2020 Fall

Introduction to Materials Science and Engineering

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Contents for previous class

Chapter 4: Imperfections in Solids

I. Point defects

- Point defects in metals/ceramics/polymers, impurities in solids

II. Dislocations-Linear defects

- Edge/ Screw/ Mix dislocation

III. Interfacial defects

- External surfaces/ Grain boundaries/ Phase boundaries (stacking fault)/ Twin boundaries/ domain boundaries

IV. Bulk or Volume defects

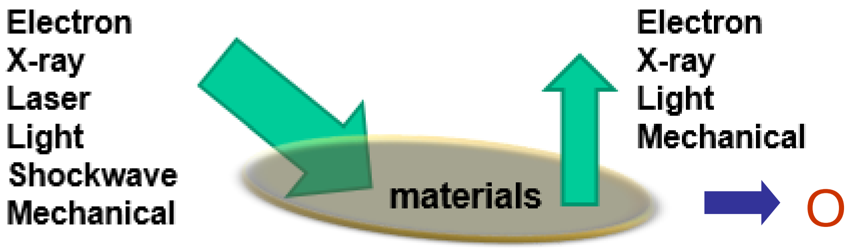
- pores/ cracks/ foreign inclusions, and other phases

V. Microscopic Examination

- Basic concepts of microscopy
- Microscopic techniques : Optical microscopy (Grain-size determination) / Electron microscopy/ Scanning probe microscopy

Chapter 4: Imperfections in Solids

- Point, Line, Area and Volume defects exist in solids.
- The number and type of defects can be varied and controlled (e.g., temperature controls vacancy concentration).
- Defects affect material properties (e.g., grain boundaries control crystal slip).
- Defects may be desirable or undesirable (e.g., dislocations may be good or bad, depending on whether plastic deformation is desirable or not).
- Observation of Microstructure: to make image from the collection of defects in the materials



➡ OM, SEM, TEM, EXAFS, AFM, SPM

Contents for today's class

Chapter 5: Diffusion

I. Introduction of diffusion

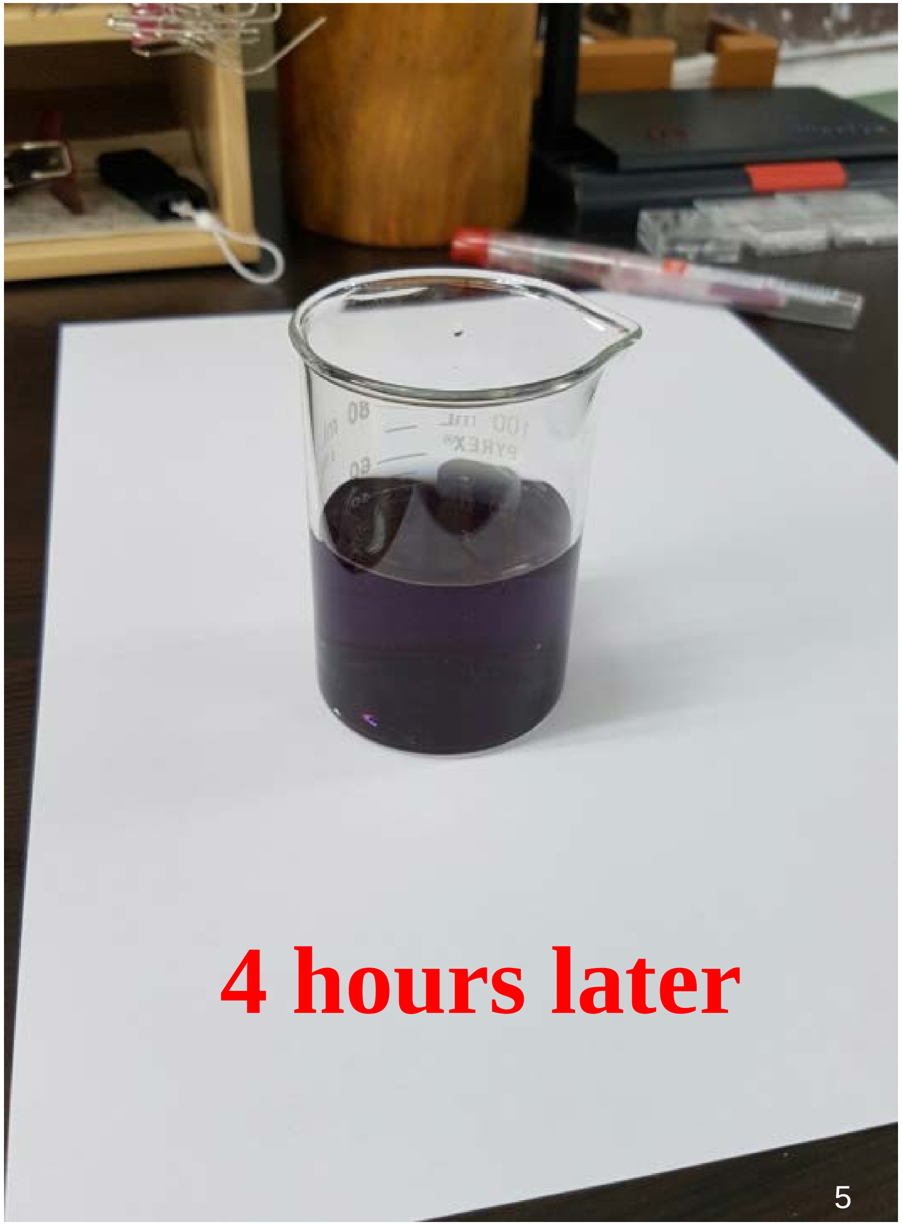
II. Diffusion mechanisms

III. Steady-state diffusion

IV. Non-steady-state diffusion

V. Factors that influences diffusion

Ink dropped in the water



4 hours later

1. Introduction of Diffusion

- atoms and molecules can be quite mobile in both liquids and solids, especially at high temp
  - Drop of ink in a beaker of water → spread, water evenly colored
  - **Intermixing at molecular level → diffusion**
- continuous motion of H_2O molecules in water at R.T. → **self-diffusion**
- atomic-scale motion (diffusion) **in liquids** is relatively rapid and easily to visualize
- more difficult to visualize diffusion **in rigid solids**, but it does occur

Diffusion

- **Diffusion: Mass transport by atomic motion**
- Heat treatments alter the properties of materials

Only possible by **atom movement**

Internal structure of material must change

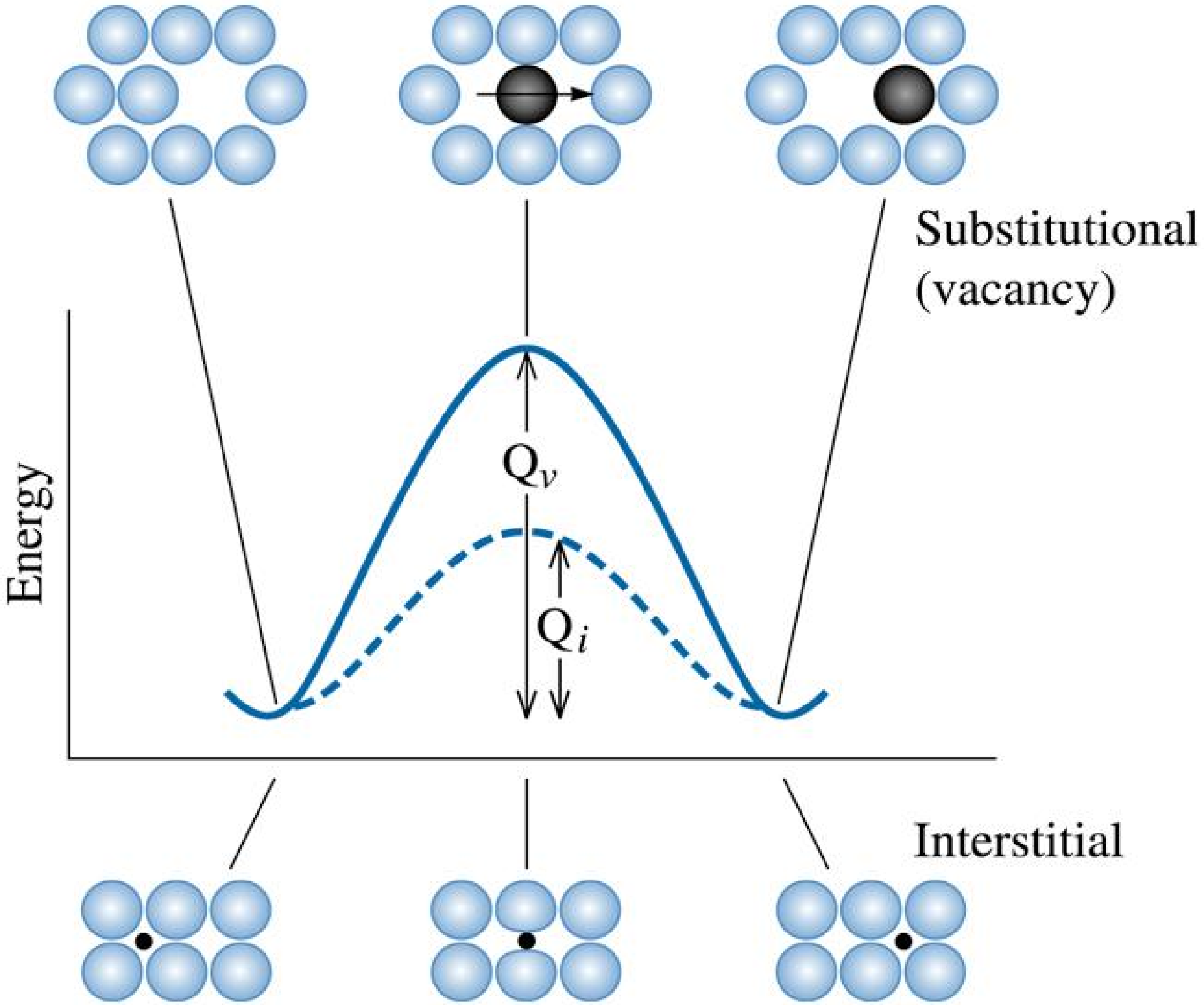
- Diffusion required for:
  - Heat treatment of metals, Ceramics sintering, Solidification, Integrated circuits, and solar cells
  - Electrical conductivity of ceramic materials
- Mechanisms
  - Gases & Liquids – random (Brownian) motion
  - Solids – vacancy diffusion or interstitial diffusion

Diffusion Concepts

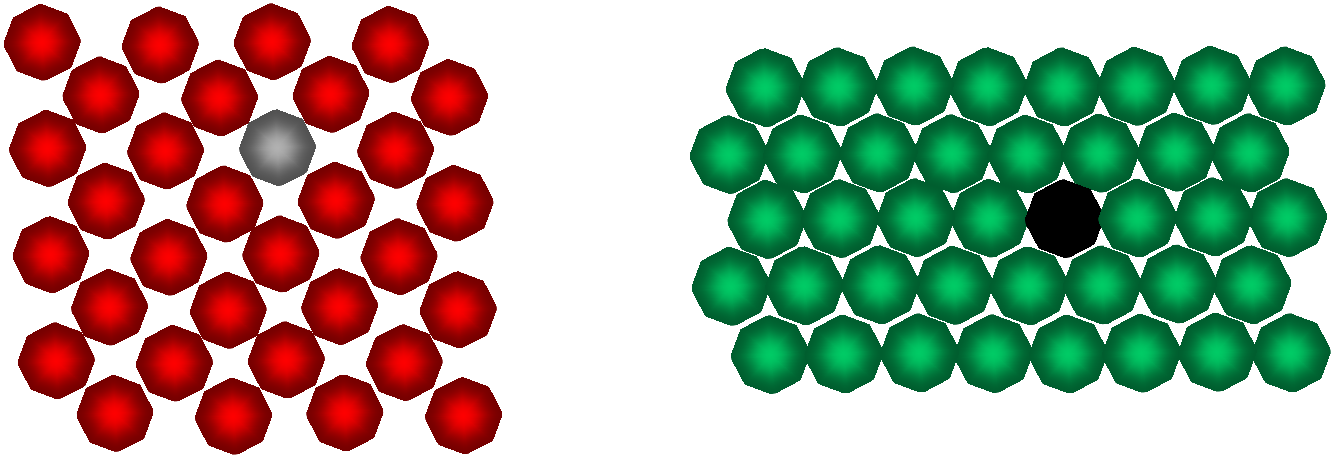
- **reactions** in solid state occur by spontaneous rearrangement of atoms into a more stable state

- for reactions to proceed from an unreacted to a reacted state, atoms must have enough energy to overcome an activation energy barrier

Diffusion Concepts



Diffusion



2. Diffusion mechanism

- Tendency to be random
  - Entropy term in the total energy ↑ → Chemical Potential ↓
- From higher concentration to lower concentration
  - few exceptions, but take it granted for now.

I. Vacancy diffusion

(a) Self-diffusion

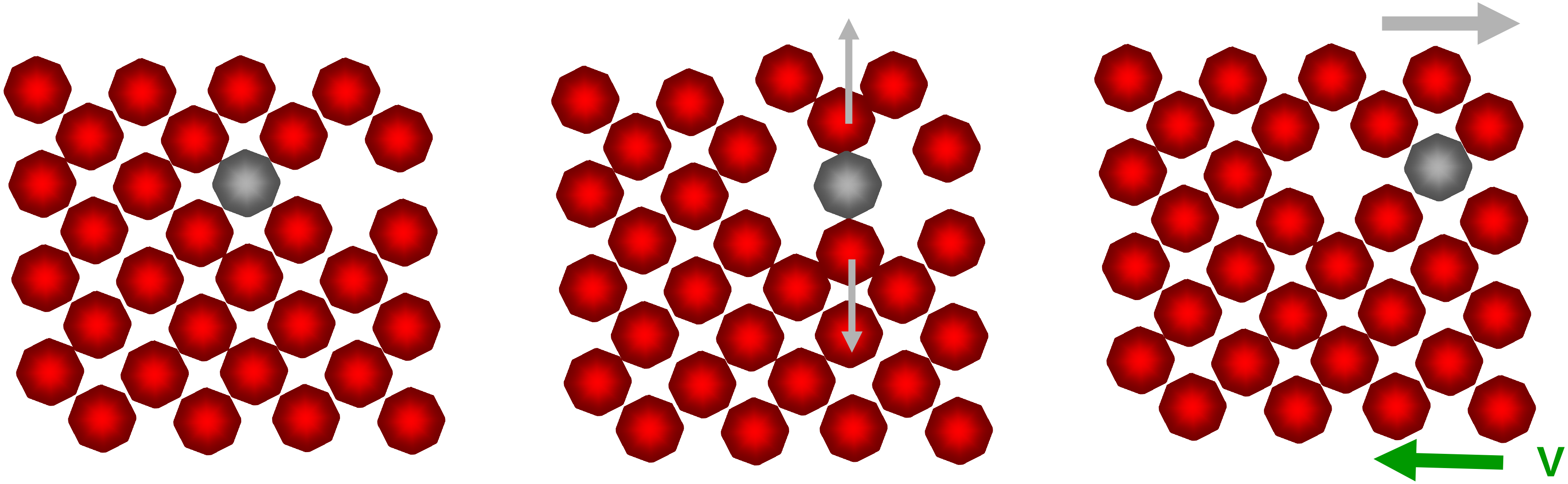
(b) Interdiffusion

II. Interstitial diffusion

I. Vacancy Diffusion

- What is needed to make solid-state diffusion happen?

→ **POINT DEFECTS**



I. Vacancy Diffusion

- **atom interchange** from a normal lattice position to an adjacent vacant lattice site

- the extent of vacancy diffusion is controlled by the concentration of these defects

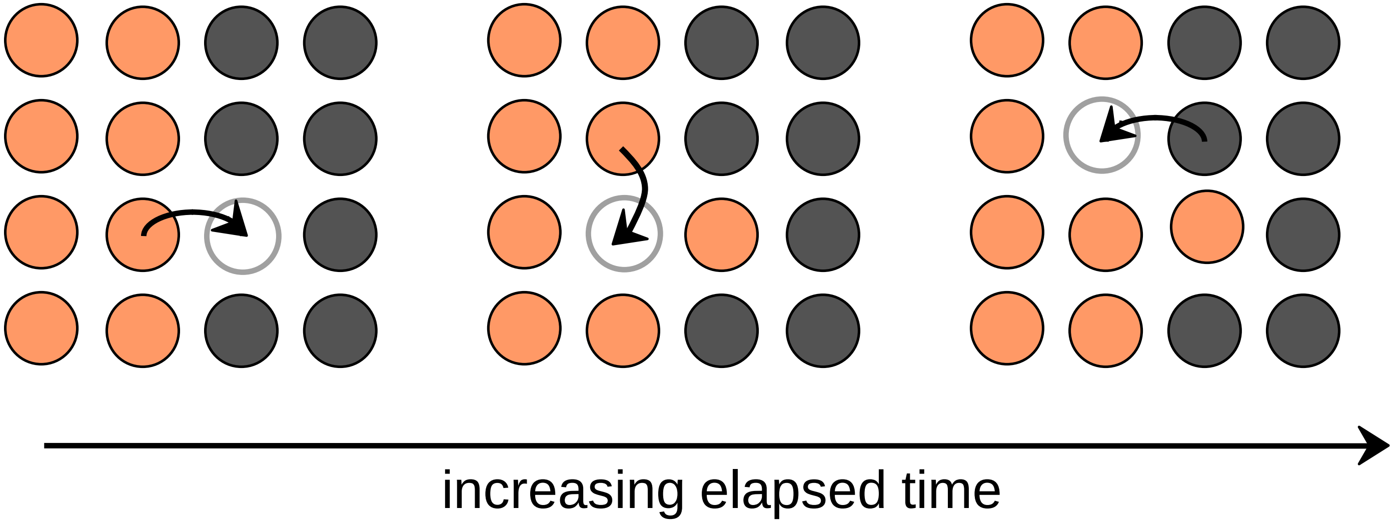
- the direction of vacancy motion is opposite to direction of diffusing atoms

- both (a) self-diffusion and (b) interdiffusion occur by this mechanism

Diffusion Mechanisms

Vacancy Diffusion:

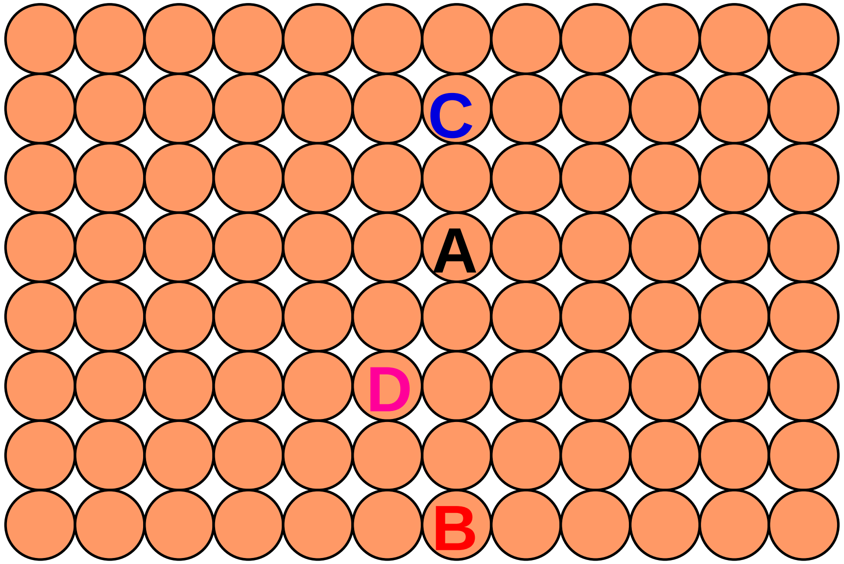
- atoms exchange with vacancies
- applies to **substitutional impurities atoms**
- rate depends on:
  -- number of vacancies
  -- activation energy to exchange.


increasing elapsed time

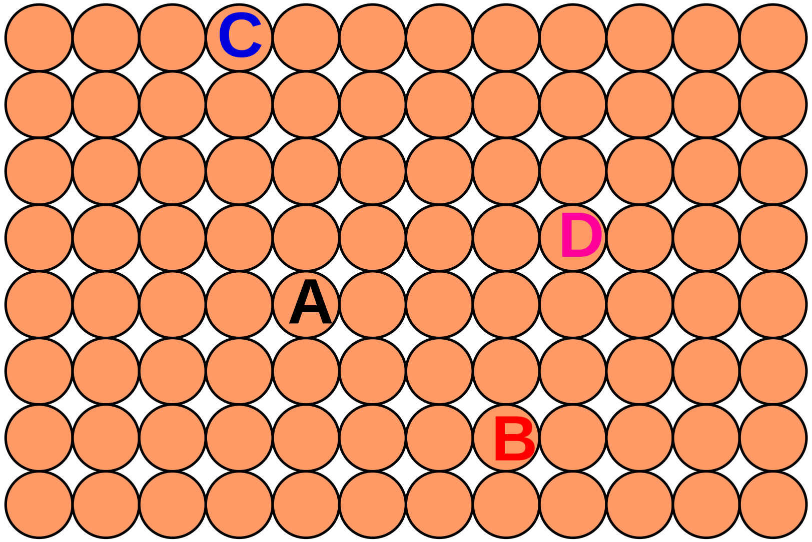
I-(a) Self-Diffusion

- Self-diffusion: In an elemental solid, atoms also migrate

Label some atoms

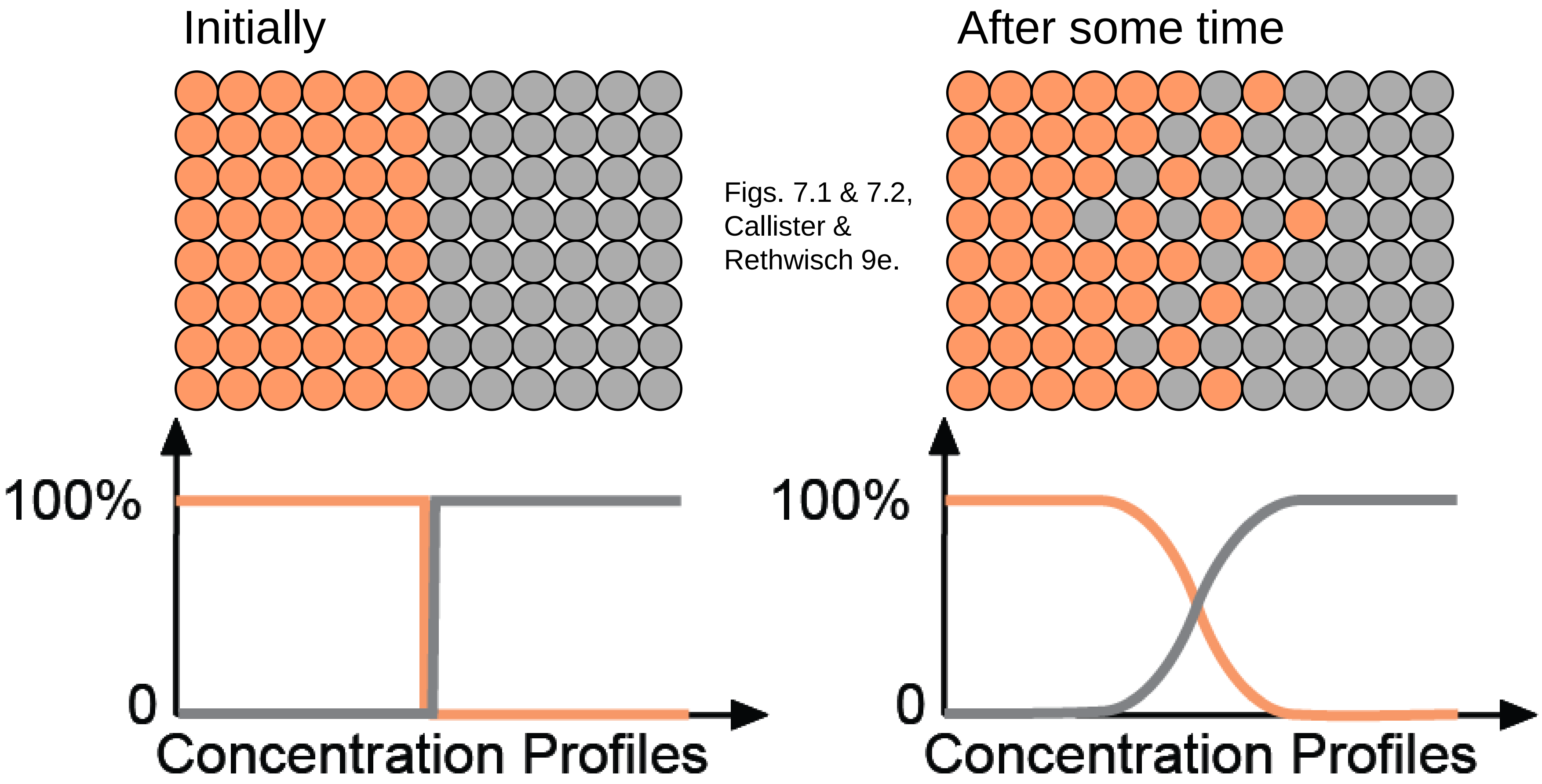


After some time



I-(b) Interdiffusion

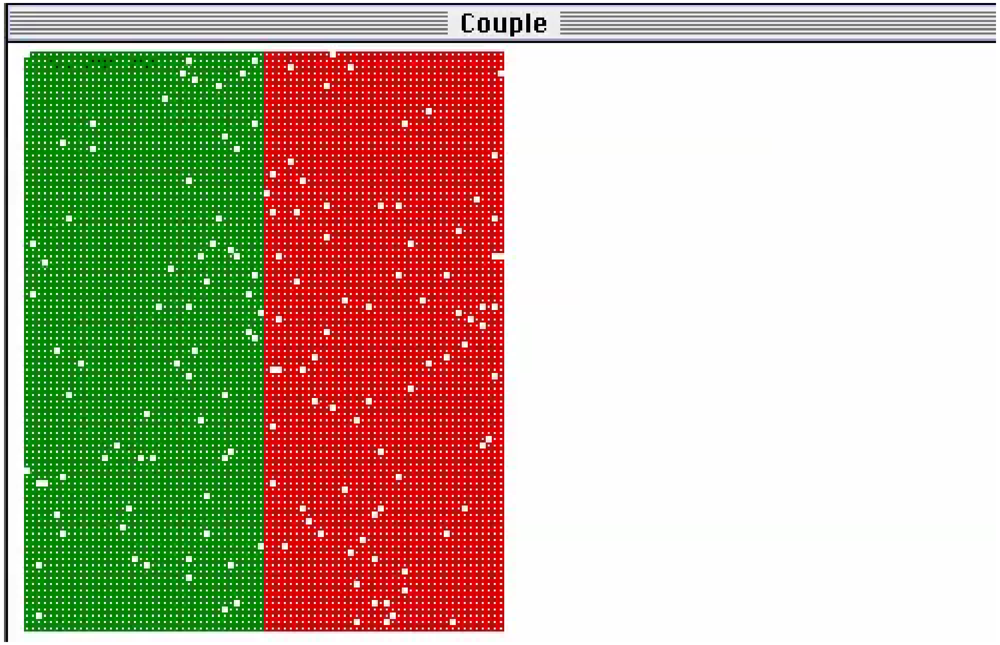
- Interdiffusion: In an alloy, atoms tend to migrate from regions of high conc. to regions of low conc.



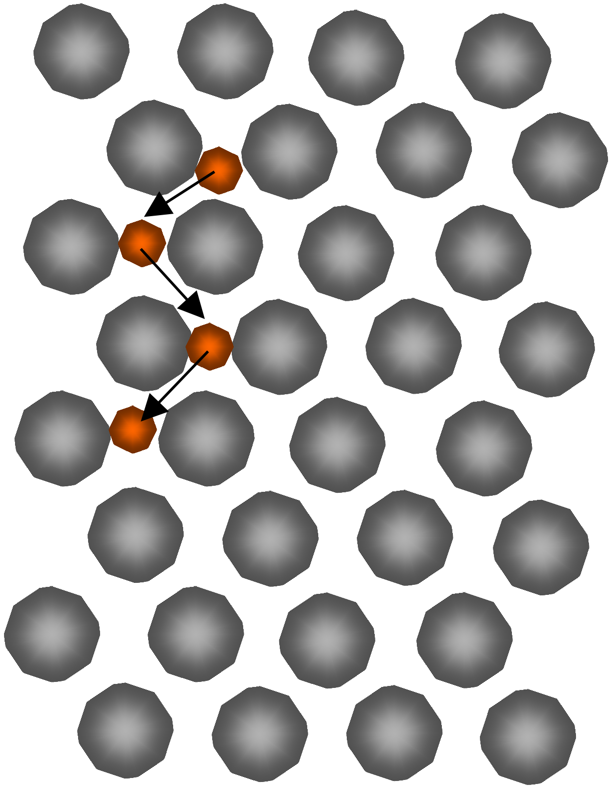
Figs. 7.1 & 7.2, Callister & Rethwisch 9e.

Diffusion Simulation

- Simulation of inter-diffusion across an interface
- Rate of substitutional diffusion depends on
  - **vacancy concentration**
  - **frequency of jumping**



II. Interstitial Diffusion



- migration of interstitial atoms from an interstitial position to adjacent empty one.
- Typical interstitial atoms: *hydrogen, carbon, nitrogen, and oxygen.*
- in most metals, interstitial diffusion occurs much more rapidly than vacancy diffusion.

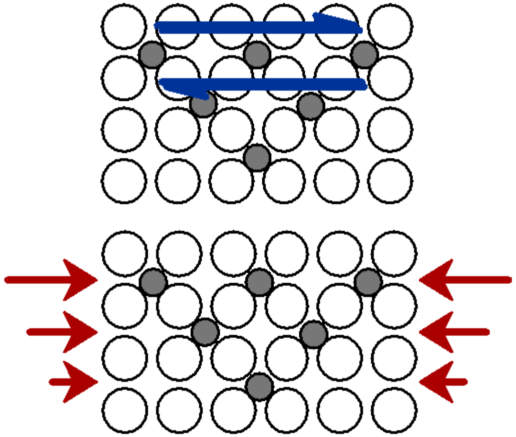
Processing Using Diffusion (1)

- Case Hardening:
  - Diffuse carbon atoms into the host iron atoms at the surface
  - Example of interstitial diffusion is a case hardened gear

Chapter-opening photograph, Chapter 7, Callister & Rethwisch 9e. (Courtesy of Surface Division, Midland-Ross.)

- Result: The presence of C atoms makes iron (steel) harder.

