10s, then quench to RT

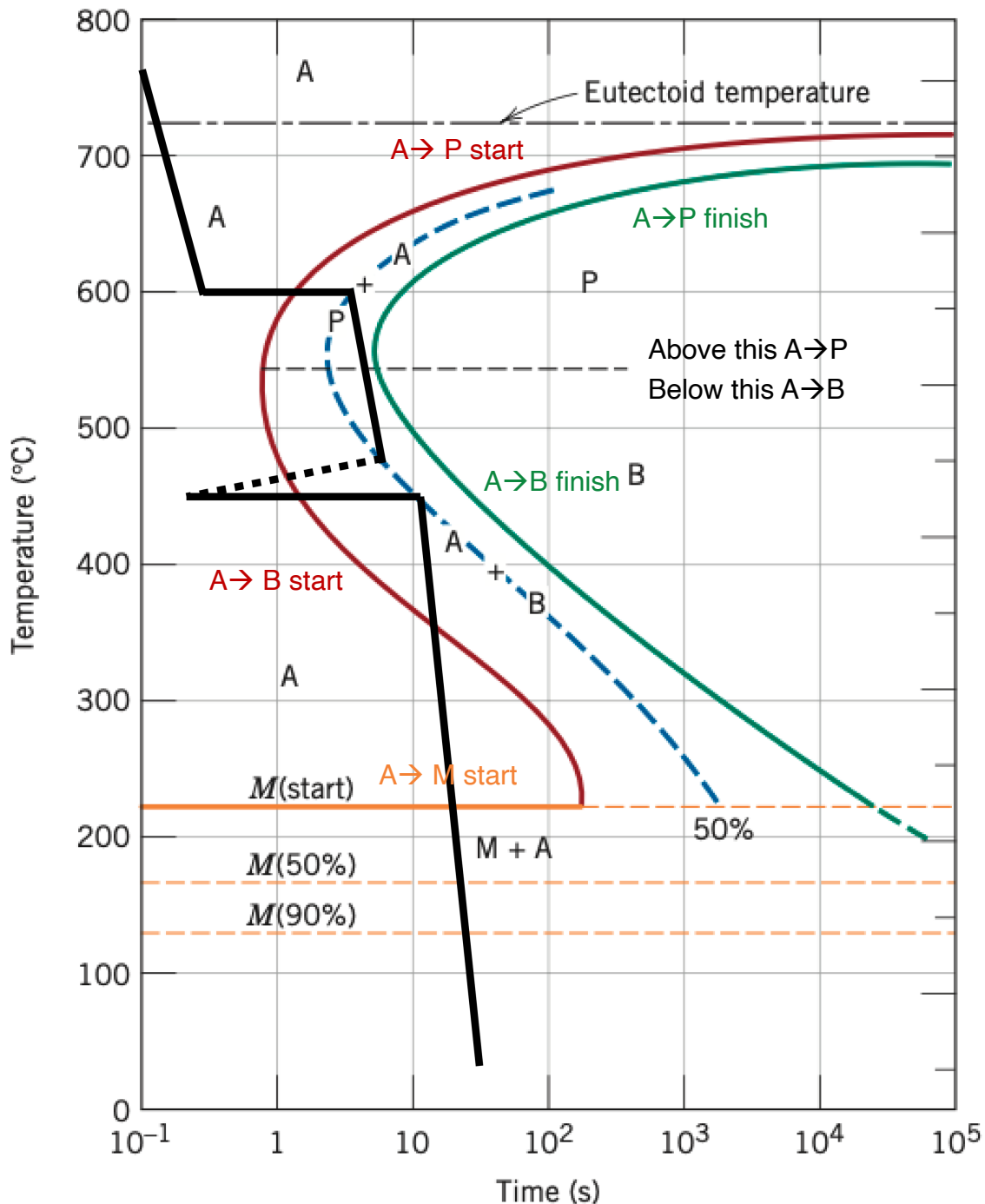
Holding at 600°C for 4s \rightarrow ~50% A + P

Assume during rapid cooling to 450°C, nothing happens

At 450°C, we start timing from 0 again to see what happens to the unstable austenite.

Holding at 450°C for 10s \rightarrow 50% of remaining A till transform into B (25% of original sample is B)

Quenching to RT transforms the remaining A to M.



IMPORTANT: Austenite and solid-state transformations

For MSE 214, **only austenite** undergoes solid-state transformations on cooling

Allowed solid-state transformations

Austenite → Ferrite
Austenite → Martensite
Austenite → Pearlite
Austenite → Bainite

Not-allowed solid-state transformations

Ferrite → Martensite
Martensite → Pearlite
Pearlite → Bainite
Etc.

Transformations can only occur if there is some austenite left to transform

No more austenite = No more transformation = Composition is “locked-in” until room temperature

