


# Advanced Materials


## Basic concepts

### ▼ Electronegativity Table

IA																	0
H																	He
2.1																	-
Li	Be															Ne	
1.0	1.5															-	
Na	Mg															Ar	
0.9	1.2															-	
		IIIB	IVB	VB	VIB	VII B	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.8	1.0	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9	1.6	1.6	1.8	2.0	2.4	2.8	-
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
0.8	1.0	1.2	1.4	1.6	1.8	1.9	2.2	2.2	2.2	1.9	1.7	1.7	1.8	1.9	2.1	2.5	-
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
0.7	0.9	1.1-1.2	1.3	1.5	1.7	1.9	2.2	2.2	2.2	2.4	1.9	1.8	1.8	1.9	2.0	2.2	-
Fr	Ra	Ac-No															
0.7	0.9	1.1-1.7															



Lower electronegativity  
(donates electrons)



Higher electronegativity  
(accepts electrons)

### ▼ Periodic table

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	2																2
H	He																He
1.008	4.0026																4.0026
Li	Be																Ne
6.94	9.0122																20.180
Na	Mg																Ar
22.990	24.305																39.948
K	Ca	Sc															Kr
39.098	40.078	44.956															83.798
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
85.468	87.62	88.906	91.224	92.906	95.94	98.906	101.07	102.91	106.42	107.87	112.41	114.82	118.71	121.76	127.60	126.90	131.29
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
132.91	137.33	138.905	178.49	180.95	183.84	186.21	190.23	192.22	195.08	196.967	200.59	204.38	207.2	208.98	209	210	222
Fr	Ra	Ac-No	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
223	226	227	261	262	263	264	265	266	267	268	269	270	271	272	273	274	275

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

Periodic table is a registered trademark of Michael Dwyer. Last updated Aug 25, 2020.

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
138.91	140.12	140.91	144.24	(145)	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.05	174.97
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
227	232.04	231.04	238.03	(237)	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(266)

### ▼ Prefixes table for measurements

Prefix	Symbol	Multiplicative Factor	Factor
tera	T	1,000,000,000,000	$10^{12}$
giga	G	1,000,000,000	$10^9$
mega	M	1,000,000	$10^6$
kilo	k	1,000	$10^3$
hector	h	100	$10^2$
deca	da	10	$10^1$
x base	—	1	—
deci	d	0.1	$10^{-1}$
centi	c	0.01	$10^{-2}$
milli	m	0.001	$10^{-3}$
micro	$\mu$	0.000001	$10^{-6}$
nano	n	0.000000001	$10^{-9}$
pico	p	0.000000000001	$10^{-12}$

#### ▼ Mol

1 mol is equivalent to  $6.022 \cdot 10^{23}$  things

#### ▼ Area and volume of a sphere

The formula for the Volume of a sphere can be used for computing the volume of an atom,

$$V = \frac{4}{3}\pi r^3$$

The formula for the Area of the surface of a sphere,

$$A = 4\pi r^2$$

## Atomic bonds

#### ▼ Ionic bonding

Ionic bonds are normal in Ceramic.

#### ▼ Properties

This type of bonding occurs between Metal and Non-metal atoms with low and high electronegativity.

There's a complete transfer of electrons, the atoms become ions with electrical charge. The Coulomb forces hold the atoms in place (it's long-range).

The bond is considered without direction and with many neighbors.

#### ▼ Consequences

Low electric conductivity and brittleness.

#### ▼ Covalent bonding

Covalent bonds are normal in Polymers

##### ▼ Properties

This type of bonding occurs between Non-metal and Non-metal atoms (or metalloids).

They follow the octet rule, where 2 atoms share electron pairs.

The bond is considered with direction and with only the immediate neighbor.

Valence = number of possible bonds

##### ▼ Consequences

Low electric conductivity, high thermal conductivity and brittle.

- Atoms of the same Kind

Equally, the sharing of an electron pair is always a nonpolar bond.

- Atoms with different electronegativities.

The uneven sharing of electron pairs always results in polar bonds. Small electrical dipole.

#### ▼ Ionic vs Covalent

Bonding between atoms of 2 elements  $A$  and  $B$ , never pure ionic bond.

Fraction of ionic bond (empirical relation):

$$f_{\text{ion}} = 1 - e^{-\frac{(x_A - x_B)^2}{4}}$$

Fraction of covalent bond (empirical relation):

$$f_{\text{cov}} = e^{-\frac{(x_A - x_B)^2}{4}}$$

These fractions are valid for both the  $A - B$  bond and a compound  $AB$ .

The fraction of the bond of a compound like  $A_aB_b$  is computed simply as the fraction of the bond  $AB$ .

#### ▼ Metallic bonding

Metallic bonds are normal in metals.

##### ▼ Properties

- This type of bonding occurs between Metal atoms.
- The Valence electrons are shared between all atoms.
- The bond is considered without direction (long-range).
- Inner electrons localized (extra covalent bond).

##### ▼ Consequences

- High electrical conductivity
- High thermal conductivity
- Reflectivity
- Ductility/Malleability.

## Secondary bonds

#### ▼ Van der Waals bonding (London bonding)

Van der Waals bonds are found in compounds with dipole-dipole interactions. Permanent dipoles result from polar covalent bonds.

Collisions might induce dipoles.

The London bonds are known for being the weakest of all types of bonding.

#### ▼ Hydrogen bond

##### ▼ Properties

Hydrogen bonds are found when a hydrogen atom exists in a covalent bond with an electronegative atom.

Interaction with a free electron pair (the proton can switch between neighbors).

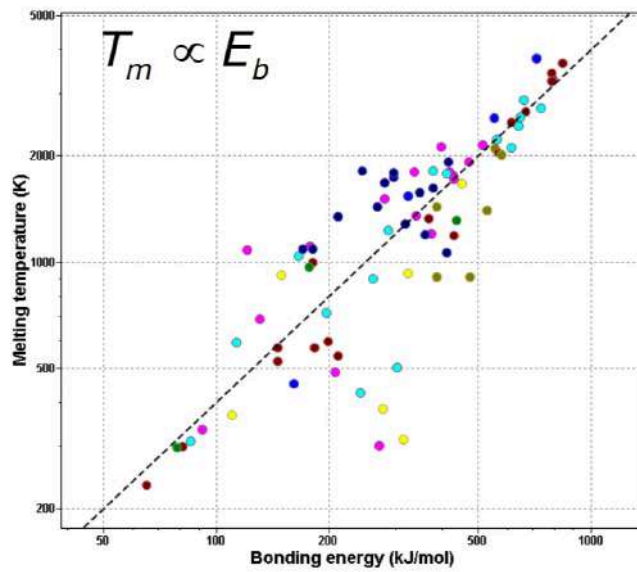
In general, the higher the molar mass, the higher the melting temperature.

##### ▼ Consequences

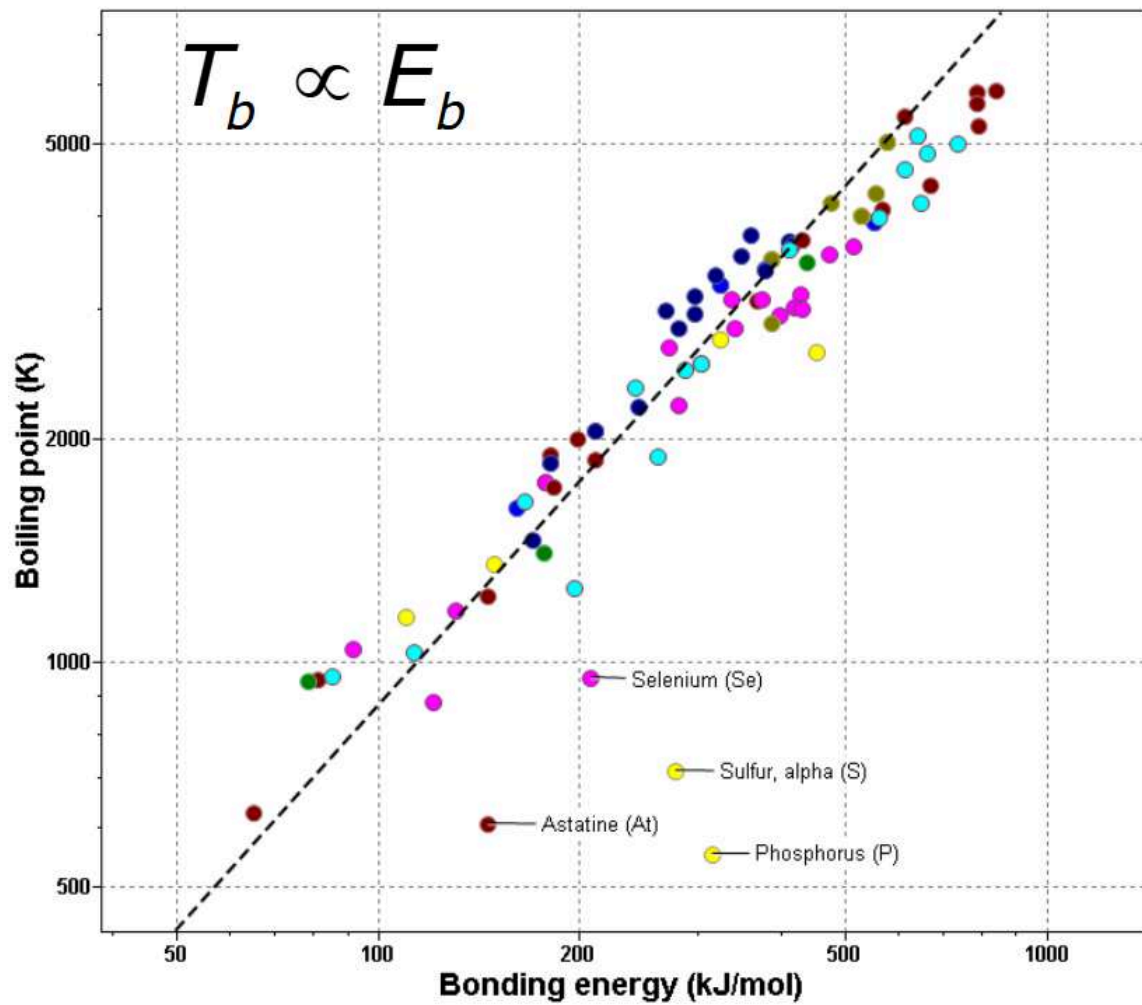
- High melting temperature
- High boiling temperature
- Low density as a solid.

# Property Correlations

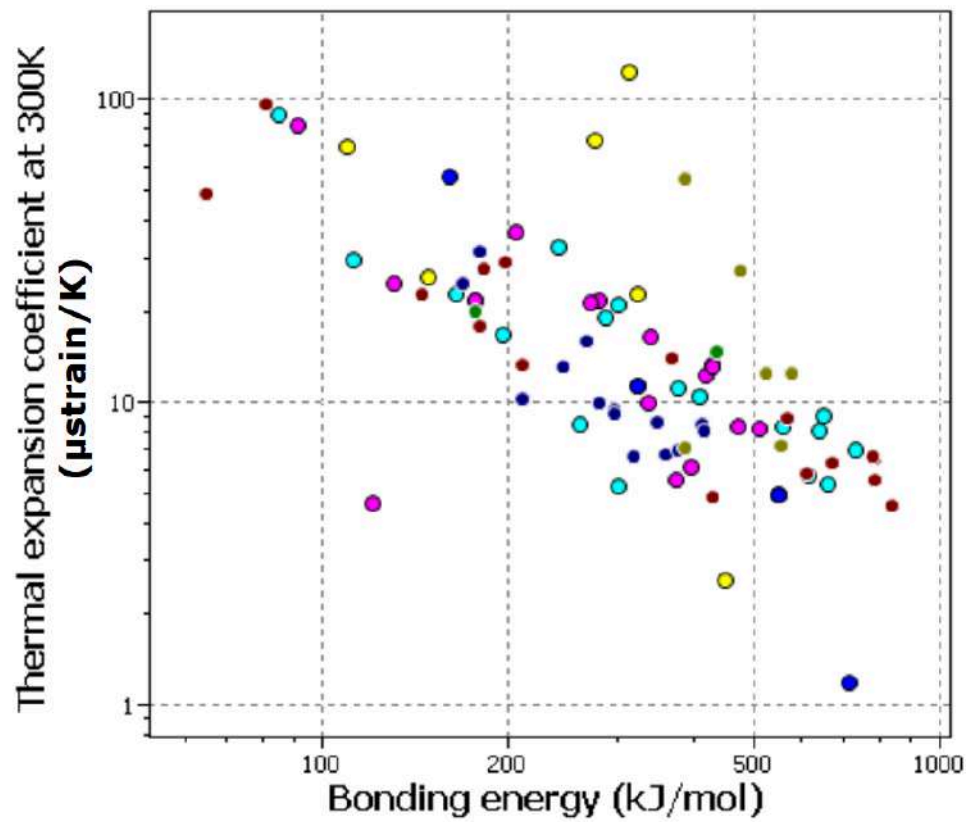
▼ Melting temperature  $T_m$  and bonding energy  $E_b$



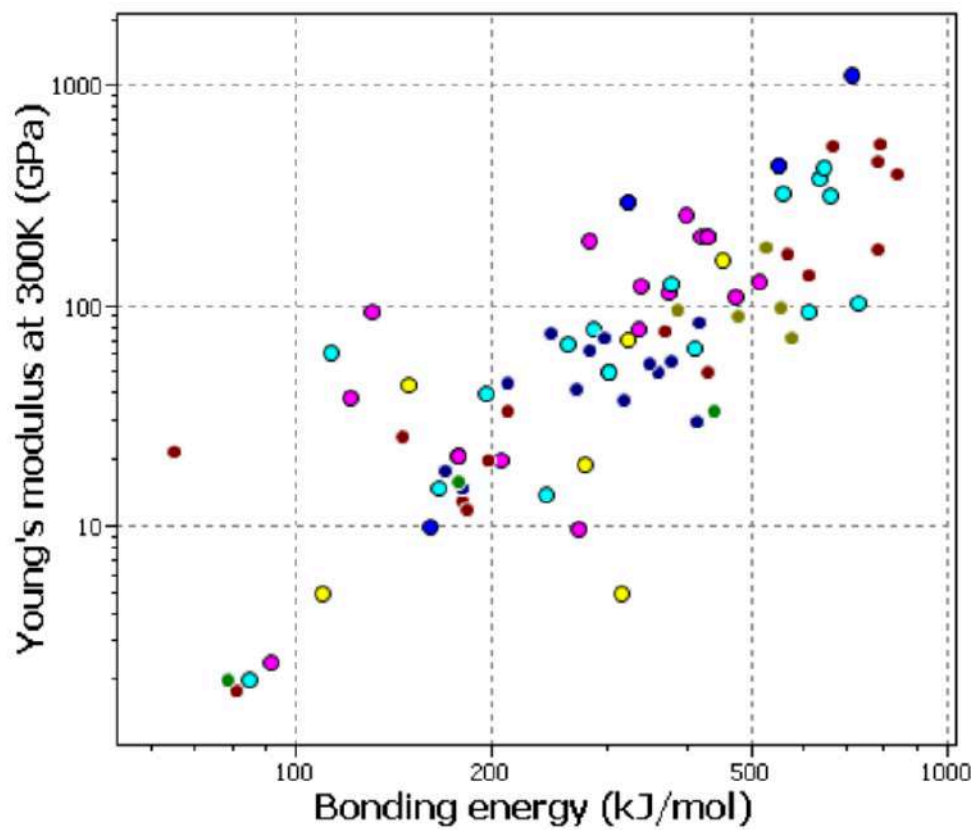
▼ Boiling temperature  $T_b$  and bonding energy  $E_b$