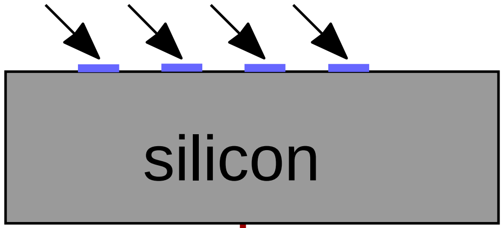
  The "Case" is
  - hard to deform: C atoms "lock" planes from shearing
  - hard to crack: C atoms put the surface in compression



Processing Using Diffusion (2)

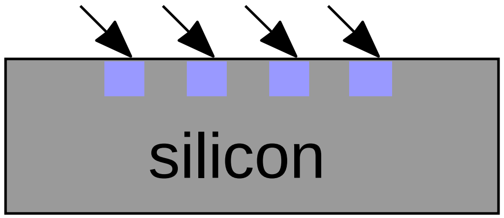
- Doping silicon with phosphorus for n-type semiconductors:
- Process:

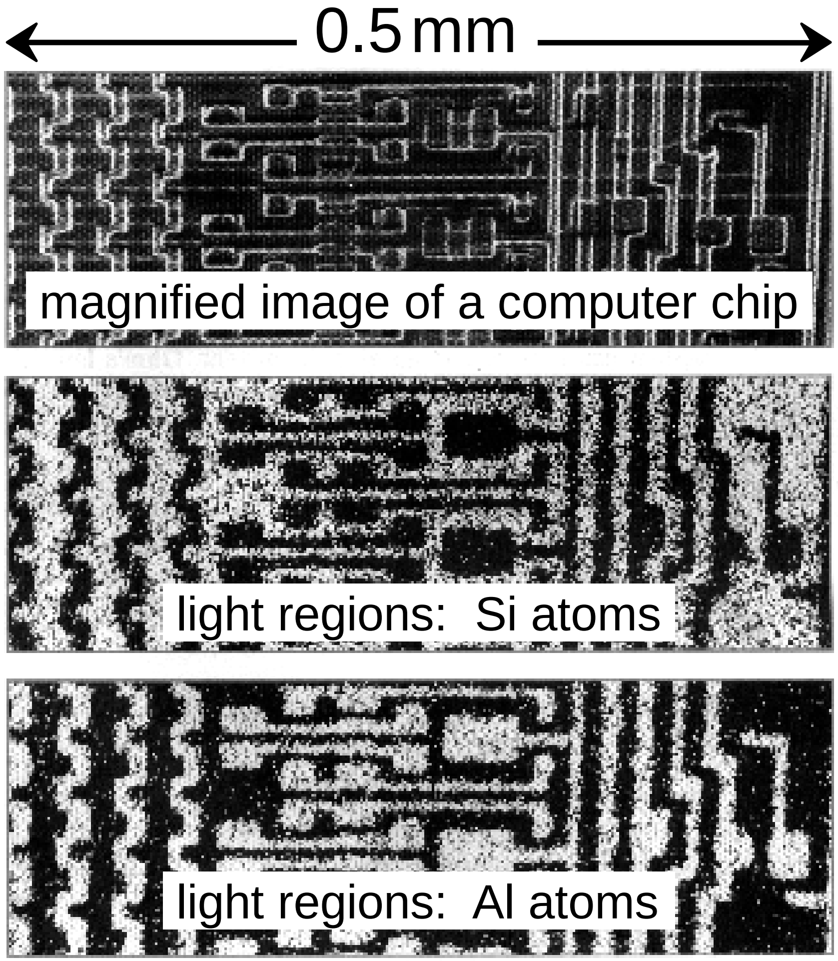
1. Deposit P rich layers on surface.



2. Heat it.

3. Result: Doped semiconductor regions.





magnified image of a computer chip

light regions: Si atoms

light regions: Al atoms

Adapted from Figure 19.27, Callister & Rethwisch 9e.

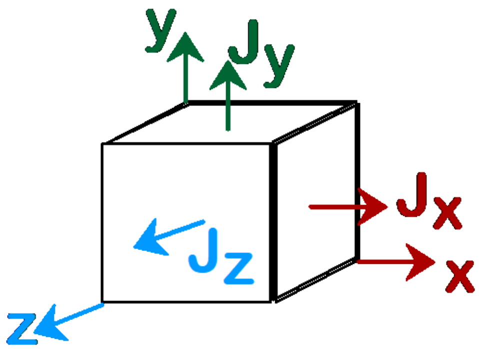
Diffusion

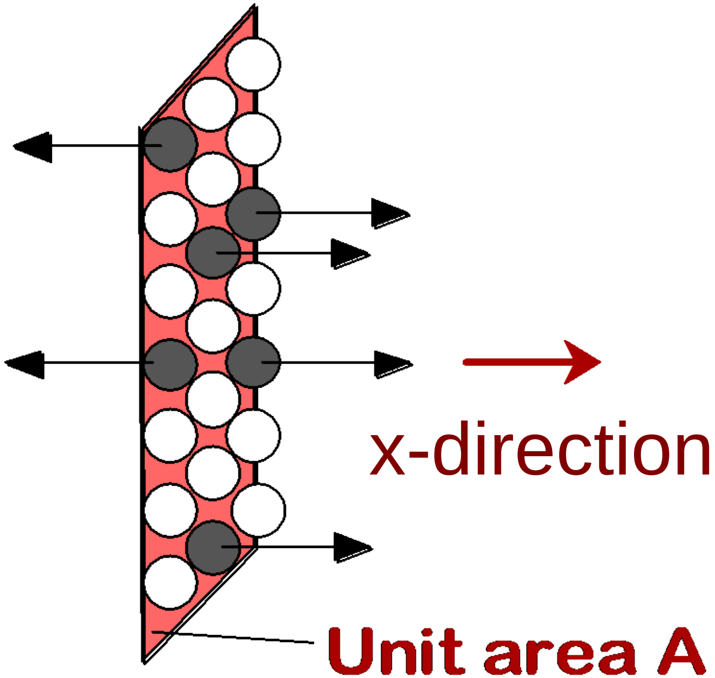
- How do we quantify the amount or rate of diffusion?

➢ Flux: # of atoms passing through a plane of unit area per unit time

$$J = \frac{1}{A}\frac{dM}{dt} \Rightarrow \left[\frac{kg}{m^2 s}\right] \text{ or } \left[\frac{atoms}{m^2 s}\right]$$

➢ Directional Quantity





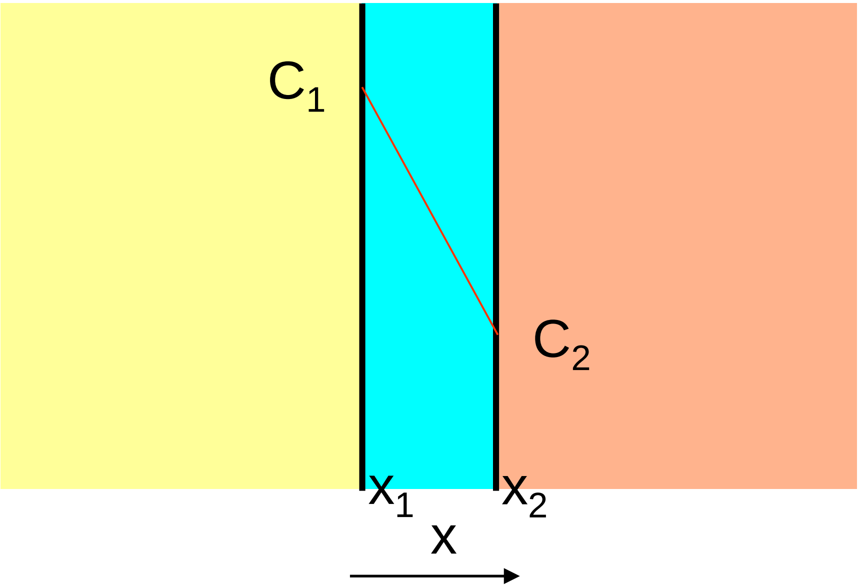
Unit area A through which atoms move.

- Flux can be measured for:
  - vacancies
  - host (A) atoms
  - impurity (B) atoms

3-I. Steady-State Diffusion

Rate of diffusion independent of time

Flux proportional to concentration gradient = $\dfrac{dC}{dx}$



Fick's first law of diffusion

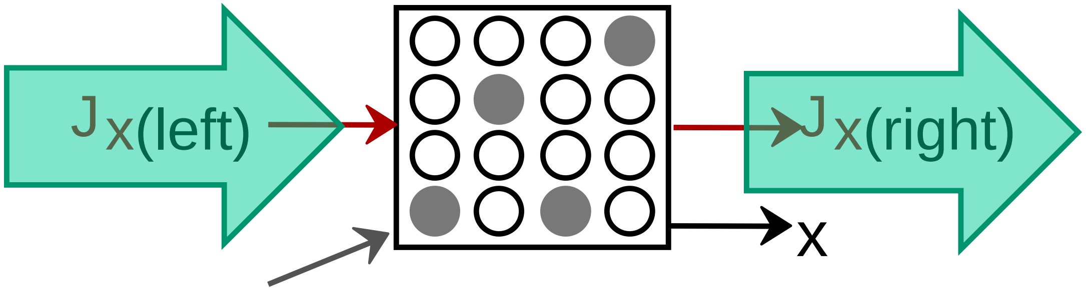
$$\boxed{J = -D\frac{dC}{dx}}$$

D ≡ diffusion coefficient

if linear $\dfrac{dC}{dx} \cong \dfrac{\Delta C}{\Delta x} = \dfrac{C_2 - C_1}{x_2 - x_1}$

Steady State Diffusion - Fick's 1st law

- Steady State: the concentration profile doesn't change with time



Concentration, C, in the box doesn't change w/time.

Steady State:

$$J_{x(left)} = J_{x(right)}$$

- Apply Fick's First Law

$$J_x = -D\frac{dC}{dx}$$

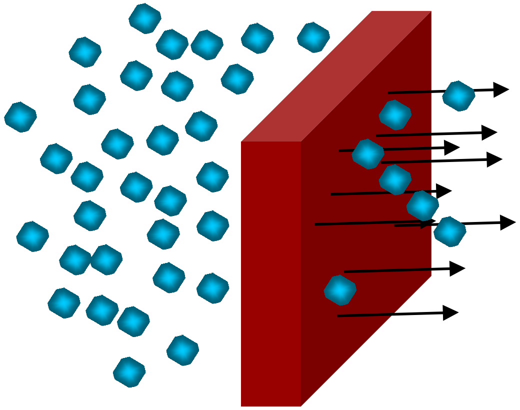
- If $J_x(\text{left}) = J_x(\text{right})$, then

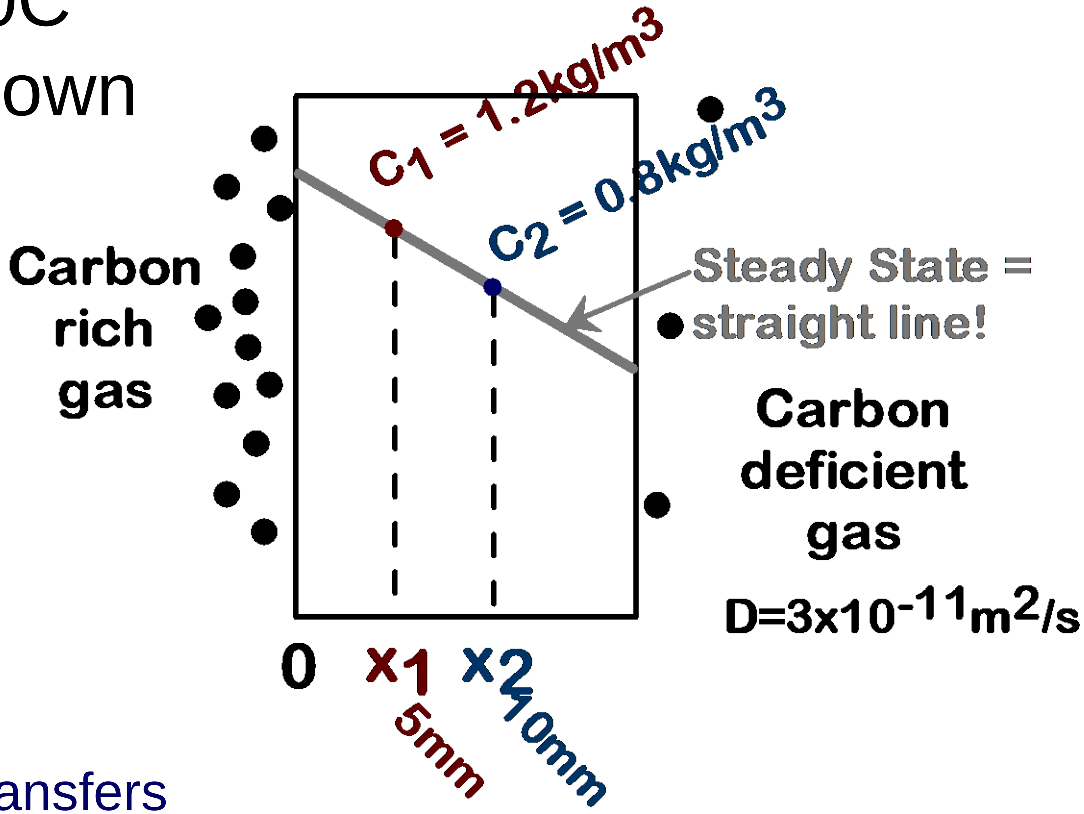
$$\left(\frac{dC}{dx}\right)_{\text{left}} = \left(\frac{dC}{dx}\right)_{\text{right}}$$

- Result: the slope, dC/dx, must be constant (i.e., slope doesn't vary with position as well as time)!

Example I: Steady State Diffusion

- Steel plate at 700C with geometry shown





➢ Q: How much carbon transfers from the rich to the deficient side?

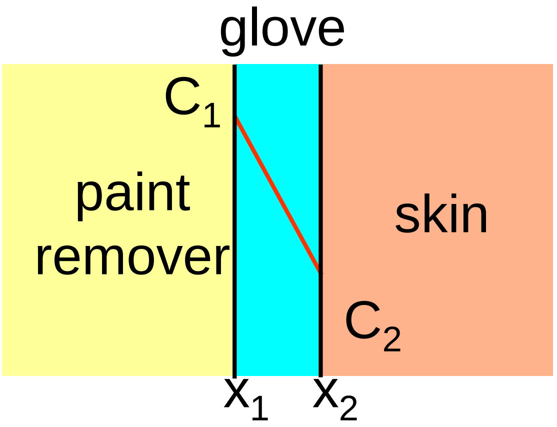
$$J = -D\frac{C_2 - C_1}{x_2 - x_1} = 2.4\times 10^{-9}\frac{\text{kg}}{\text{m}^2\text{s}}$$

Example II: Chemical Protective Clothing (CPC)

- Methylene chloride is a common ingredient of paint removers. Besides being an irritant, it also may be absorbed through skin. When using this paint remover, protective gloves should be worn.
- If butyl rubber gloves (0.04 cm thick) are used, what is the diffusive flux of methylene chloride through the glove?
- Data:
  - diffusion coefficient in butyl rubber: $D = 110 \times 10^{-8}\ \text{cm}^2/\text{s}$
  - surface concentrations: $C_1 = 0.44\ \text{g/cm}^3$
    $C_2 = 0.02\ \text{g/cm}^3$

Example (cont).

- **Solution** – assuming linear conc. gradient



$$J = -D\frac{dC}{dx} \cong -D\frac{C_2 - C_1}{x_2 - x_1}$$

Data:

$D = 110 \text{ x } 10^{-8}\ \text{cm}^2/\text{s}$

$C_1 = 0.44\ \text{g/cm}^3$

$C_2 = 0.02\ \text{g/cm}^3$

$x_2 - x_1 = 0.04\ \text{cm}$

$$J = -(110 \text{ x } 10^{-8}\ \text{cm}^2/\text{s})\frac{(0.02\ \text{g/cm}^3 - 0.44\ \text{g/cm}^3)}{(0.04\ \text{cm})} = \boxed{1.16 \text{ x } 10^{-5}\ \frac{\text{g}}{\text{cm}^2\text{s}}}$$

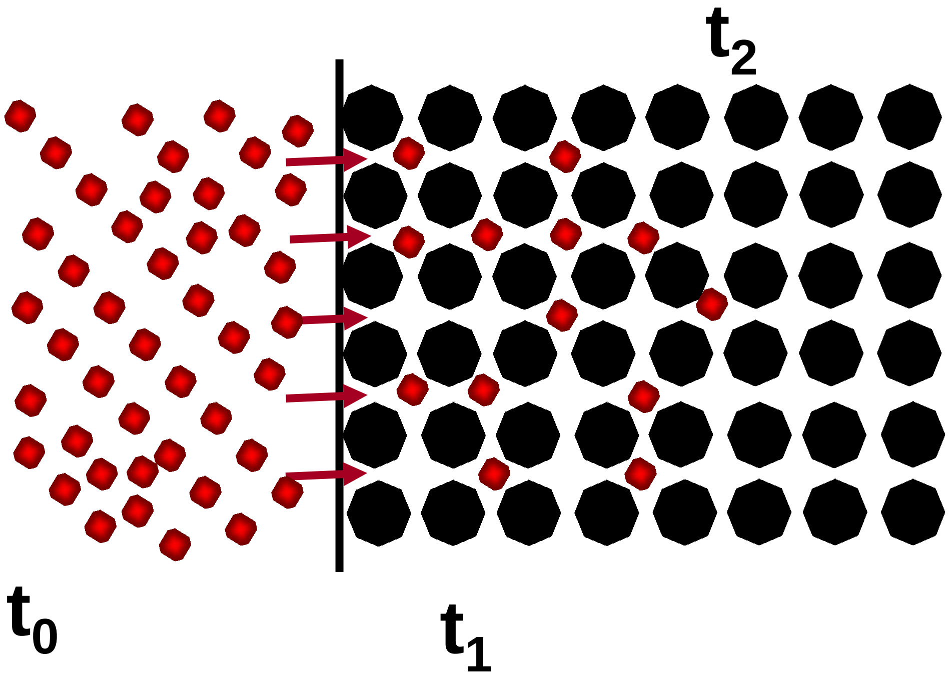
3-II. Non-steady State Diffusion

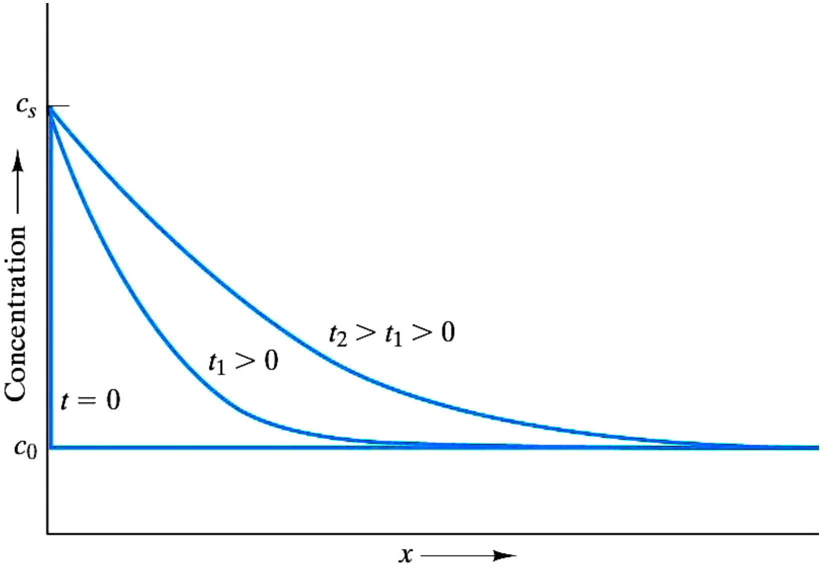
- The concentration of diffusing species is a function of both time and position $C = C(x,t)$
- In this case Fick's Second Law is used

Fick' s Second Law $$\boxed{\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}}$$

Non Steady State Diffusion

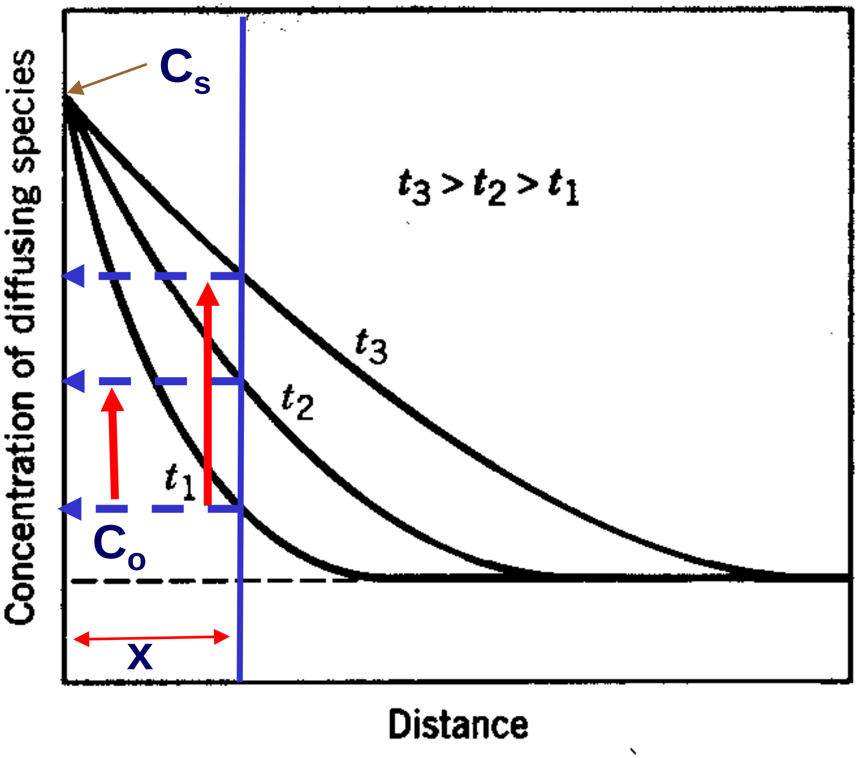
- steady-state diffusion not commonly encountered in engineering materials
- in most cases the concentration of solute atoms at any point in the material changes with time → **non-steady state diffusion**





Fick’s Second Law

Fick’s second law applies for non-steady state cases

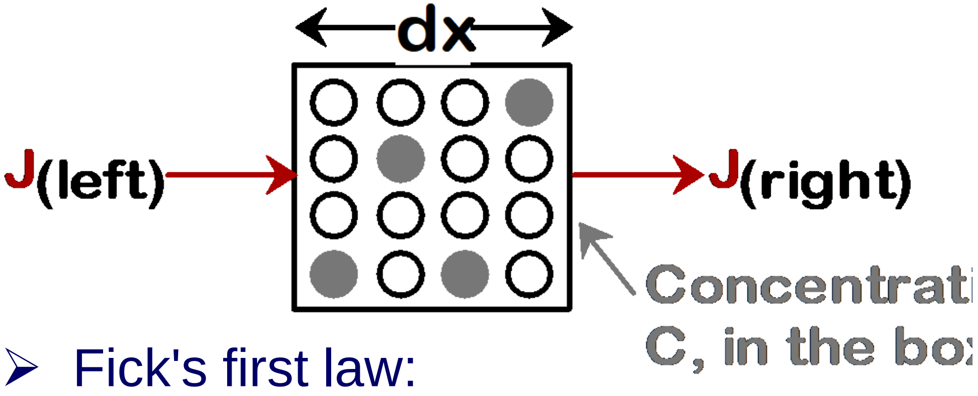


$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial C}{\partial x} \right)$$

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

Fick’s Second Law

- Concentration profile, C(x), changes w/ time



➢ To conserve matter:

$$\boxed{\frac{J(\text{right}) - J(\text{left})}{dx}} = -\frac{dC}{dt}$$

$$\boxed{\frac{dJ}{dx}} = -\frac{dC}{dt}$$

➢ Fick's first law:

$$J = -D\frac{dC}{dx}$$ or

$$\boxed{\frac{dJ}{dx}} = -D\frac{d^2C}{dx^2}$$ (if D does not vary with x)

equate

➢ Governing Eqn.:

$$\boxed{\frac{dC}{dt} = D\frac{d^2C}{dx^2}}$$

➢ Fick's second law:

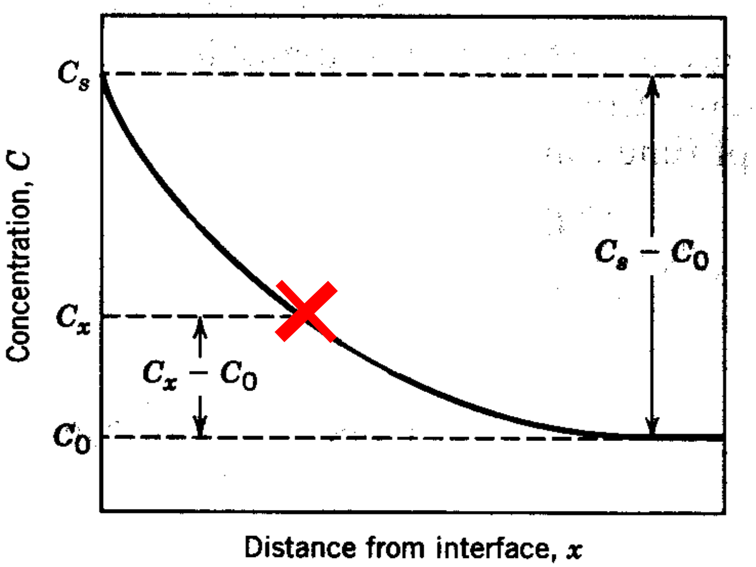
Fick’s Second Law

- To solve Fick’s second law, physically meaningful boundary conditions must be specified
- A practical and important solution is for a semi-infinite solid in which the surface concentration is held constant
- boundary conditions:

For $t = 0, C = C_0$ at $0 \le x \le \infty$

For $t > 0, C = C_s$ (the constant surface concentration) at $x = 0$

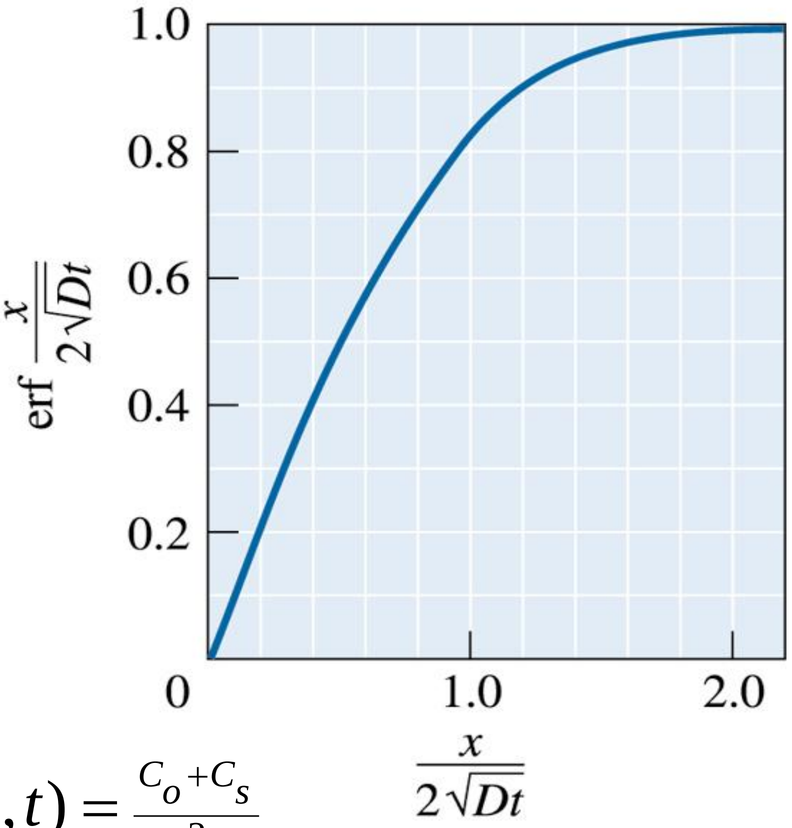
$C = C_0$ at $x = \infty$



$$\frac{C_x - C_0}{C_S - C_0} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

Error Function

z	erf(z)	z	erf(z)
0.00	0.0000	0.70	0.6778
0.01	0.0113	0.75	0.7112
0.02	0.0226	0.80	0.7421
0.03	0.0338	0.85	0.7707
0.04	0.0451	0.90	0.7969
0.05	0.0564	0.95	0.8209
0.10	0.1125	1.00	0.8427
0.15	0.1680	1.10	0.8802
0.20	0.2227	1.20	0.9103
0.25	0.2763	1.30	0.9340
0.30	0.3286	1.40	0.9523
0.35	0.3794	1.50	0.9661
0.40	0.4284	1.60	0.9763
0.45	0.4755	1.70	0.9838
0.50	0.5205	1.80	0.9891
0.55	0.5633	1.90	0.9928
0.60	0.6039	2.00	0.9953
0.65	0.6420		



effective penetration distance: $C(x_{eff},t)=\frac{C_o+C_s}{2}$

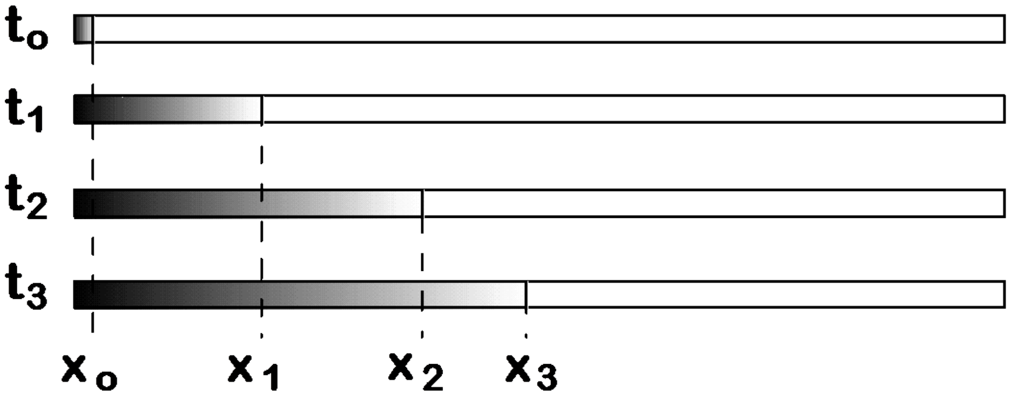
$$0.5=erf\left(\frac{x_{eff}}{2\sqrt{Dt}}\right) \quad \mathrm{erf}(0.5)\approx 0.5$$

$$\boxed{x_{eff}\approx\sqrt{Dt}}$$

in general $x_{eff}=\gamma\sqrt{Dt}$

Diffusion Demo: Analysis

- The experiment: we recorded combinations of t and x that kept C constant



$$\frac{C(x_i, t_i) - C_o}{C_s - C_o} = 1 - \mathrm{erf}\left(\frac{x_i}{2\sqrt{Dt_i}}\right)$$ = (constant here)

➢ Diffusion depth given by:

$$x_i \propto \sqrt{Dt_i}$$

Non-steady State Diffusion

- Copper diffuses into a bar of aluminum.

Surface conc., C_S of Cu atoms

pre-existing conc., C_o of copper atoms

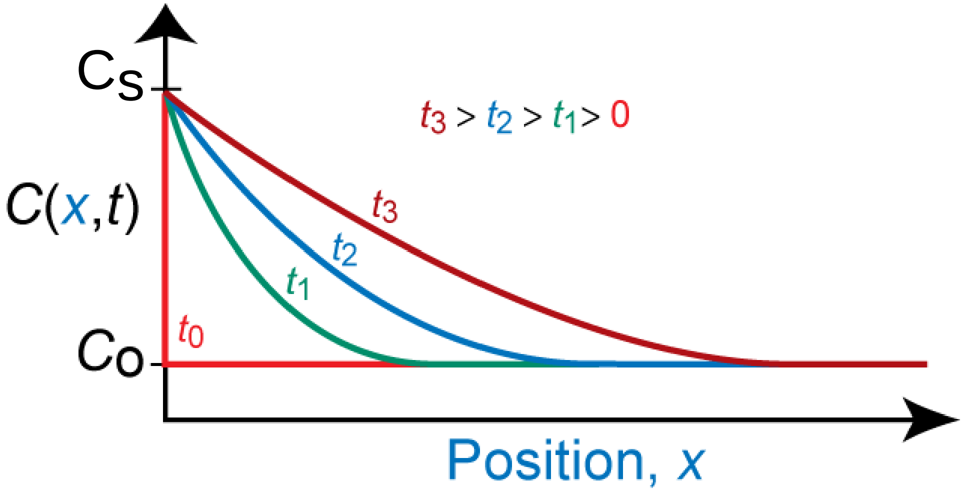


Fig. 7.5, Callister & Rethwisch 9e.

B.C. at $t = 0$, $C = C_o$ for $0 \leq x \leq \infty$

at $t > 0$, $C = C_S$ for $x = 0$ (constant surface conc.)