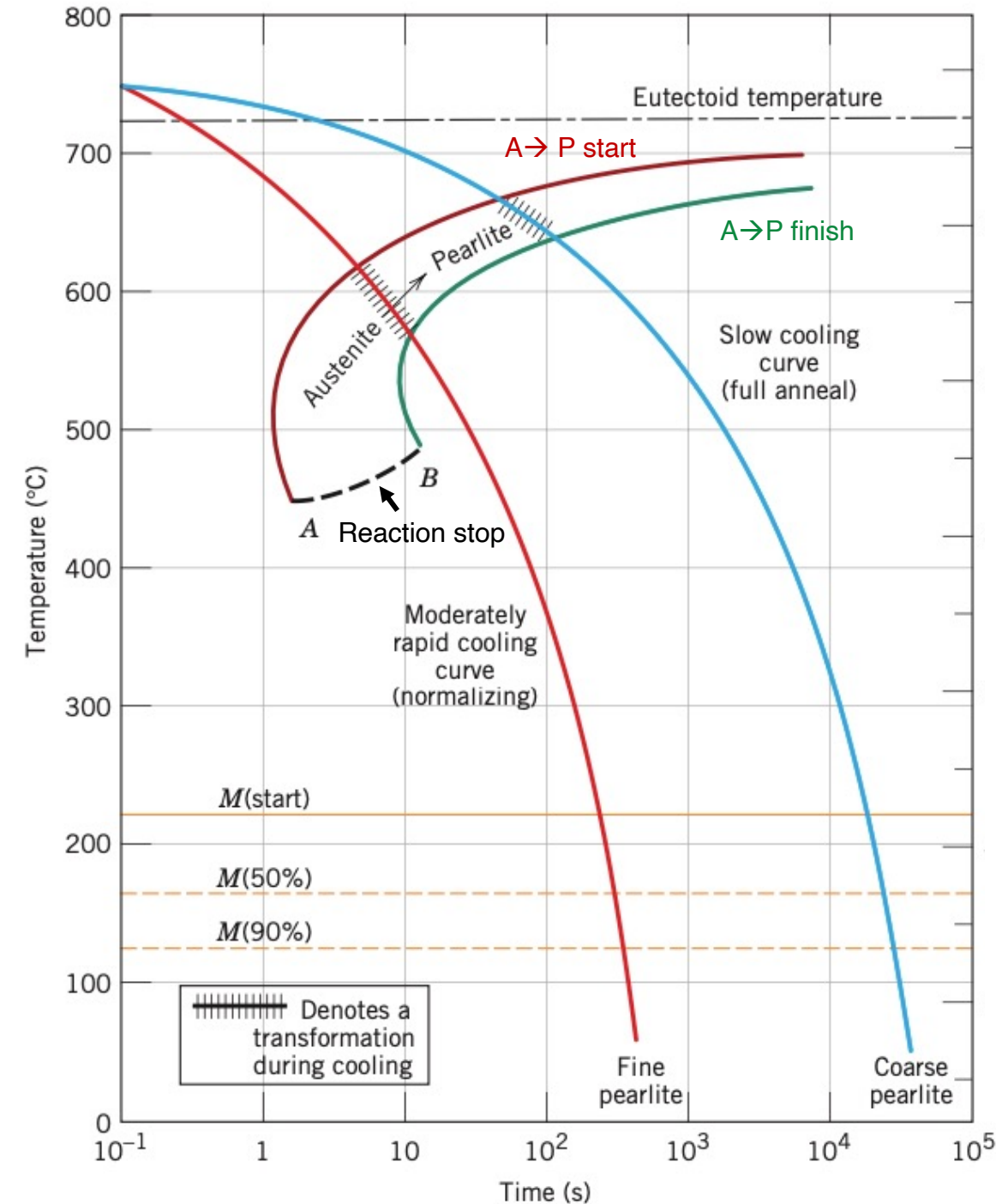
← CCT diagram

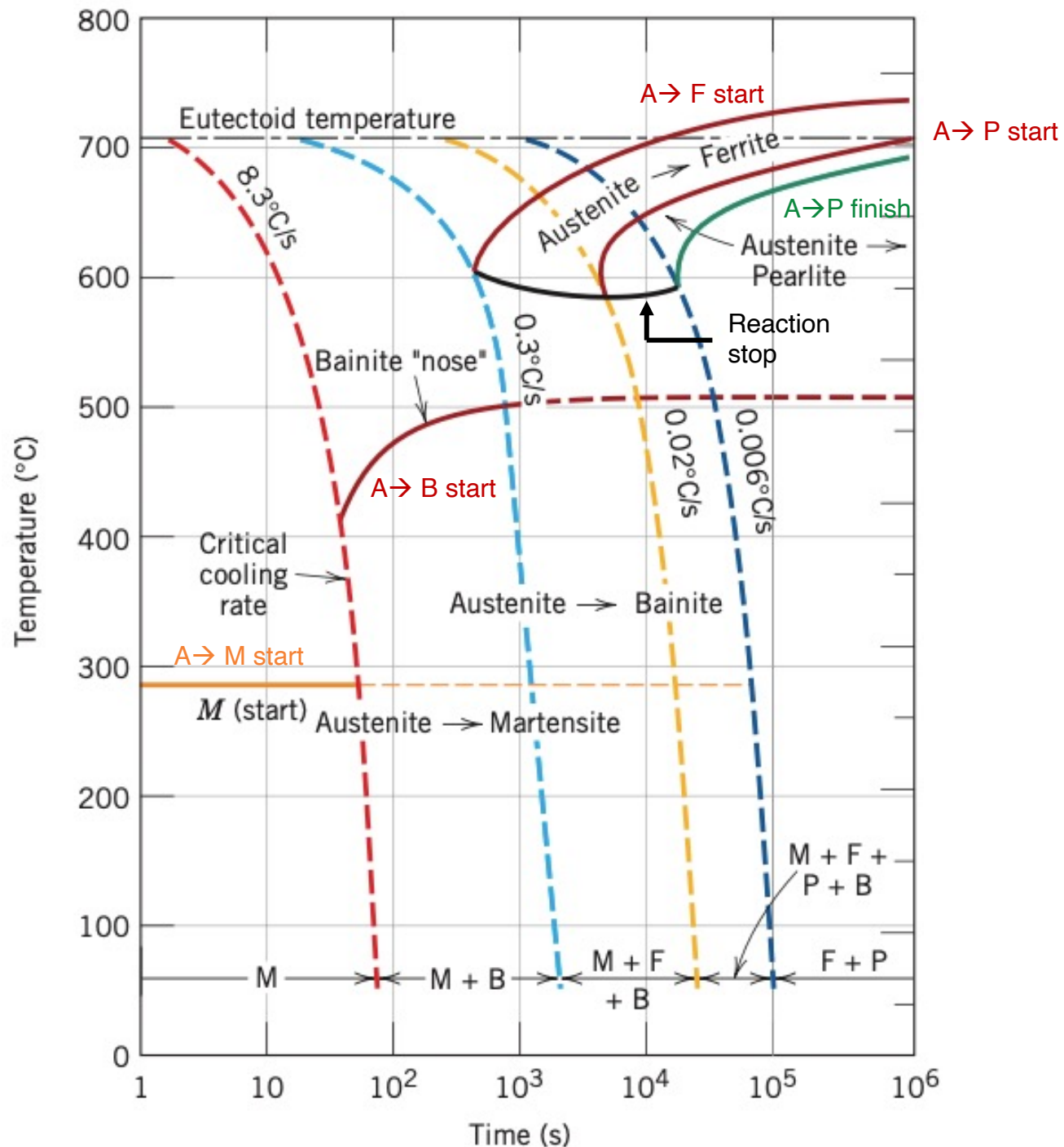
CCT diagrams can look similar to TTT diagrams!

Cooling curves (cooling at different rates) superimposed onto CCT diagrams

Transformation starts when the cooling curve intersects the beginning reaction curve and is completed when it crosses the completion curve.

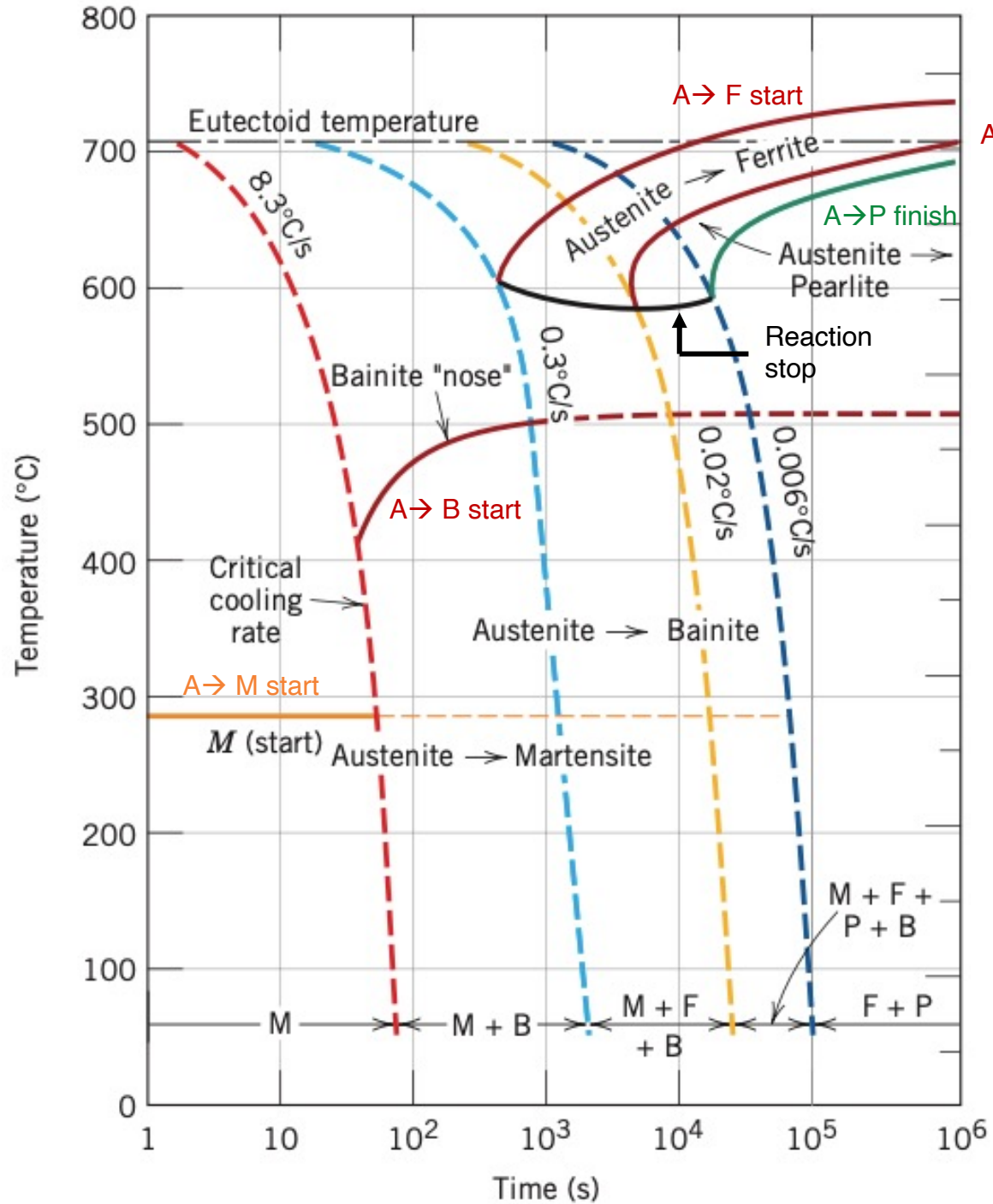
If the cooling curve exits the region before crossing the completion curve, only some fraction of the metal transformed