▼ Thermal expansion coefficient and bonding energy  $E_b$



▼ Elastic modulus  $E$  and bonding energy  $E_b$

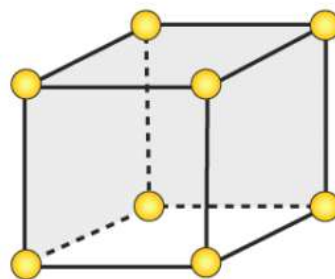


# Crystal structure

## ▼ Cubic lattices

### ▼ Simple cubic (sc)

#### ▼ Basics



Simple cubic unit cell



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Atoms in unit cell: 1

Coordination number (# of nearest neighbors): 6

#### ▼ Along the edges:

- Atoms touch each other
- Distance between centers:  $a$
- Distance between neighbors: 0

#### ▼ Along the diagonals:

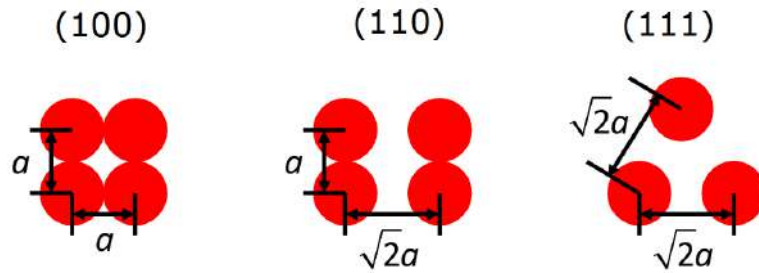
- Atoms do not touch each other
- Distance between centers:  $\sqrt{2}a$
- Distance between neighbors:  $\sqrt{2}a - 2R$

#### ▼ Along the volume diagonals:

- Atoms do not touch each other
- Distance between centers:  $\sqrt{3}a$
- Distance between neighbors:  $\sqrt{3}a - 2R$
- Ratio between edge length and atomic radius:  $\frac{a}{R} = 2$
- Atomic packing factor:  $APF = \frac{\pi}{6} \approx 0.52$
- closest packed direction:  $\langle 100 \rangle$
- Closest packed planes:  $\{100\}$  (Not close-packed)

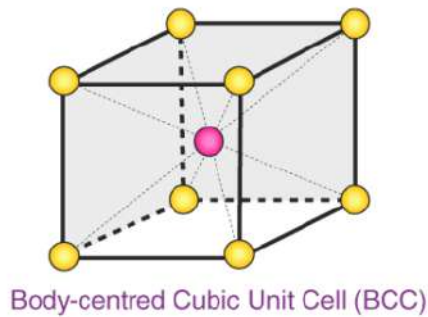


## ▼ Crystallographic planes



## ▼ Body-centered cubic (bcc)

## ▼ Basics

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Atoms in unit cell: 2

Coordination number (# of nearest neighbors): 8

## ▼ Along the edges:

- Atoms do not touch each other
- Distance between centers:  $a$
- Distance between neighbors:  $a - 2R$

## ▼ Along the diagonals:

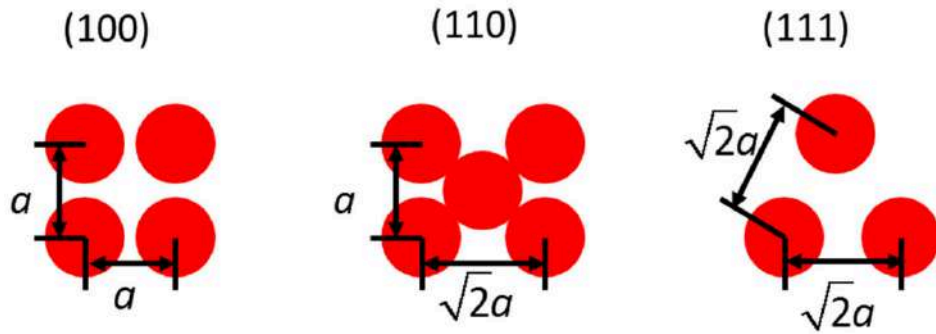
- Atoms do not touch each other
- Distance between centers:  $\sqrt{2}a$
- Distance between neighbors:  $\sqrt{2}a - 2R = \sqrt{2}a - \frac{\sqrt{3}a}{2}$

## ▼ Along the volume diagonals:

- Atoms touch each other
- Distance between centers:  $\frac{\sqrt{3}a}{2}$
- Distance between neighbors: 0

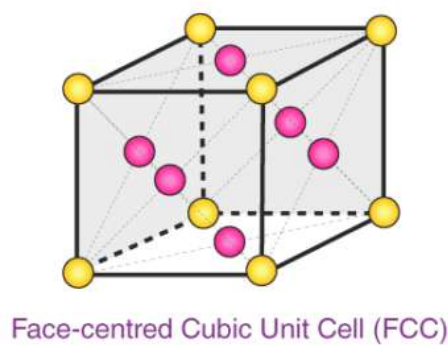
- Ratio between edge length and atomic radius:  $\frac{a}{R} = \frac{4}{\sqrt{3}}$
- Atomic packing factor:  $APF = \frac{\sqrt{3}\pi}{8} \approx 0.68$
- closest packed direction:  $\langle 111 \rangle$
- Closest packed planes:  $\{110\}$  (Not close-packed)

▼ Crystallographic planes



▼ Face-centered cubic (fcc)

▼ Basics



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Atoms in unit cell: 4

Coordination number (# of nearest neighbors): 12

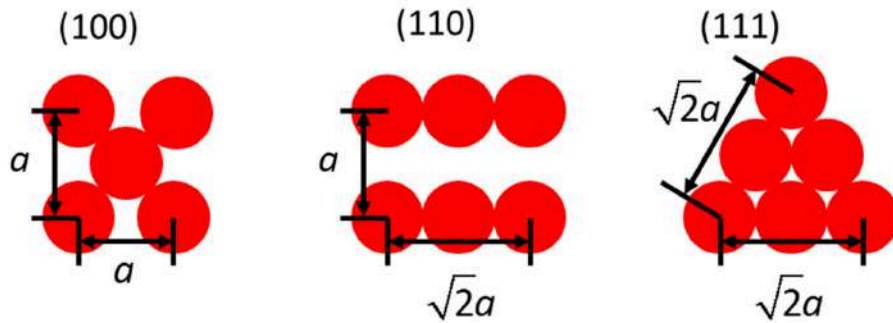
▼ Along the edges:

- Atoms do not touch each other
- Distance between centers:  $a$
- Distance between neighbors:  $a - 2R$

▼ Along the diagonals:

- Atoms touch each other
- Distance between centers:  $\frac{\sqrt{2}a}{2}$

- Distance between neighbors: 0
- ▼ Along the volume diagonals:
  - Atoms do not touch each other
  - Distance between centers:  $\sqrt{3}a$
  - Distance between neighbors:  $\sqrt{3}a - 2R$
- Ratio between edge length and atomic radius:  $\frac{a}{R} = 2\sqrt{2}$
- Atomic packing factor:  $APF = \frac{\sqrt{2}\pi}{6} \approx 0.74$
- closest packed direction:  $\langle 110 \rangle$
- Closest packed planes:  $\{111\}$  (Close-packed)
- ▼ Crystallographic planes



▼ Atomic packing factor and mass density

Naïve idea,

$$\rho_{theo} = \frac{m_{at}}{V_{at}} = \frac{m_{at}}{\frac{4\pi}{3} R_{at}^3}$$

Crystalline lattice,

$$\rho = \frac{N_{at} m_{at}}{V_{unitcell}} = \frac{N_{at} m_{at}}{a^3}$$

Atomic packing factor,

$$APF = \frac{N_{at} m_{at}}{V_{unitcell}} = \frac{N_{at} m_{at}}{a^3}$$

$m_{at}$ , mass of an atom  
 $V_{at}$ , volume of an atom  
 $R_{at}$ , radius of an atom  
 $N_{at}$ , number of atoms in the unit cell  
 $a$ , edge length of a unit cell  
 $\rho_{theo}$ , theoretical density  
 $\rho$ , mass density in lattice

### ▼ Crystallography

#### ▼ Crystallographic points - notation $x_j y_j z_j$

basis:  $\vec{r}_j = x_j \vec{a} + y_j \vec{b} + z_j \vec{c}$

length of the vectors:  $|\vec{r}| = a \sqrt{x^2 + y^2 + z^2}$

#### ▼ Crystallographic direction - notation $[u \ v \ w]$

Find the three components of the vector along the three axes of the unit cell. recalculate the resulting components to obtain integers, the three integers (indices  $u \ v \ w$ ) are written without separation within square brackets.

- If one of the indices becomes negative, it is indicated by a bar on top of it, like  $[u \ \bar{v} \ w]$ .
- If one of the indices is 10 or above it is separated by a dot from the next, like  $[10. \ 2 \ 3]$ .
- If you don't want to refer to a specific direction, but all crystallographic equivalents are meant, angle brackets are used  $\langle u \ v \ w \rangle$ .

#### ▼ Crystallographic plane - notation $(h \ k \ l)$

Find the intersections of the plane with the axis of the unit cell.

If the plane does not intersect an axis (because both are parallel, this is accounted as infinity).

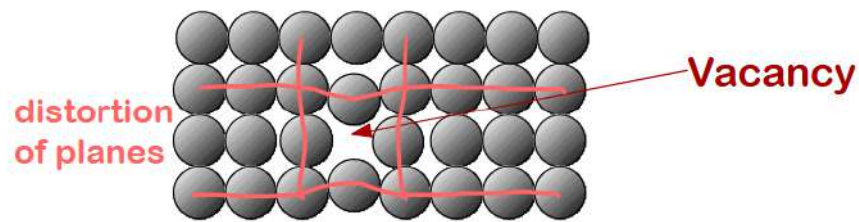
After finding the intersections we use reciprocal values  $\left(\frac{1}{x}\right)$  and recalculate so that they become integers.

- If one of the values is negative we denote it with a bar over it, like  $(2, \ \bar{1}, \ 0)$ .
- If you don't want to refer to a specific plane, but all crystallographic equivalents are meant, curly brackets are used  $\{h \ k \ l\}$ .

## Lattice defects

### ▼ 0-dimensional: point defects

#### ▼ Vacancies



Vacancies exist in thermal equilibrium.

Equilibrium density of vacancies is given by:

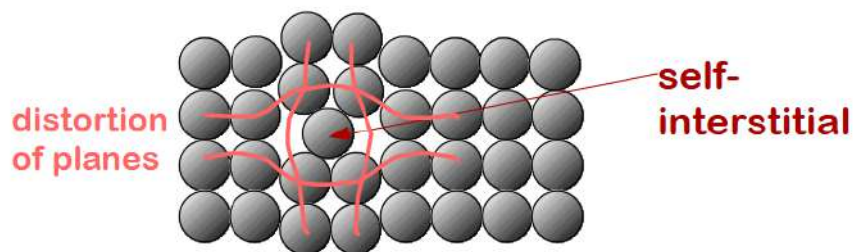
$$C_V = \frac{N_V}{N} = e^{-\frac{Q_V}{kT}}$$

$N_V$  denotes the number of vacancies

$N$  denotes the number of lattice sites

$k = 1.38 \times 10^{-23} \text{ J/K}$  denotes the Boltzmann constant

#### ▼ Self-interstitial atoms (SIA)



High formation energy: No self-interstitial atoms in thermal equilibrium in metals.

High mobility

#### ▼ 1-dimensional: line defects

##### ▼ Dislocations

Extra lattice plane inserted in crystal, not extending through all of the crystal (half-plane) ending in dislocation line.

The burgers vector is the displacement vector that defines the slip direction.

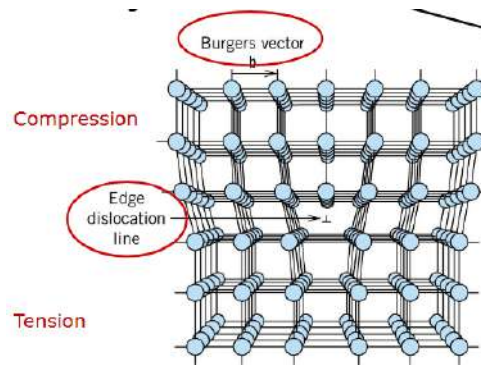
##### ▼ Dislocation density

Is the dislocation line length per volume, the formula is:

$$\rho = \frac{L}{V}$$

$L$ , denotes the dislocation length

$V$ , denotes the volume



### ▼ Slip systems in metals

Plastic deformation = deformation motion = slip (or glide)

Slip system: slip plane  $\{hkl\}$  + slip direction  $\langle uvw \rangle$  closest packed plane + closest packed direction planes with largest distance + Burgers vector

Lattice	Examples	Close(st) packed planes (hkl)	Close(st) packed directions [uvw]	Slip systems
fcc	Al, Cu, Ag, Au, Ni, ...	$\{111\}$ = close-packed	$\langle 110 \rangle$ face diagonals	$4 \times 3 = 12$
bcc	Cr, W, ...	$\{110\}$ = not close-packed	$\langle 111 \rangle$ volume diagonals	$6 \times 2 = 12$

### ▼ 2-dimensional: area (planar) defects

#### ▼ Grain boundaries

Separate 2 grains, (2 regions of the same crystal structure), but of different crystallographic orientation.

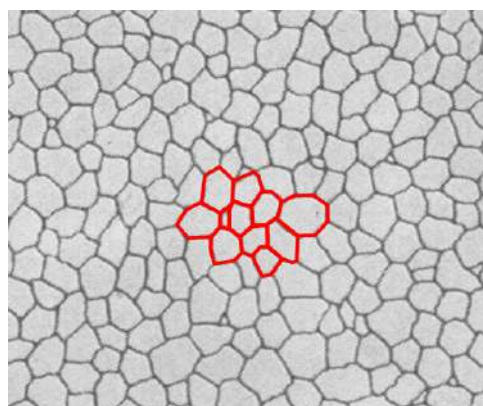
The boundary density  $S_V$  can be calculated by:

$$S_V = \frac{S}{V} \approx \frac{2}{D}$$

$D$  defined by the grain size

$S$  the surface area of the average grain

$V$  Volume

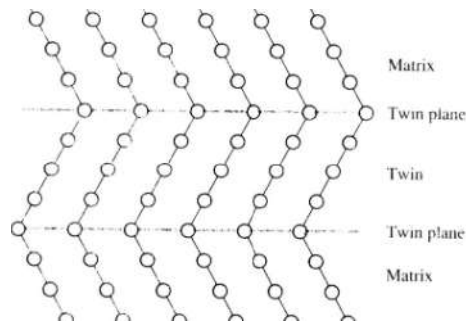


▼ Twin boundaries in polycrystals

Twin = mirrored crystalline lattice

Coherent boundaries on well-defined lattice planes (fcc {111})

Twin formation causes shear.



▼ 3-dimensional: volume (bulk) defects

▼ Self defects

Clusters of point defects.

Pore = an agglomerate of vacancies

▼ Alloys

▼ Types of alloys:

Most types of alloys can be categorized into three principle types:

▼ Solid solutions

Otherwise known as foreign atoms in crystal lattice, this type of alloy is known for unordered atoms in the same lattice.

▼ Mixture of different metallic phases

This type of alloy is known for its distinct phases with different composition and possibly different lattices.

▼ Intermetallic compounds

Are known for atoms ordered in possibly different lattice.

▼ Point defects in alloys

In a solid solution, foreign atoms (impurities) in the crystal lattice of host atoms can show up in 2 ways:

1. Interstitial atoms, sitting between lattice sites, or an interstitial solid solution

▼ Requirements for possible interstitial atoms in solid solutions

Foreign atoms on interstitial sites, only small atoms in holes (as B, C, N, O).