$C = C_o$ for $x = \infty$

Solution:

$$\boxed{\frac{C(x,t)-C_o}{C_s-C_o}=1-\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)}$$

$C(x,t)$ = Conc. at point x at time t

$\operatorname{erf}(z)$ = error function

$$=\frac{2}{\sqrt{\pi}}\int_0^z e^{-y^2}dy$$

$\operatorname{erf}(z)$ values are given in Table 7.1

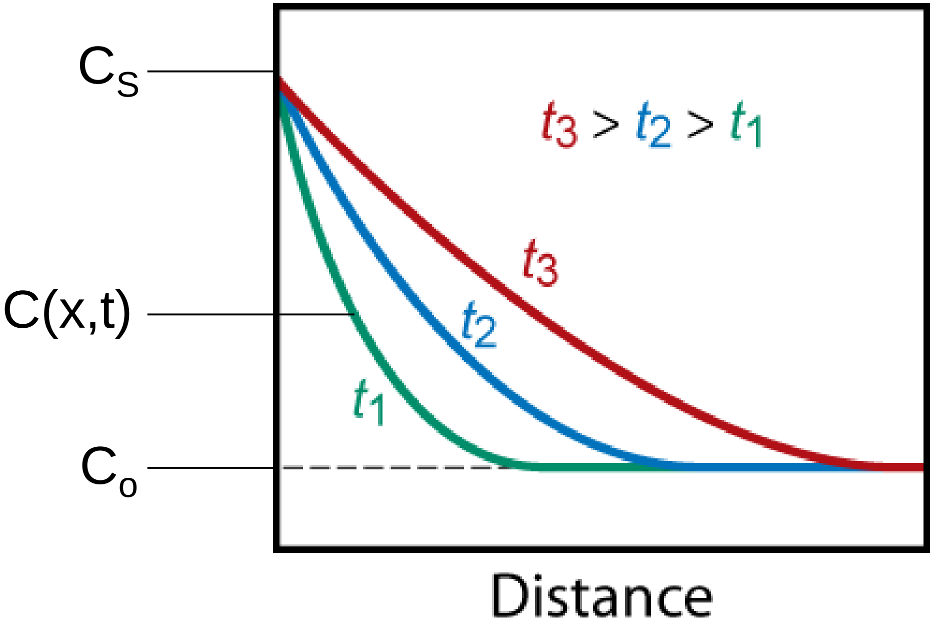


Fig. 7.5, Callister & Rethwisch 9e.

Example: Non-steady State Diffusion

- Sample Problem: An FCC iron-carbon alloy initially containing 0.20 wt% C is carburized at an elevated temperature and in an atmosphere that gives a surface carbon concentration constant at 1.0 wt%. If after 49.5 h the concentration of carbon is 0.35 wt% at a position 4.0 mm below the surface, determine the temperature at which the treatment was carried out.

- Solution: use Eqn. 7.5

$$\frac{C(x,t)-C_o}{C_s-C_o}=1-\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Solution (cont.):

$$\frac{C(x,t)-C_o}{C_s-C_o}=1-\text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

- t = 49.5 h
- C_x = 0.35 wt%
- C_o = 0.20 wt%

x = 4 x 10^{-3} m

C_s = 1.0 wt%

$$\frac{C(x,t)-C_o}{C_s-C_o}=\frac{0.35-0.20}{1.0-0.20}=1-\text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)=1-\text{erf}(z)$$

$\therefore$ erf(z) = 0.8125

Solution (cont.):

We must now determine from Table 7.1 the value of z for which the error function is 0.8125. An interpolation is necessary as follows

z	erf(z)
0.90	0.7970
z	0.8125
0.95	0.8209

$$\frac{z - 0.90}{0.95 - 0.90} = \frac{0.8125 - 0.7970}{0.8209 - 0.7970}$$

$$z = 0.93$$

Now solve for D

$$z = \frac{x}{2\sqrt{Dt}} \Longrightarrow D = \frac{x^2}{4z^2 t}$$

$$\therefore D = \left(\frac{x^2}{4z^2 t}\right) = \frac{(4 \text{ x } 10^{-3}\text{m})^2}{(4)(0.93)^2(49.5 \text{ h})}\frac{1 \text{ h}}{3600 \text{ s}} = 2.6 \text{ x } 10^{-11} \text{ m}^2/\text{s}$$

Solution (cont.):

$$D = D_o \exp\left(-\frac{Q_d}{RT}\right)$$

- To solve for the temperature at which *D* has the above value, we use a rearranged form of Equation (8.9a);

$$T = \frac{Q_d}{R(\ln D_o - \ln D)}$$

from Table 8.2, for diffusion of C in FCC Fe

$D_o = 2.3 \times 10^{-5}$ m^2/s $Q_d = 148{,}000$ J/mol

$$\therefore \quad T = \frac{148{,}000 \text{ J/mol}}{(8.314 \text{ J/mol-K})(\ln 2.3\text{x}10^{-5} \text{ m}^2/\text{s} - \ln 2.6\text{x}10^{-11} \text{ m}^2/\text{s})}$$

$$\boxed{T = 1300 \text{ K} = 1027^\circ \text{ C}}$$

4. Factors Influencing Diffusion

- Temperature
- Diffusion Coefficient (D)
- Time
- Dependence on Bonding and Crystal Structure
- Types of Diffusion - volume diffusion, grain boundary diffusion, surface diffusion
- Dependence on Concentration of Diffusing Species and Composition of Matrix

4-I. Diffusion and Temperature

(a) Diffusion coefficient increases with increasing T

$$D = D_o \exp\left(-\frac{Q_d}{RT}\right)$$

D = diffusion coefficient [m^2/s]

D_o = pre-exponential [m^2/s]

Q_d = activation energy [J/mol or eV/atom]

R = gas constant [8.314 J/mol-K]

T = absolute temperature [K]

Diffusion Exercise

Example: Determine D_{cu} in Ni at 500°C.

Q_d = 256 kJ/mol

D_O= 2.7 x 10^{-5} m^2/sec

T = 500 + 273 = 773 K

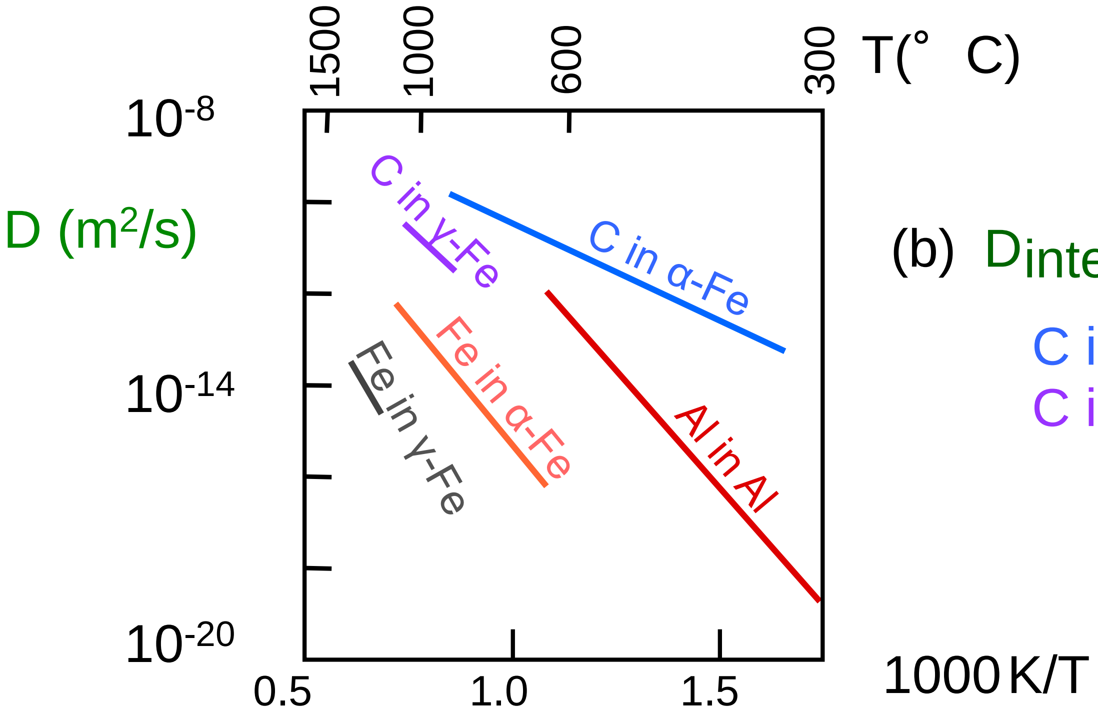
R = 8.31 J/mol-K

$$D = 2.7 \times 10^{-5} \cdot \exp\left(-\frac{256000}{8.31 \times 773}\right)$$

D = 1.33 x 10^{-22} m^2/sec

4-I. Diffusion and Temperature

D has exponential dependence on T

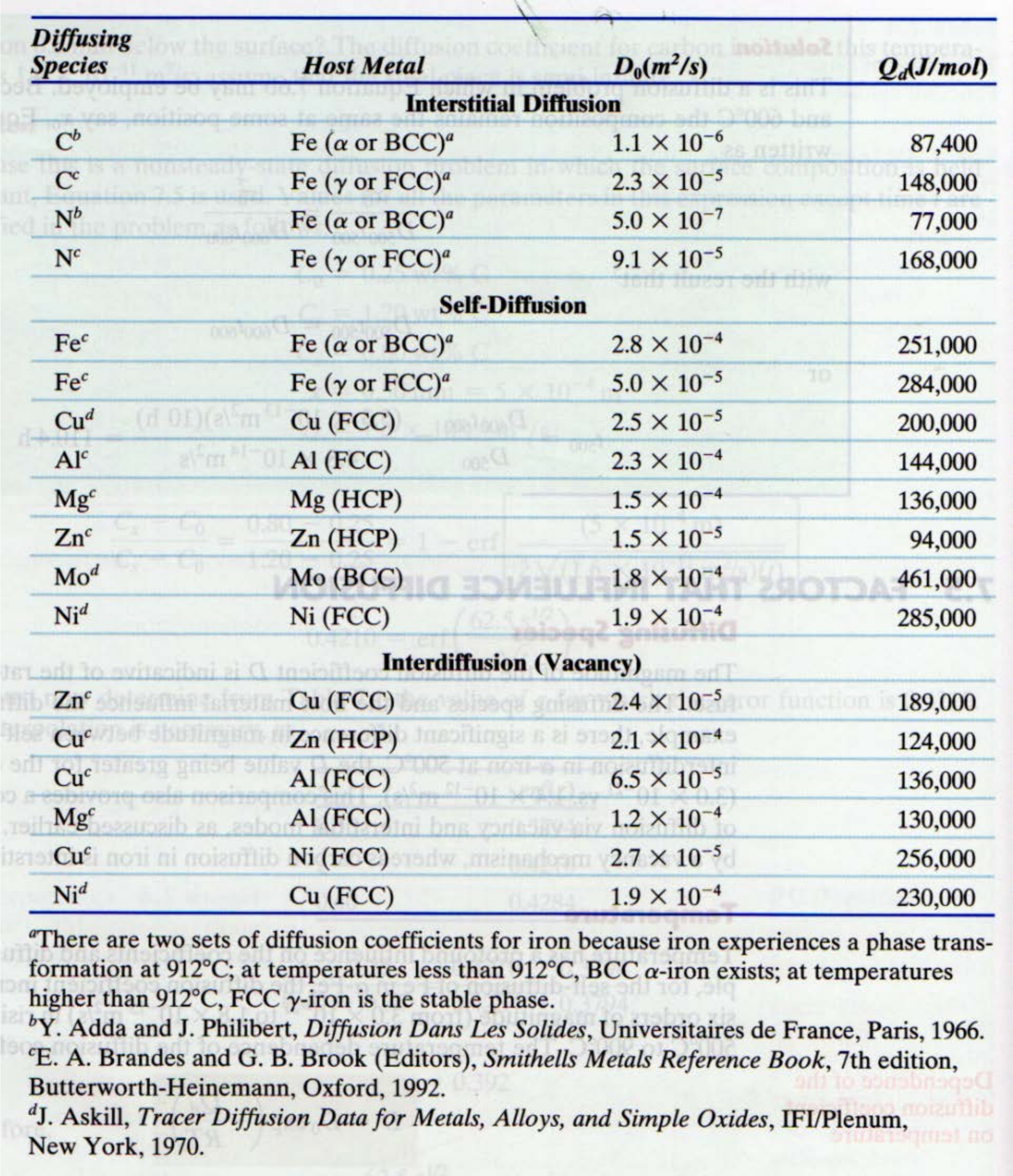


(b) $D_{interstitial}$ >> $D_{substitutional}$

$D_{interstitial}$	$D_{substitutional}$
C in α-Fe	Al in Al
C in γ-Fe	Fe in α-Fe
	Fe in γ-Fe

Adapted from Fig. 7.7, Callister & Rethwisch 9e.
(Data for Fig. 7.7 taken from E.A. Brandes and G.B. Brook (Ed.) Smithells Metals Reference Book, 7th ed., Butterworth-Heinemann, Oxford, 1992.)

Table 7.2



Diffusing Species	*Host Metal*	$D_0(m^2/s)$	$Q_d(J/mol)$
Interstitial Diffusion			
C[b]	Fe (α or BCC)[a]	1.1×10^{-6}	87,400
C[c]	Fe (γ or FCC)[a]	2.3×10^{-5}	148,000
N[b]	Fe (α or BCC)[a]	5.0×10^{-7}	77,000
N[c]	Fe (γ or FCC)[a]	9.1×10^{-5}	168,000
Self-Diffusion			
Fe[c]	Fe (α or BCC)[a]	2.8×10^{-4}	251,000
Fe[c]	Fe (γ or FCC)[a]	5.0×10^{-5}	284,000
Cu[d]	Cu (FCC)	2.5×10^{-5}	200,000
Al[c]	Al (FCC)	2.3×10^{-4}	144,000
Mg[c]	Mg (HCP)	1.5×10^{-4}	136,000
Zn[c]	Zn (HCP)	1.5×10^{-5}	94,000
Mo[d]	Mo (BCC)	1.8×10^{-4}	461,000
Ni[d]	Ni (FCC)	1.9×10^{-4}	285,000
Interdiffusion (Vacancy)			
Zn[c]	Cu (FCC)	2.4×10^{-5}	189,000
Cu[c]	Zn (HCP)	2.1×10^{-4}	124,000
Cu[c]	Al (FCC)	6.5×10^{-5}	136,000
Mg[c]	Al (FCC)	1.2×10^{-4}	130,000
Cu[c]	Ni (FCC)	2.7×10^{-5}	256,000
Ni[d]	Cu (FCC)	1.9×10^{-4}	230,000

[a] There are two sets of diffusion coefficients for iron because iron experiences a phase transformation at 912°C; at temperatures less than 912°C, BCC α-iron exists; at temperatures higher than 912°C, FCC γ-iron is the stable phase.

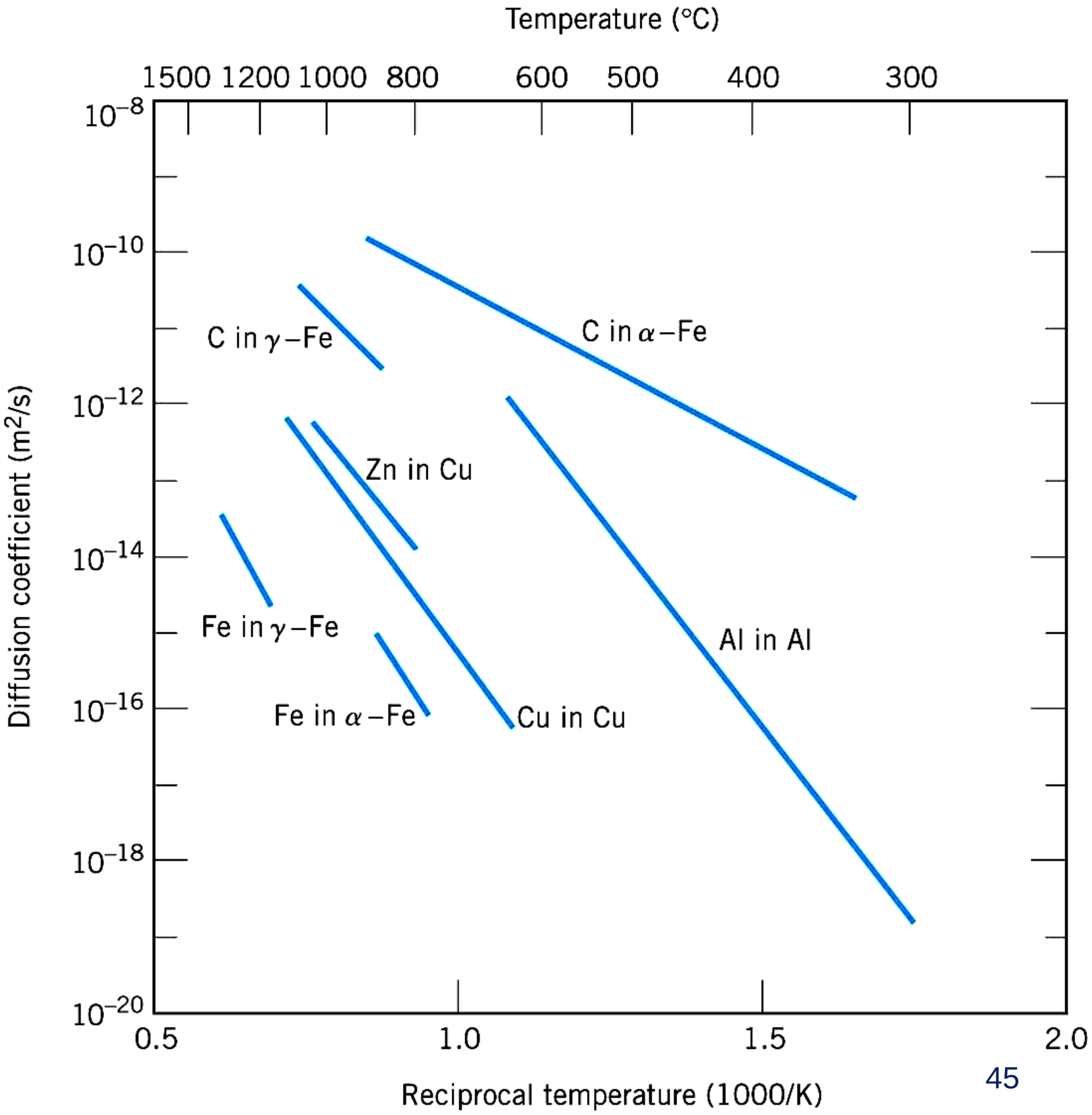
[b] Y. Adda and J. Philibert, *Diffusion Dans Les Solides*, Universitaires de France, Paris, 1966.

[c] E. A. Brandes and G. B. Brook (Editors), *Smithells Metals Reference Book*, 7th edition, Butterworth-Heinemann, Oxford, 1992.

[d] J. Askill, *Tracer Diffusion Data for Metals, Alloys, and Simple Oxides*, IFI/Plenum, New York, 1970.

Factors Influencing Diffusion temperature

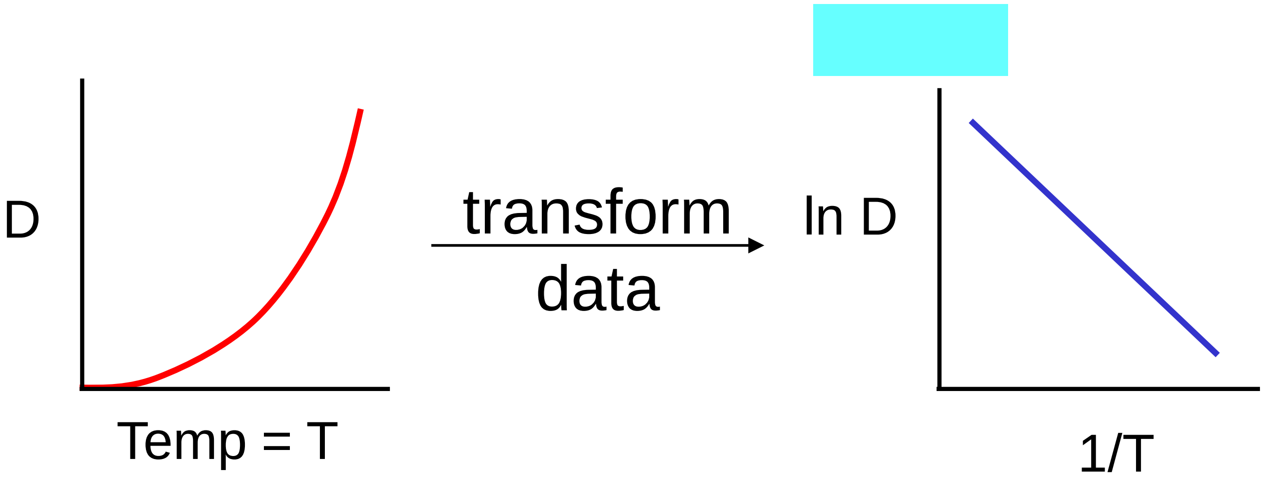
- ***Arrhenius plot*** of relationship between diffusion coefficient and reciprocal of temperature for different elements



Example: At 300° C the diffusion coefficient and activation energy for Cu in Si are

D(300° C) = 7.8 x 10^{-11} m^2/s, Q_d = 41.5 kJ/mol

(c) What is the diffusion coefficient at 350° C?



$$\ln D_2 = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T_2}\right) \quad \text{and} \quad \ln D_1 = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T_1}\right)$$

$$\therefore \quad \ln D_2 - \ln D_1 = \ln\frac{D_2}{D_1} = -\frac{Q_d}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Example (cont.)

$$D_2 = D_1 \exp\left[-\frac{Q_d}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

$T_1 = 273 + 300 = 573\,\mathrm{K}$

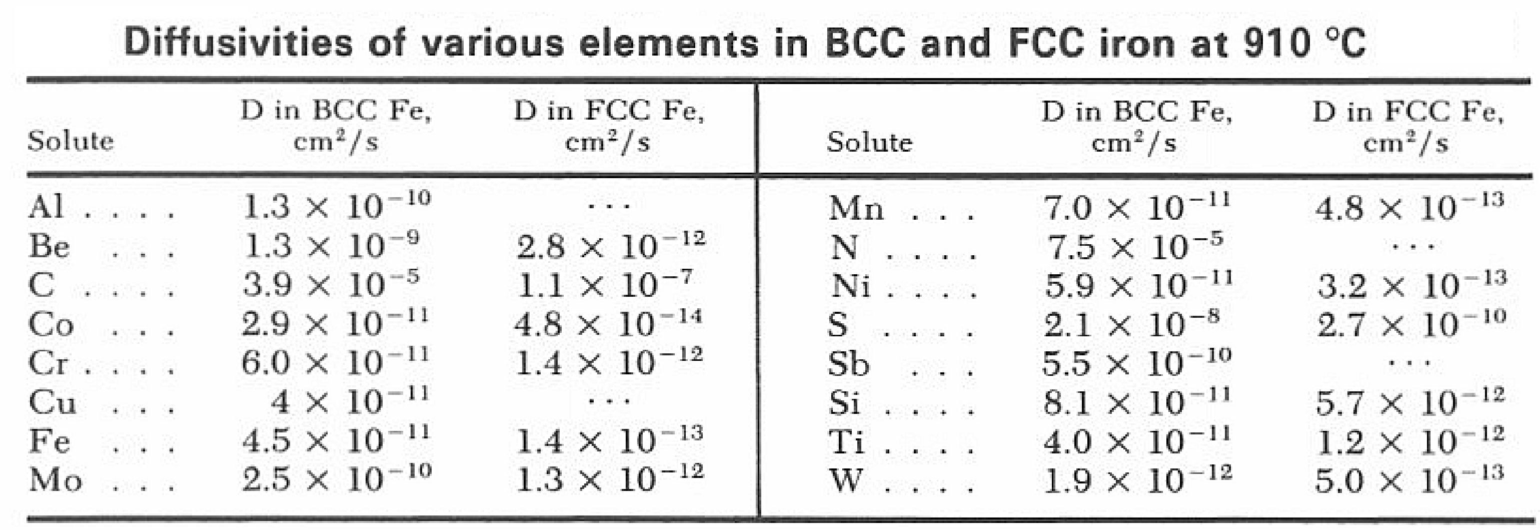
$T_2 = 273 + 350 = 623\,\mathrm{K}$

$$D_2 = (7.8 \text{ x } 10^{-11}\ \mathrm{m}^2/\mathrm{s}) \exp\left[\frac{-41{,}500 \text{ J/mol}}{8.314 \text{ J/mol-K}}\left(\frac{1}{623 \text{ K}} - \frac{1}{573 \text{ K}}\right)\right]$$

$$\boxed{D_2 = 15.7 \text{ x } 10^{-11}\ \mathrm{m}^2/\mathrm{s}}$$

4-II. Factors Influencing Diffusion crystal structure

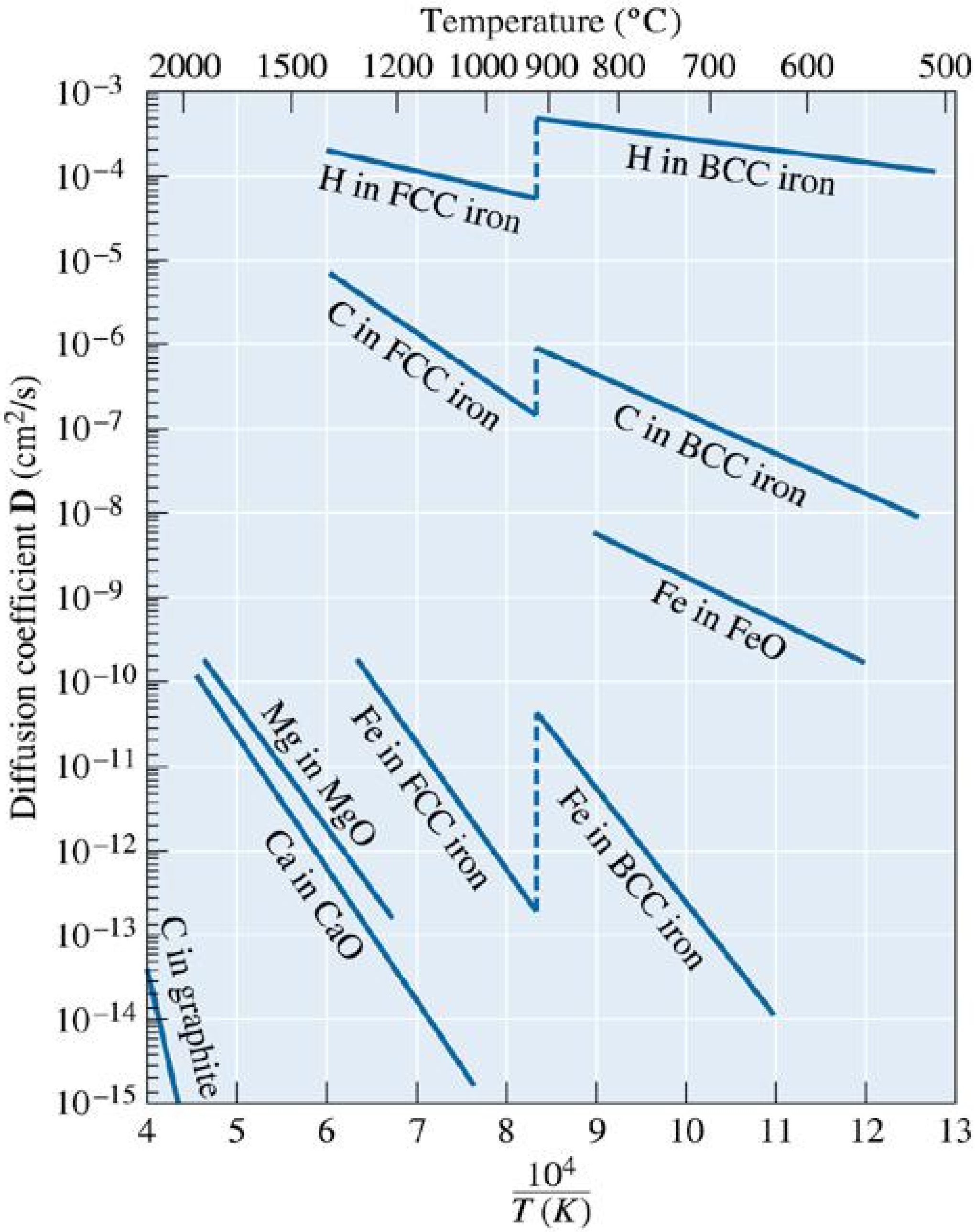
- The crystal structure of the metal affects the diffusion rate:
  - Diffusivities of different elements in BCC-Fe are higher than in FCC-Fe at the same temperature (e.g. 910ºC)
  - Reasons for faster diffusion in BCC compared with FCC iron
    - BCC iron lattice is slightly more open; it has lower packing factor than FCC
    - BCC lattice has a coordination number of 8 compared with 12 in FCC → fewer bonds must be broken when elements diffuse in BCC iron



Diffusivities of various elements in BCC and FCC iron at 910 °C

Solute	D in BCC Fe, cm²/s	D in FCC Fe, cm²/s	Solute	D in BCC Fe, cm²/s	D in FCC Fe, cm²/s
Al	1.3×10^{-10}	. . .	Mn . . .	7.0×10^{-11}	4.8×10^{-13}
Be . . .	1.3×10^{-9}	2.8×10^{-12}	N	7.5×10^{-5}	. . .
C	3.9×10^{-5}	1.1×10^{-7}	Ni	5.9×10^{-11}	3.2×10^{-13}
Co . . .	2.9×10^{-11}	4.8×10^{-14}	S	2.1×10^{-8}	2.7×10^{-10}
Cr	6.0×10^{-11}	1.4×10^{-12}	Sb . . .	5.5×10^{-10}	. . .
Cu . . .	4×10^{-11}	. . .	Si	8.1×10^{-11}	5.7×10^{-12}
Fe . . .	4.5×10^{-11}	1.4×10^{-13}	Ti	4.0×10^{-11}	1.2×10^{-12}
Mo . . .	2.5×10^{-10}	1.3×10^{-12}	W	1.9×10^{-12}	5.0×10^{-13}

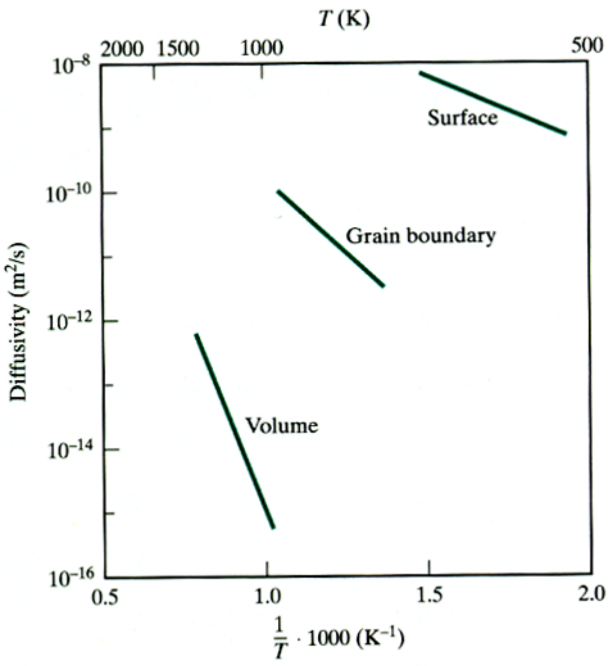
G.F. Carter. "Principles of Physical & Chemical Metallurgy". American Society for Metals (1979)