General rules:

- At room temperature, no more austenite (A)
- If the cooling curve crosses a finish line, it means all A transformed → No more further transformations
- If the cooling curve crosses a stop line, it does not mean all the A was consumed. It just means that the A→X reaction stopped. Some A and X left. The remaining A can transform
- If the cooling curve crosses a new reaction A→X before it finishes/stops the previous one, assume that both reactions happen.

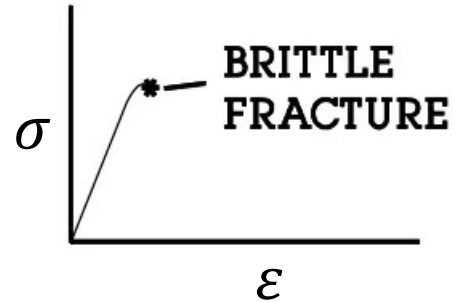
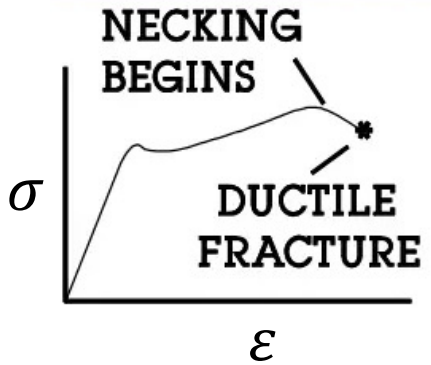


Questions on CCT (if any) will be qualitative:

What phases are there?

~~What percentage of martensite is present at room temperature?~~

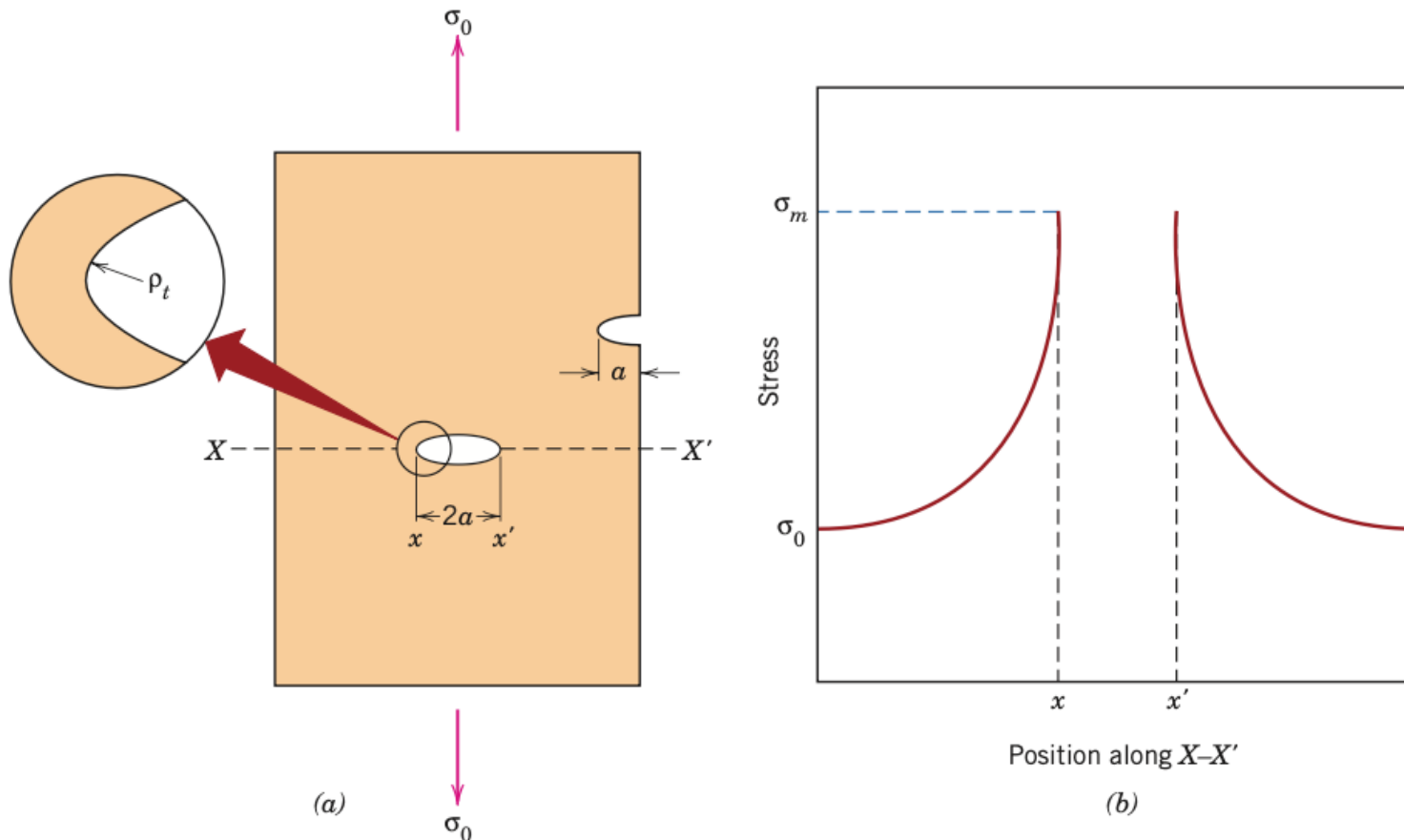
Ductile vs Brittle Fracture



	Ductile	Brittle
Energy absorption before failure	High	Little
Plastic deformation at the crack front	Significant	Little to none
Crack growth rate	Stable / Slow	Unstable/ Rapid
Force required to maintain crack growth	Yes	No

Cracks act as stress concentrators

Consider an elliptical crack of width $2a$ in the center of a body subjected to an applied stress σ_0



Magnitude of localized stress decreases with distance away from the crack tip

Far from the crack tip, the stress is just the applied stress σ_0

Maximum stress at the crack tip

$$\sigma_m = 2\sigma_0 \sqrt{\frac{a}{\rho_t}}$$

a : length of surface crack or half the length of an internal crack

ρ_t : the radius of curvature of the crack tip

Fracture Toughness

$$\sigma_c = \sqrt{\frac{2E\gamma}{\pi a}}$$

For a crack of length a , σ_c is the stress required for crack propagation

$$\sigma_c \sqrt{\pi a} = \sqrt{2E\gamma} \rightarrow \text{Material properties}$$

$$\sigma_c \sqrt{\pi a} = K_c \rightarrow \text{Critical stress intensity factor or Fracture Toughness}$$

More generally:

$$K_c = Y \sigma_c \sqrt{\pi a}$$

Y : Dimensionless geometric constant

K_c has units of $\text{MPa} \sqrt{m}$

Why is K_c important?