2. Substitutional atoms, substitute atoms on lattice sites, or substitutional solid solution (metals are usually substitutional)

▼ Complete miscibility for substitutional solid solution requires (according to Hume-Rothery rules):

1. The same crystal structure.
2. The difference in atomic radius is not more than 15%
3. Similar electronegativity
4. Same valence

If these are not met, this can lead to partial miscibility or immiscibility.

▼ Composition of binary alloys

▼ Weight percentage and atomic percentage

Weight percentage formally known as mass fraction, can be calculated as:

Atomic percentage formally known as amount fraction, can be calculated as:

$$C_A = \frac{m_A}{m_A + m_B}$$

$$C_B = \frac{m_B}{m_A + m_B}$$

$$C_A^* = \frac{n_A}{n_A + n_B}$$

$$C_B^* = \frac{n_B}{n_A + n_B}$$

To properly convert from one to the other we can do as such:

$$m_A = n_A \mu_A \quad \mu_A = \frac{m_A}{n_A}$$

$$C_A = \frac{n_A \mu_A}{n_A \mu_A + n_B \mu_B} = \frac{C_A^* \mu_A}{C_A^* \mu_A + C_B^* \mu_B}$$

$$C_A^* = \frac{C_A / \mu_A}{C_A / \mu_A + C_B / \mu_B}$$

Density of a binary alloy can be calculated by:

$$\rho = \frac{m}{V} = \frac{m_A + m_B}{V}$$

▼ Naïve estimate: additivity of volumes

$$V = \frac{m_A + m_B}{\rho} \approx V_A + V_B = \frac{m_A}{\rho_A} + \frac{m_B}{\rho_B}$$

$$\rho \approx \frac{1}{\frac{C_A}{\rho_A} + \frac{C_B}{\rho_B}}$$

▼ Lattice constant  $a$  of solid solutions:



Vegard's rule says:

$$a_{ss} = C_A^* a_A + C_B^* a_B$$

▼ Interstitial sites in cubic lattices

$r_H$  is the radius of the atom in the interstitial site  
 $R_{at}$  is the radius of the original atom in the lattice

- Simple cubic lattice

$$r_H/R_{at} = 0.732$$

- Face-centered cubic lattice

$$r_H/R_{at} = 0.414$$

- Body-centered cubic lattice

$$r_H/R_{at} = 0.150$$

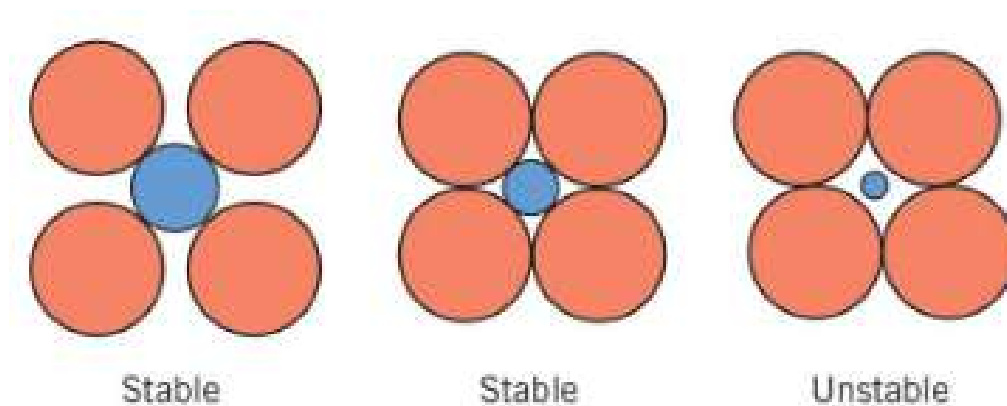
## Structures of ceramics

▼ Ionic crystals  $A^{n+}X^{n-}$

- Smaller cations  $A^{n+}$  (missing electrons), ion radius  $R_A$
- Larger anions  $X^{n-}$  (extra electrons), ion radius  $R_X$

Depending on the ratio  $R_A/R_X$  (or  $R_X/R_A$  in case  $R_A > R_X$ ), we can find how many larger anions fit around a smaller cation.

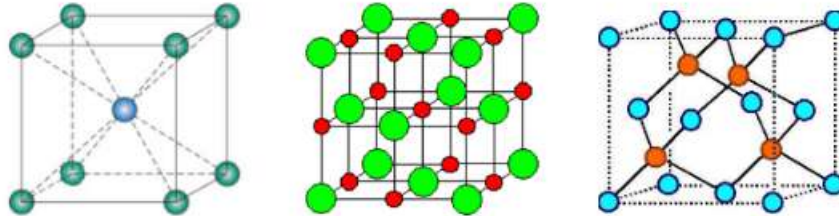
Slightly too small cations are unstable, while slightly too large cations push anions from each other.



▼ Structure types

Depending on the ionic radii  $R_A/R_X$  ratio, different types of structures exist.

$R_A/R_X$ range	>0.732	0.414-0.732	<0.414
Structure type	CsCl	NaCl	ZnS
$R_A/R_X$ comp.	0.92	0.56	0.40



#### ▼ Mass density

With 2 different types of atoms in the crystal lattice the mass density formula changes and therefore is now generalized to:

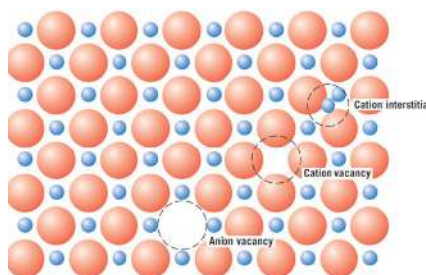
$$\rho = \frac{N_1 m_1 + N_2 m_2}{N_A V_{\text{unitcell}}}$$

$N_1, N_2$  numbers in the unit cell  
 $m_1, m_2$  Molar masses  
 $N_A$  Avogadro constant

#### ▼ Lattice defects

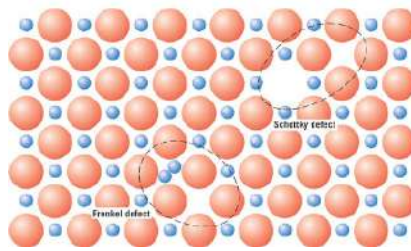
##### ▼ Crystalline ceramics

##### ▼ Point defects



These types of lattice defects make the lattice electrically charged and do not exist in equilibrium.

##### ▼ Point defect pairs



These types of lattice defects do not make the lattice electrically charged and are relevant for optical properties and AC conductivity.

#### ▼ Dislocations

Motion may or may not lead to neighboring ions with the same charge.

Low number of slip systems.

- Grain boundaries

#### ▼ General for all ceramics

##### ▼ Pores

These cause a lower density and related properties (conductivities, strength).

- Microcracks

## Structures of polymers

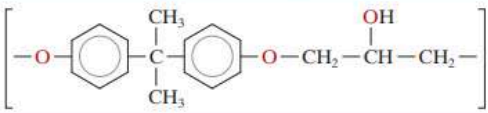
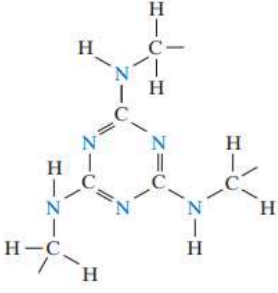
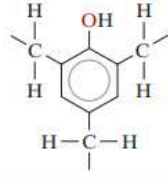
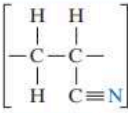
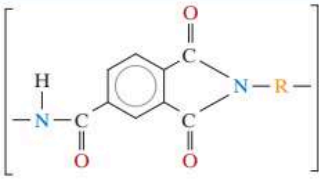
The meaning of the term polymer is many parts and an individual part is called a monomer

#### ▼ Monomer

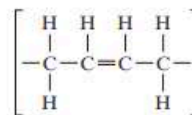
A monomer is defined by an individual molecule before being assembled into a polymer. The bonds inside monomers are always covalent.

Monomers must be able to react in chemical reactions with other monomers, like an extra pair from a double bond or a reaction by releasing a small molecule like  $H_2O$ .

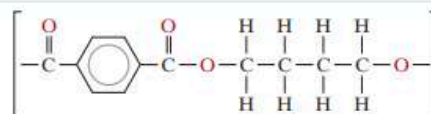
#### ▼ Common polymers and their repeat units

Chemical Name	Repeat Unit Structure
Epoxy (diglycidyl ether of bisphenol A, DGEPA)	
Melamine-formaldehyde (melamine)	
Phenol-formaldehyde (phenolic)	
Polyacrylonitrile (PAN)	
Poly(amide-imide) (PAI)	

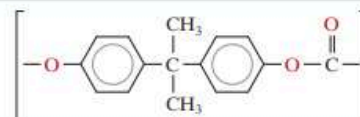
Polybutadiene



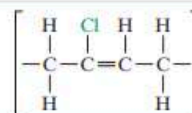
Poly(butylene terephthalate) (PBT)



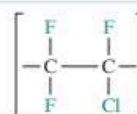
Polycarbonate (PC)



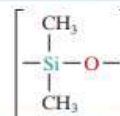
Polychloroprene



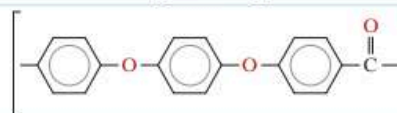
Polychlorotrifluoroethylene



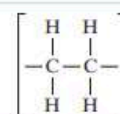
Poly(dimethyl siloxane) (silicone rubber)



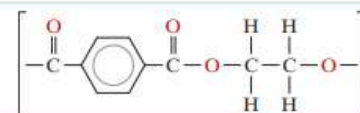
Polyetheretherketone (PEEK)



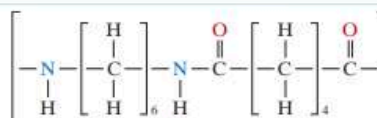
Polyethylene (PE)



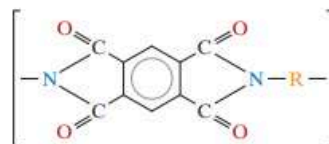
Poly(ethylene terephthalate) (PET)



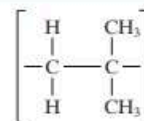
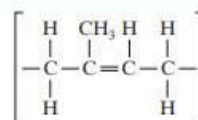
Poly(hexamethylene adipamide) (nylon 6,6)



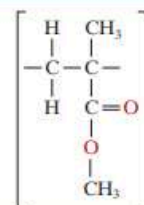
Polyimide



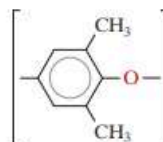
Polyisobutylene

*cis*-Polyisoprene (natural rubber)

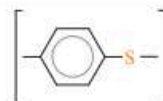
Poly(methyl methacrylate) (PMMA)



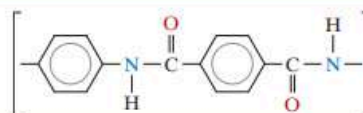
Poly(phenylene oxide) (PPO)



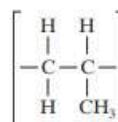
Poly(phenylene sulfide) (PPS)



Poly(paraphenylene terephthalamide) (aramid)



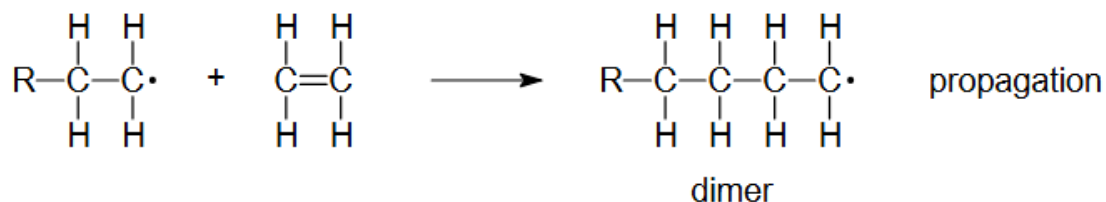
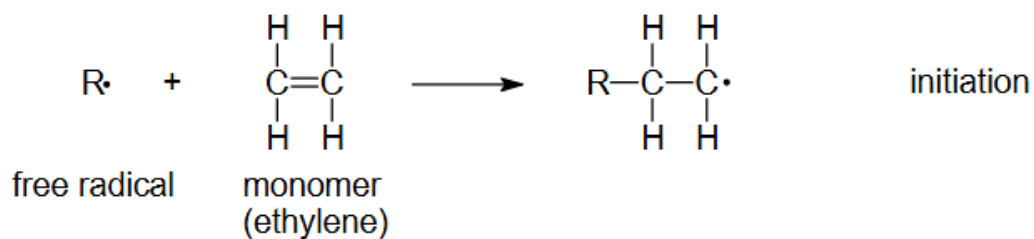
Polypropylene (PP)



Polystyrene (PS)	$\left[ \begin{array}{cc} \text{H} & \text{H} \\   &   \\ -\text{C} & -\text{C}- \\   &   \\ \text{H} & \text{C}_6\text{H}_5 \end{array} \right]$
Polytetrafluoroethylene (PTFE)	$\left[ \begin{array}{cc} \text{F} & \text{F} \\   &   \\ -\text{C} & -\text{C}- \\   &   \\ \text{F} & \text{F} \end{array} \right]$
Poly(vinyl acetate) (PVAc)	$\left[ \begin{array}{cc} & \text{O}=\text{C}-\text{CH}_3 \\ &   \\ \text{H} & \text{O} \\   &   \\ -\text{C} & -\text{C}- \\   &   \\ \text{H} & \text{H} \end{array} \right]$
Poly(vinyl alcohol) (PVA)	$\left[ \begin{array}{cc} \text{H} & \text{H} \\   &   \\ -\text{C} & -\text{C}- \\   &   \\ \text{H} & \text{OH} \end{array} \right]$
Poly(vinyl chloride) (PVC)	$\left[ \begin{array}{cc} \text{H} & \text{H} \\   &   \\ -\text{C} & -\text{C}- \\   &   \\ \text{H} & \text{Cl} \end{array} \right]$
Poly(vinyl fluoride) (PVF)	$\left[ \begin{array}{cc} \text{H} & \text{H} \\   &   \\ -\text{C} & -\text{C}- \\   &   \\ \text{H} & \text{F} \end{array} \right]$
Poly(vinylidene chloride) (PVDC)	$\left[ \begin{array}{cc} \text{H} & \text{Cl} \\   &   \\ -\text{C} & -\text{C}- \\   &   \\ \text{H} & \text{Cl} \end{array} \right]$
Poly(vinylidene fluoride) (PVDF)	$\left[ \begin{array}{cc} \text{H} & \text{F} \\   &   \\ -\text{C} & -\text{C}- \\   &   \\ \text{H} & \text{F} \end{array} \right]$

### ▼ Polymerization

Chain polymerization can be caused by the reaction of a free radical and a monomer.