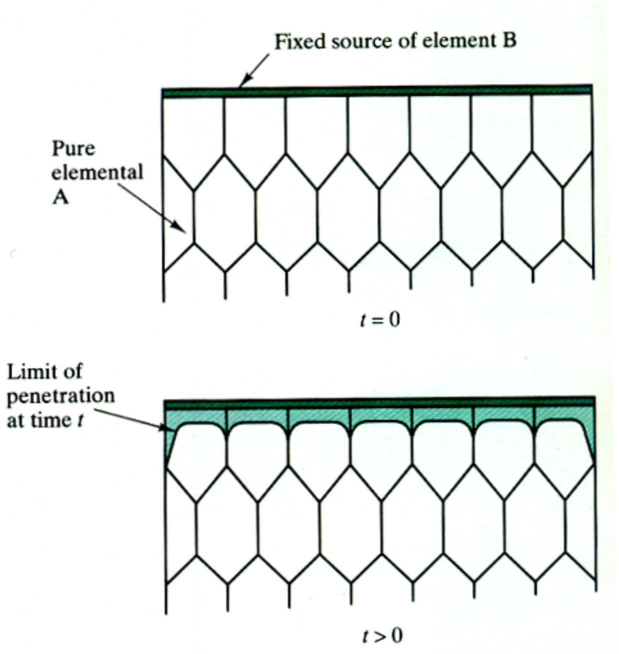


Increase in Temperature

III. Factors Influencing Diffusion_grain boundary

- Diffusion is faster along grain boundaries than through grains:
  - More open structure at grain boundaries than the interior grain
  - Much lower activation energy for diffusion in grain boundaries compared to transgranular diffusion

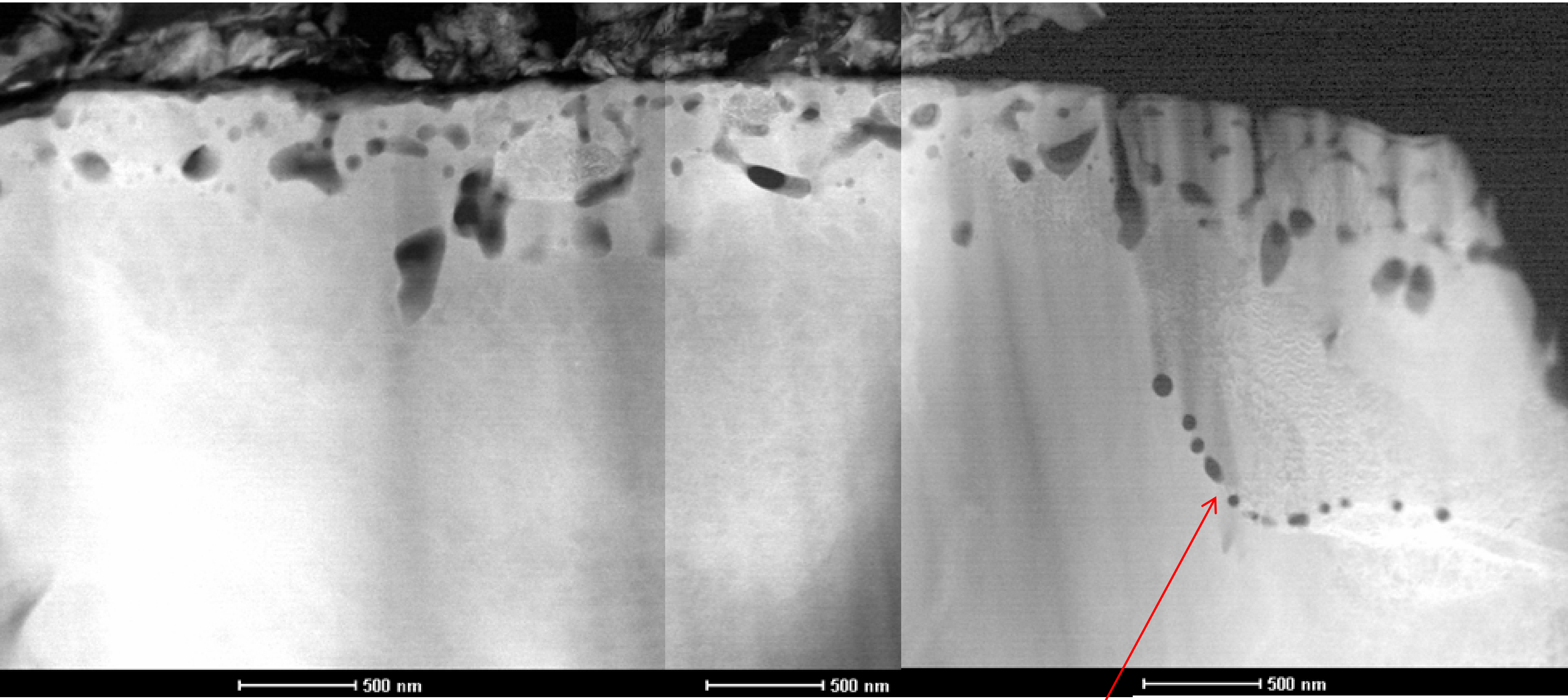




$Q_{volume} > Q_{gb} > Q_{surface}$

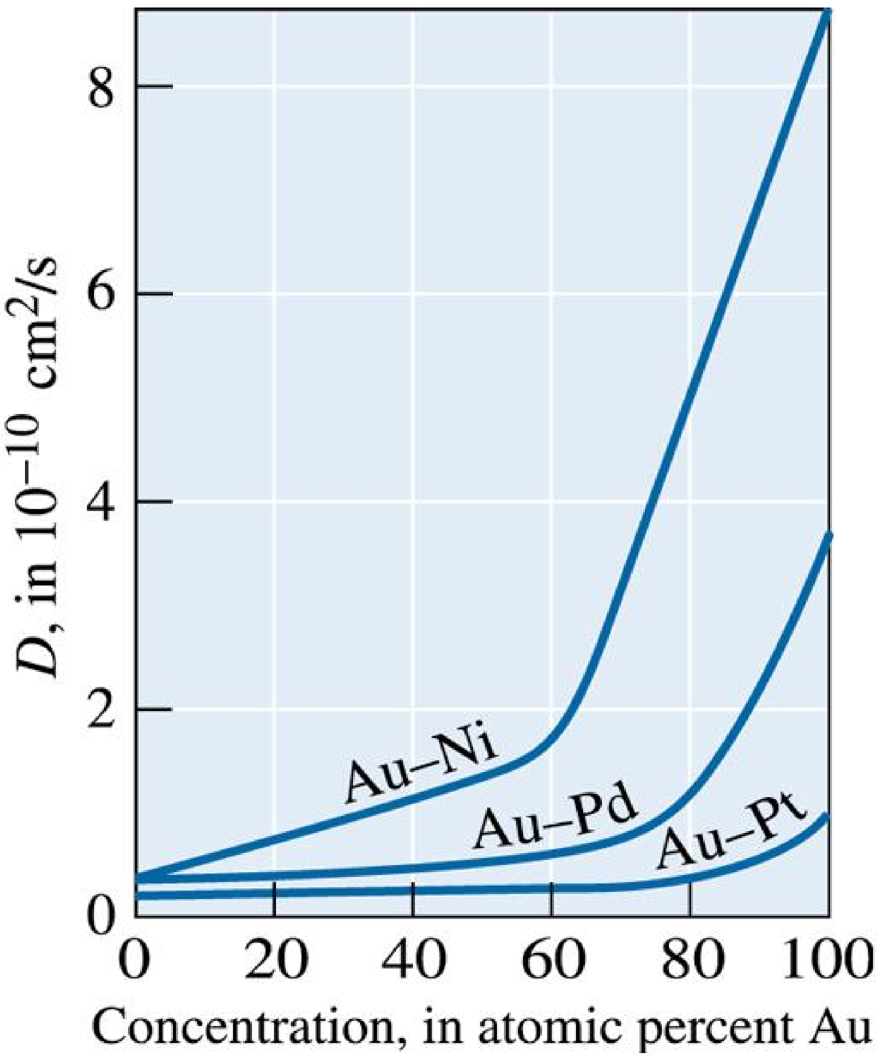
$D_{volume} < D_{gb} < D_{surface}$

Oxidation – Grainboundary diffusion



Grain boundary

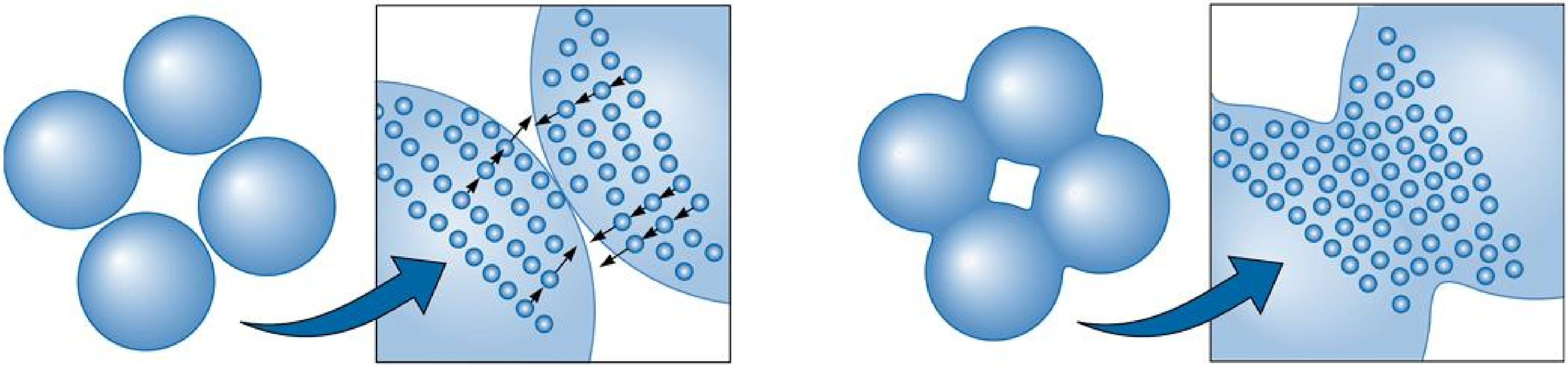
IV. Factors Influencing Diffusion
: concentration of diffusing species



The dependence of diffusion coefficient of Au on concentration of Au

5. Diffusion and Materials Processing

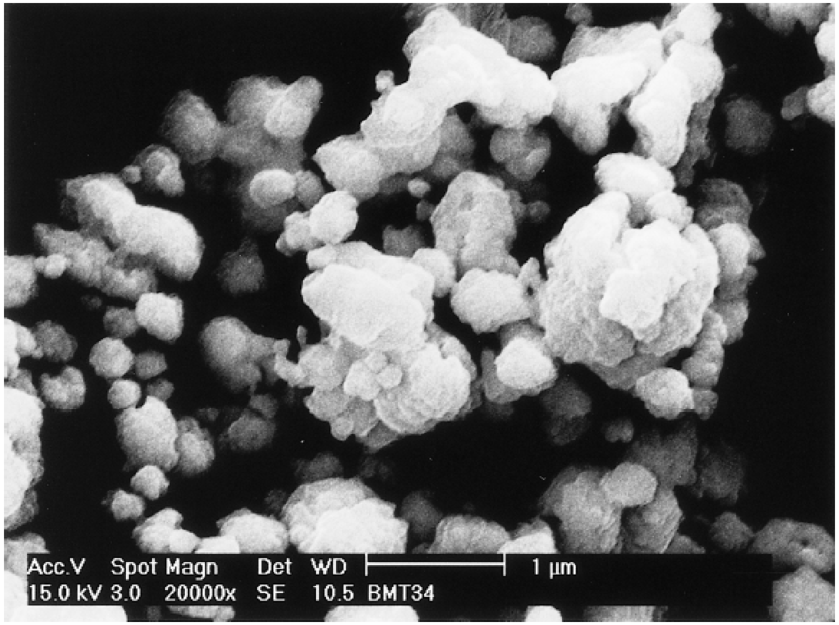
- **Powder metallurgy** - A method for producing monolithic metallic parts
- **Sintering** - A high-temperature treatment used to join small particles
- **Grain growth** - Movement of grain boundaries by diffusion in order to reduce the amount of grain boundary area
- **Diffusion bonding** - A joining technique in which two surfaces are pressed together at high pressures and temperatures



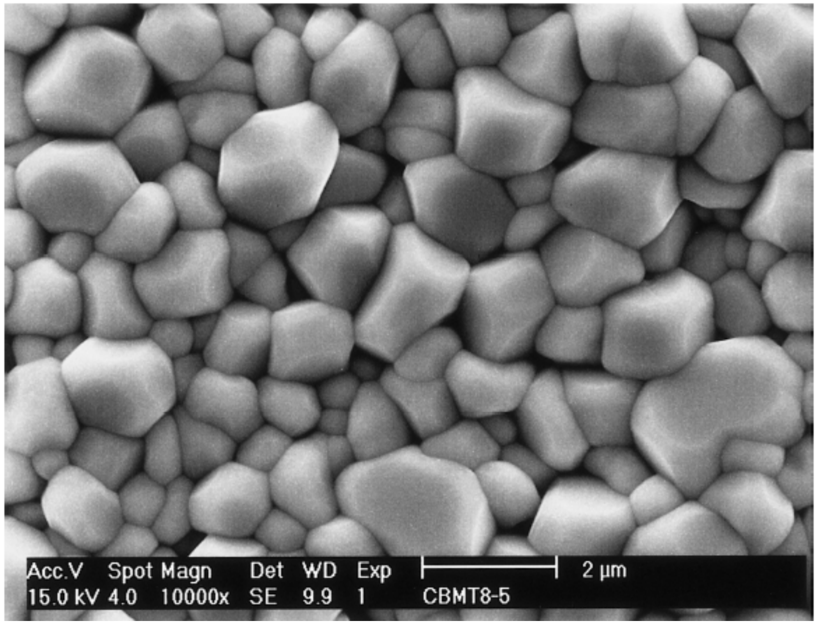
Compacted product

Partly sintered product

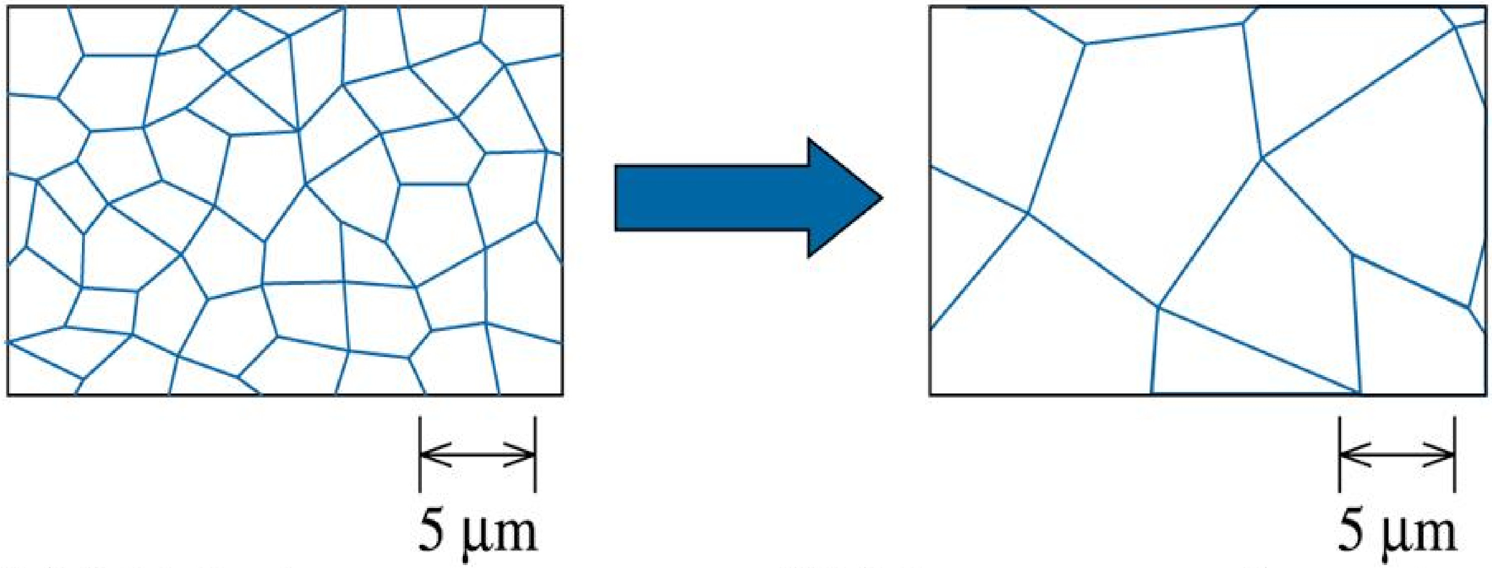
(a, b) Diffusion processes during **sintering and powder metallurgy**. Atoms diffuse to points of contact, creating bridges and reducing the pore size



Particles of barium magnesium tantalate (BMT) ($Ba(Mg_{1/3}Ta_{2/3})O_3$) powder are shown. This ceramic material is useful in making electronic components known as dielectric resonators that are used for wireless communications.

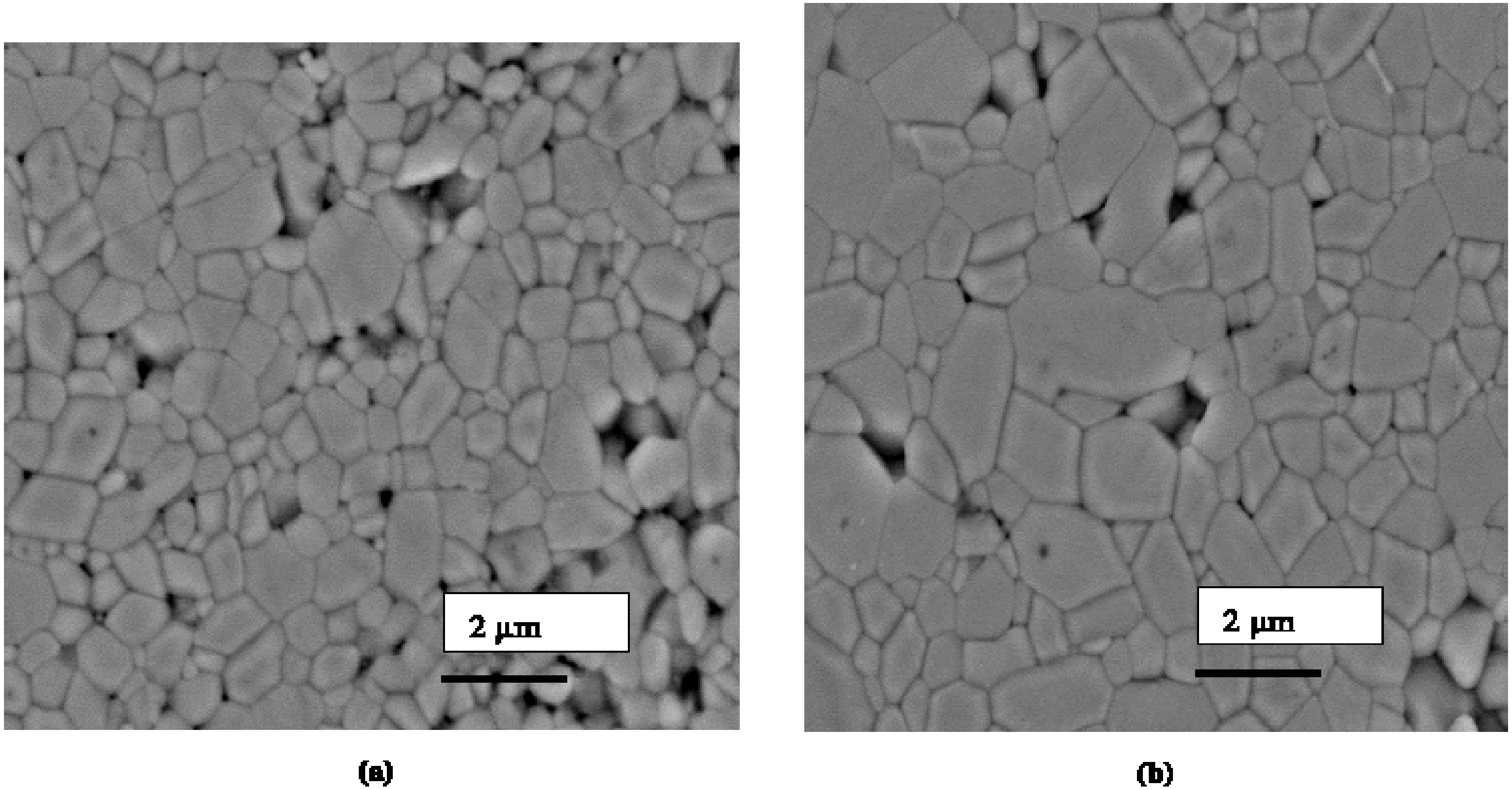


The microstructure of BMT ceramics obtained by compaction and **sintering** of BMT powders.

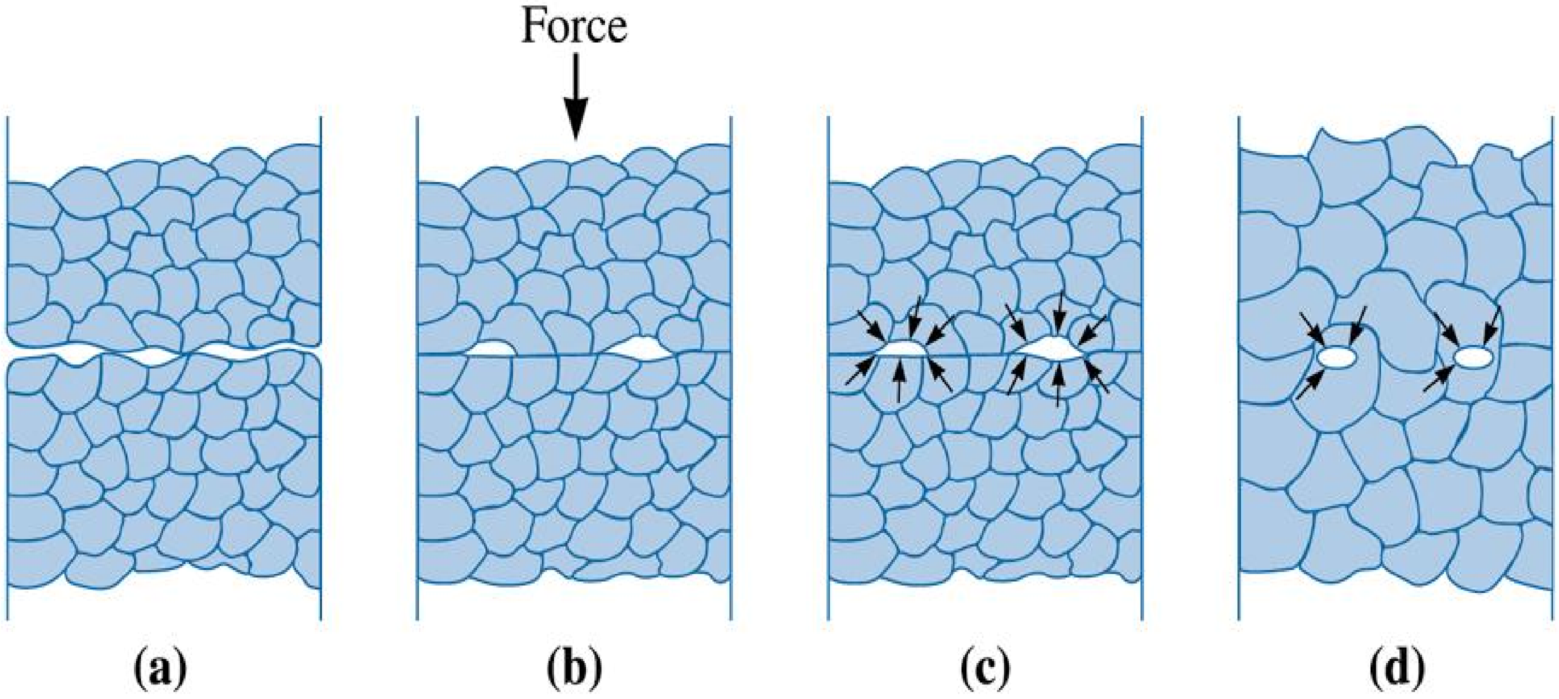


(a) Initial microstructure **(b)** Microstructure after grain growth

Grain growth occurs as atoms diffuse across the grain boundary from one grain to another

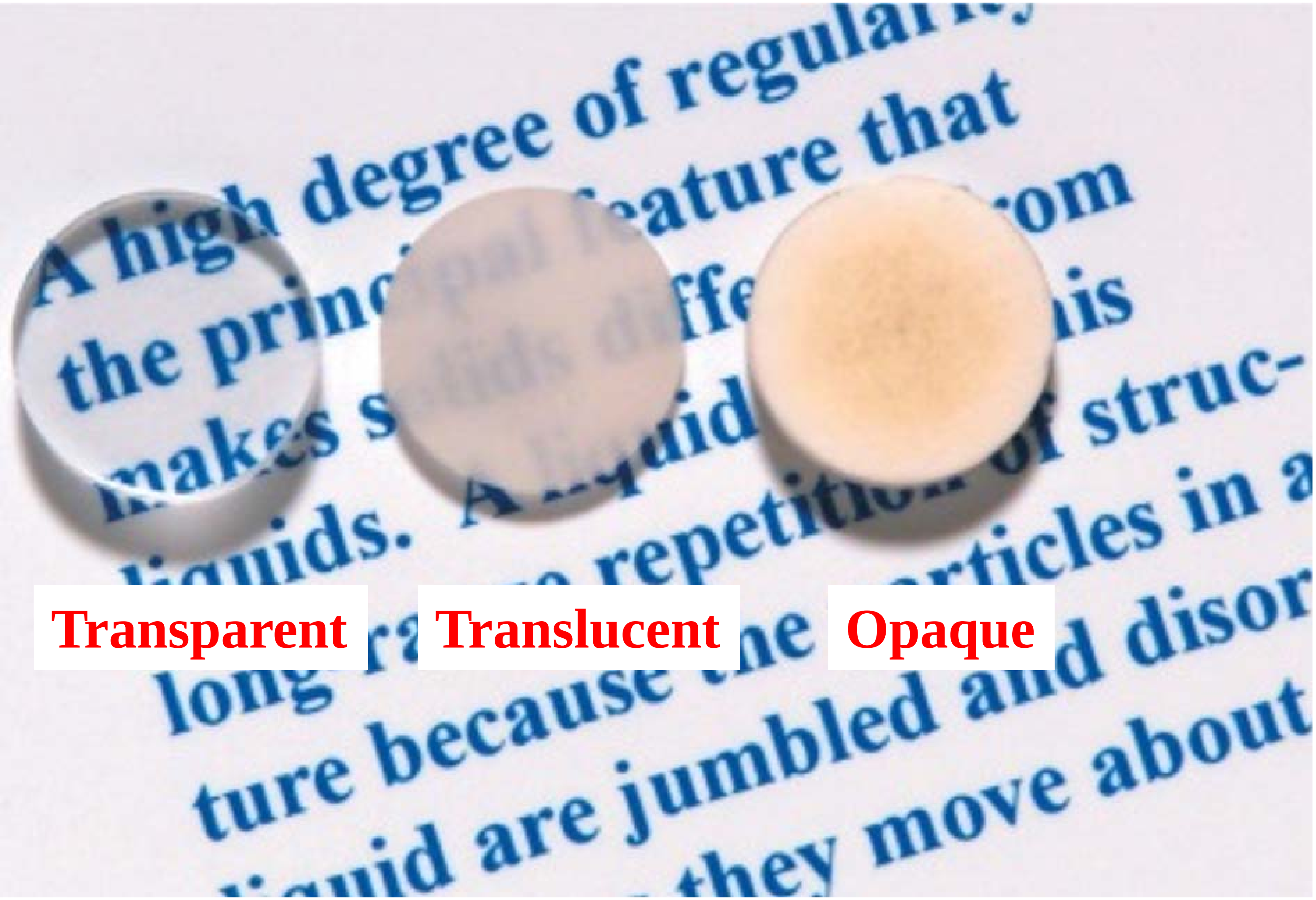


Grain growth in alumina ceramics can be seen from the SEM micrographs of alumina ceramics. (a) The left micrograph shows the microstructure of an alumina ceramic sintered at 1350^{o}C for 150 hours. (b) The right micrograph shows a sample sintered at 1350^{o}C for 300 hours.



The steps in **diffusion bonding**: (a) Initially the contact area is small; (b) application of pressure deforms the surface, increasing the bonded area; (c) grain boundary diffusion permits voids to shrink; and (d) final elimination of the voids requires volume diffusion

Void Effect on the optical properties



Summary

Chapter 5: Diffusion

I. Introduction of diffusion

: Movement of atoms to reduce its chemical potential μ.

⇨ **driving force: Reduction of G**

Down-hill diffusion movement of atoms from a high C_B region to low C_B region.

Up-hill diffusion movement of atoms from a low C_B region to high C_B region.

II. Diffusion mechanisms

Vacancy diffusion vs. Interstitial diffusion

(a) Self-diffusion

(b) Interdiffusion

III. Steady-state diffusion

Concentration varies with position.

Fick’s Frist law:

$$\boxed{J = -D\frac{dC}{dx}}$$

Estimation of Diffusion Depth:

$$\frac{C_x - C_0}{C_S - C_0} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

IV. Non-steady-state diffusion

Concentration varies with time and position.