If you know K_c and a , you can solve for stress needed to cause fracture (σ_c)

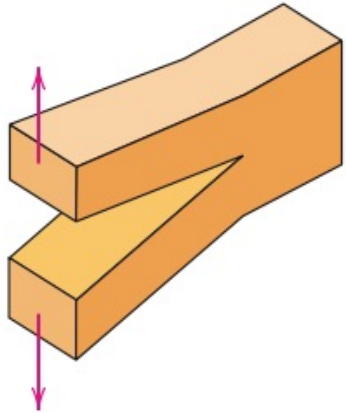
If you know K_c and the stress in the system (σ_c), you can solve for the maximum crack size that can be tolerated before fracture (a)

Note 1: K_c is independent of sample thickness only when sample thickness is much greater than crack dimensions

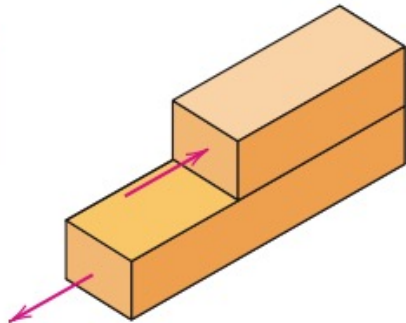
Note 2: The constant value K_c is the one that is most often reported. It is called the *plane strain fracture toughness*

There are different kinds of Fracture Toughness

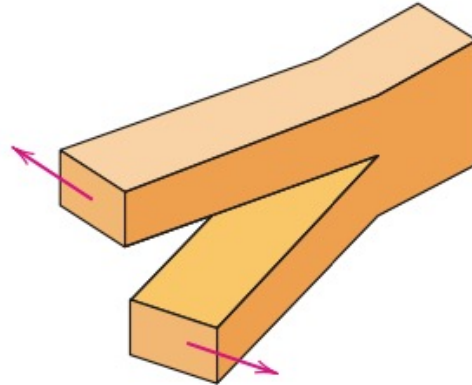
Mode I
(Opening)



Mode II
(In-plane shear)

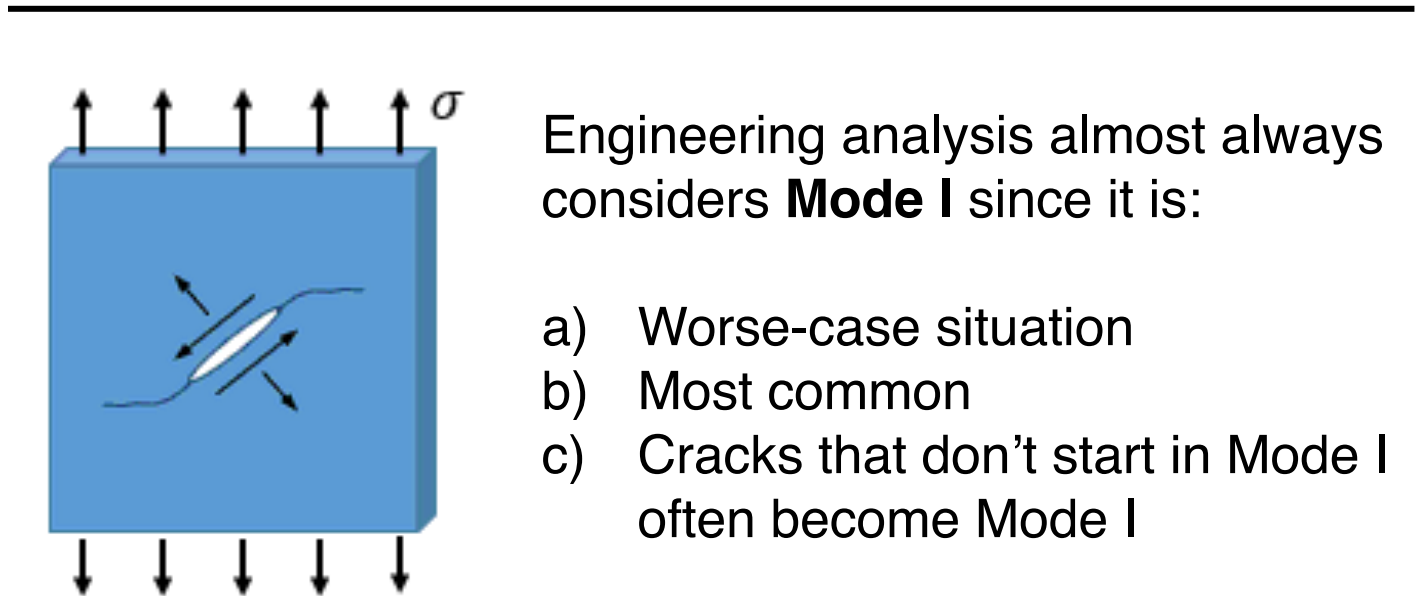


Mode III
(Out-of-plane shear)



Each loading mode has its own associated fracture toughness value!

$$K_{Ic}, K_{IIc}, K_{IIIc}$$



Engineering analysis almost always considers **Mode I** since it is:

- a) Worse-case situation
- b) Most common
- c) Cracks that don't start in Mode I often become Mode I

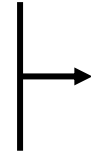
Material

K_{Ic}
MPa√m

Aluminum alloy ^a (7075-T651)	24
Aluminum alloy ^a (2024-T3)	44
Titanium alloy ^a (Ti-6Al-4V)	55
Alloy steel ^a (4340 tempered @ 260°C)	50.0
Alloy steel ^a (4340 tempered @ 425°C)	87.4
Polystyrene (PS)	0.7–1.1
Poly(methyl methacrylate) (PMMA)	0.7–1.6
Polycarbonate (PC)	2.2

Fatigue — Fracture from cyclic stresses

Form of fracture in structures subjected to dynamic and fluctuating stresses

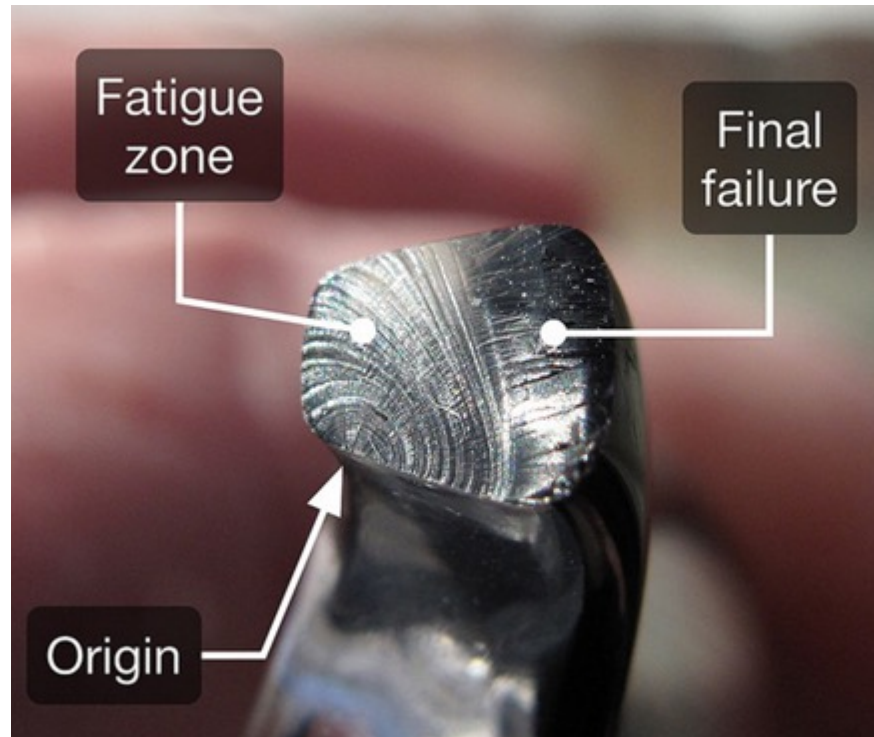


Here, fracture can occur at a stress level **much lower** than the tensile or yield strength