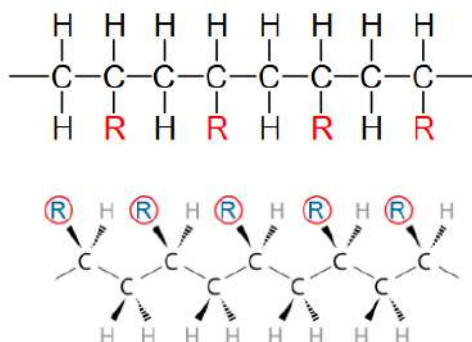


### ▼ Stereoisomerism

Also known as the arrangement of side groups, these can be:

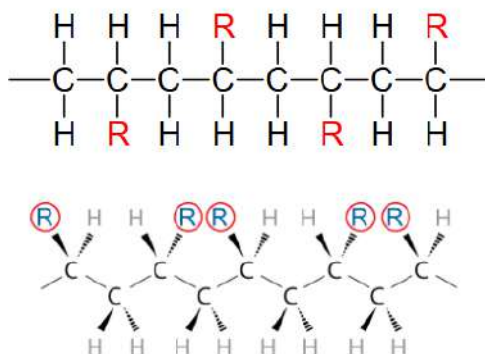
#### ▼ Isotactic

R groups on the same side, like:



#### ▼ Syndiotactic

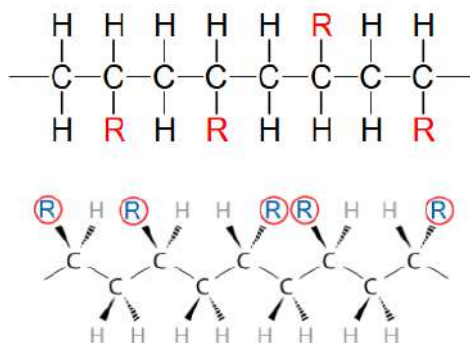
R groups on alternate sides, like:





## ▼ Atactic

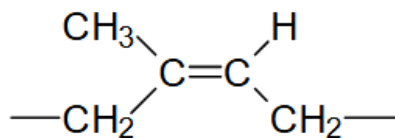
R groups at random positions, like:



## ▼ Geometrical Isomerism

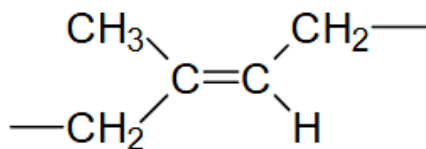
## ▼ Cis

Where the chain continues on the same side, like:



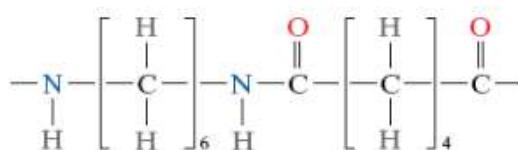
## ▼ Trans

Where the chain varies from monomer to monomer, like:



## ▼ Co-polymers

Consist of 2 distinct monomers, like:



An advantage of this is a better spatial distribution of not-miscible polymer types.

To calculate degree of polymerization we need to use the average molar mass of the monomers

#### ▼ Molar mass (Molar weight)

The more monomers in a chain,

- The longer the chain
- The higher the molar mass
- The higher the melting temperature

The molar mass of a chain molecule is calculated using:

$$M = nm$$

$m$  Molar mass of the repeating unit  
 $n$  Number of repeating units

Average molar mass (number weighted) can be calculated using:

$$\bar{M}_n = \sum x_i M_i$$

$x_i$  is the fraction of all chains that have molar mass  $M_i$

#### ▼ Degree of polymerization

IUPAC's definition is the number of monomers in a chain and its calculated by:

$$N = M/m$$

$M$ , is the molar mass of the chain  
 $m$ , is the molar mass of the monomer

In the case of co-polymers:

$$\bar{m}, \text{ is the average molar mass of monomers}$$

The degree of polymerization is not the number of repeat units, but the number of monomers.

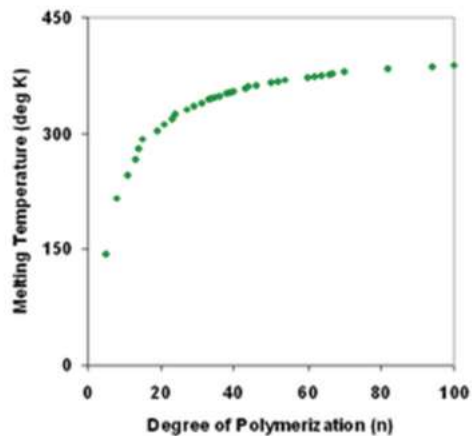
Chain length distribution, degree of polymerization:

$$\bar{N} = \bar{M}_n/m \text{ or } \bar{N} = \bar{M}_n/\bar{m}$$

$\bar{M}_n$ , is the number weighted average molar mass

#### ▼ Structure-property relation

- ▼ Degree of polymerization vs melting temperature



A higher melting temperature means:

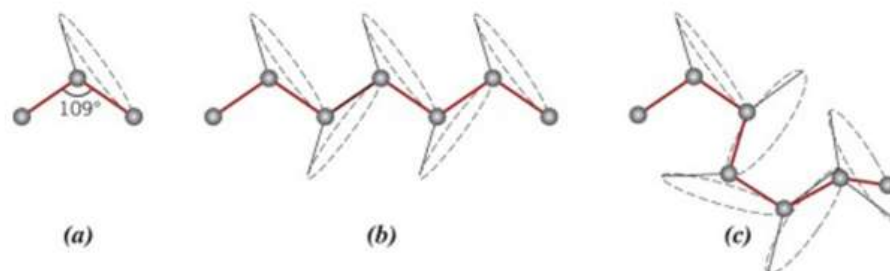
- High molar mass
- Low chain flexibility (large side groups, double bonds or aromatic rings, strong secondary bonds)

A lower melting temperature means:

- (more) Side branches
- randomly ordered side groups (atactic)

#### ▼ Bonds

Carbon has 4 bonds, with a bond angle of  $\theta_{CC} = 109^\circ$  and a bond length of  $d_{CC} = 0.154 \text{ nm}$



Carbon skeleton has free rotation around single bonds, so to accurately measure the straightened chain length we do:

$$L = N_{CC} d_{CC} \sin(\theta_{CC}/2)$$

$d_{CC}$ , is the bond length

$N_{CC}$ , is the number of single C-C bonds along the chain

#### ▼ Flexible chains with different shapes (conformation)

The average start to end distance is calculated using:

$$r = d_{CC} \sqrt{N_{CC}}$$

$$d_{CC} = 0.154 \text{ nm}$$

#### ▼ Stiff monomers and stiff chains

These are called stiff if they have no rotational degree of freedom, 2 examples are double bonds and aromatic rings

#### ▼ Chains "knitted" into each other

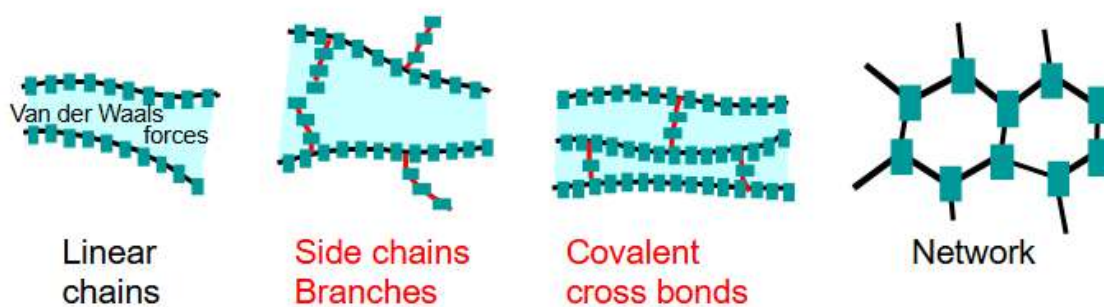
Where each monomer:

- Does not recognize the end of its chain.
- Can not distinguish between own and alien chains
- can not pass through other parts of the chain



#### ▼ Interactions between chains

- Along chains, covalent bonds are expected.
- Between chains, secondary bonds (or covalent bonds) are expected.



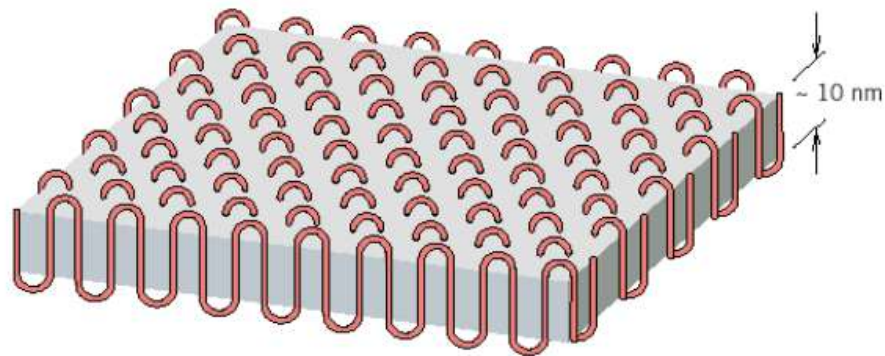
#### ▼ Thermoplastic versus thermoset

	Thermoplastic	Thermoset
Heating	Softening (and melting)	Neither becoming softer nor melting

	Thermoplastic	Thermoset
Cooling	Harder	Becomes hard during manufacturing
Typically	Chains with few branches	Network with cross bonds
Bonds	Secondary bonds (Van der Waals)	Covalent cross bonds
Manufacturing	High temperature and high pressure	Hardening during cooling or radiation
	Reversible	Irreversible
Degradation	At too high temperatures	At too high temperatures

### ▼ Crystallinity

Can be defined by crystalline regions (spherulites). Thin platelets with folded chains, chains are locally straightened.



### ▼ Semi-crystalline polymers

Polymers with both amorphous and crystalline regions. Where the crystalline regions act as cross-links.

Maximum crystallinity is around 80%.

These types of polymers are known for:

- Higher density
- Higher melting temperature
- Being mechanically stronger
- Not being translucent

### ▼ Density of semi-crystalline polymers

- Density of crystalline regions  $\rho_c$

- Density of amorphous regions  $\rho_a < \rho_c$
- Good to note that the relation between density ( $\rho_{sc}$ ) and volume fraction  $f_c$  are linear, while density ( $\rho_{sc}$ ) and crystallinity ( $x$ ) are not

Semi-crystalline polymers have a density that can be calculated:

$$\rho_{sc} = f_c \rho_c + (1 - f_c) \rho_a$$

Where  $f_c$  denotes the volume fraction of crystalline regions and is calculated:

$$f_c = \frac{\rho - \rho_a}{\rho_c - \rho_a}$$

And lastly the crystallinity (mass fraction) can be calculated:

$$x = \frac{m_c}{m_{sc}} = \frac{f_c \rho_c}{\rho_{sc}} = \frac{\rho_c}{\rho_{sc}} \frac{\rho_{sc} - \rho_a}{\rho_c - \rho_a}$$

## Imaging

### ▼ Methods

#### ▼ Diffraction

Visualization of atoms in a crystal

Source - Visual light

#### ▼ Microscopy

Visualization of 2D image

Source - Electrons

#### ▼ Tomography

Visualization of 3D image

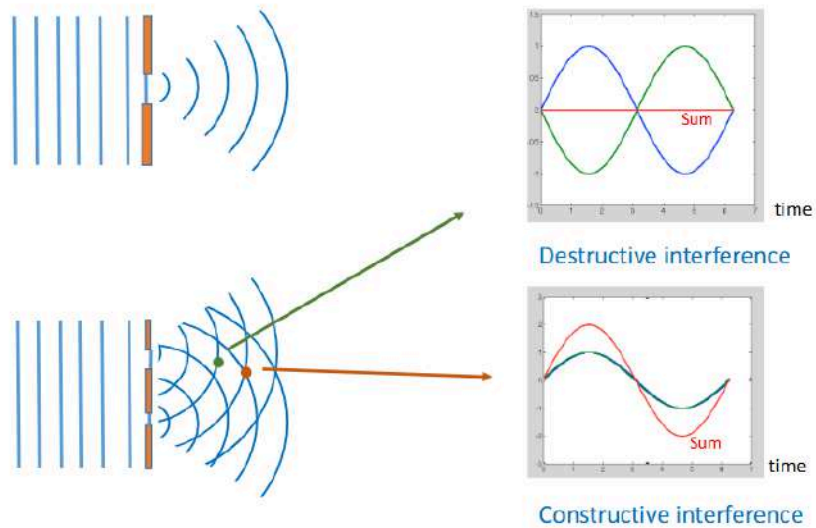
Source - X-rays

#### ▼ Cantilever arm

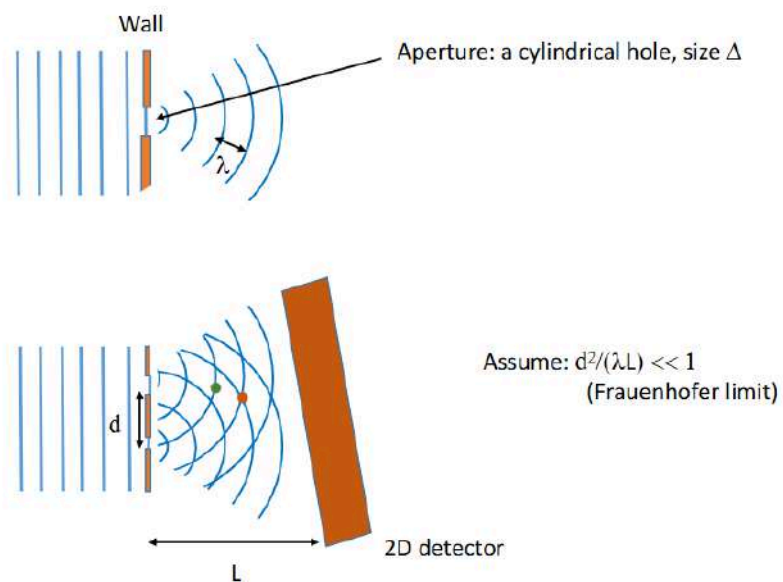
Visualization of surface studies

Source - Scanning probe

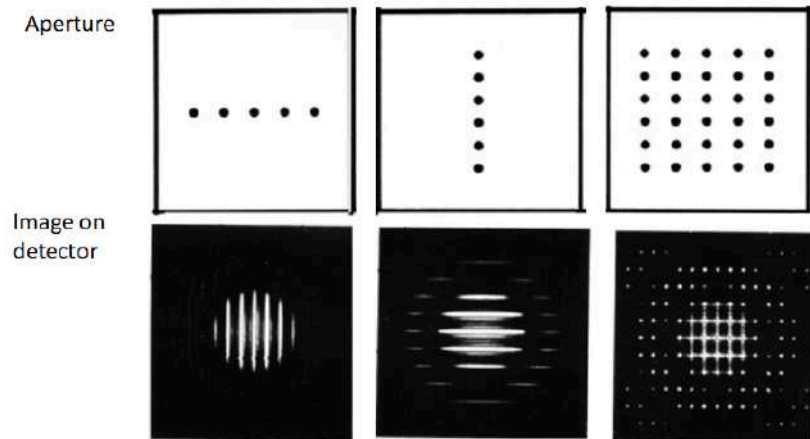
### ▼ Diffraction in 2D: interference of waves



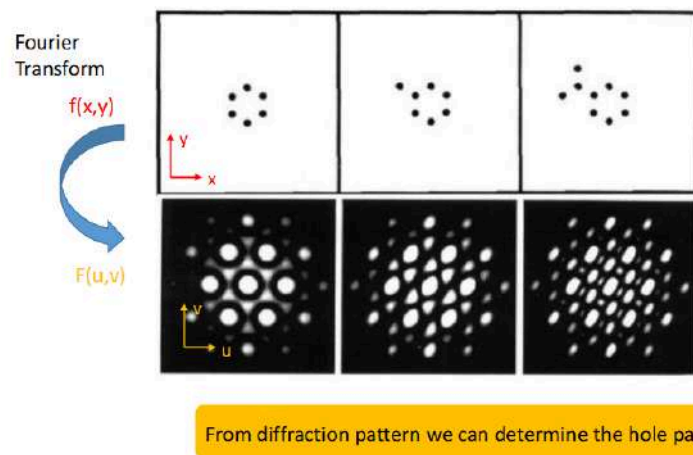
▼ Diffraction in 3D: interference of waves