Fick’s Second law:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

Diffusion coefficient:

$$\boxed{D = D_0 exp\left(\frac{Q_d}{RT}\right)}$$

V. Factors that influences diffusion

Diffusion **FASTER** for...	Diffusion **SLOWER** for...
open crystal structures	close-packed structures
lower melting T materials	higher melting T materials
materials w/secondary bonding	materials w/covalent bonding
smaller diffusing atoms	larger diffusing atoms
cations	anions
lower density materials	higher density materials

2020 Fall

Introduction to Materials Science and Engineering

10. 08. 2020

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Contents for previous class

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H3 : Chapter 5 example (10 판기준, 9판은 7장)

IH : Chapter 5 연습문제

중간고사

29일 혹은 30일 4-7시/ 6-9시, 31일 9-12시/ 1시-4시

시험범위

1장부터 – 8장까지, 12장 일부, 14장 포함 (10판 기준)/ 10장까지 (9판 기준)

주교재 – 영문기준 270 page까지 + 435-455 & 512-544 pages

Lecture notes 1~14

Contents for previous class

Chapter 1: Introduction

Chapter 2-4:

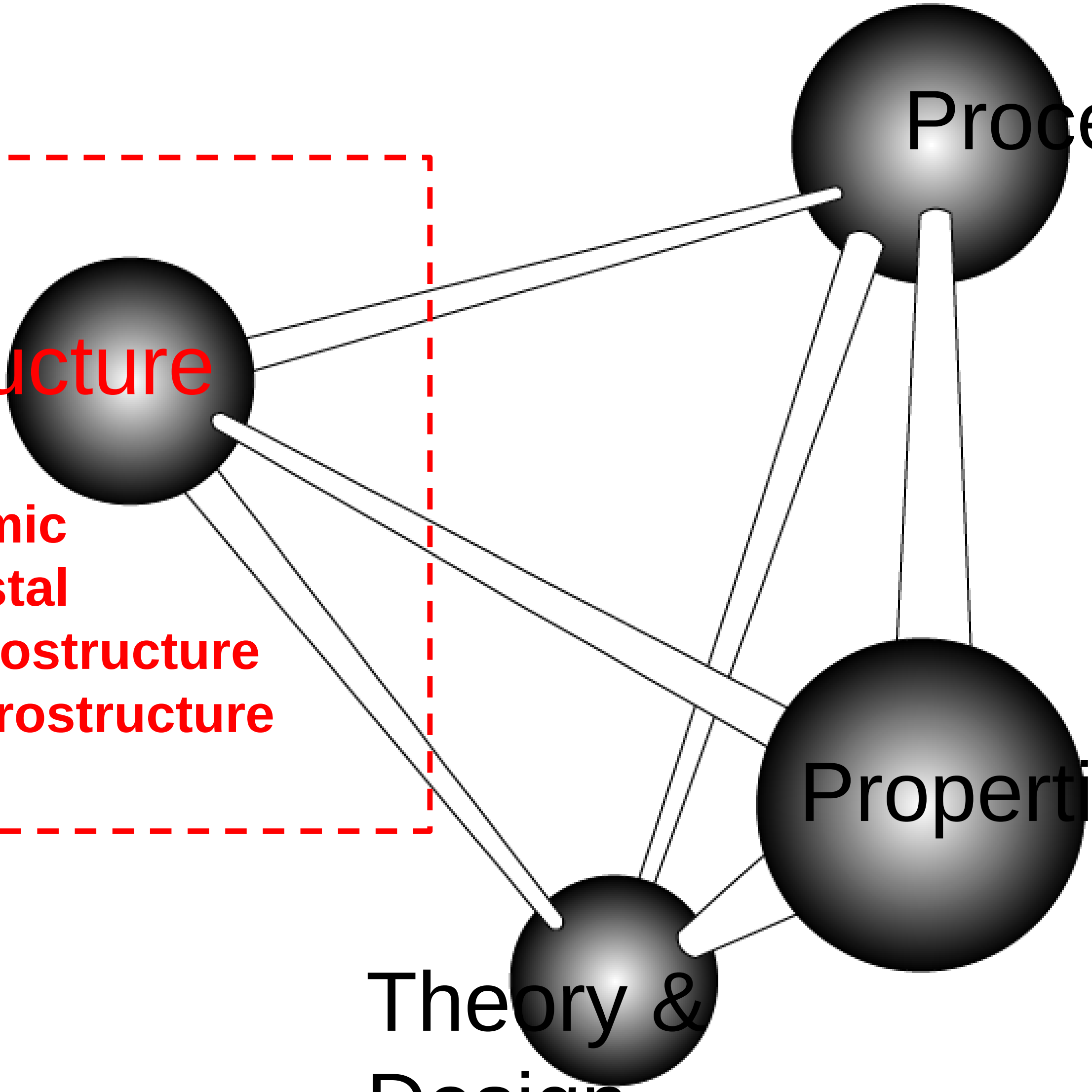
Atomic structure and interatomic **bonding**

Fundamentals of **crystallography**
The structure of **crystalline solid**
Structure of Polymers

Imperfections in solids

Chapter 5: **Diffusion**

Materials Science and Engineering



Processing

- Sintering
- Heat treatment
- Thin Film
- Melt process
- Mechanical

Structure

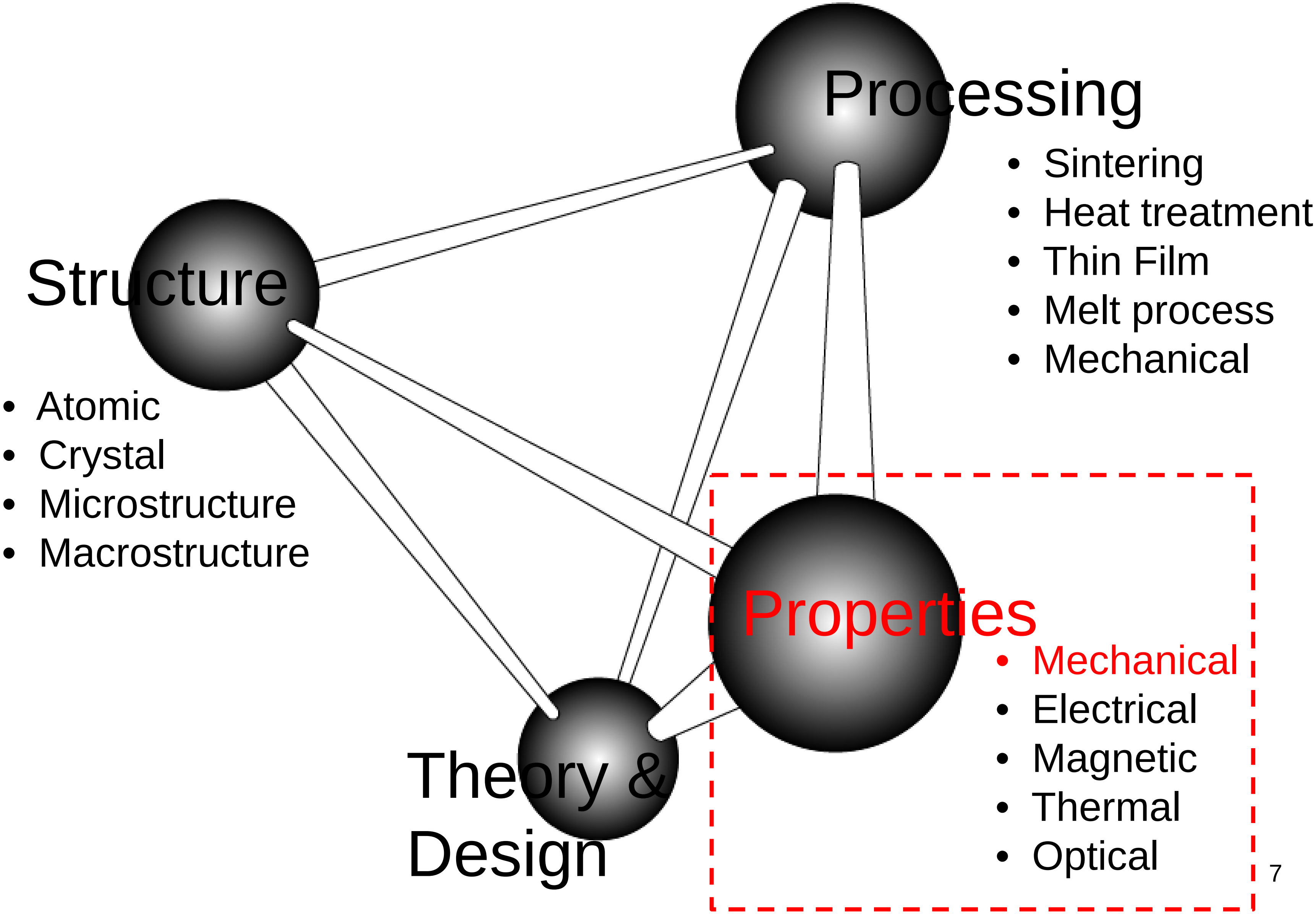
- **Atomic**
- **Crystal**
- **Microstructure**
- **Macrostructure**

Properties

- Mechanical
- Electrical
- Magnetic
- Thermal
- Optical

Theory &
Design

Materials Science and Engineering



Processing

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- Atomic
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Properties

- Mechanical
- Electrical
- Magnetic
- Thermal
- Optical

Theory & Design

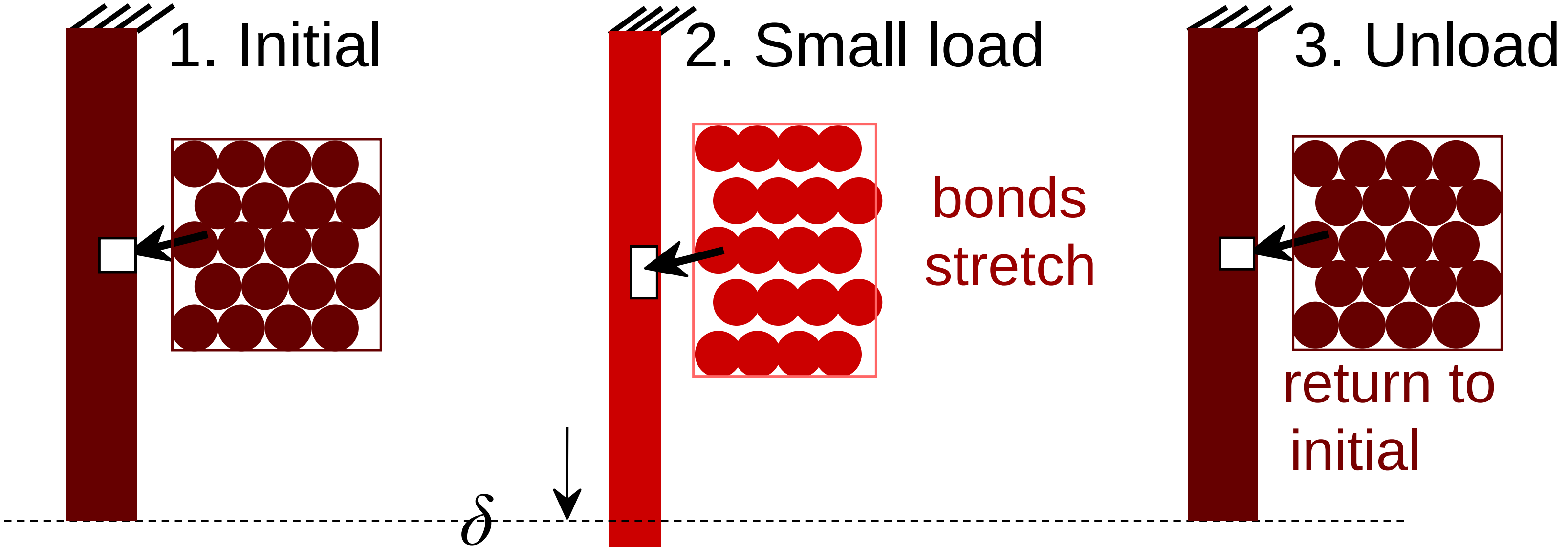
Contents for today's class

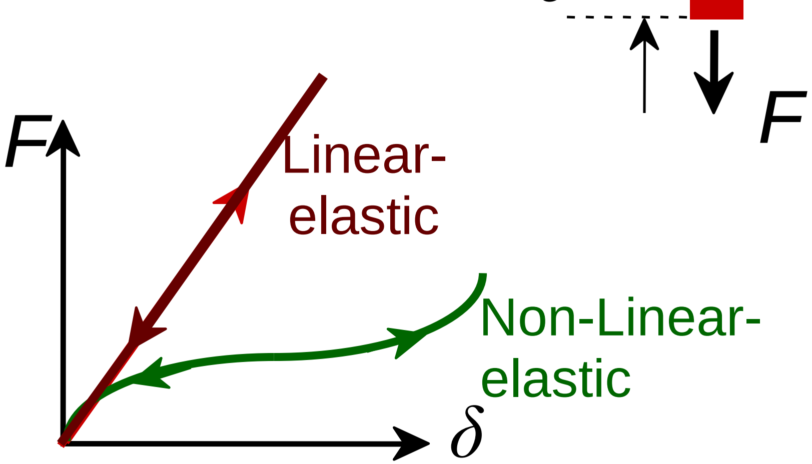
Chapter 6: Mechanical Properties of Metals

- **Stress and strain**:
  What are they and why are they used instead of load and deformation?
- **Elastic behavior:**
  When loads are small, how much deformation occurs?
  What materials deform least?
- **Plastic behavior:**
  At what point do dislocations cause permanent deformation?
  What materials are most resistant to permanent deformation?
- **Toughness and ductility:**
  What are they and how do we measure them?

- Load - The force applied to a material during testing
- Stress - Force or load per unit area of cross-section over which the force or load is acting
- Strain - Elongation change in dimension per unit length
- Engineering stress - The applied load, or force, divided by the original cross-sectional area of the material
- Engineering strain - The amount that a material deforms per unit length in a tensile test
- True stress The load divided by the actual cross-sectional area of the specimen at that load
- True strain The strain calculated using actual and not original dimensions, given by $\varepsilon_t \ln(l/l_0)$
- Young's modulus (E) - The slope of the linear part of the stress-strain curve in the elastic region, same as modulus of elasticity
- Shear modulus (G) - The slope of the linear part of the shear stress-shear strain curve

Elastic Deformation

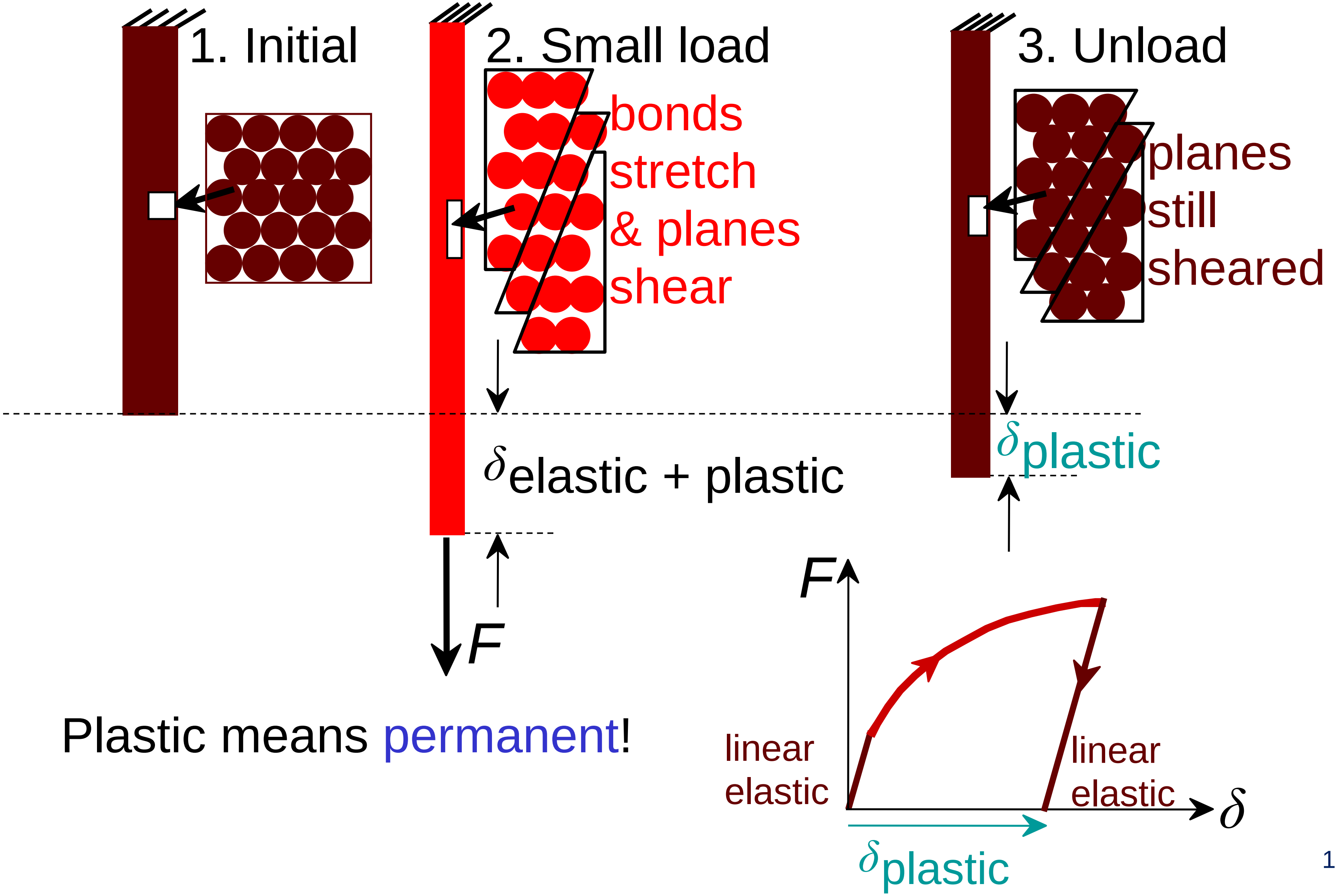




Elastic means reversible!

https://www.youtube.com/watch?v=SIFfY-MS3yA

Plastic Deformation (Metals)



1. Initial

2. Small load

bonds stretch & planes shear

$\delta_{\text{elastic + plastic}}$

F

3. Unload

planes still sheared

δ_{plastic}

Plastic means permanent!

F

linear elastic

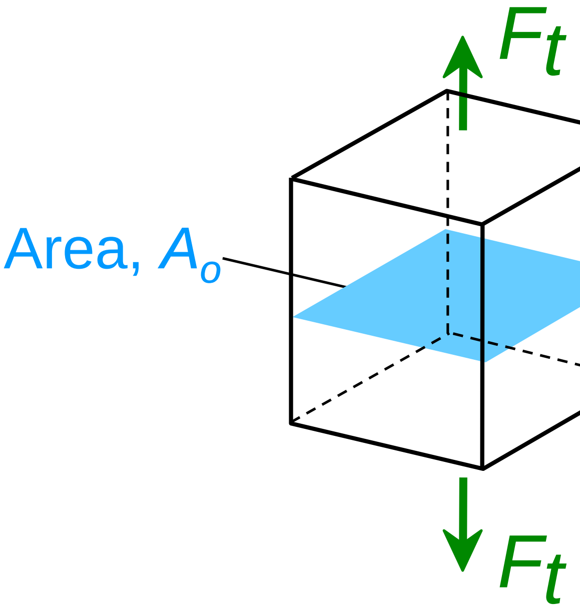
linear elastic

δ

δ_{plastic}

II. Engineering Stress

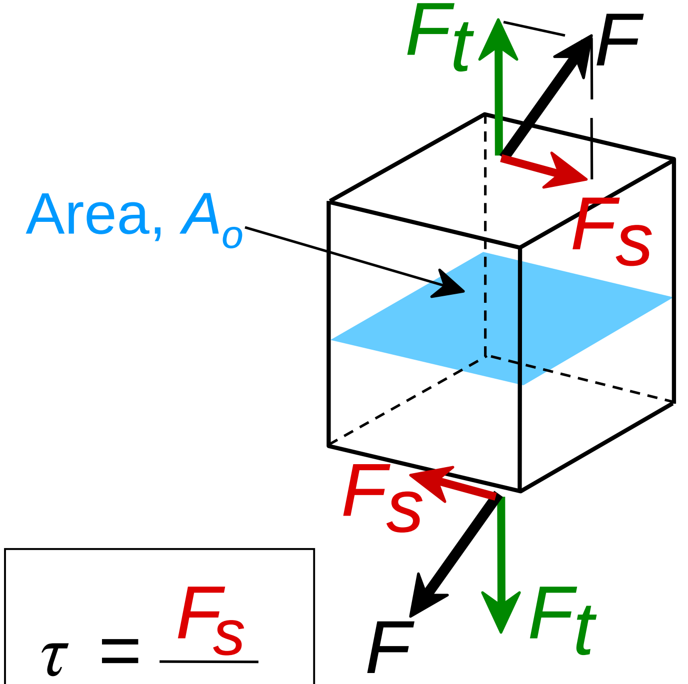
- Tensile stress, σ:



$$\sigma = \frac{F_t}{A_o} = \frac{\text{N}}{\text{m}^2}$$

original cross-sectional area before loading

- Shear stress, τ:

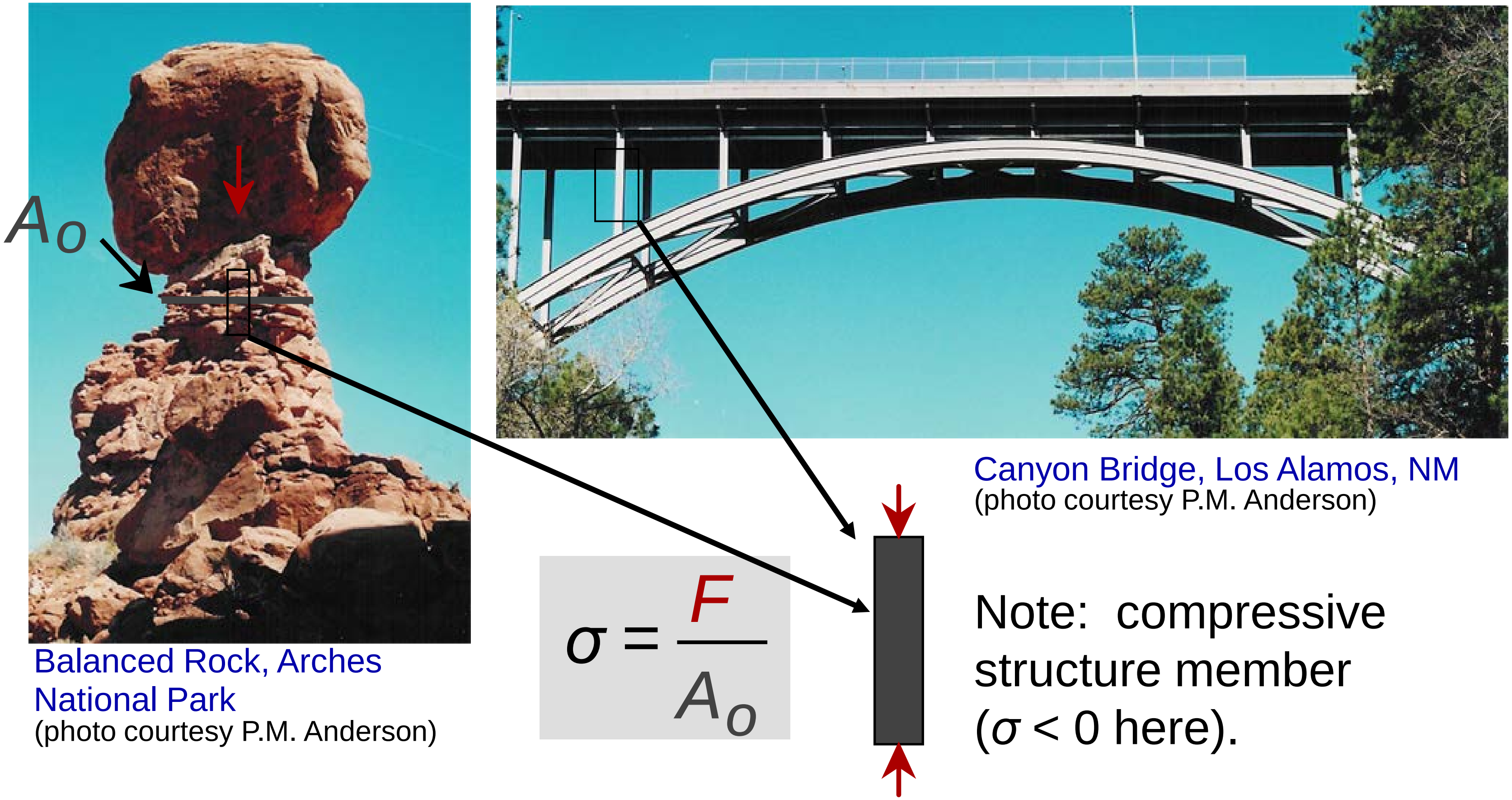


$$\tau = \frac{F_s}{A_o}$$

∴ Stress has units: N/m^2

II. Common States of **Stress**

a. Simple **compression**:



Balanced Rock, Arches National Park
(photo courtesy P.M. Anderson)

Canyon Bridge, Los Alamos, NM
(photo courtesy P.M. Anderson)

$$\sigma = \frac{F}{A_o}$$

Note: compressive structure member ($\sigma < 0$ here).

II. Common States of **Stress**

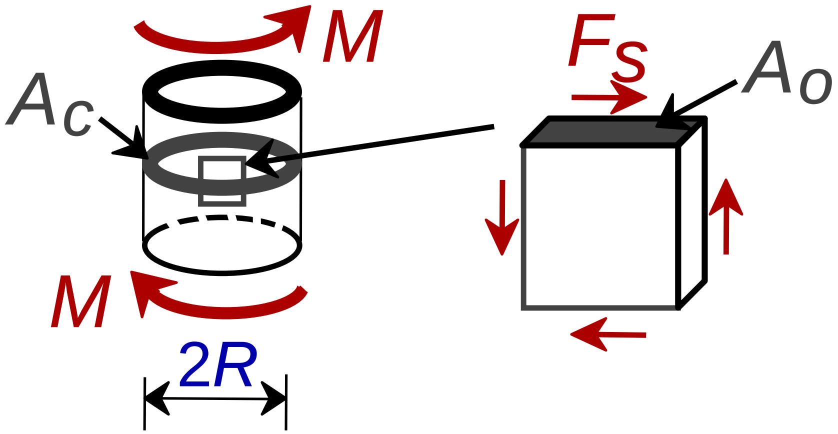
b. Simple tension: cable

A_o = cross-sectional area (when unloaded)

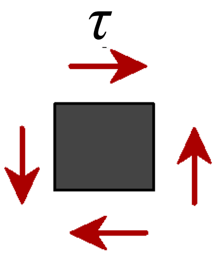
$$\sigma = \frac{F}{A_o}$$

Ski lift (photo courtesy P.M. Anderson)

c. Torsion (a form of shear): drive shaft



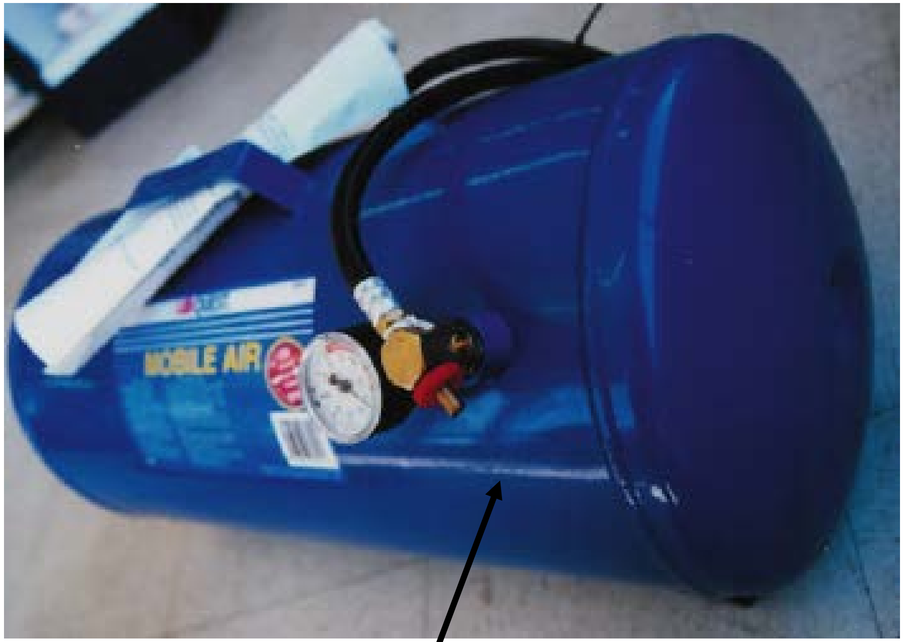
$$\tau = \frac{F_s}{A_o}$$



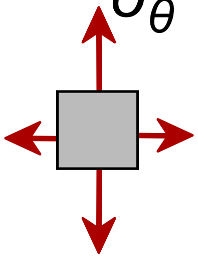
Note: $\tau = M/A_cR$ here.

II. Common States of **Stress**

d. Bi-axial tension:



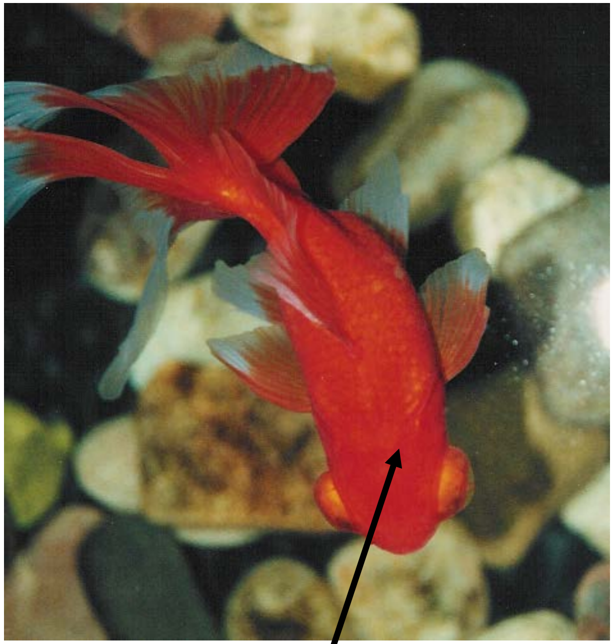
Pressurized tank
(photo courtesy
P.M. Anderson)



$\sigma_\theta > 0$

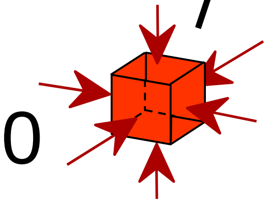
$\sigma_z > 0$

e. Hydrostatic compression:



Fish under water

(photo courtesy
P.M. Anderson)

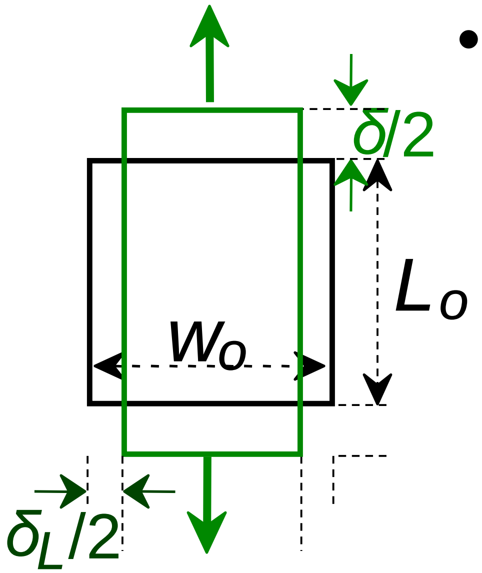


$\sigma_h < 0$

III. Engineering Strain

- **Tensile strain:**

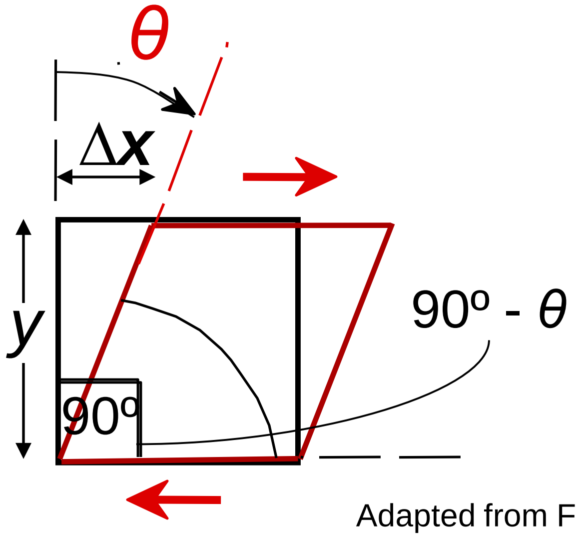
$$\varepsilon = \frac{\delta}{L_o}$$



- **Lateral strain:**

$$\varepsilon_L = \frac{-\delta_L}{w_o}$$

- **Shear strain:**



$$\gamma = \Delta x / y = \tan \theta$$

Strain is always dimensionless.

Adapted from Fig. 8.1 (a) and (c), *Callister & Rethwisch 9e.*

Stress-Strain Testing

- **Typical tensile test machine**

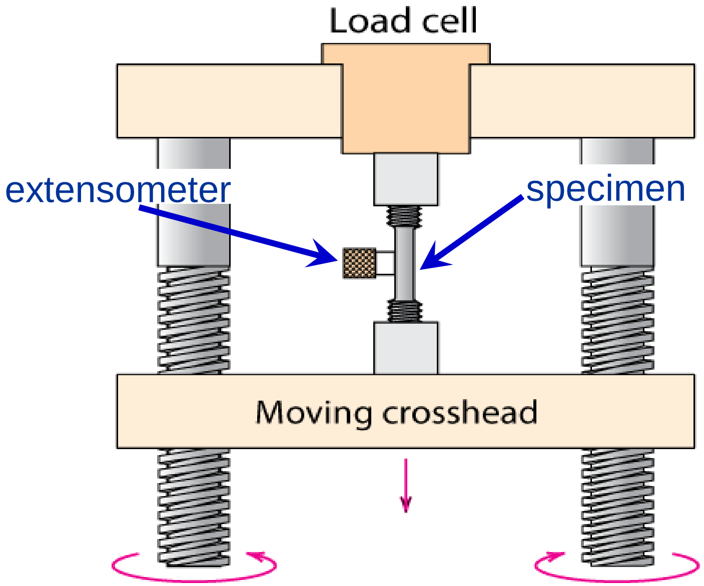
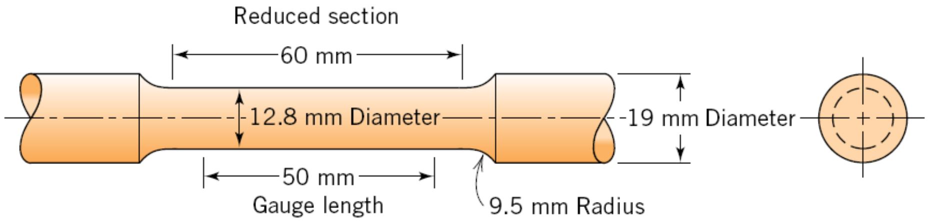


Fig. 8.3, *Callister & Rethwisch 9e.*

(Taken from H.W. Hayden, W.G. Moffatt, and J. Wulff, *The Structure and Properties of Materials*, Vol. III, *Mechanical Behavior*, p. 2, John Wiley and Sons, New York, 1965.)