Fatigue fracture is often sudden and without warning

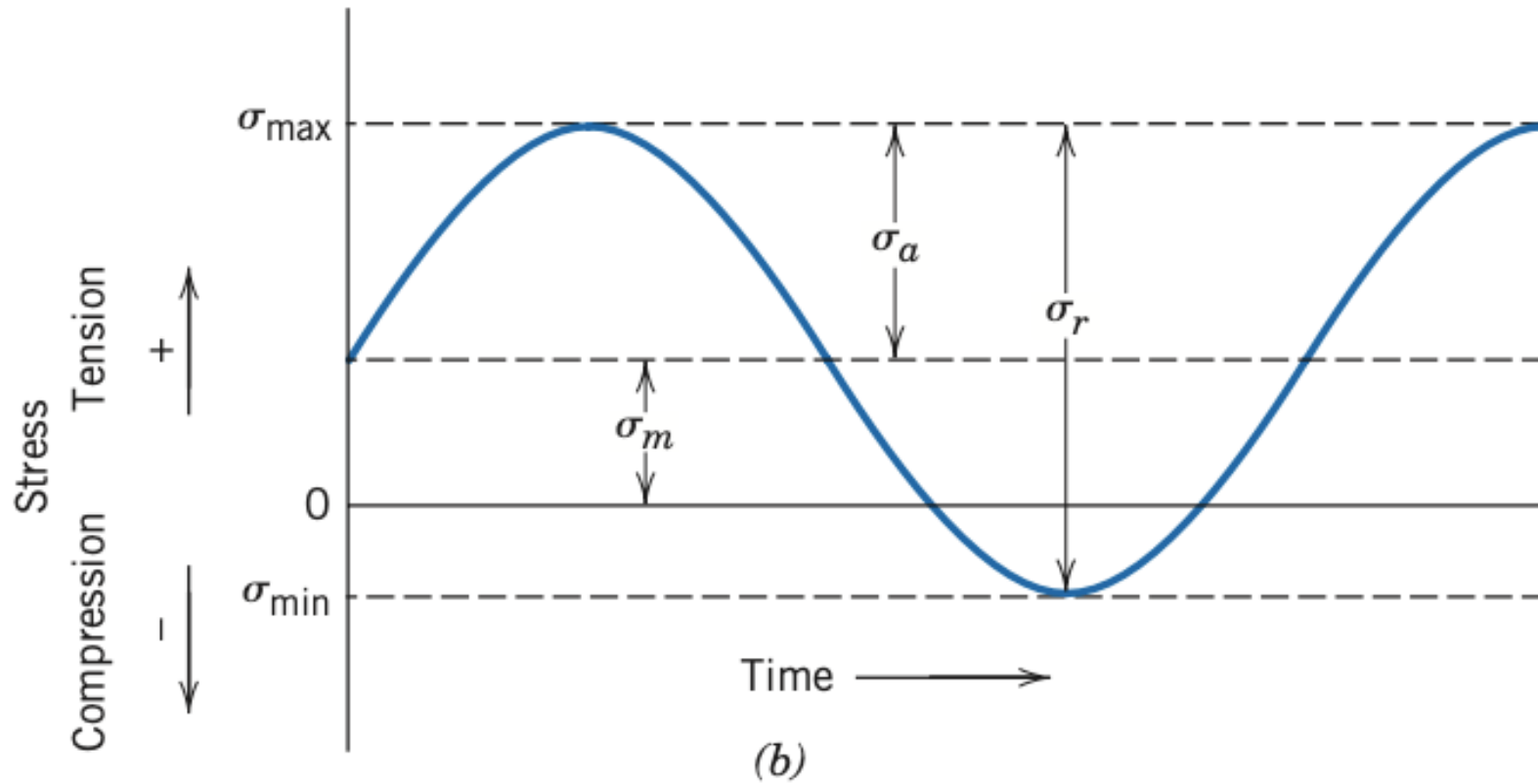
Fatigue fracture is brittle-like even in normally ductile metals

Little to no plastic deformation associated with fracture



Fatigue fracture looks like brittle failure!

Parameters to characterize a stress cycle



σ_m = mean stress
 σ_r = range of stress
 σ_a = stress amplitude

Mean stress

$$\sigma_m = \frac{\sigma_{max} + \sigma_{min}}{2}$$

Range of stress

$$\sigma_r = \sigma_{max} - \sigma_{min}$$

Stress amplitude

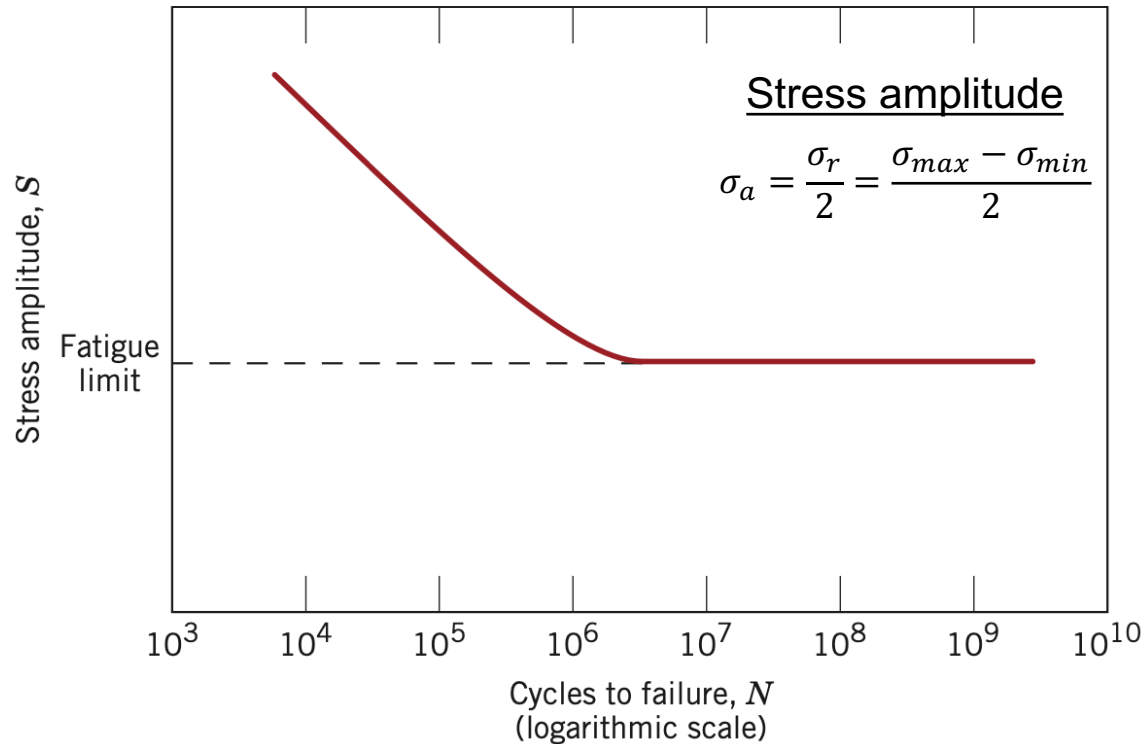
$$\sigma_a = \frac{\sigma_r}{2} = \frac{\sigma_{max} - \sigma_{min}}{2}$$