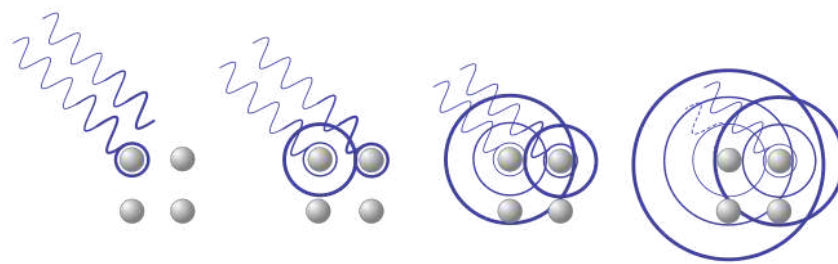
▼ Diffraction: interference of waves



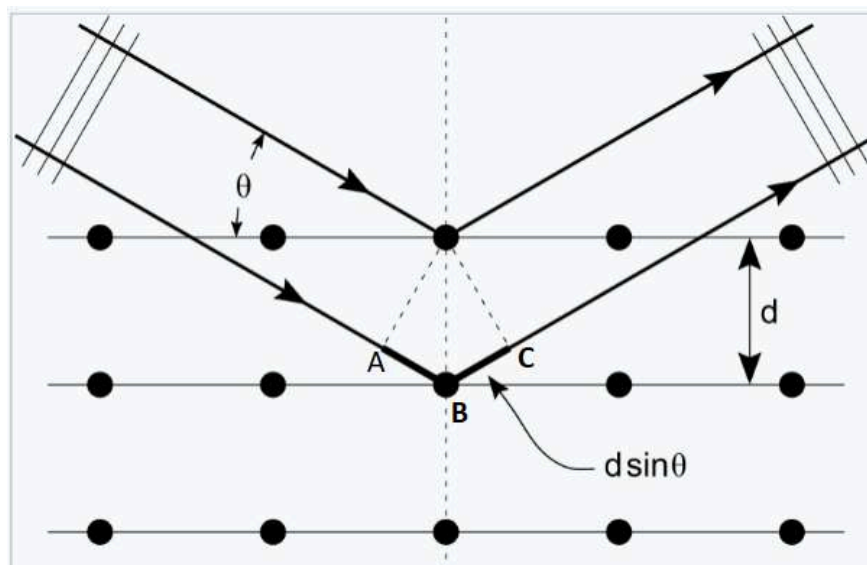
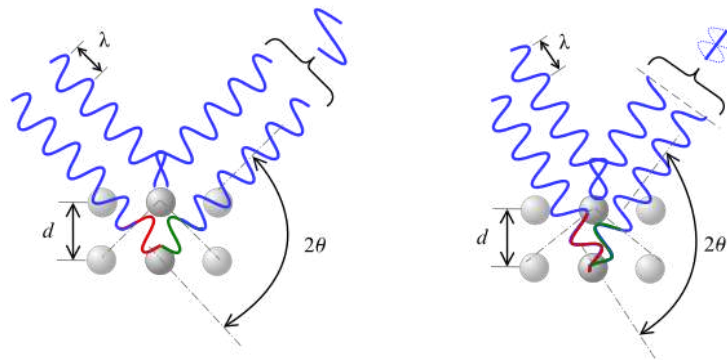
More holes  
=> Sharper pattern



### ▼ Bragg diffraction







In phase:

$$n\lambda = |AB| + |BC|$$

$$n\lambda = d_{hkl} \sin \theta + d_{hkl} \sin \theta$$

▼ Bragg's law:

$$n\lambda = 2d_{hkl} \sin \theta$$

For every  $d_{hkl}$  (it depends on the plane) we can measure a scattering angle  $2\theta$ .  $n$  is the refractive index (for vacuum/air:  $n = 1$ )

▼ Crystallography

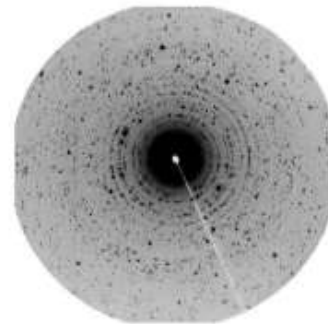
Due to the fact atoms are extremely small, they leave very narrow spots on the detector with extreme enhanced intensity

▼ X-ray diffraction

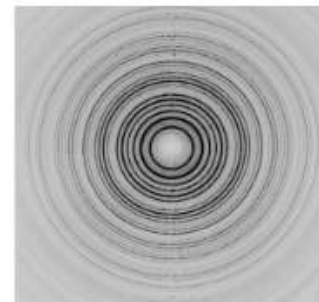
▼ Example of a single-crystal



▼ Example of more crystals

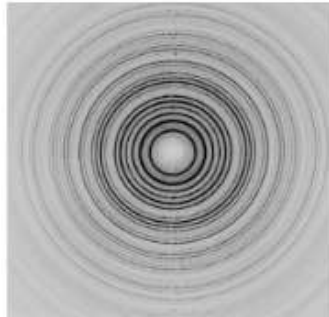


▼ Example of Powder

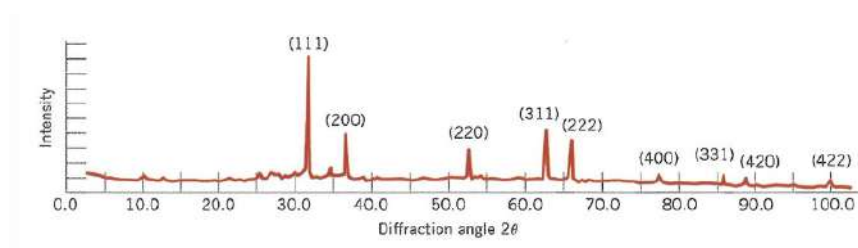


▼ Powder diffraction (more deeply)

▼ Example of X-ray diffraction of powder



Due to it being a powder X-ray diffraction, we can see the radius varies with the intensity as fct (Fourier computed tomographic imaging). We can write the radius as the diffraction angle  $2\theta$  and graph intensity versus the diffraction angle as such:



Each of these graphs is unique to a specific element and their lattice.

#### ▼ Cubic symmetry

In crystals in cubic lattices the  $d_{hkl}$  can be calculated using:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Not every planes in every lattice contain reflections. We can find what planes contain reflections with the following table:

Crystal structure	Reflections present	First 6 indices
Simple	All	100,110,111,200,210,211
FCC	$h, k$ and $l$ are either all even or all odd	111,200,220,311,222,400
BCC	$(h + k + l)$ has to be even	110,200,211,220,310,222

#### ▼ Important formulas

$$n\lambda = 2d_{hkl} \sin \theta$$

Where,  

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

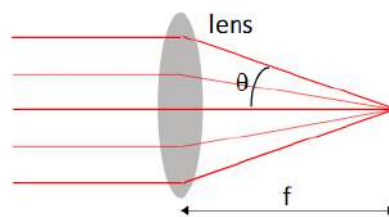
$n$  is the refractive index, its 1 for vacuum/air

$\lambda$  is the length of the wave

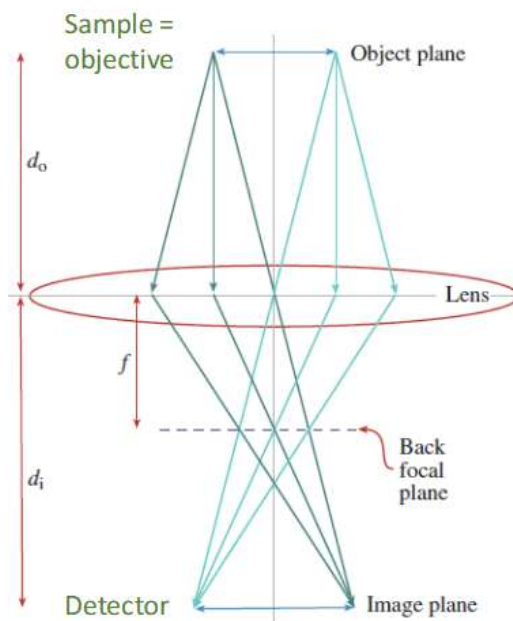
$2\theta$  is the diffraction angle

### ▼ Microscopy

#### ▼ Focal length:



#### ▼ General graph:



- Lens/lensmakers equation:

$$\frac{1}{d_i} + \frac{1}{d_o} = \frac{1}{f}$$

- Magnification:

$$M = \frac{d_i}{d_o}$$

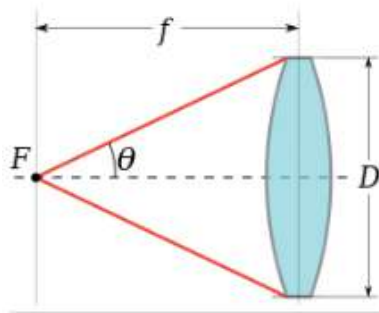
- Spatial resolution

▼ Numerical aperture:

$$NA = n \sin \theta \approx n \frac{D/2}{f}$$

$D$ , is the diameter of the lens

$n$ , refractive index for vacuum/air:  $n = 1$

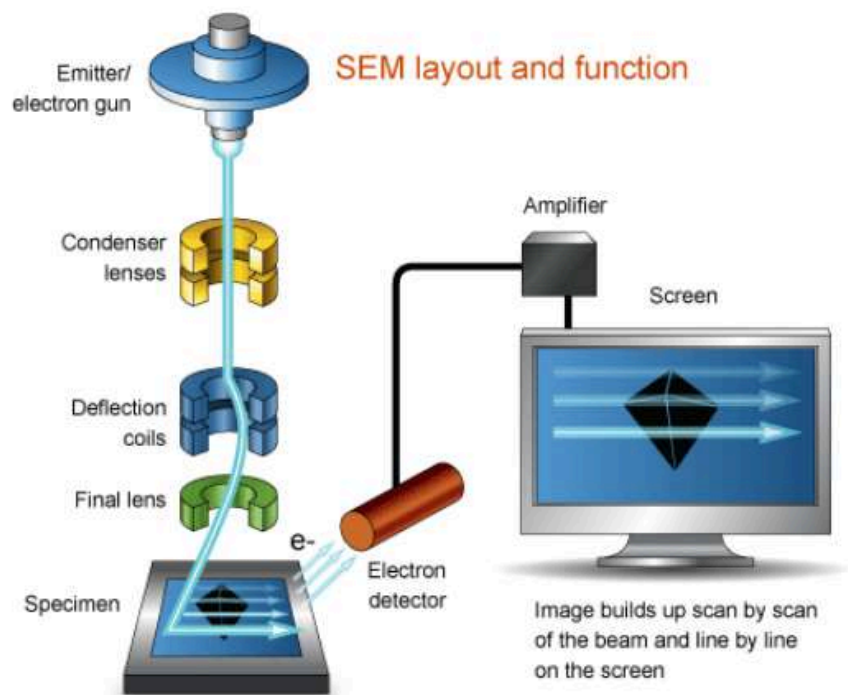


▼ Diffraction limit:

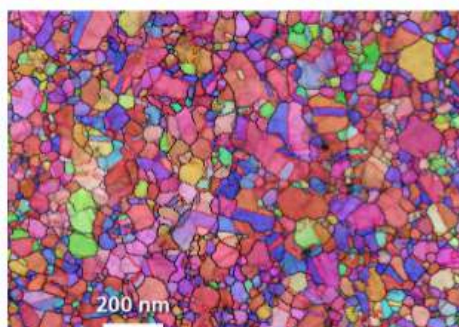
$$\text{Res} \geq 0.6 \frac{\lambda}{NA} = 0.6 \frac{\lambda}{n \sin \theta}$$

	Visual light	Electrons	X-rays
<b>Wavelength</b>	500 nm	0.03 nm	0.1 nm
<b>NA</b>	Up to 1	0.01	Towards 0.01
<b>Resolution</b>	500 nm	0.3 nm	Towards 10 nm
<b>Use</b>	Grains	Atoms	Towards domains

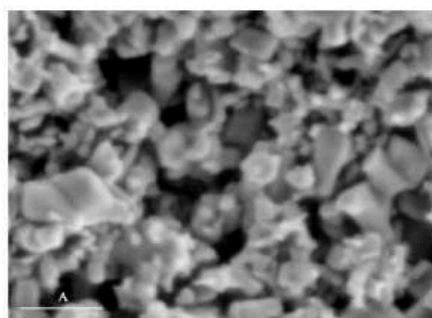
▼ Scanning electron microscopy (SEM)



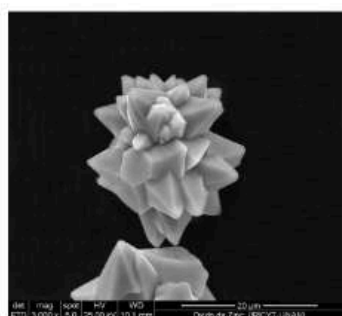
Typically in vacuum



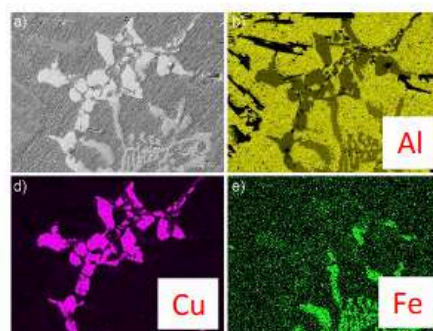
Nano-size grains



Porous structures



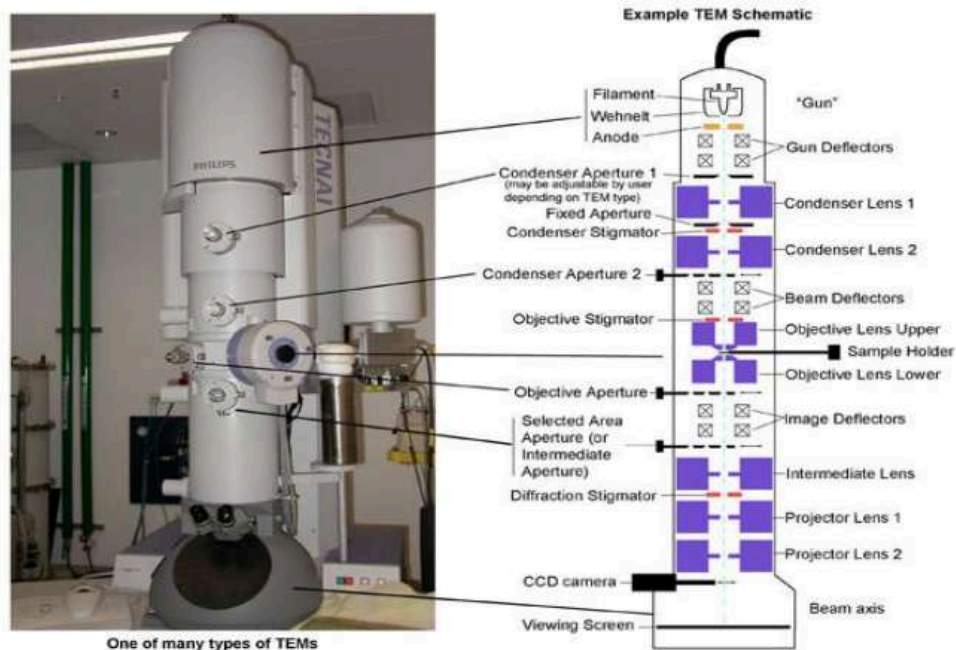
Small stuff on surface



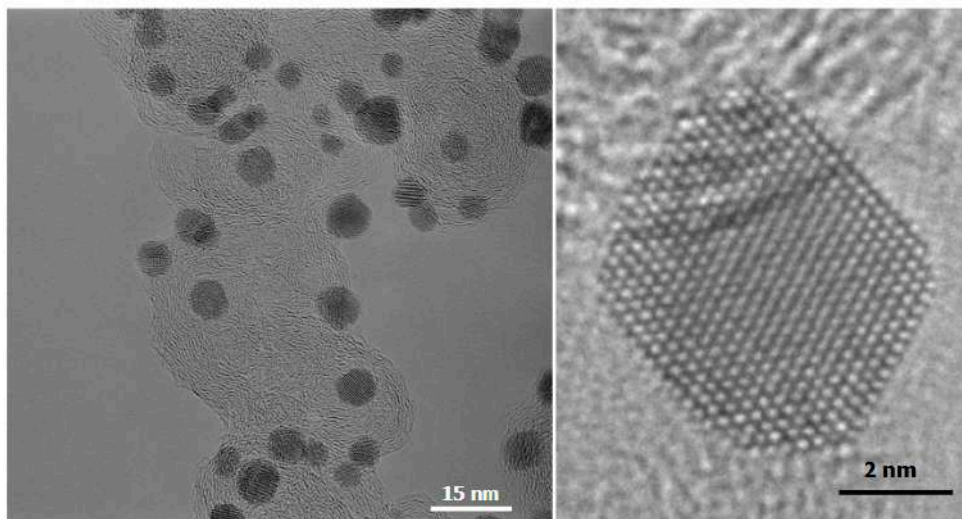
Chemical map of Al alloy

▼ Transmission electron microscope (TEM)