- **Typical tensile specimen**



➢ **Other types of tests:**

- compression: brittle materials (e.g. concrete)

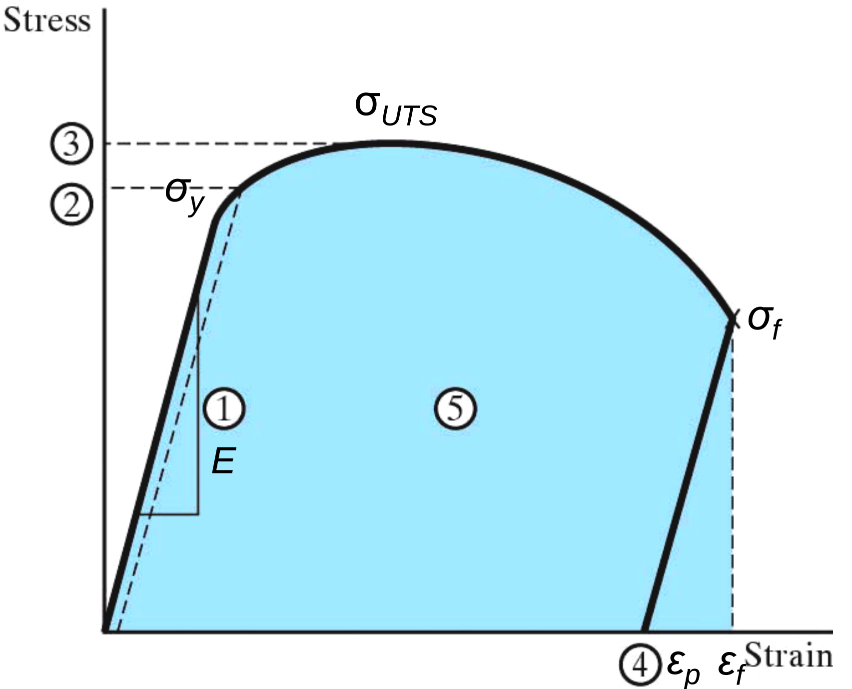
- torsion: cylindrical tubes, shafts

Tensile testing of a steel specimen

IV. Deformation

- Elastic vs. Plastic region
- Key points

  1. Elastic modulus (=Young's modulus), E
  2. 0.2% (0.002 strain) yield stress, σ_y
  3. Ultimate yield stress, σ_{UTS}
  4. Ductility, ε_p
  5. Toughness ⟹ $\boxed{\int \sigma d\varepsilon}$
  6. Fracture stress, σ_f
  7. Fracture strain, ε_f



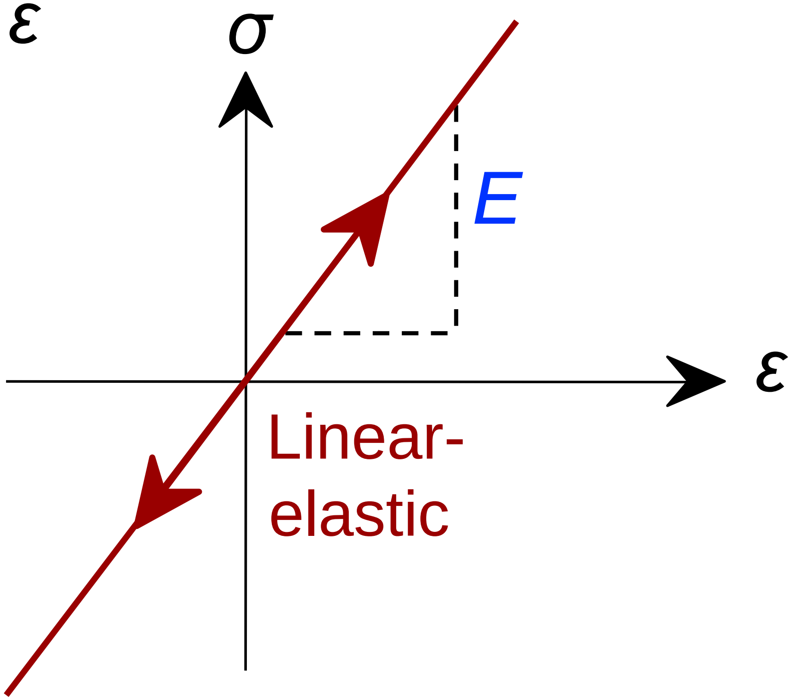
a. Elastic Properties

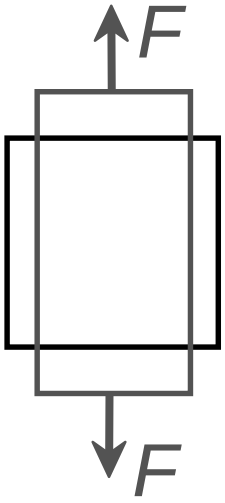
(1) Modulus of Elasticity, *E*:

(also known as Young's modulus)

- **Hooke's Law:**

$$\sigma = E\,\varepsilon$$





simple
tension
test

Properties from Bonding: E

- Slope of stress strain plot (which is proportional to the elastic modulus, E) depends on bond strength of metal

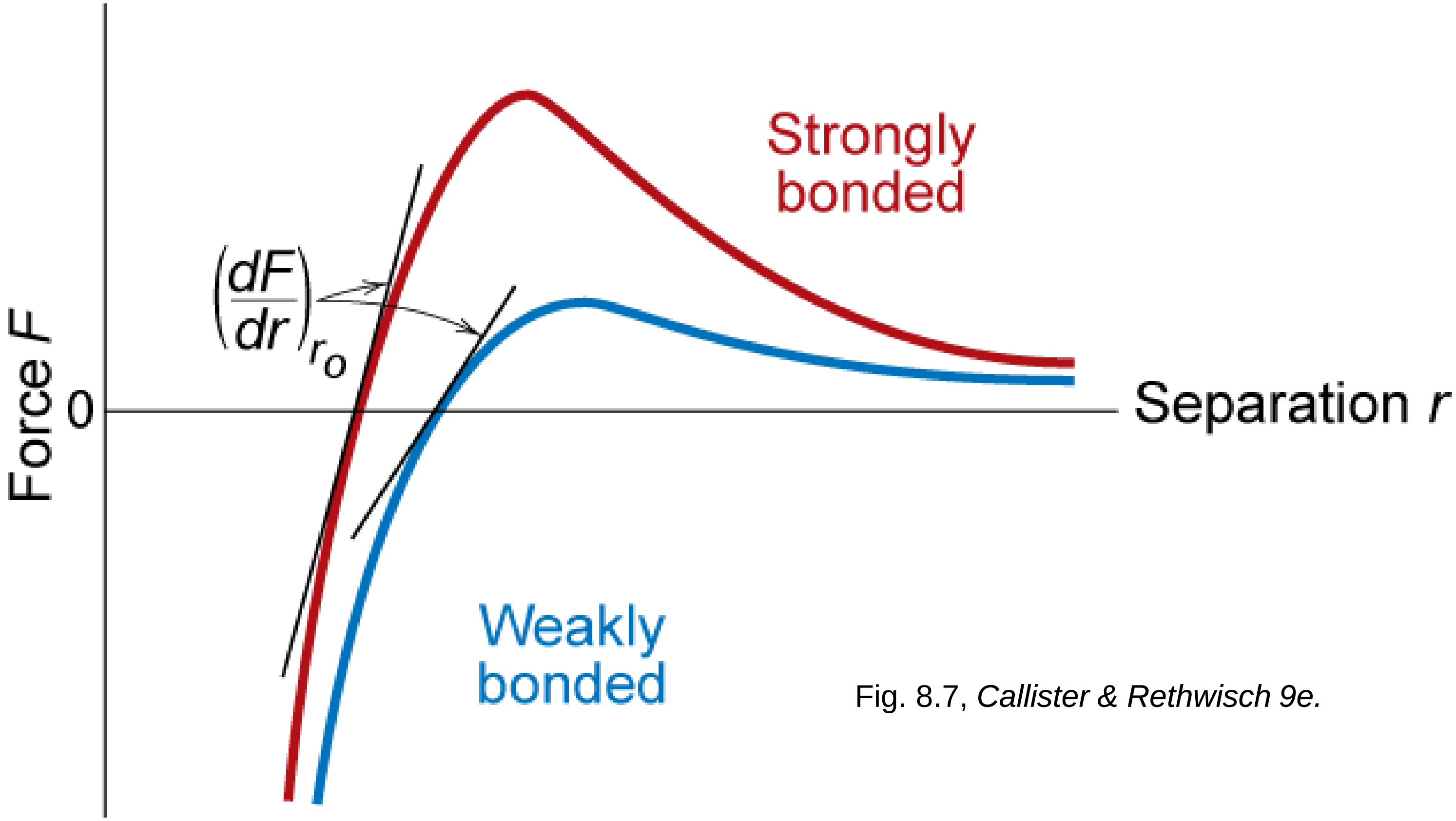
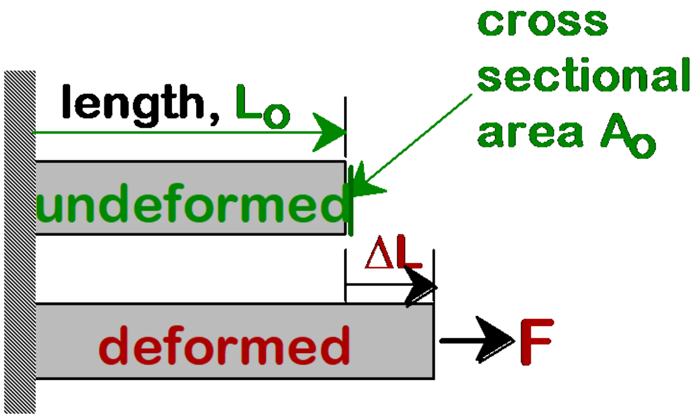


Fig. 8.7, *Callister & Rethwisch 9e.*

Properties from Bonding: E

- Elastic (Young's) modulus, E (Y)



Elastic modulus

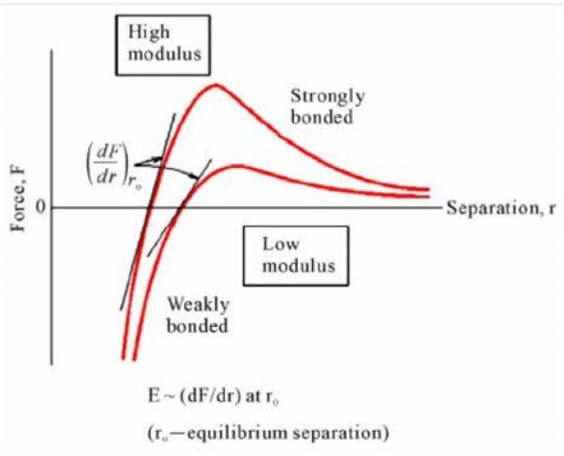
$$\frac{F}{A_o} = E\frac{\Delta L}{L_o}$$

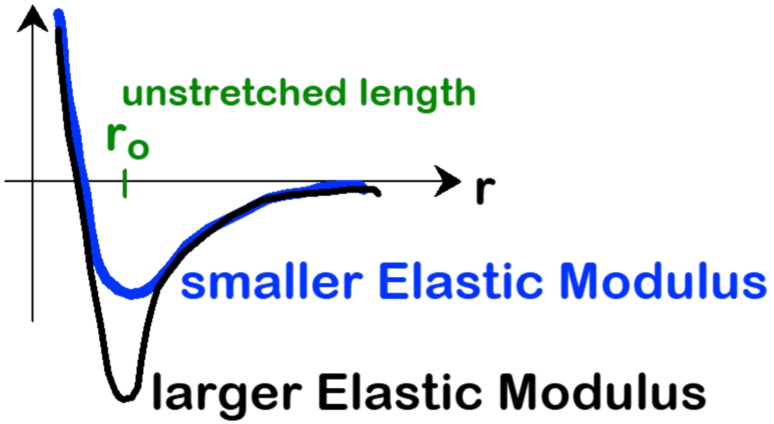
$$\sigma = E\varepsilon$$

- E ~ curvature at r_o (the bottom of the well)

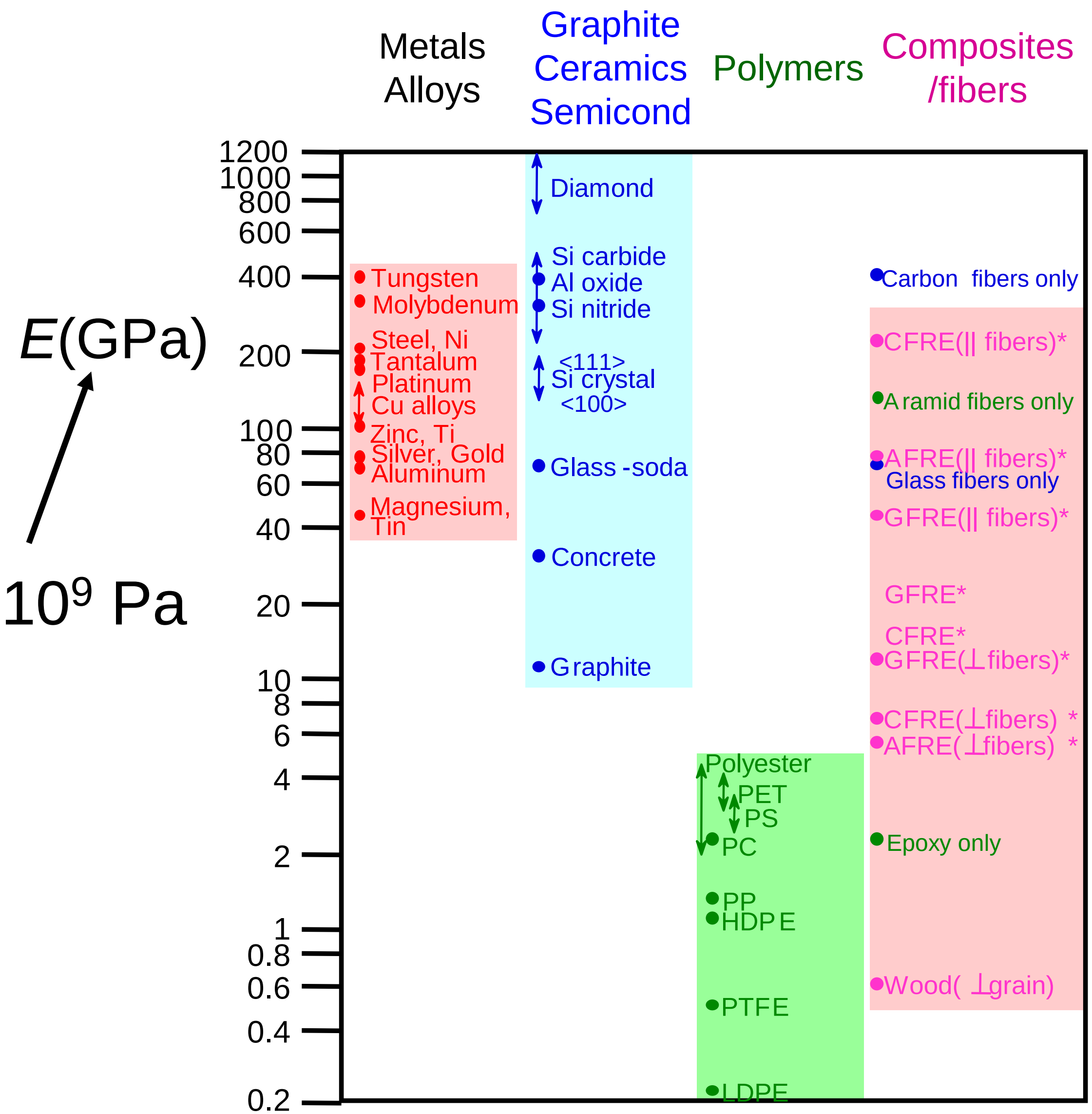
$$Y \sim \left(\frac{d^2E}{dr^2}\right)_{r_o}$$

E is larger if E_o is larger





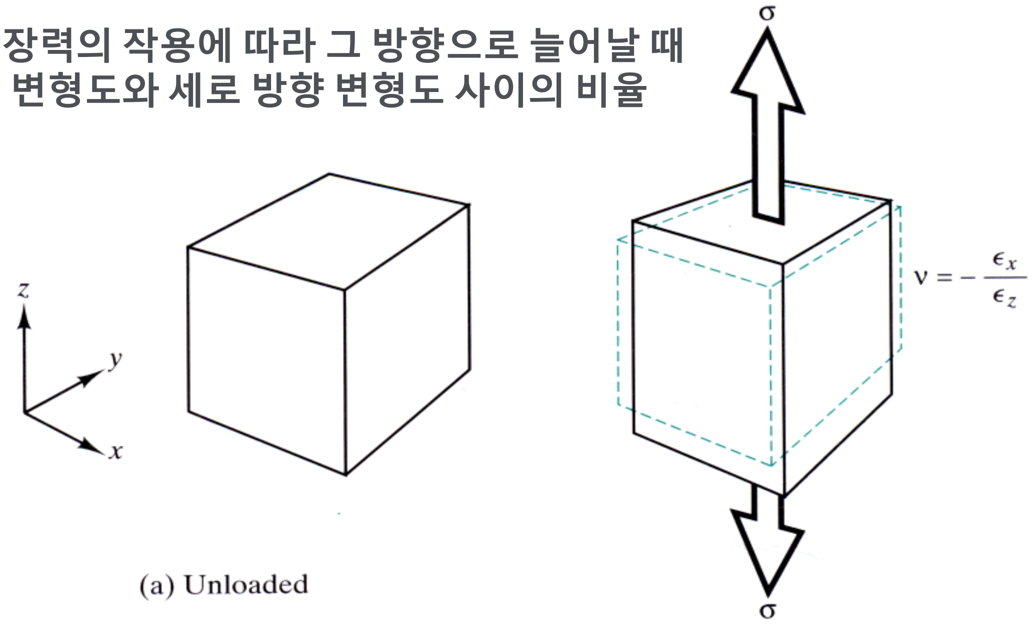
Young’s Moduli: Comparison



Based on data in Table B.2, *Callister & Rethwisch 9e.*
Composite data based on reinforced epoxy with 60 vol% of aligned carbon (CFRE), aramid (AFRE), or glass (GFRE) fibers.

(2) Poisson's ratio, ν

재료가 인장력의 작용에 따라 그 방향으로 늘어날 때
가로 방향 변형도와 세로 방향 변형도 사이의 비율



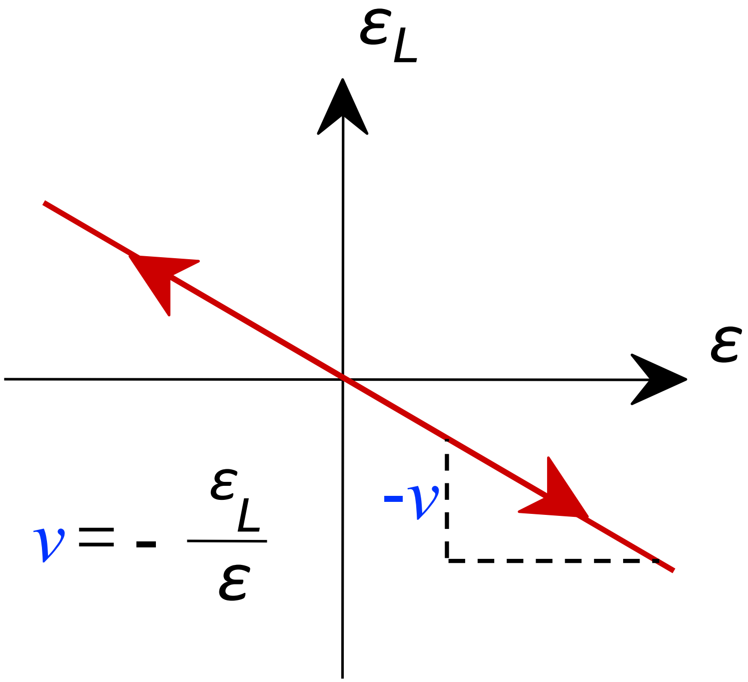
(a) Unloaded

(b) Loaded

Poisson's ratio

$$\nu = -\frac{\varepsilon_x}{\varepsilon_z}$$

Estimation of ν



$$\nu = -\frac{\varepsilon_L}{\varepsilon}$$

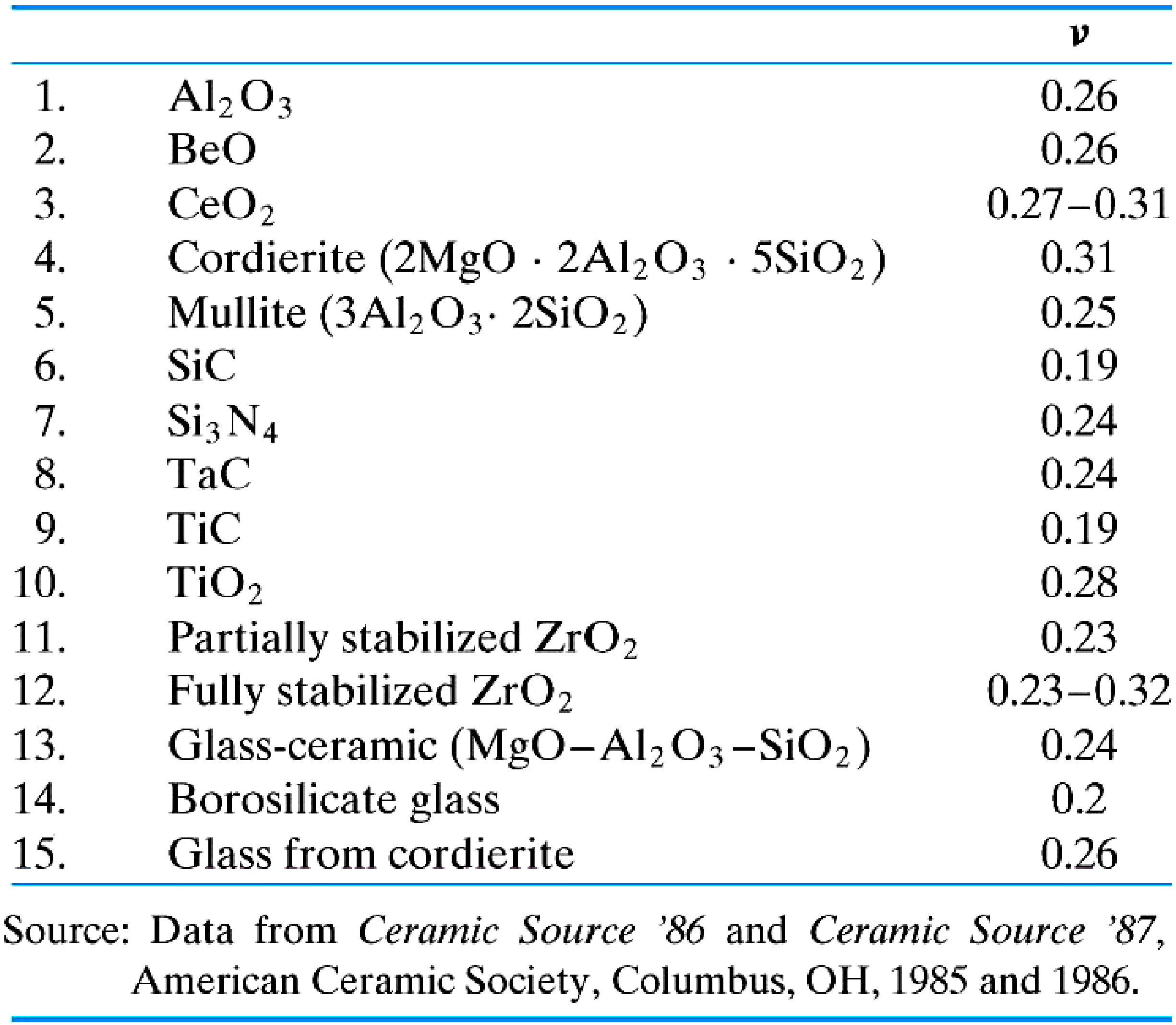
Units:
E: [GPa] or [psi]
ν: dimensionless

$\nu > 0.50$ density increases

$\nu < 0.50$ density decreases
(voids form)

Measured values of Poisson's ratio

metals: ν ~ 0.33
ceramics: ν ~ 0.25
polymers: ν ~ 0.40



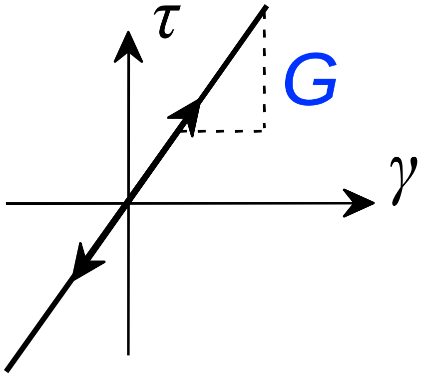
		ν
1.	Al_2O_3	0.26
2.	BeO	0.26
3.	CeO_2	0.27–0.31
4.	Cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$)	0.31
5.	Mullite ($3Al_2O_3 \cdot 2SiO_2$)	0.25
6.	SiC	0.19
7.	Si_3N_4	0.24
8.	TaC	0.24
9.	TiC	0.19
10.	TiO_2	0.28
11.	Partially stabilized ZrO_2	0.23
12.	Fully stabilized ZrO_2	0.23–0.32
13.	Glass-ceramic ($MgO-Al_2O_3-SiO_2$)	0.24
14.	Borosilicate glass	0.2
15.	Glass from cordierite	0.26

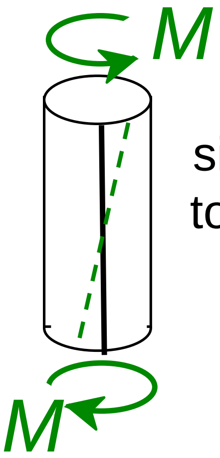
Source: Data from *Ceramic Source '86* and *Ceramic Source '87*, American Ceramic Society, Columbus, OH, 1985 and 1986.

(3) Other Elastic Properties

- **Elastic Shear modulus, *G*:**

$$\tau = G\gamma$$

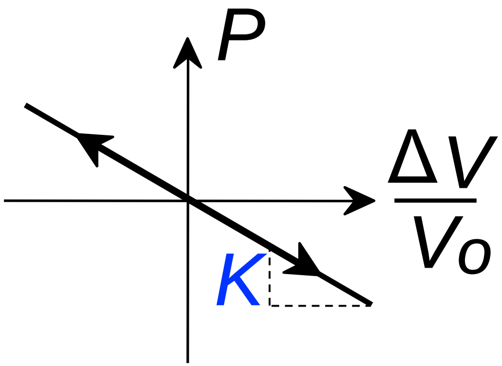


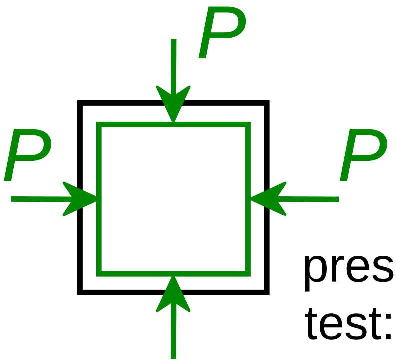


simple torsion test

- **Elastic Bulk modulus, K:**

$$P = -K\frac{\Delta V}{V_o}$$





pressure test: Init. vol $=V_o$. Vol chg. $= \Delta V$

- **Special relations for isotropic materials:**

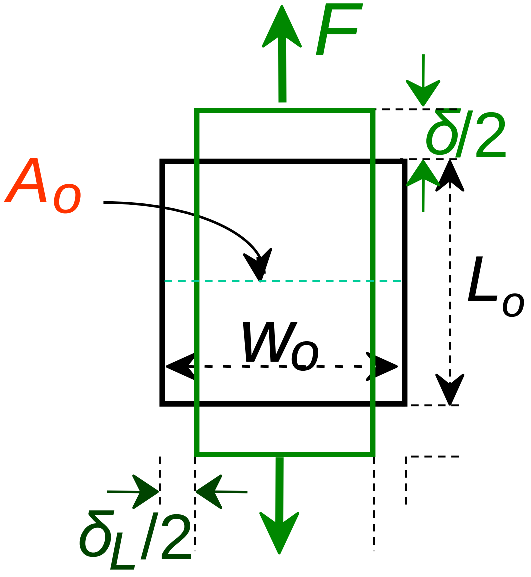
$$G = \frac{E}{2(1+\nu)} \qquad K = \frac{E}{3(1-2\nu)}$$

(4) Useful Linear Elastic Relationships

- **Simple tension:**

$$\delta = \frac{FL_o}{EA_o}$$

$$\delta_L = -\nu \frac{Fw_o}{EA_o}$$

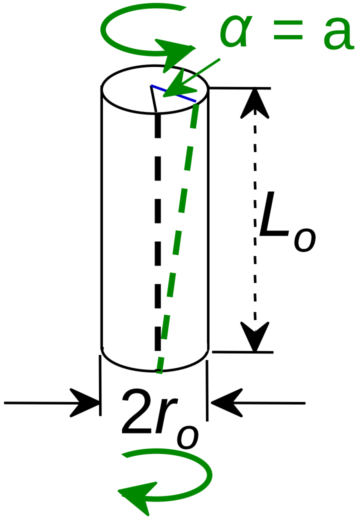


- **Simple torsion:**

$$\alpha = \frac{2ML_o}{\pi r_o^4 G}$$

M = moment

α = angle of twist

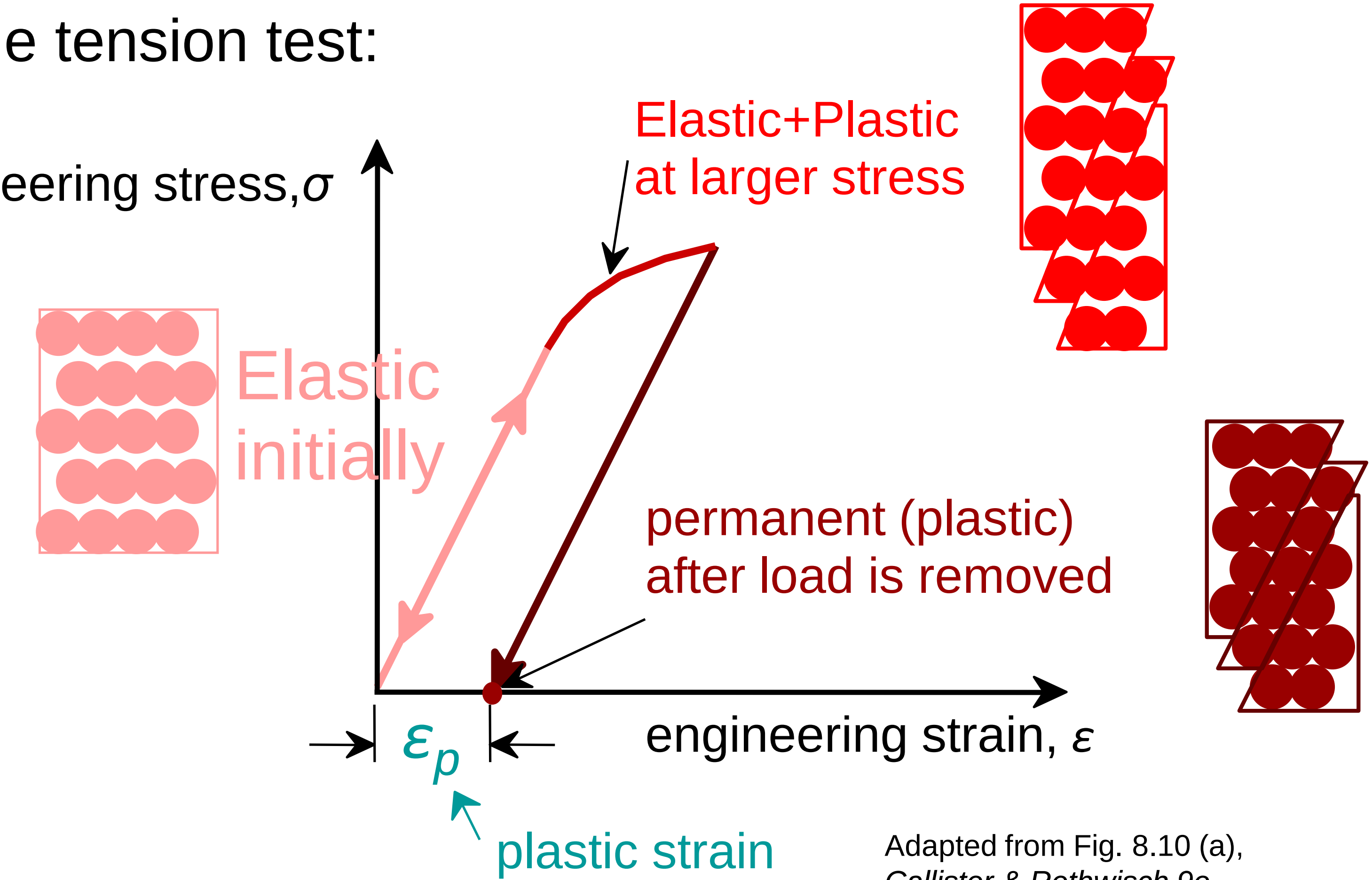


- Material, geometric, and loading parameters all contribute to deflection.
- Larger elastic moduli minimize elastic deflection.