Stress ratio

$$R = \frac{\sigma_{min}}{\sigma_{max}}$$

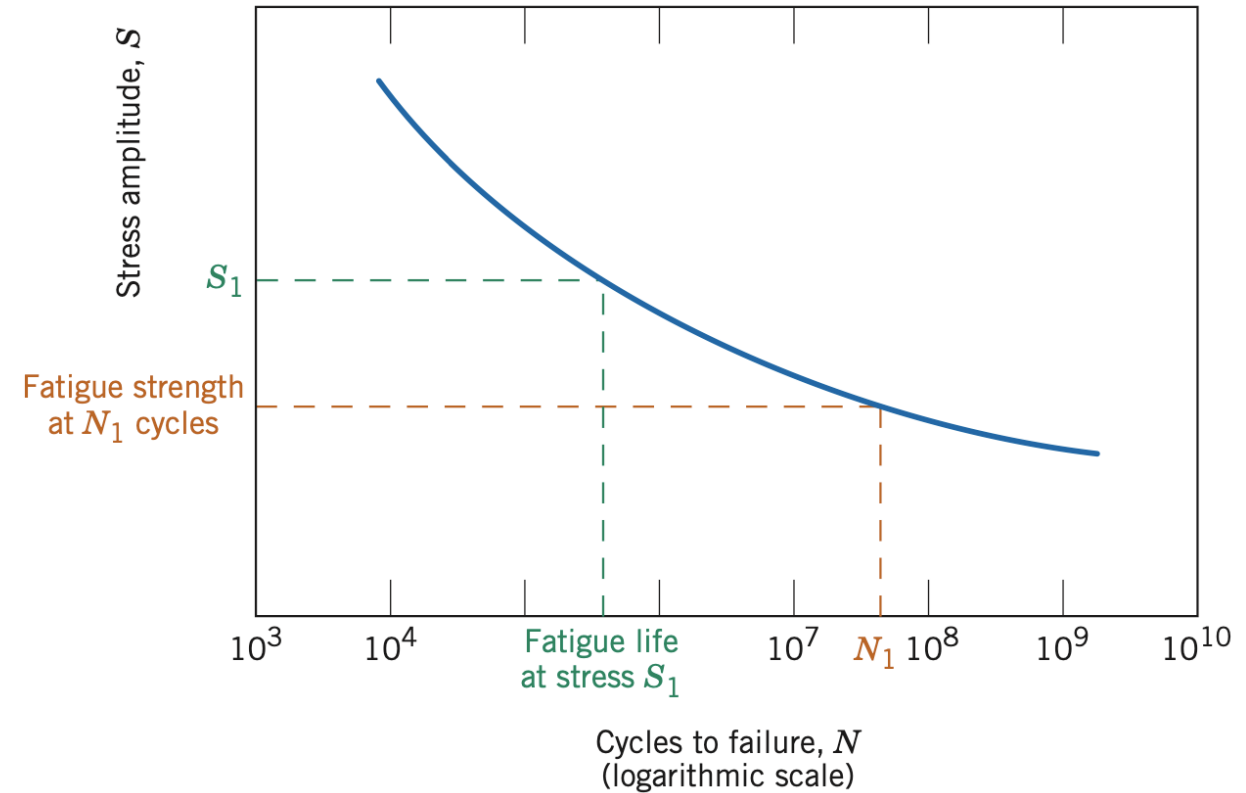
S-N Curve (Applied Stress vs. Number of cycles to failure)

Possesses a fatigue limit



No fatigue fracture below the fatigue limit
(Seen in some ferrous and titanium alloys)

Does not possess a fatigue limit



Fatigue fracture will occur eventually
Fatigue strength is defined with respect to a
specified number to failure
(Often seen in non-ferrous alloys)

Miner's Rule

$$\sum_{i=1}^k \frac{n_i}{N_i} = C$$

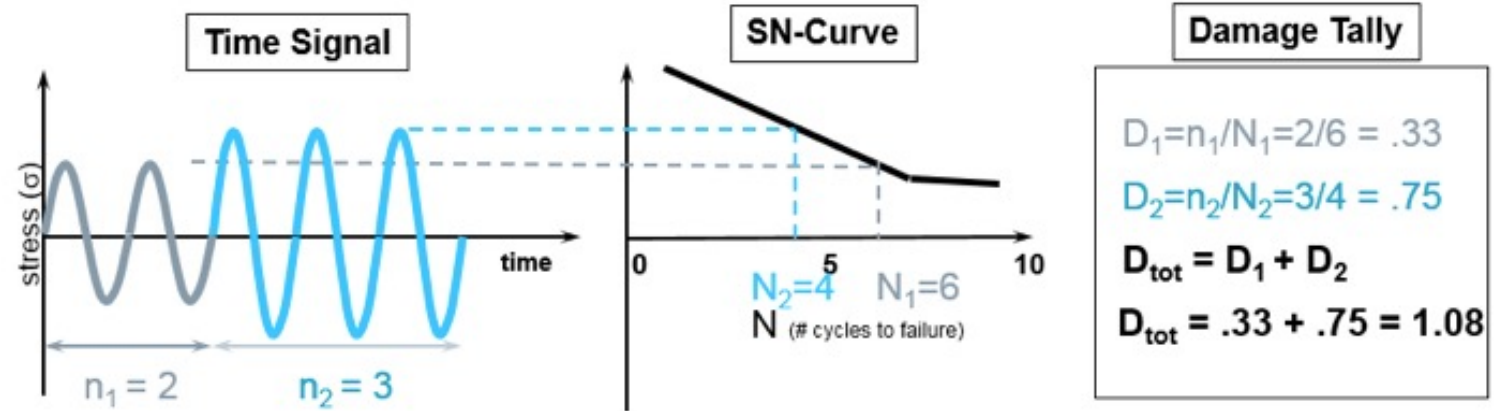
n_i is the number of cycles accumulated at stress S_i

N_i is the average number of cycles to failure at stress S_i

C is the fraction of life consumed
Sometimes denoted as D

Can think of Miner's rule as determining the fraction of life consumed at each stress level and then summing them to predict how much "life" is left

Limitations of Miner's Rule



Independent damage: Damage from each stress cycle is independent of the previous stress cycles

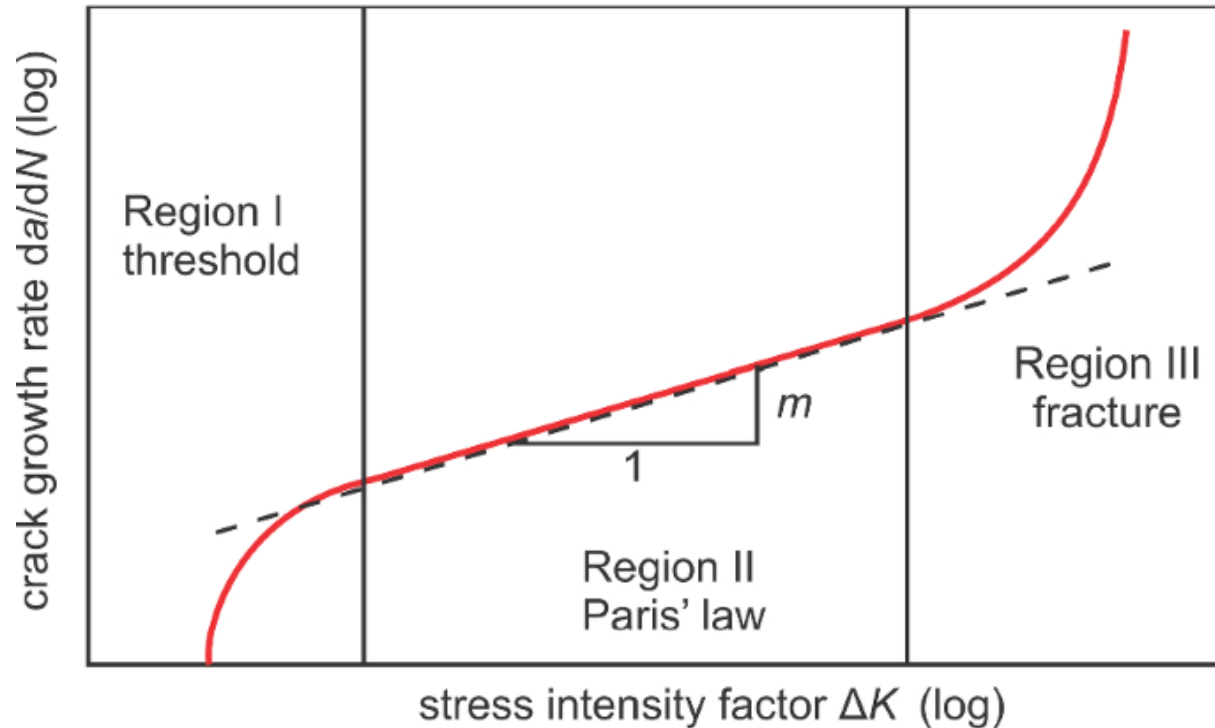
No effect of load sequence: The order of applied stress does not matter. High stress \rightarrow Low stress = Low stress \rightarrow High stress