Always in vacuum



#### ▼ Imaging of materials

	Light	Electrons	X-rays	Scanning probe
Resolution	500 nm	0.3 nm	10-100 nm	0.1 nm
Depth	None	100 nm	1 mm	None
Field of view	Large	Small	Medium	Small
Diffraction	-	+	+	-
Environment	All	Vacuum	All	All
Access	Lab	Uni center	Uni center or synchrotron	Lab

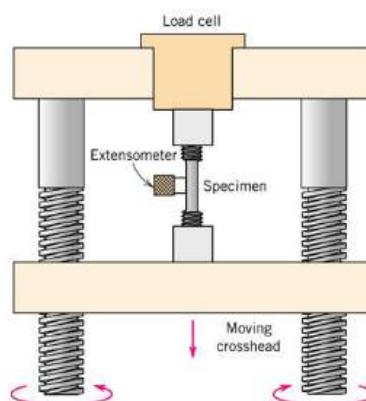
# Mechanical testing

## ▼ Tensile test

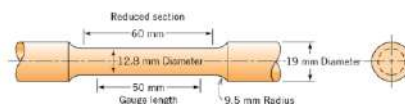
### ▼ Tensile testing

To do the tensile test we exert a force on a specimen to elongate and then graph the force vs the elongation.

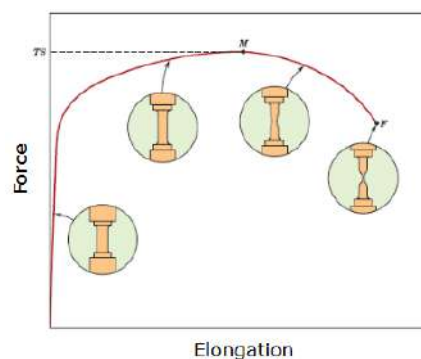
### ▼ Example system



### ▼ Example specimen



### ▼ Example graph



- (Normal) Force  $F_n$

Depends on the initial cross-section  $A_0$  of the specimen (a specimen twice as thick requires twice the force).



- Elongation  $\Delta l$

Depends on the initial length  $l_0$  of the specimen (a specimen with twice the length achieves twice the elongation).

▼ Measurements

▼ The stress  $\sigma$

can be calculated:

$$\sigma = \frac{F_n}{A_0}$$

Its unit is Pa (Pascal), although we often use MPa.

$$\begin{aligned} 1 \text{ Pa} &= 1 \text{ N/m}^2 \\ 1 \text{ MPa} &= 10^6 \text{ N/m}^2 \end{aligned}$$

Tensile stress refers to when  $\sigma > 0$

Compressive stress refers to when  $\sigma < 0$

Shear stress  $\tau$  refers to the tangential force

▼ The strain (relative elongation)  $\varepsilon$

can be calculated:

$$\varepsilon = \frac{\Delta l}{l_0} = \frac{l - l_0}{l_0}$$

Its unit is 1 m/m or dimensionless (%)

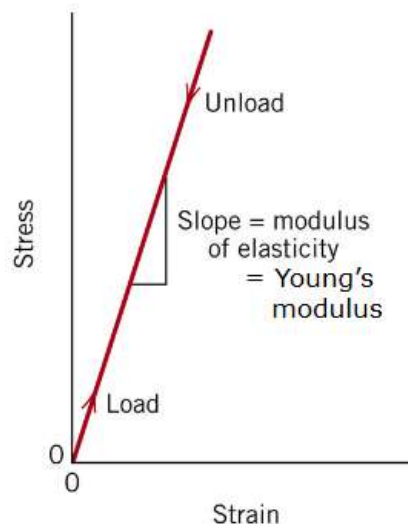
Elongation due to tension refers to  $\varepsilon > 0$

Contraction due to compression refers to  $\varepsilon < 0$

Shear strain  $\gamma = \tan \theta$ , where  $\theta$  is the angle at which the body inclined

▼ Strain-stress slope

In the very beginning of the stress-strain chart, the line is actually linear and the slope of that line is the defined as modulus of elasticity or Young's modulus.



### ▼ Elastic properties

According to Hooke's law, there is a proportionality factor between stress and strain,  $E$ , which we call Elastic modulus, Young's modulus, or E-modulus. This is usually expressed in GPa (giga-Pascal), although we must convert to the proper unit for normal calculations.

$$\sigma = E\varepsilon$$

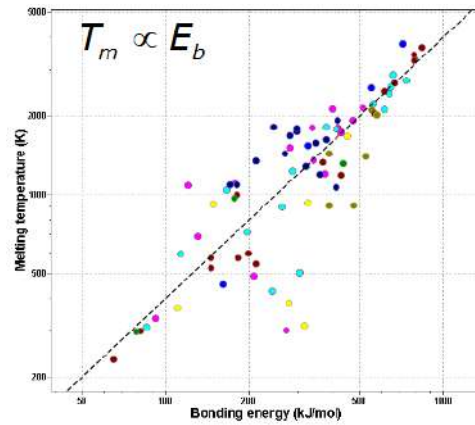
The Elastic modulus is only dependent on elongation, stress, strain, the influence of impurities and temperature.

	$E$	$T_m$
Pb	16 GPa	327 °C
Al	71 GPa	660 °C
Cu	130 GPa	1084 °C
Fe	210 GPa	1538 °C
W	411 GPa	3422 °C

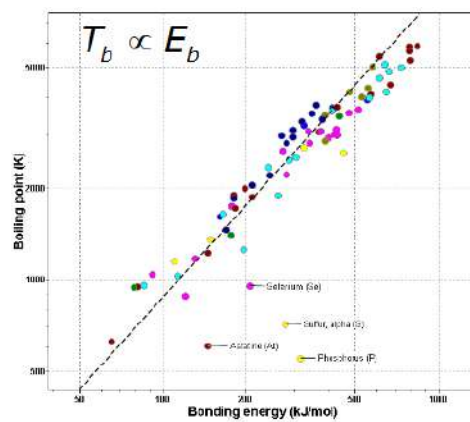
And there is a correlation between Young's modulus and the melting temperature of materials, where the higher the melting temperature of a material the higher the Young's modulus since both are controlled by the bonding energy.

### ▼ Property correlations

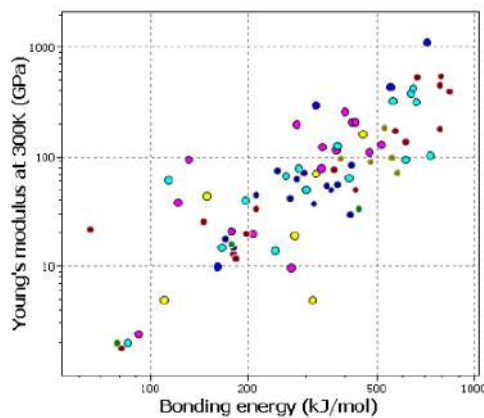
#### ▼ Melting temperature and bonding energy



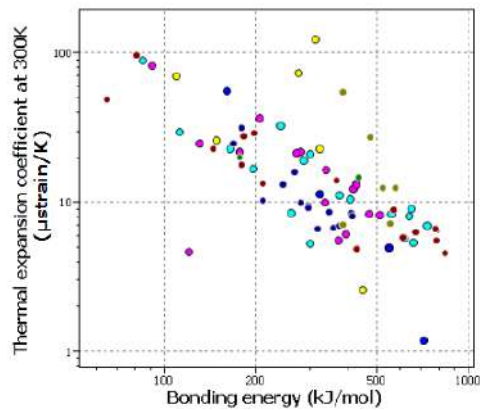
▼ Boiling temperature and bonding energy



▼ Young's modulus of elements at 300 kelvin and their corresponding bonding energy



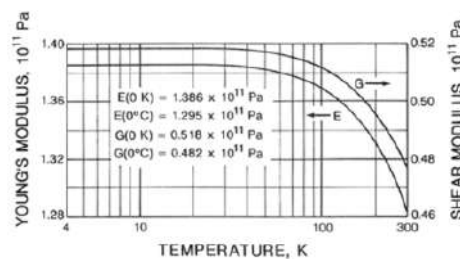
▼ Thermal expansion coefficient and bonding energy



#### ▼ Young's modulus/shear modulus and temperature

Young's modulus decreases with temperature, due to thermal oscillations. The same thing can also be said about shear modulus.

Below we can see how Young's modulus and the shear modulus of copper changes with the change of temperature.



#### ▼ Young's modulus and crystallography

Anisotropy (usually)

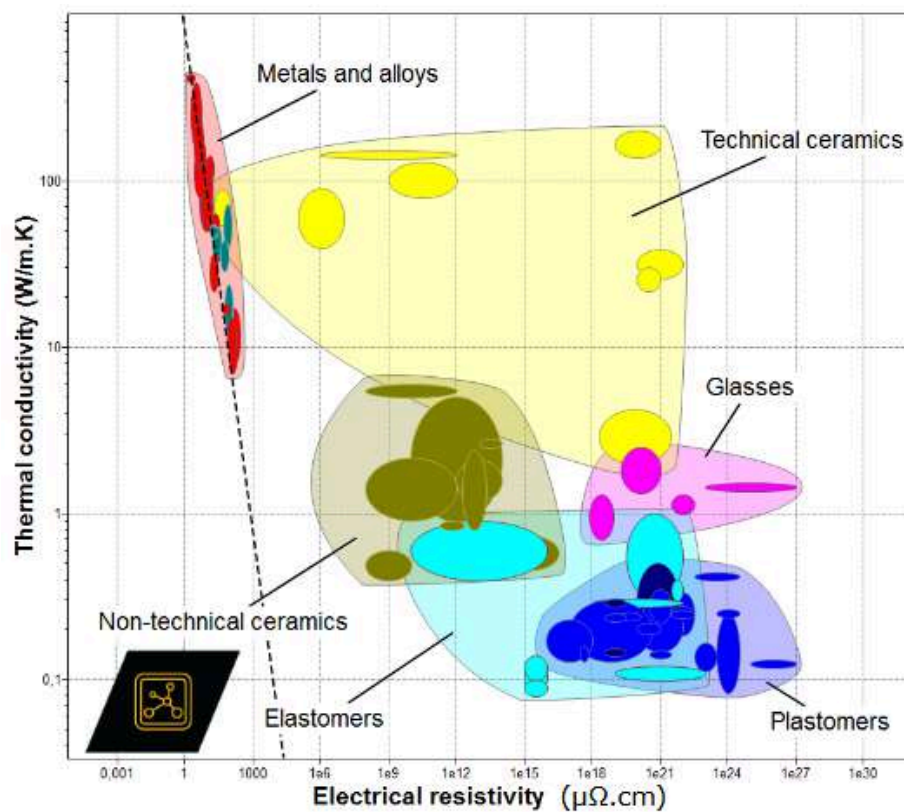
►

It's true for most cubic lattices, relevant for single crystals.

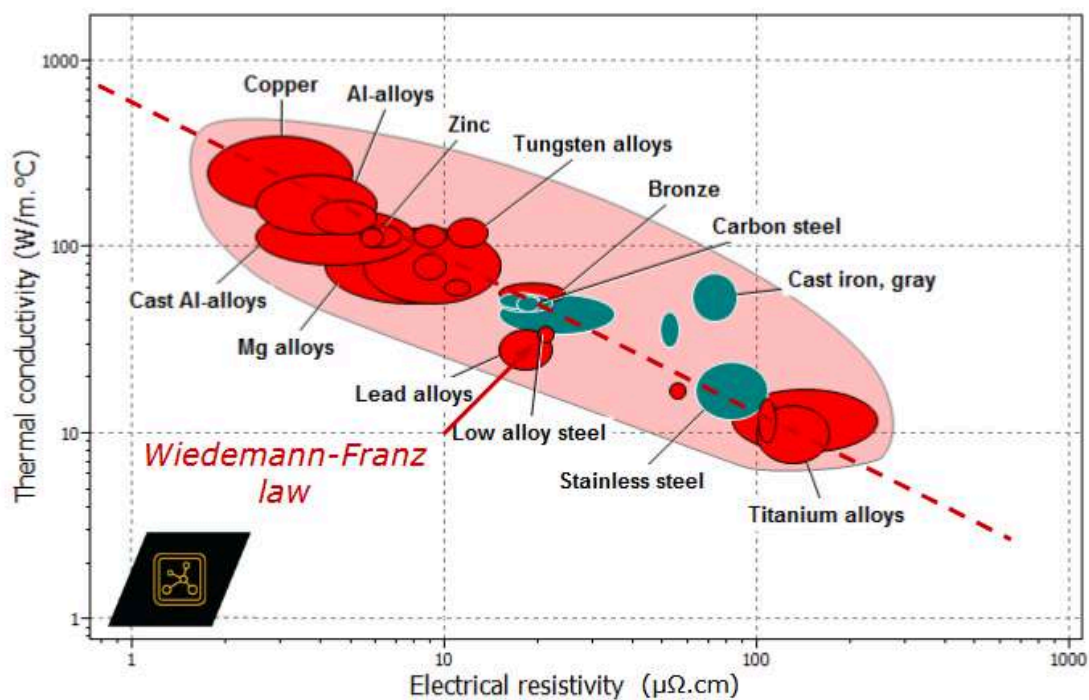
#### ▼ Table of examples

		Modulus of Elasticity (GPa)	
Metal	[100]	[110]	[111]
Aluminium	63.7	72.6	76.1
Copper	66.7	130.3	191.1
Iron	125.0	210.5	272.2
Tungsten	384.6	384.6	384.6

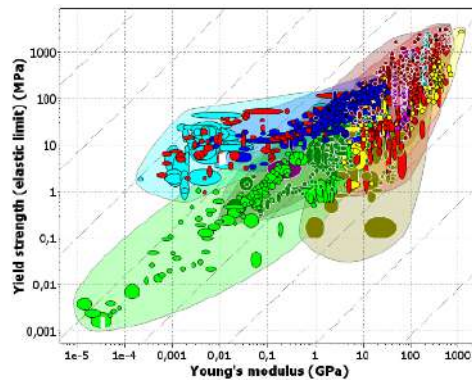
▼ Thermal conductivity and electrical resistivity (all materials)



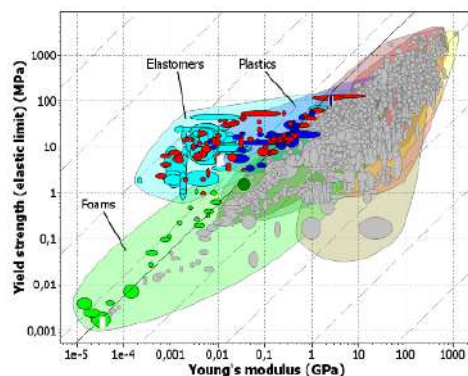
▼ Thermal conductivity and electrical resistivity (Metals and Alloys)



▼ Yield strength and Young's modulus



▼ Theoretical yield strength (defect-free material)



▼ Young's modulus of alloys

▼ Substitutional solid solutions

Depends on composition and alloy type

▼ Example of Cu and Ni

Alloy	E/GPa
Cu	115
Cu 10 wt% Ni	130
Cu 25 wt% Ni	145
Cu 30 wt% Ni	150
Cu 44 wt% Ni	165
Ni	207

▼ Intermetallic compound

Depends on different crystal structure, different bonds, different elastic moduli.