Plastic (Permanent) Deformation

(at lower temperatures, i.e. $T < T_{melt}/3$)

- Simple tension test:



engineering stress, σ

Elastic+Plastic at larger stress

Elastic initially

permanent (plastic) after load is removed

ε_p

plastic strain

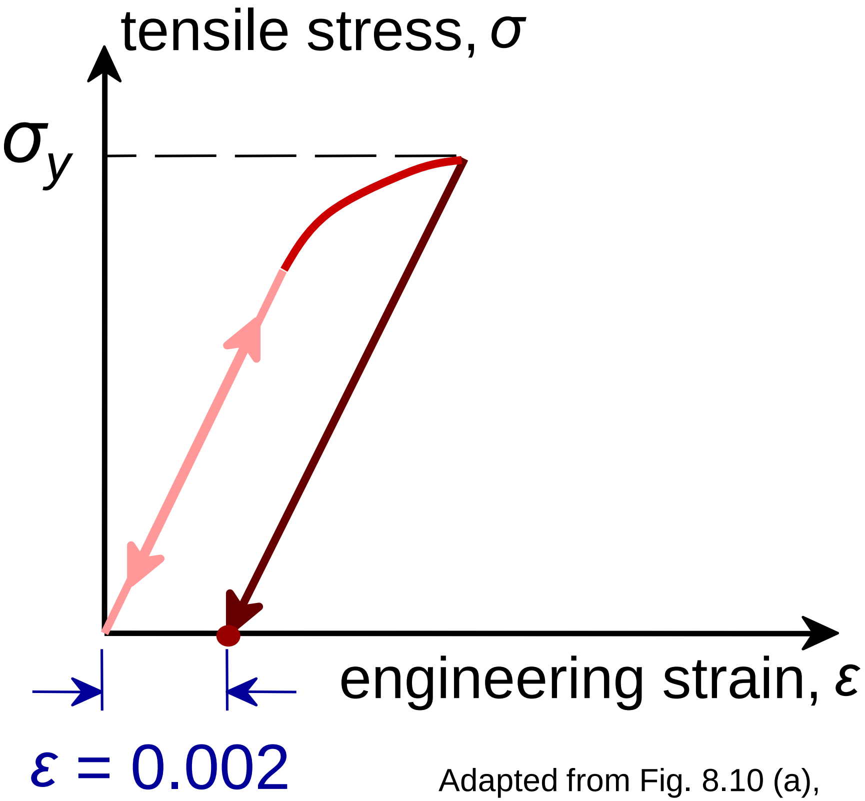
engineering strain, ε

Adapted from Fig. 8.10 (a), *Callister & Rethwisch 9e.*

b. Yield Strength, σ_y

- **Stress at which *noticeable* plastic deformation has occurred.**

when $\varepsilon = 0.002$



Adapted from Fig. 8.10 (a), *Callister & Rethwisch 9e.*

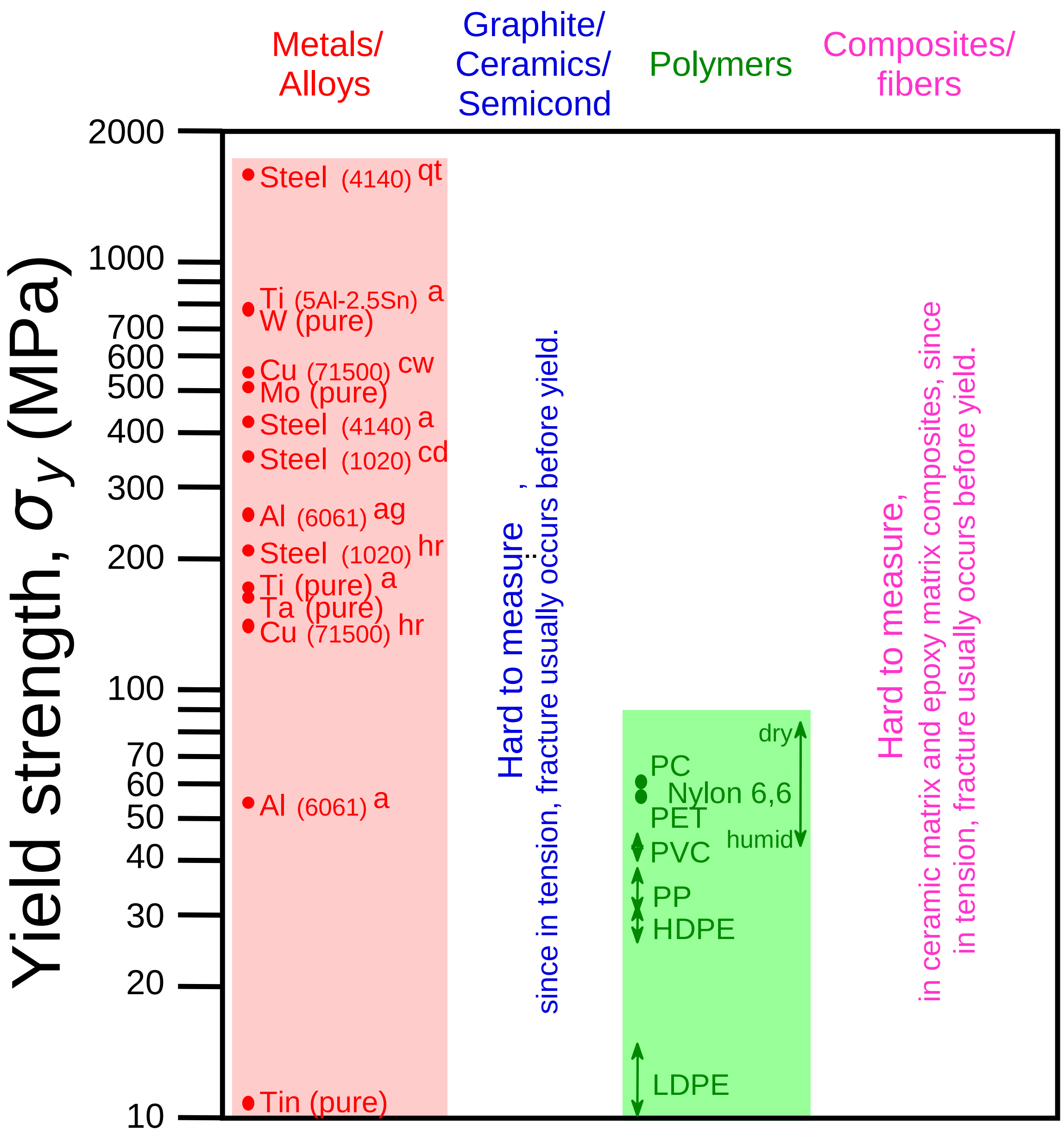
σ_y = yield strength

Note: for 2 inch sample

$\varepsilon = 0.002 = \Delta z / z$

$\therefore\ \Delta z = 0.004$ in

Yield Strength : Comparison



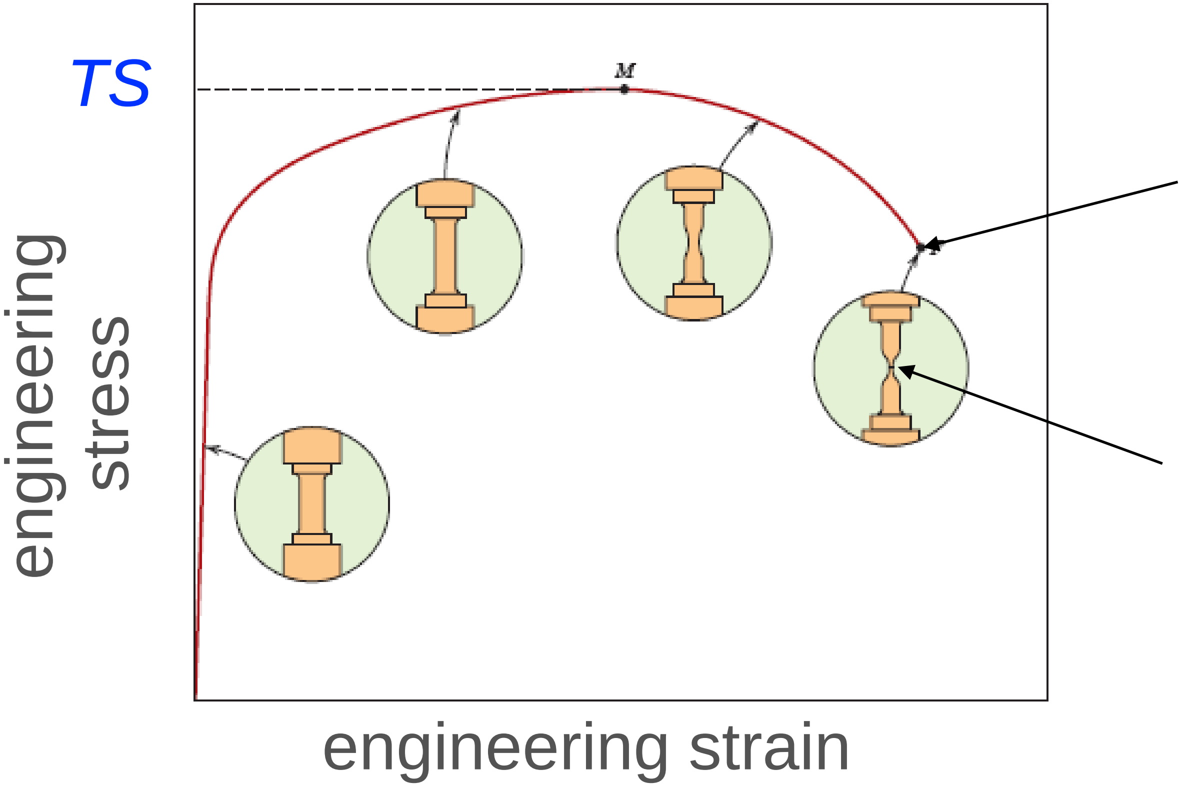
Room temperature values

Based on data in Table B.4, *Callister & Rethwisch 9e.*

a = annealed
hr = hot rolled
ag = aged
cd = cold drawn
cw = cold worked
qt = quenched & tempered

c. Tensile Strength, TS

- Maximum stress on engineering stress-strain curve.



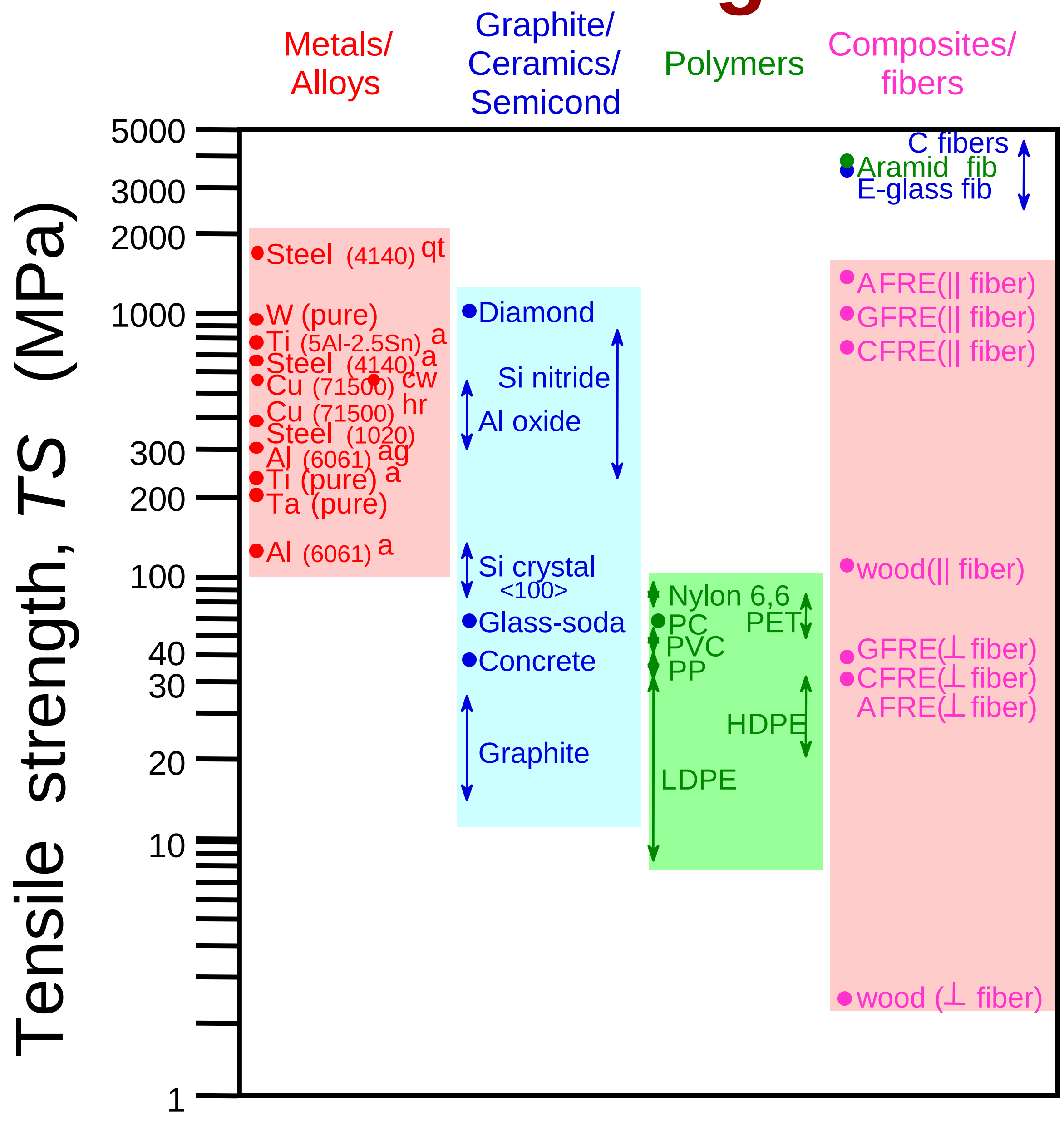
Adapted from Fig. 8.11, *Callister & Rethwisch 9e.*

F = fracture or
ultimate
strength

Neck – acts
as stress
concentrator

- Metals: occurs when noticeable necking starts.
- Polymers: occurs when polymer backbone chains are aligned and about to break.

Tensile Strength: Comparison



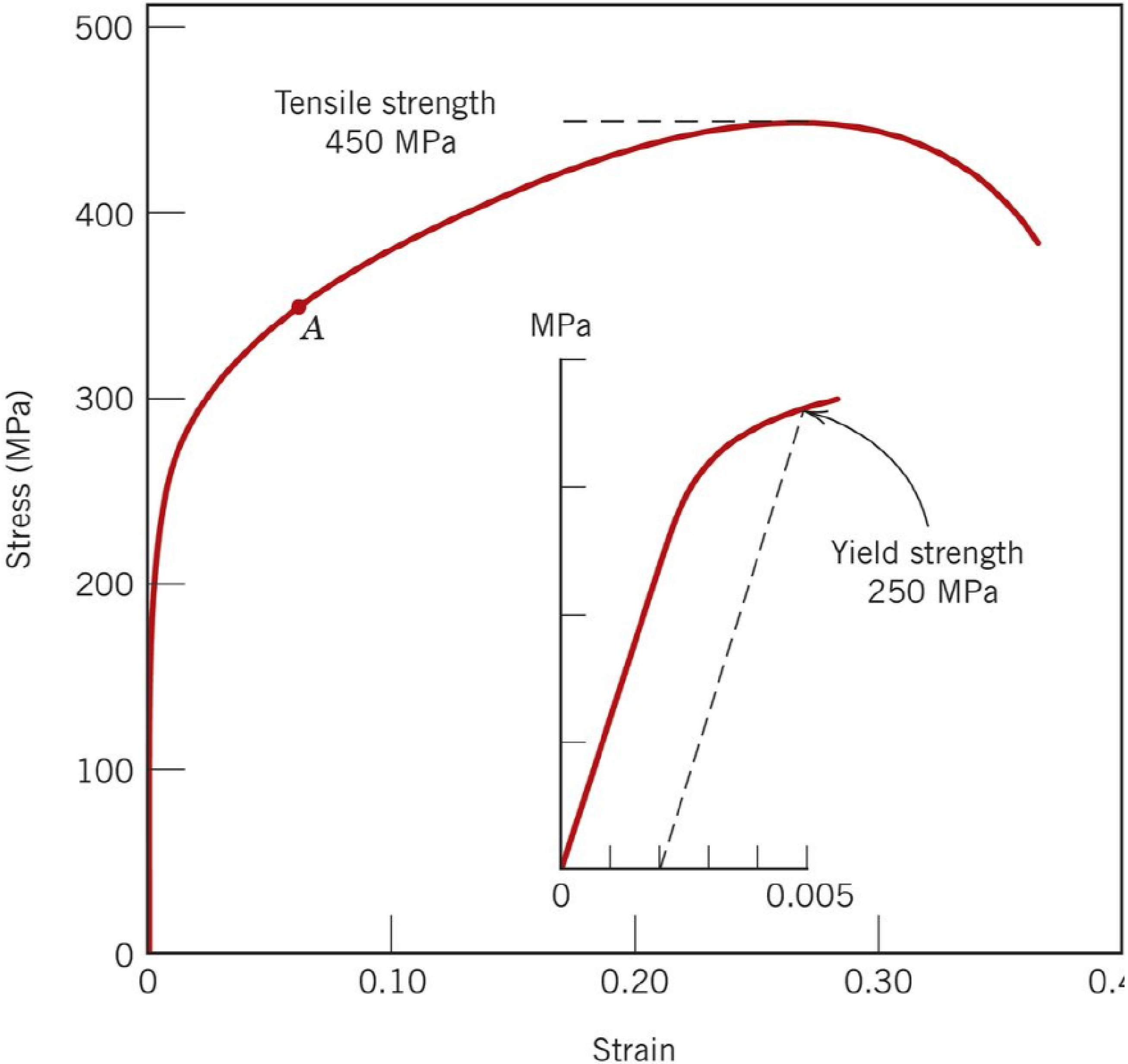
Room temperature values

Based on data in Table B4, *Callister & Rethwisch 9e.*

a = annealed
hr = hot rolled
ag = aged
cd = cold drawn
cw = cold worked
qt = quenched & tempered

AFRE, GFRE, & CFRE = aramid, glass, & carbon fiber-reinforced epoxy composites, with 60 vol% fibers.

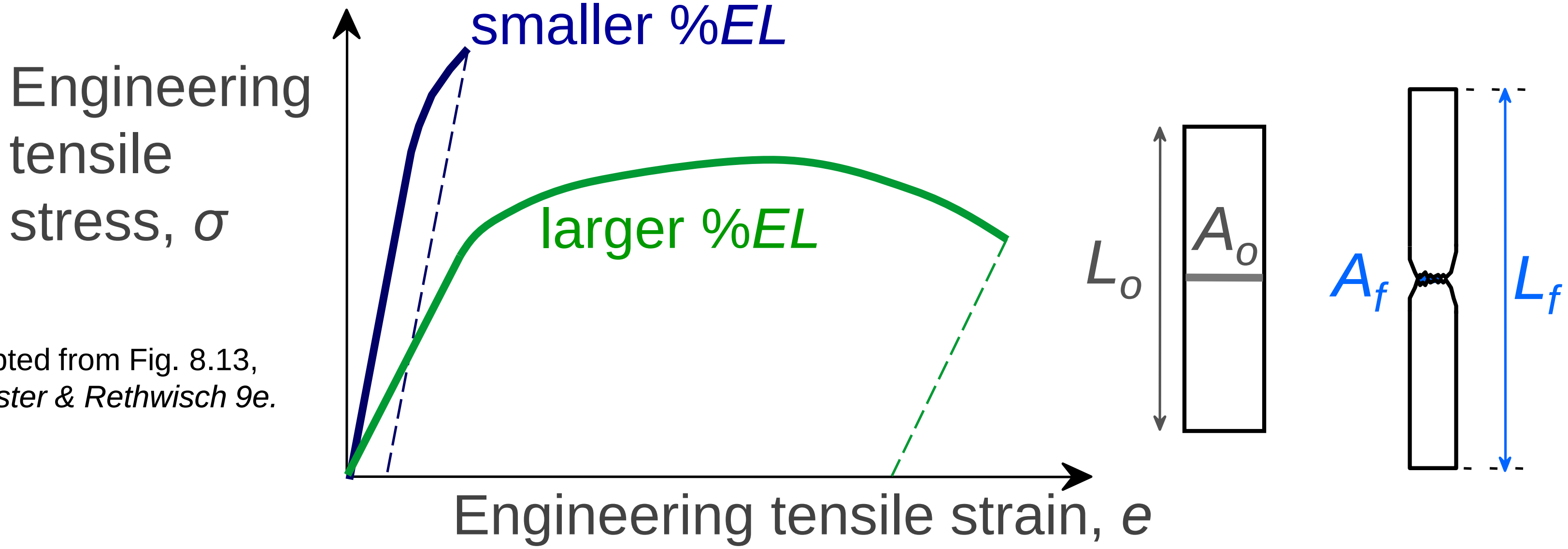
Figure 6.12 in the textbook



d. Ductility

- **Plastic tensile strain at failure**:

$$\%EL = \frac{L_f - L_o}{L_o} \times 100$$



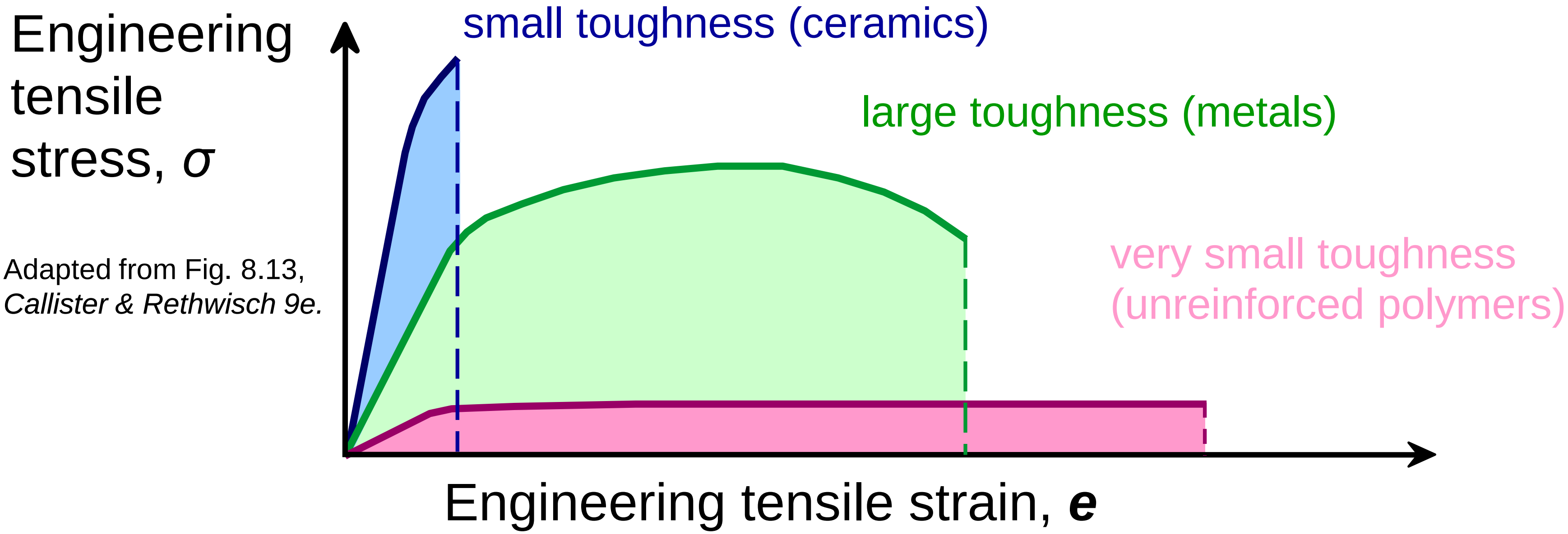
Adapted from Fig. 8.13, *Callister & Rethwisch 9e.*

- Another ductility measure:

$$\%RA = \frac{A_o - A_f}{A_o} \times 100$$

e. Toughness

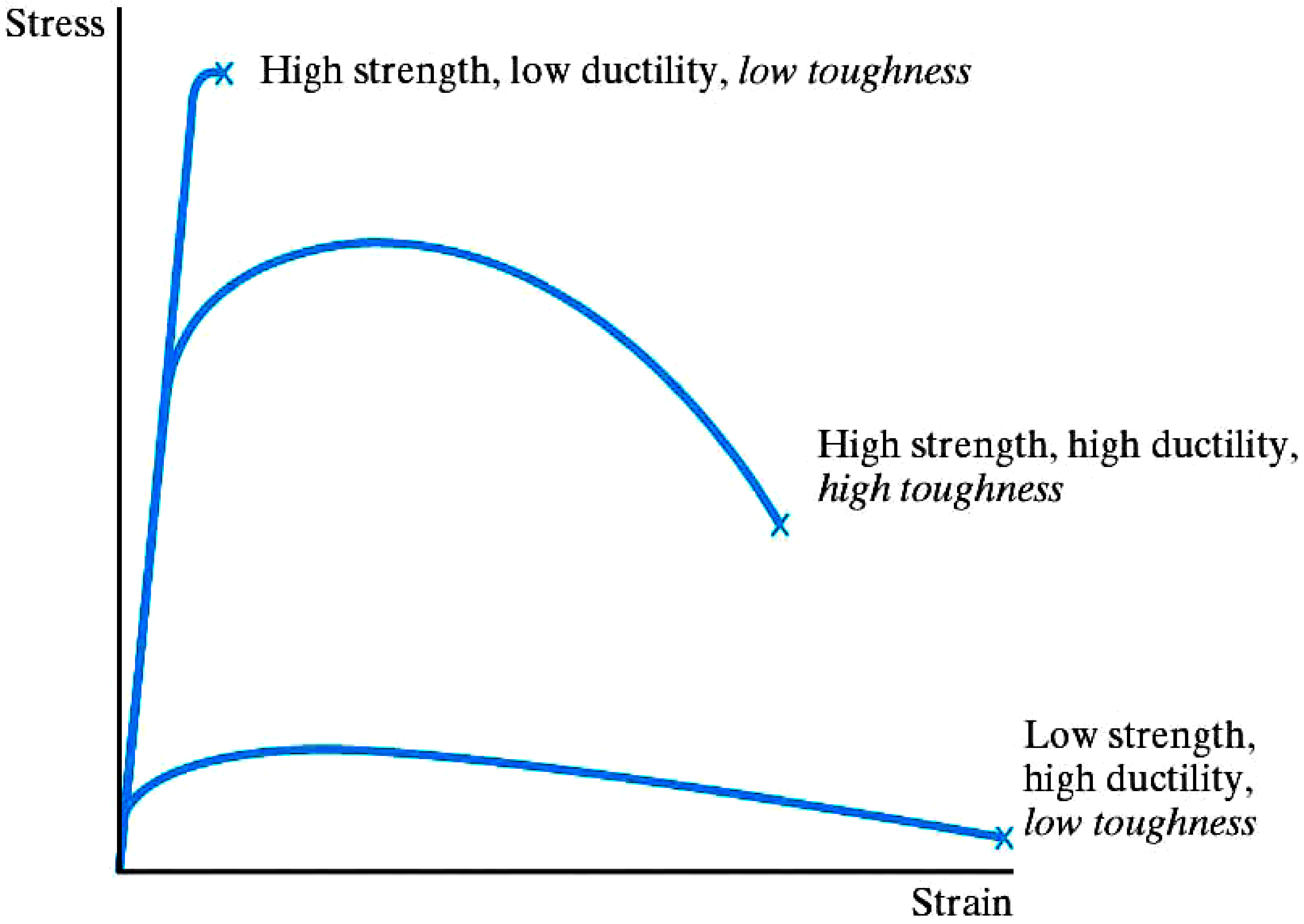
- **Energy to break a unit volume of material**
- Approximate by the area under the stress-strain curve.