Linear accumulation of damage: Damage from each stress level is additive. Ignores possibility of higher-order effects

Does not include probability: Only uses average values, ignores probabilistic component of fatigue fracture

Paris' Law (Crack growth equation)

Crack growth equations are used to calculate the size of a fatigue crack growing from cyclic loads



Typical plot of crack growth vs stress intensity range

$$\Delta K = K_{max} - K_{min}$$

Maximum and minimum stress intensity factors in a stress cycle

Paris' Law

$$\frac{da}{dN} = C(\Delta K)^m$$

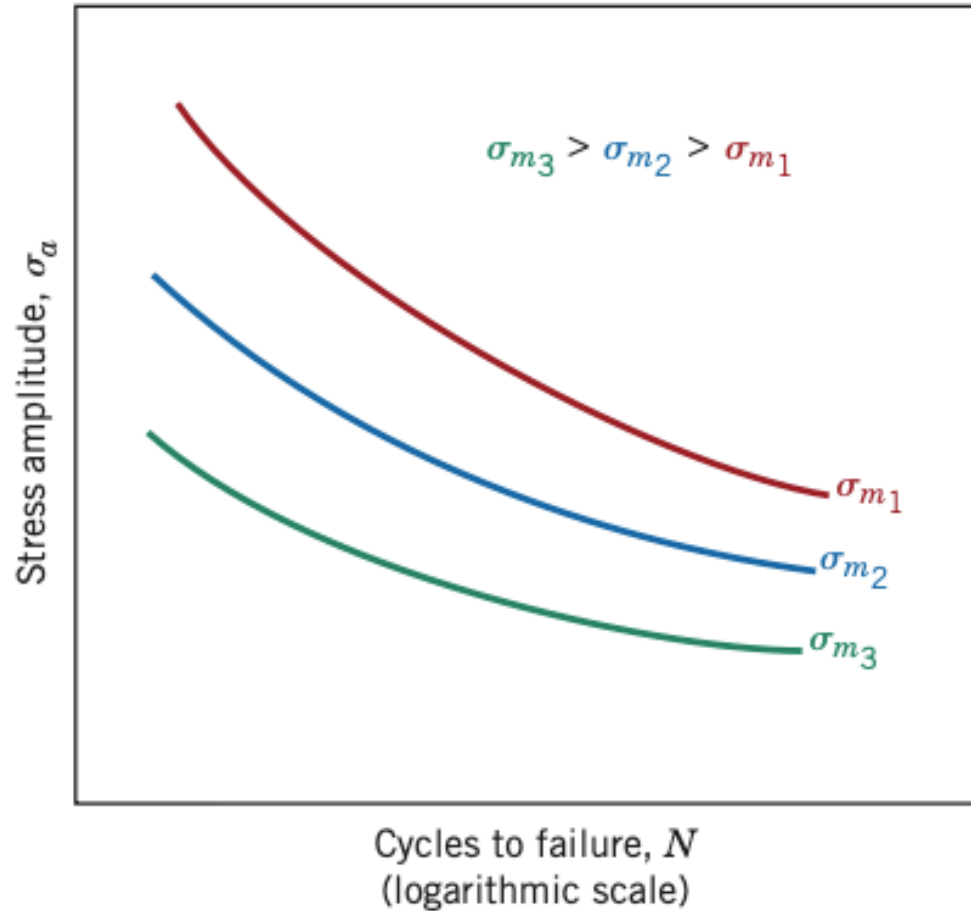
C and m are determined experimentally

Paris' law only holds for mid-range of crack growth.

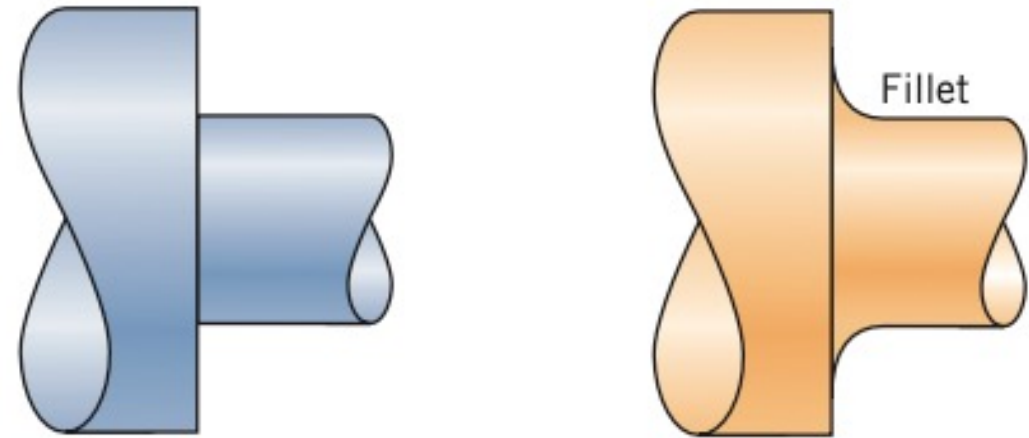
Can be used to estimate cycles to failure

What affects fatigue?

Mean stress level



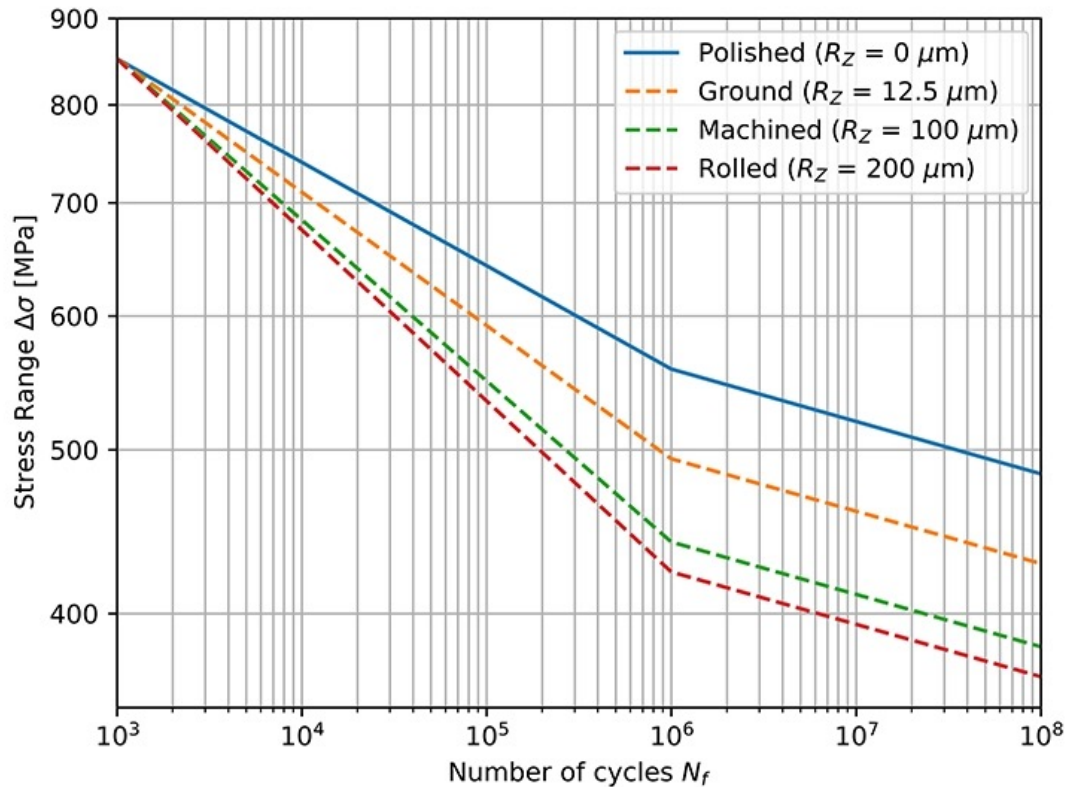
Design of part



Sharp corners can act as stress concentrators and initiate a surface crack. This surface crack can initiate fatigue crack propagation