▼ Mixture of phases

Depends on rule of mixtures, Young's modulus depends on spatial arrangement

## ▼ Elastic behavior cross-contraction

Change in extension perpendicular to load

In general

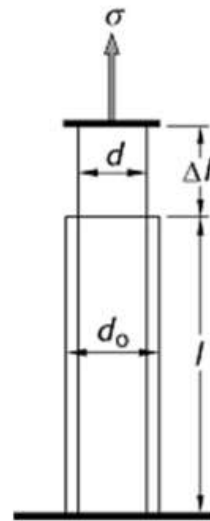
$$\Delta l > 0$$

$$\Delta d < 0$$

Poisson's ratio:

$$\nu = -\frac{\Delta d/d_0}{\Delta l/l_0} = -\frac{\varepsilon_x}{\varepsilon_z}$$

For a load along the z-direction.  $0.25 \leq \nu \leq 0.35$  (most times 0.3).



If there is volume conservation then  $\nu = 0.5$

## ▼ Shear test

▼ Shear stress  $\tau$ :

$$\tau = \frac{F_s}{A_0}$$

▼ Shear strain  $\gamma$ :

$$\gamma = \frac{\Delta x}{h_0}$$

▼ Shear modulus  $G$  (Elastic isotropic materials):

$$G = \frac{E}{2(1 + \nu)}$$

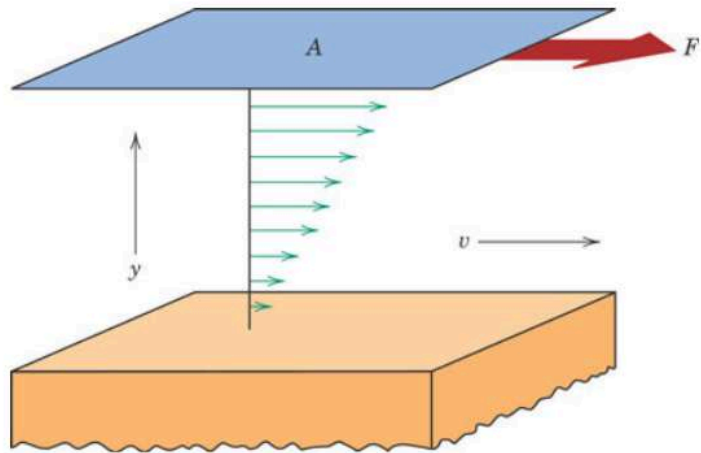
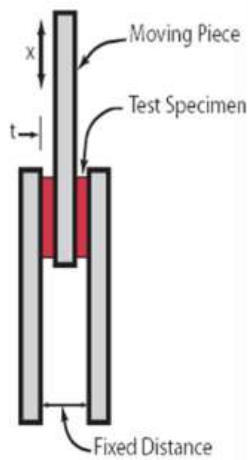
▼ Hooke's law

$$\tau = G\gamma$$

▼ Theoretical critical shear stress  $\tau_{th}$ :

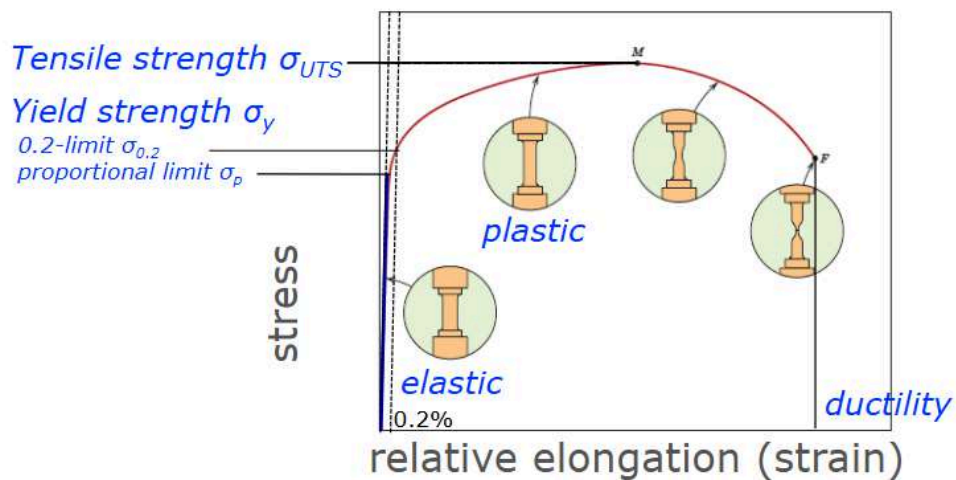
$$\tau_{th} = \frac{G}{20}$$

▼ Example of shear test



▼ Tensile testing

Elastic behavior is reversible, while plastic behavior is not.



$\sigma_p$ , the last stress value in the elastic region  
 $\sigma_{0.2}$ , stress value at intersection of stress-strain curve  
 and  $\sigma = E(\epsilon + 0.002)$   
 $\sigma_{UTS}$ , tensile strength or fracture strength

- $\sigma_p$ , proportional limit, the last stress value in the elastic region
- $\sigma_y$ , yield strength, can be considered proportional limit if  $y$  is not defined



- $\sigma_{0.2}$ , stress at 0.2-limit, stress value at the intersection of the stress-strain curve, and  $\sigma = E(\epsilon + 0.002)$
- $\sigma_{UTS}$ , tensile strength (or fracture strength), highest strength measured
- It's important to note that even after yielding, the elastic strain continues to increase (entering plastic region does not mean elastic strain stops)
- ductility or maximal strain before fracture is the last value of strain
- Resilience, is the area under the flow curve in the elastic region has unit of Pa

#### ▼ Theoretical yield strength

In most cases, the theoretical yield strength is larger than the real yield strength, and in these cases, defects are expected at the theoretical yield strength. Elastomers do not follow this since their theoretical yield strength is lower than their actual yield strength.

$$\sigma_{th} = E/20$$

#### ▼ Tensile properties

##### ▼ Ductility

Otherwise known as the amount of strain to fracture,  $\epsilon_f$

Shows the ability for shape changes without fracture

The opposite is known as brittleness

- Strain to fracture  $\epsilon_f$

Brittle for  $\epsilon_f < 0.1\%$

Ductile for  $\epsilon_f > 10\%$

Super-plastic for  $\epsilon_f \approx 1000\%$

- Depends on:

Material, temperature and crystal structure (number of slip systems)

##### ▼ Toughness

Otherwise known as the area under stress-strain curve up to the point of fracture.

Gives us the necessary mechanical work until fracture.

Shows the resistance to fracture

Brittle materials are less tough

Toughness can be expressed in any of the following units,

$$1 \frac{J}{m^3} = 1 \frac{Nm}{m^3} = 1 \frac{N}{m^2} = 1Pa$$

### ▼ Resilience (modulus of resilience)

Otherwise known as the area under the stress-strain curve before yielding. Gives us the necessary mechanical work until yielding.

Shows stored energy density in the elastic region

- Energy the material can absorb without yielding (unit is Pascal):

$$\frac{\sigma_y^2}{2E}$$

Materials with the ability to absorb energy and remain elastic have a high resilience, therefore have a high  $\sigma_y$  and a low  $E$

Resilience can be expressed in any of the following units,

$$1 \frac{J}{m^3} = 1 \frac{Nm}{m^3} = 1 \frac{N}{m^2} = 1Pa$$

## Strengthening

### ▼ Strengthening mechanisms

There are multiple ways of strengthening here's a couple:

- Increase resistance against plastic deformation
- Affect the mobility of dislocation
- Create obstacles for dislocation movement

Pores and vacancies do not contribute to the strength.

Lattice defects are obstacles for dislocation motion.

	Defect	Strengthening mechanism
0D	Solute atoms	Solid solution hardening
1D	Dislocations	Work hardening
2D	Grain or phase boundaries	Grain boundary strengthening
3D	Precipitates	Precipitation hardening

Depending on temperature, chemical composition, crystal structure and microstructure:

$$\sigma_y = \sigma_0 + \Delta\sigma_{ss} + \Delta\sigma_{disl} + \Delta\sigma_{gb} + \Delta\sigma_{prec}$$

### ▼ Work-hardening or strain-hardening

Dislocation density increases with plastic deformation

The glide of mobile dislocations is hindered by other dislocation

Strengthening effect:

$$\sigma = \sigma_0 + \sigma_{\text{disl}}$$

$$\sigma_{\text{disl}} = M\alpha Gb\sqrt{\rho}$$

$M$ , Taylor factor

$\alpha$ , Interaction coefficient

$G$ , Shear modulus

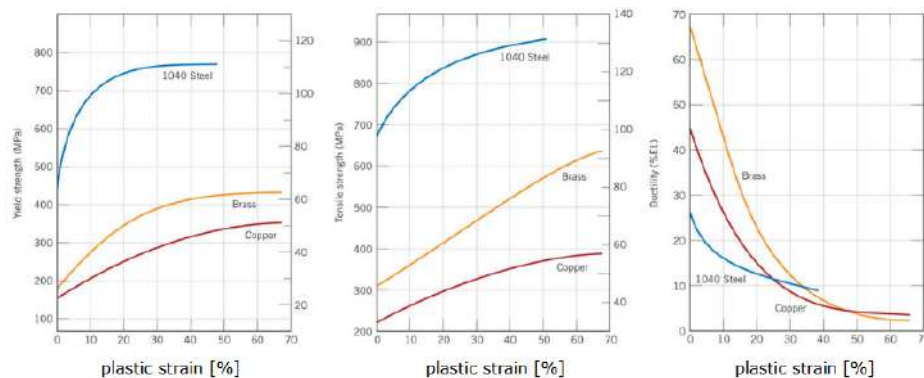
$b$ , Burgers vector

$\rho$ , Dislocation density

Work hardening from increased dislocation density

Ductility is reduced

▼ Examples of Mechanical properties after pre-deformation

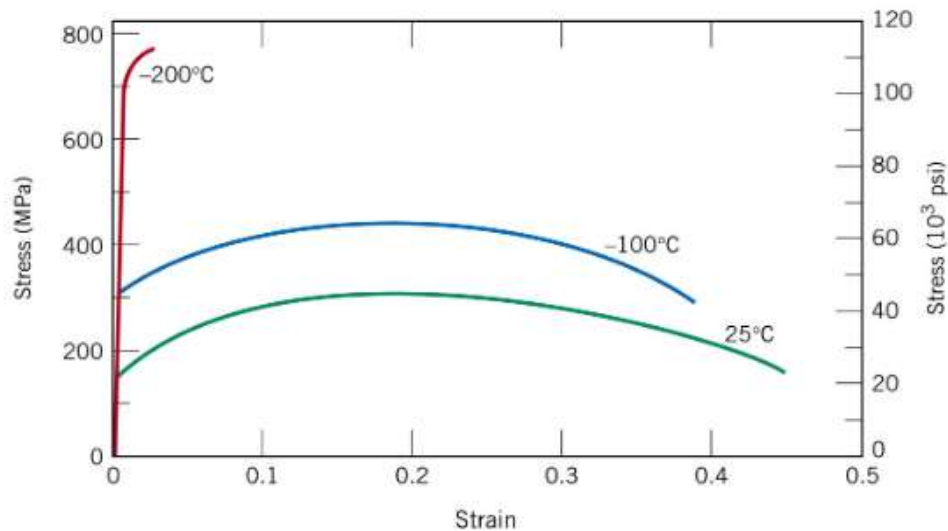


Where the plastic strain [%] is the plastic strain from pre-deformation

▼ Dependence on temperature

In general with increasing temperature:

- Strength decreases
- Ductility increases



#### ▼ Grain boundary strengthening

Dislocations cannot pass the grain boundary and therefore accumulate at the grain boundaries and the stress concentrates at the grain boundaries

The internal stress affects the plastically undeformed neighbor grain and activates slip systems

Hall-Petch relation:

$$\sigma = \sigma_0 + \Delta\sigma_{gb}$$

$$\Delta\sigma_{gb} = \frac{k_y}{\sqrt{D}}$$

$k_y$ , Denotes the Hall-Petch coefficient  
 $D$ , Is the grain size

Strengthening by grain refinement → Nanoscale structures

The grain refinement improves strength, but does not impair toughness

#### ▼ Strengthening in alloys

Often in 2 metal alloys even if individually both metals have lower tensile strength their mixture will have a higher tensile strength, the same thing can be said about yield strength.

One thing that isn't better when there is a mixture of those metals is their ductility, it will be lower for alloys than the individual metals.

#### ▼ Particle strengthening with coherent particles

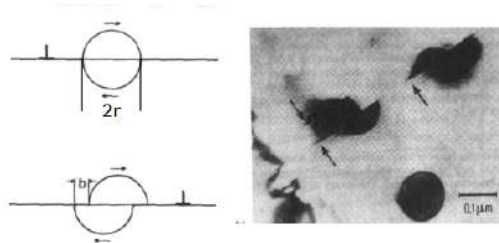
Dislocations can intersect coherent precipitates, where they create an interface with energy  $\gamma$

$$\Delta\sigma_{\text{pcoh}} = \frac{\gamma r}{l + 2r}$$

$r$ , Is the particle radius

$l$ , Is the particle distance

$\gamma$ , Is the interface energy



#### ▼ Particle strengthening with incoherent particles

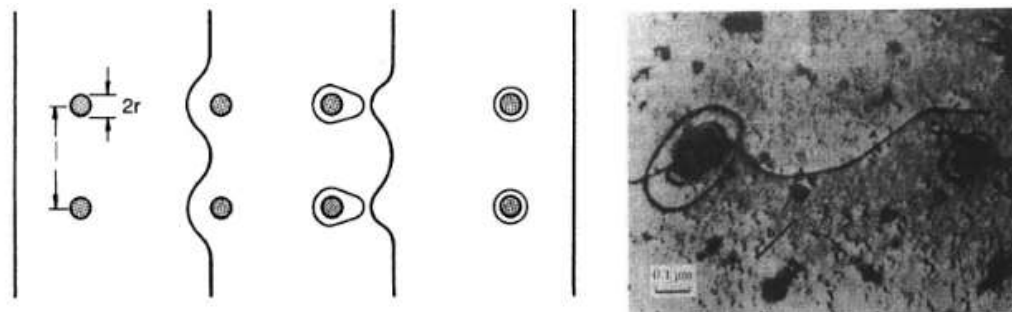
Dislocations cannot intersect incoherent particles, instead they circumvent precipitate (Orowan mechanism)

$$\Delta\sigma_{\text{pincoh}} = \frac{Gb}{l}$$

$G$ , Is the shear modulus

$b$ , Is the Burgers vector

$l$ , Is the particle distance



#### ▼ The 4 mechanical properties

Highest level	Stiff	Strong	Hard	Ductile
Lowest level	Compliant	Weak	Soft	Brittle
	Elastic behavior	Tensile strength	Hardness	Toughness

Note that toughness doesn't only depend on ductility.

#### ▼ Hardness

Otherwise known as the resistance of materials to (localized) plastic deformation.

Hardness is measured with the indentation of the diamond indenter with a given force since diamond is the hardest of all materials.