Adapted from Fig. 8.13, *Callister & Rethwisch 9e.*

Brittle fracture: elastic energy
Ductile fracture: elastic + plastic energy

Tensile Test



f. Resilience, U_r

- Ability of a material to store energy
  - Energy stored best in elastic region

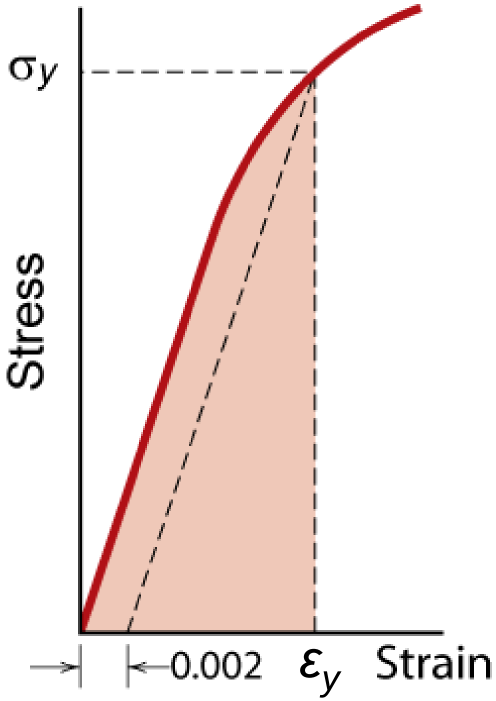


Fig. 8.15, *Callister & Rethwisch 9e.*

$$U_r = \int_0^{\epsilon_y} \sigma \, d\epsilon$$

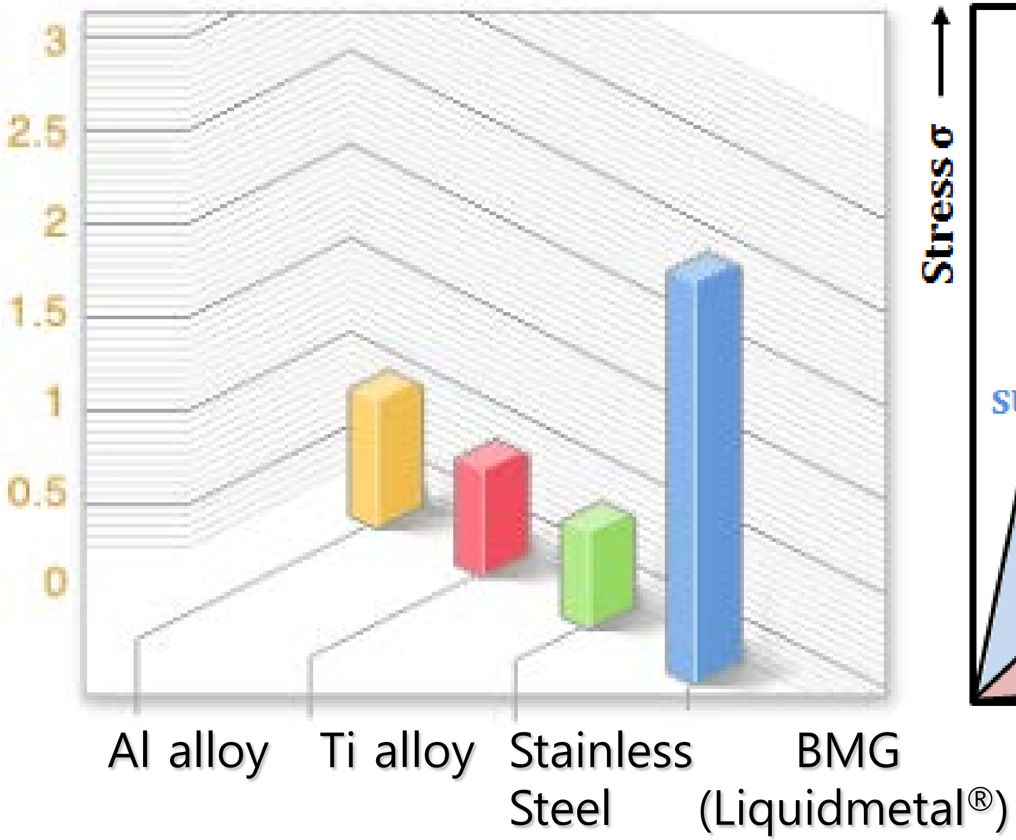
If we assume a linear stress-strain curve this simplifies to

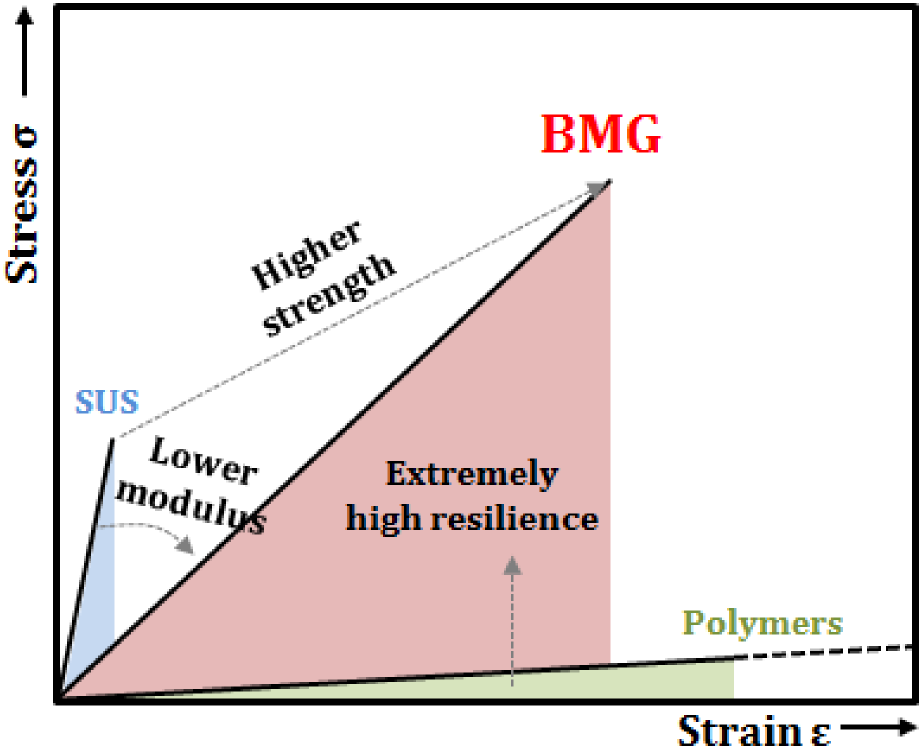
$$U_r \cong \frac{1}{2}\sigma_y \varepsilon_y$$

Large elastic strain limit of BMGs

Elastic Strain Limit

[as % of Original Shape]





* **Resilience: ability to return to the original form, position, etc. →** $U = \frac{\sigma_y 2}{2E}$

Large elastic strain limit of BMGs

VI. Elastic Strain Recovery

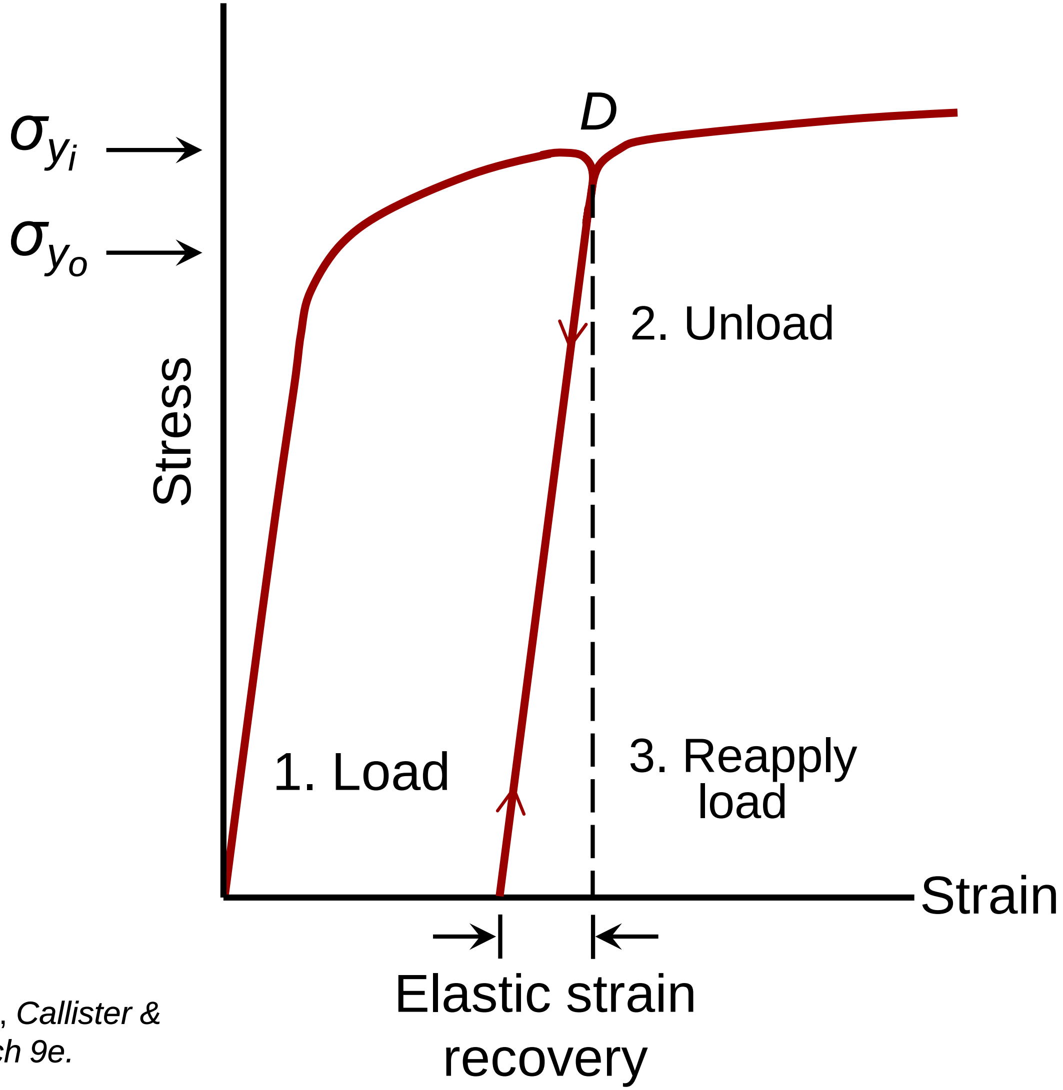
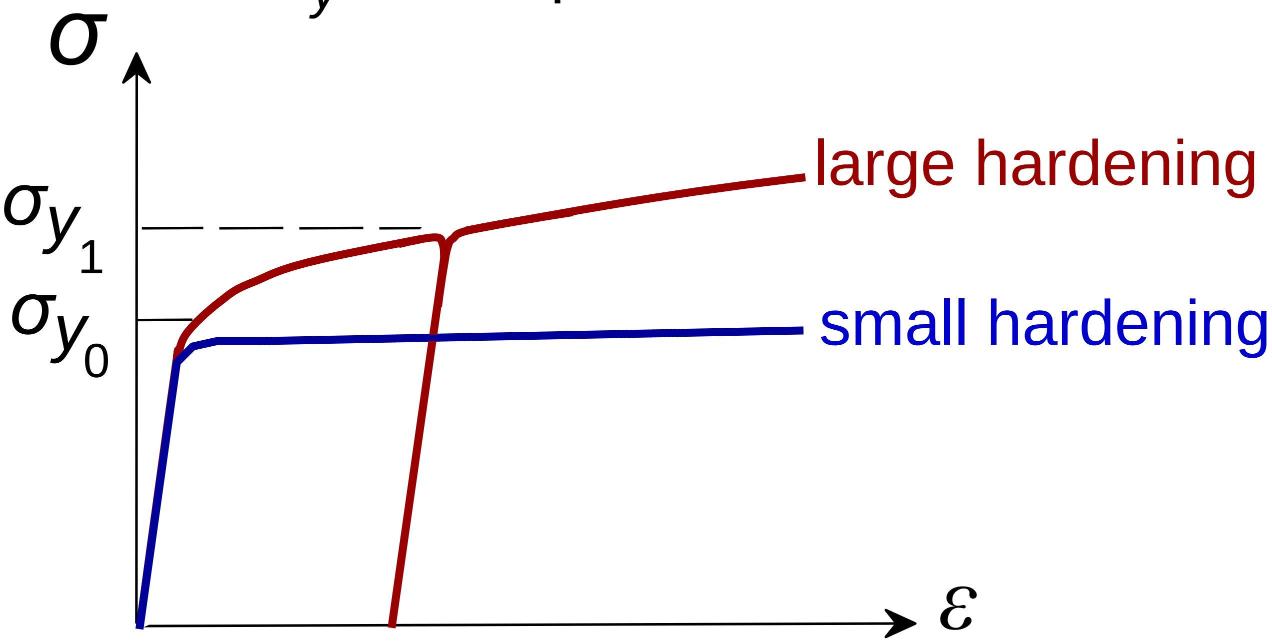


Fig. 8.17, *Callister & Rethwisch 9e.*

VII. Hardening

- An increase in σ_y due to plastic deformation.



- Curve fit to the stress-strain response:

$$\sigma_T = K\left(\varepsilon_T\right)^n$$

hardening exponent:
n = 0.15 (some steels)
to n = 0.5 (some coppers)

"true" stress (F/A)

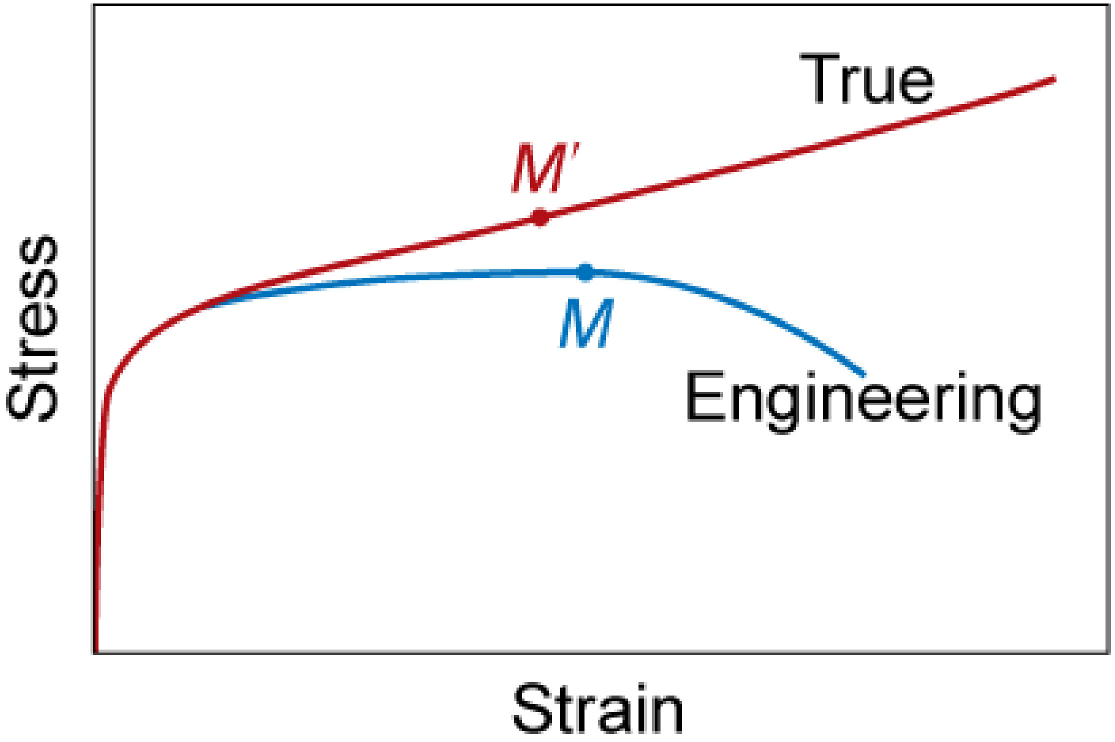
"true" strain: $\ln(\ell/\ell_o)$

VIII. True Stress & Strain

Note: *Cross-sectional area* changes when sample stretched

- True stress $\sigma_T = F/A_i$
- True strain $\epsilon_T = \ln\left(\ell_i/\ell_o\right)$

$$\boxed{\begin{aligned}\sigma_T &= \sigma\left(1+\epsilon\right)\\ \epsilon_T &= \ln\left(1+\epsilon\right)\end{aligned}}$$

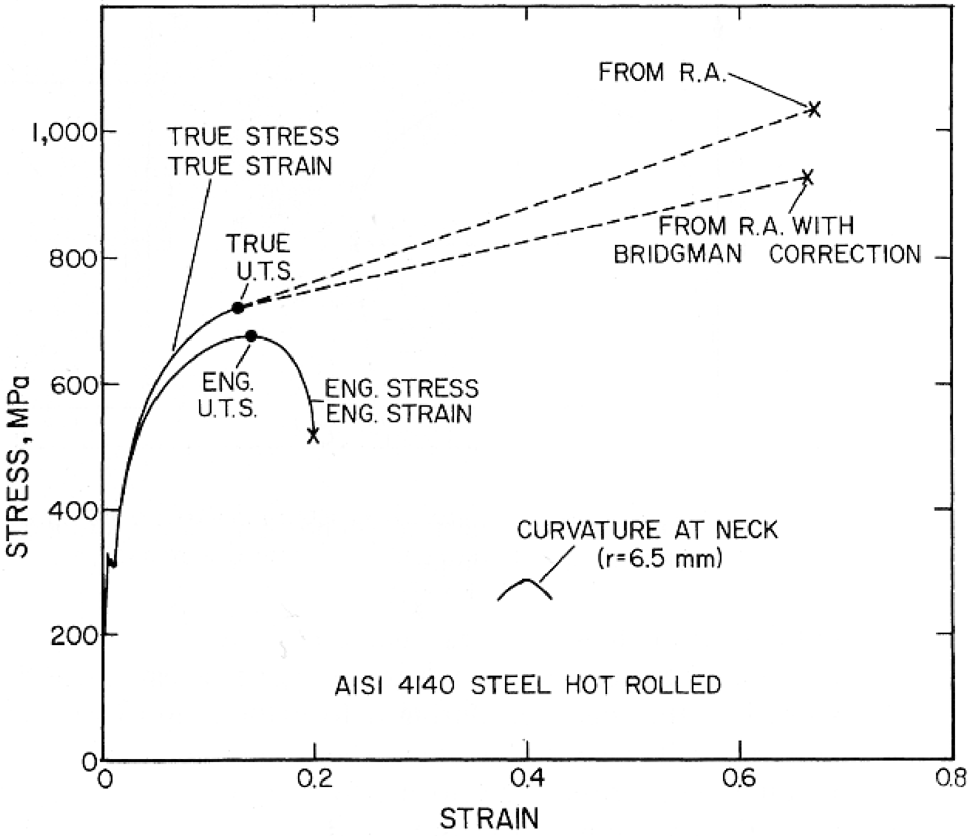


Adapted from Fig. 8.16,
Callister & Rethwisch 9e.

Necking – Work hardening

Represented as $\sigma = \sigma_0 + K\varepsilon^n$

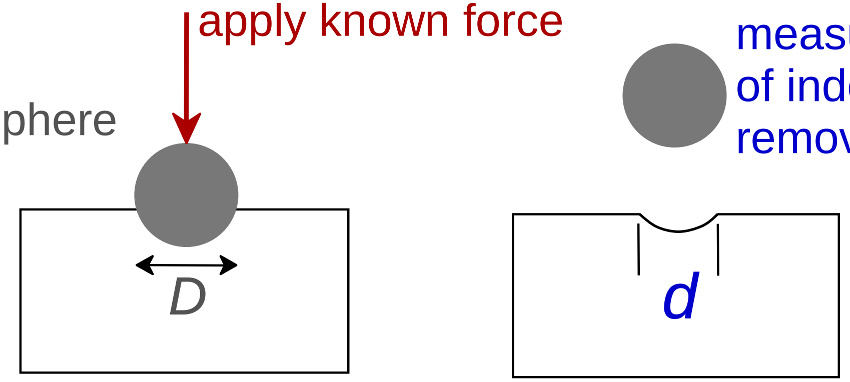
Hollomon's eq



What is *n*? -> meaning from the relationship of stress-strain

IX. Hardness

- Resistance to permanently indenting the surface.
- Large hardness means:
  - -- resistance to plastic deformation or cracking in compression.
  - -- better wear properties.



apply known force

e.g.,
10 mm sphere

measure size
of indent after
removing load

Smaller indents
mean larger
hardness.


most plastics

brasses Al alloys

easy to machine steels

file hard

cutting tools

nitrided steels

diamond

increasing hardness

Hardness: Measurement

- Rockwell
  - No major sample damage
  - Each scale runs to 130 but only useful in range 20-100.
  - Minor load 10 kg
  - Major load 60 (A), 100 (B) & 150 (C) kg
    - A = diamond, B = 1/16 in. ball, C = diamond

- HB = Brinell Hardness
  - *TS* (psia=pounds per square inch) = 500 x HB
  - *TS* (MPa) = 3.45 x HB

Hardness: Measurement

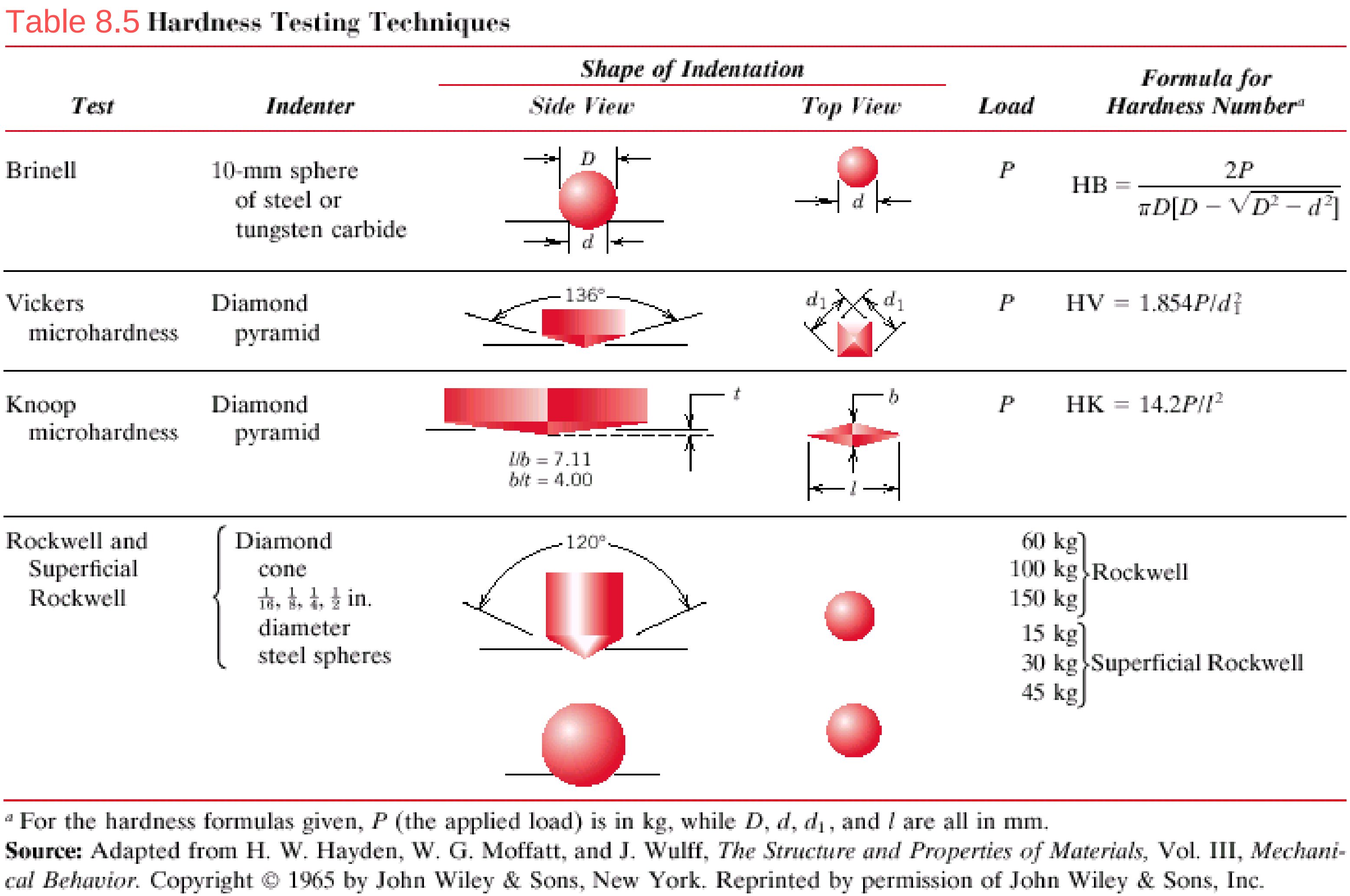


Table 8.5 **Hardness Testing Techniques**

Test	Indenter	Shape of Indentation: Side View	Shape of Indentation: Top View	Load	Formula for Hardness Number[a]
Brinell	10-mm sphere of steel or tungsten carbide	D d	d	P	$\mathrm{HB} = \dfrac{2P}{\pi D\left[D - \sqrt{D^2 - d^2}\right]}$
Vickers microhardness	Diamond pyramid	136°	d_1 d_1	P	$\mathrm{HV} = 1.854P/d_1^2$
Knoop microhardness	Diamond pyramid	t $l/b = 7.11$ $b/t = 4.00$	b l	P	$\mathrm{HK} = 14.2P/l^2$
Rockwell and Superficial Rockwell	Diamond cone $\frac{1}{16}$, $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$ in. diameter steel spheres	120°		60 kg 100 kg 150 kg	Rockwell
				15 kg 30 kg 45 kg	Superficial Rockwell

[a] For the hardness formulas given, P (the applied load) is in kg, while D, d, d_1, and l are all in mm.

Source: Adapted from H. W. Hayden, W. G. Moffatt, and J. Wulff, *The Structure and Properties of Materials*, Vol. III, *Mechanical Behavior.* Copyright © 1965 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

X. Variability in Material Properties

- Elastic modulus is material property
- Critical properties depend largely on sample flaws (defects, etc.). Large sample to sample variability.
- Statistics
  - Mean

$$\bar{x} = \frac{\sum^{n} x_n}{n}$$

  - Standard Deviation

$$s = \left[\frac{\sum^{n} \left(x_i - \bar{x} \right)^2}{n-1} \right]^{\frac{1}{2}}$$

where *n* is the number of data points

XI. Design or Safety Factors

- Design uncertainties mean we do not push the limit.
- Factor of safety, *N*

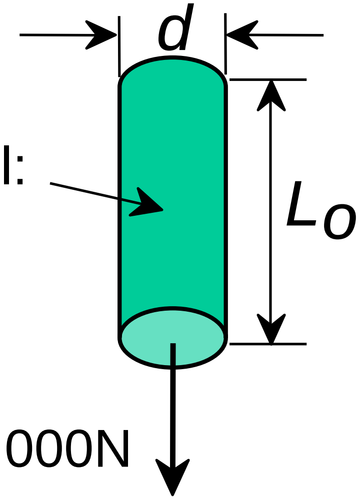
$$\sigma_{working} = \frac{\sigma_y}{N}$$

Often *N* is between 1.2 and 4

- Example: Calculate a diameter, *d*, to ensure that yield does not occur in the 1045 carbon steel rod below. Use a factor of safety of 5.

$$\underbrace{\sigma_{working}}_{\frac{220{,}000\text{N}}{\pi\left(d^2/4\right)}} = \frac{\sigma_y}{\underbrace{N}_{5}}$$

1045 plain carbon steel:
σ_y = 310 MPa
TS = 565 MPa



F = 220,000N

$$\boxed{d = 0.067 \text{ m} = 6.7 \text{ cm}}$$

Summary

Chapter 8: Mechanical Properties of Metals

- Stress and strain: These are size-independent measures of load and displacement, respectively.

- Elastic behavior: This reversible behavior often shows a linear relation between stress and strain. To minimize deformation, select a material with a large elastic modulus (*E* or *G*).

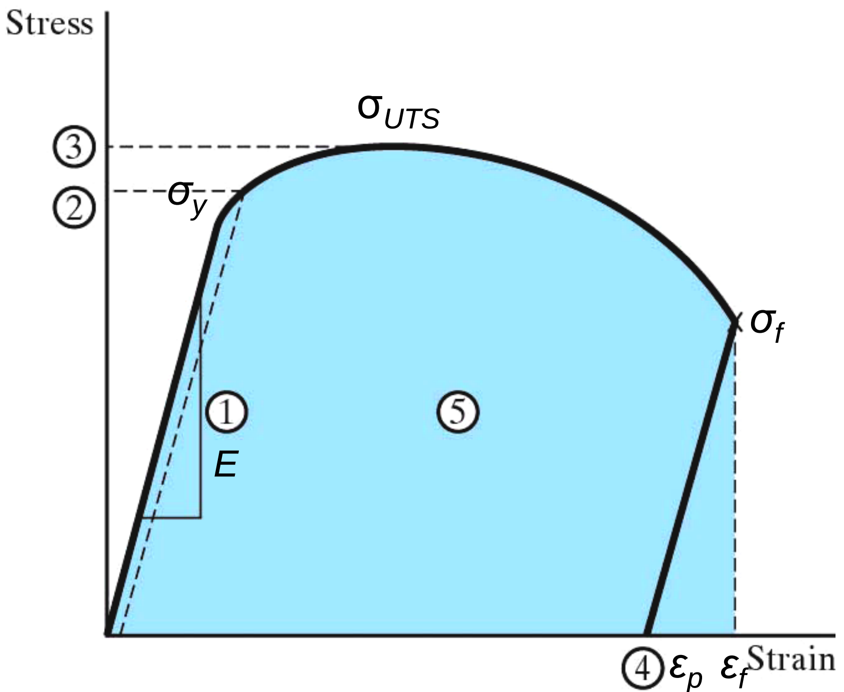
- Plastic behavior: This permanent deformation behavior occurs when the tensile (or compressive) uniaxial stress reaches σ_y.

- Toughness: The energy needed to break a unit volume of material.

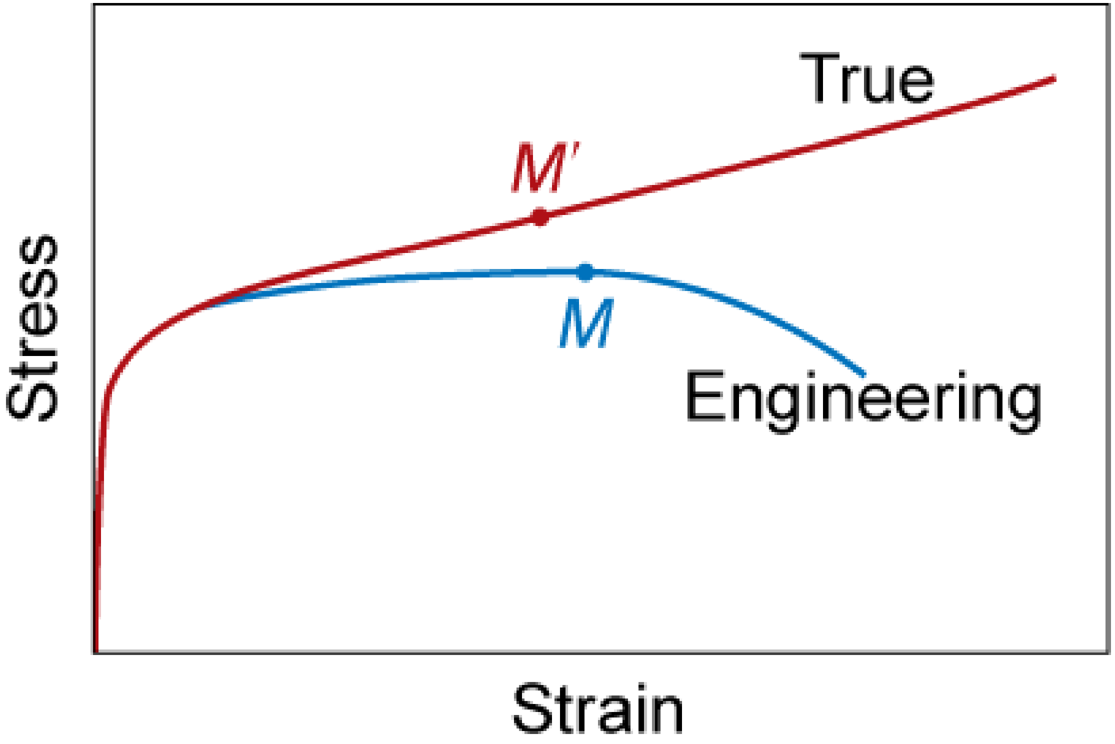
- Ductility: The plastic strain at failure.

Deformation

- Elastic vs. Plastic region
- Key points
    1. Elastic modulus (=Young's modulus), E
    2. 0.2% (0.002 strain) yield stress, σ_y
    3. Ultimate yield stress, σ_{UTS}
    4. Ductility, ε_p
    5. Toughness → $\int \sigma d\varepsilon$
    6. Fracture stress, σ_f
    7. Fracture strain, ε_f



Engineering vs True Stress & Strain



Adapted from Fig. 8.16, *Callister & Rethwisch 9e.*

Variability in Material Properties : need to Statistics

Material design considering Safety factor:

$$\sigma_{working} = \frac{\sigma_y}{N}$$

Often N is between 1.2 and 4