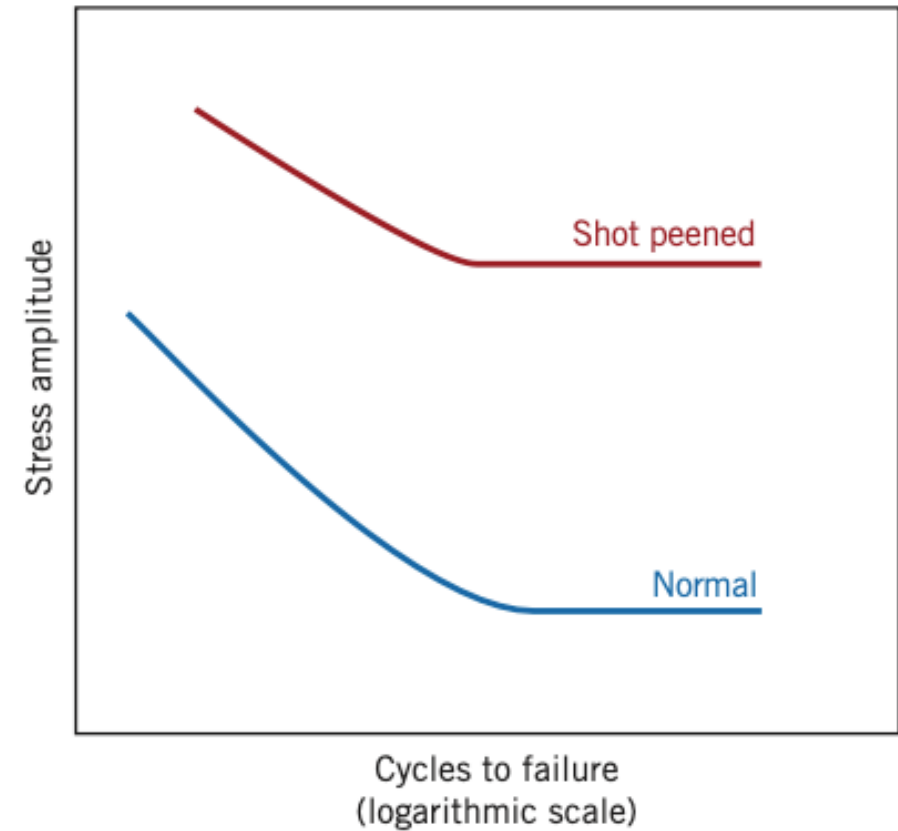
What affects fatigue?

Surface Treatment (Polishing)



Polishing removes surface flaws that could initiate fatigue cracking

Surface Treatment (Shot peening)

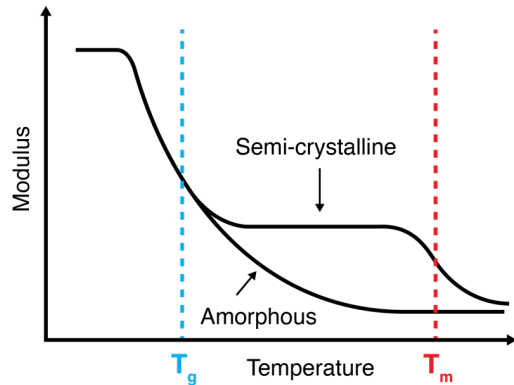
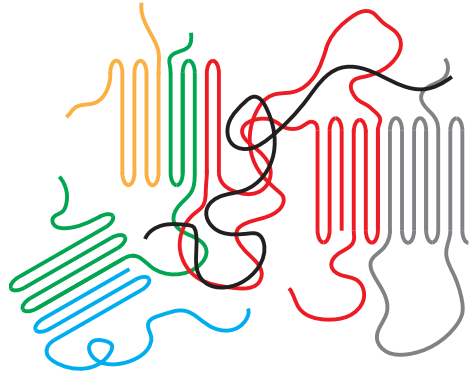
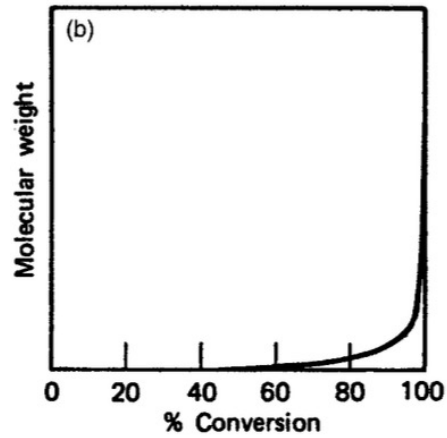


Cracks can only grow in tension

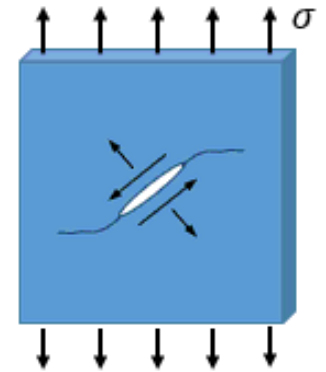
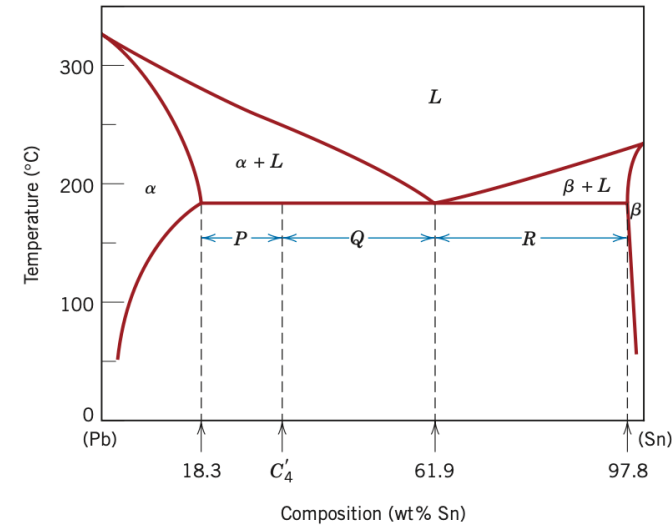
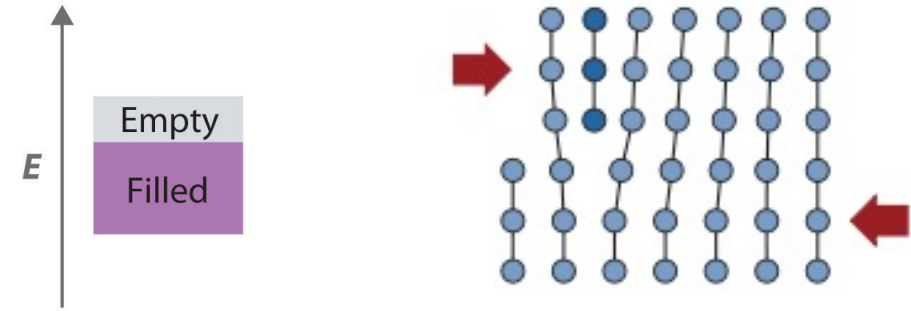
Shot peening induces a compressive stress onto the surface. Need to overcome this stress before crack can grow

MSE 214: Summary

Polymers



Metals



I hope this class helped you understand materials a little better and gave you a better appreciation for the wonders of chemistry!