Qualitatively we measure hardness with the Mohs scale to see which materials scratch others

Quantitatively we measure hardness value from the size of indentation marks on the material

#### ▼ Hardness testing

Vickers hardness:

$$HV = 2 \sin 68^\circ \times \frac{P}{d_1^2} = 1.854 \times \frac{P}{d_1^2}$$

$$HV = 0.1891 \times \frac{F}{d_1^2}$$

$P$ , Is the force applied in kgf (kp)

$F$ , Is the force applied

$d_1$ , Is the size of diagonal left imprinted

Brinell's Hardness:

$$HB \approx 0.95 \times HV$$

Relation between Brinell hardness and tensile strength

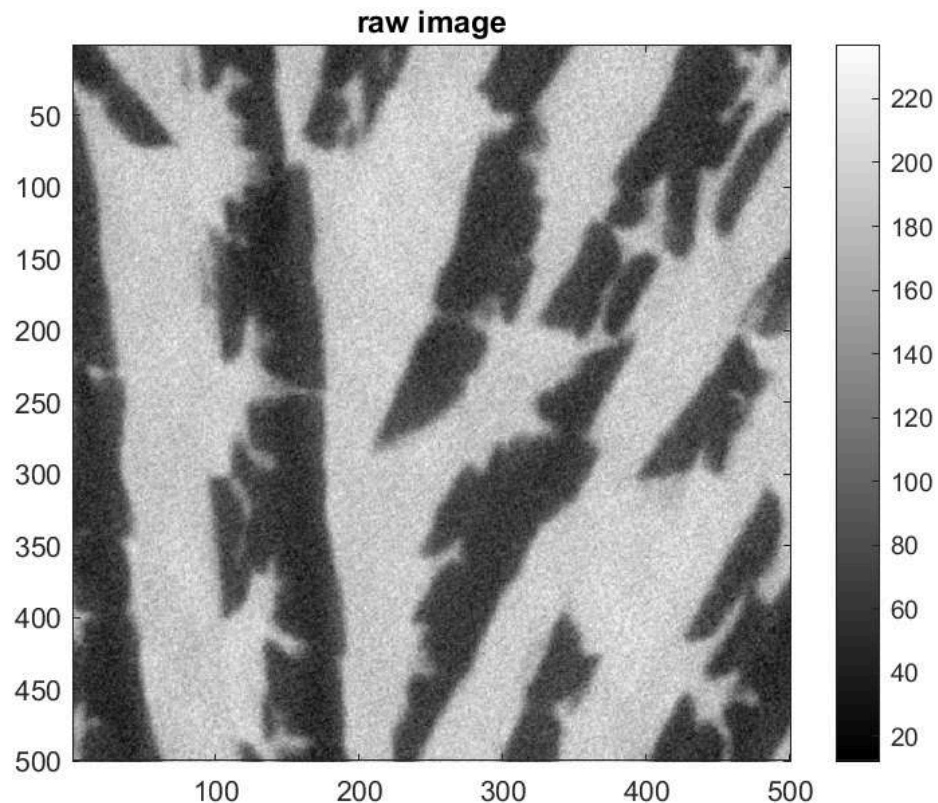
$$UTS \approx c_{\text{emp}} HB$$

## Quantitative 3D imaging

#### ▼ Segmentation

Segmentation is useful for analyzing, visualizing, and measuring the given data. For example, a digital image is made up of just numbers. For x-ray tomography it is related to how absorbing the material "in" each voxel is. And we decide how those numbers are mapped to colors on screen.

#### ▼ Raw x-ray tomography example



#### ▼ Pixel vs Voxel

2D images consist of Pixels (picture elements), while 3D images consist of voxels (volume elements).

Voxel sizes are given like  $[X \ Y \ Z]$ .

#### ▼ Threshold segmentation

Segmenting the data into different values means we must define regions for each phase far from an interface. To do this we find the mean of bright and dark phase samples and find the mean of that

#### ▼ Data filtering (noise reduction)

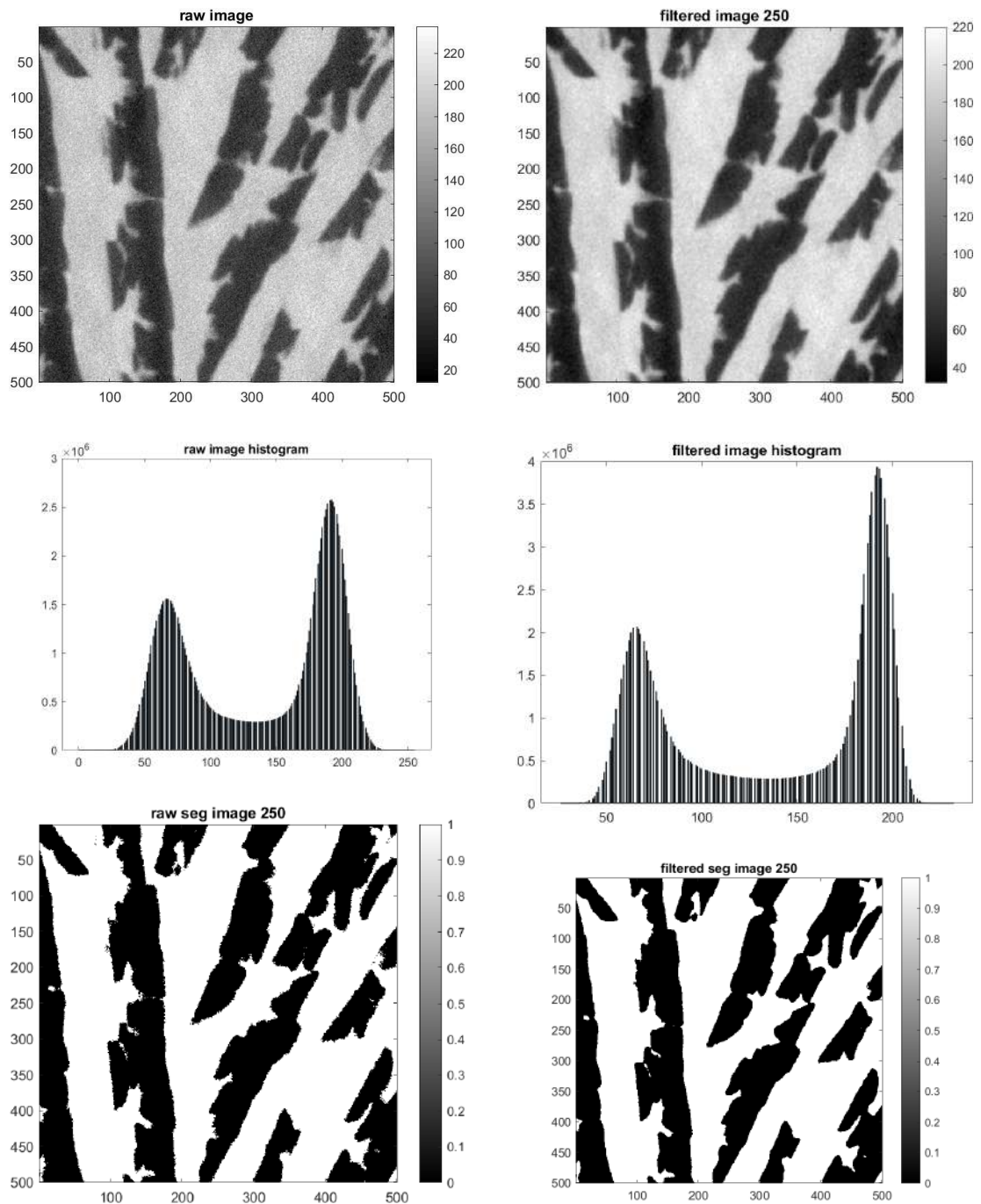
We assume that neighbouring voxels are likely to be the same phase, so instead of looking at the intensity of one voxel, we consider all the intensity values in a neighbourhood around the voxel

To reduce the noise of raw images, we use a median filter on the data.

#### ▼ MATLAB code

```
B = medfilt3(vol,[3,3,3],"symmetric");
```

#### ▼ Example before and after filtering



As you can see, without noise reduction the data would be 'fuzzier'

All data filters have drawbacks, like the removal of small features and rounding of sharp edges

To have the best result, we should always:

- Apply the least intrusive filter that allows us to segment the data, don't apply a filter if it isn't necessary (a small filter is often useful and sufficient)



- Understand the properties of the filter we are using (make sure we aren't removing important structural features)

## Electrical and Thermal properties

### ▼ Basic definitions (electrical)

$$V = RI$$

Resistance,  $R$   
 Electric potential,  $V$   
 Electric current,  $I$

Units:  $\Omega$  ( $V/A$ )  
 Units: Volt  $V$  ( $J/C$ )  
 Units: Amperes  $A$  ( $C/s$ )

$$C = 1/R$$

Conductance,  $C$

Units:  $\Omega^{-1}$

$$J = I/A$$

Current density,  $J$   
 Area,  $A$

Units:  $A/m^2$   
 Units:  $m^2$

$$\varepsilon = V/l$$

Electric field intensity,  $\varepsilon$   
 Length,  $l$

Units:  $V/m$   
 Units:  $m$

### ▼ Ohm's law defining a linear relation

$$J = \varepsilon/\rho = \sigma\varepsilon$$

$$\rho = RA/l$$

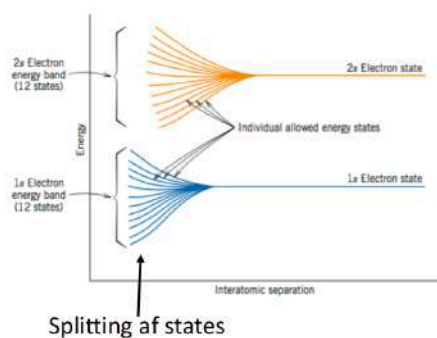
Resistivity,  $\rho$ Units:  $\Omega m$ 

$$\sigma = 1/\rho$$

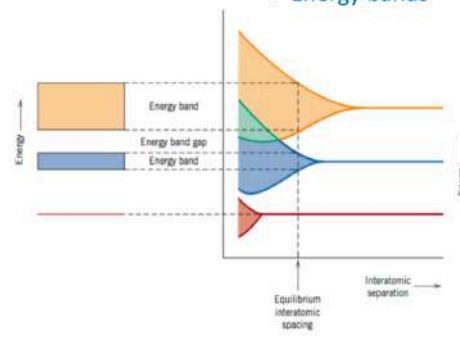
Conductivity,  $\sigma$ Units:  $\Omega^{-1} m^{-1}$ 

## ▼ Energy bands

Bohrs model for 12 atoms

Bohrs model for  $N_A$  atoms

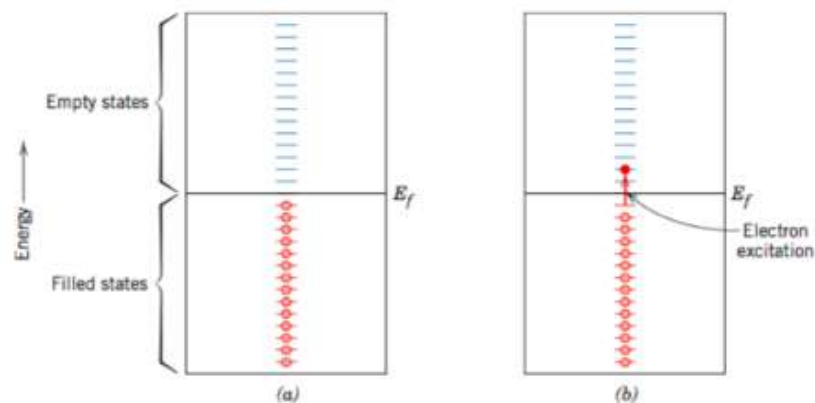
=&gt; Energy bands



## ▼ Fermi energy and thermal excitation (position of 'holes' and electrons)

- Metal:

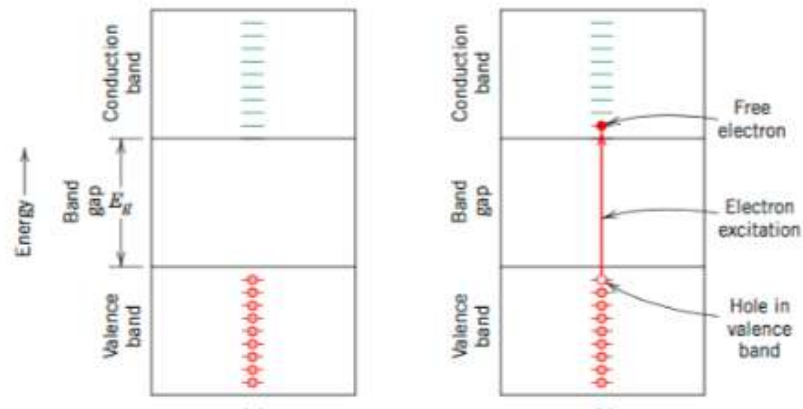
$$\sigma \approx 10^7 (\Omega m)^{-1}$$



- Insulator:

$$\text{Band gap} > 2eV$$

$$\sigma \approx 10^{-20} - 10^{-10} (\Omega m)^{-1}$$



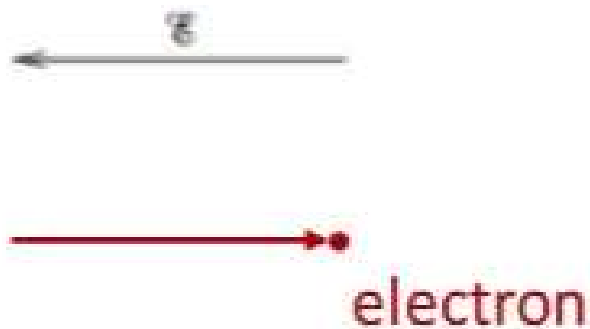
- Semiconductor:

$$\text{Band gap} < 2eV$$

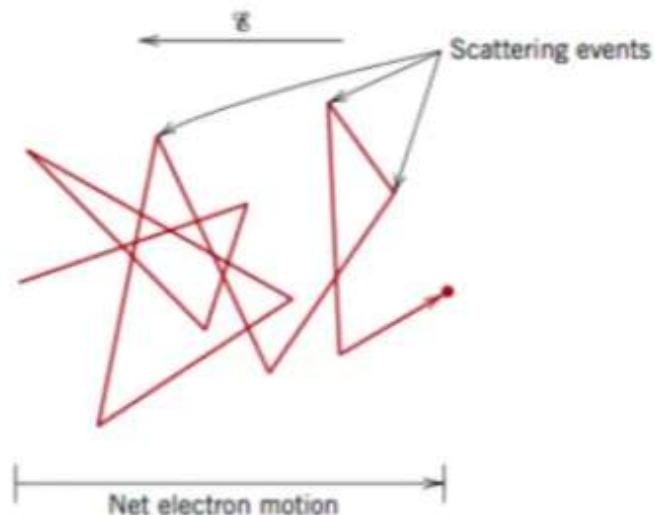
$$\sigma \approx 10^6 - 10^4 (\Omega m)^{-1}$$

#### ▼ Cause of Resistance

In a perfect crystal lattice the movement of the electron can look like:



However, in imperfect crystal lattices with defects like Impurities, Vacancies, Dislocations, Vibrations (heat), etc. can make the movement of the electron look like:



### ▼ Electron mobility

$$J = n|e|v_d$$

$$|e| = 1.6 \times 10^{-19} \text{ C}$$

Electron density,  $n$   
Drift (net) velocity,  $v_d$

Units:  $m^{-3}$   
Units:  $m/s$

$$v_d = \mu_e \mathcal{E}$$

Electron mobility,  $\mu_e$

Units:  $m^2/(Vs)$

Note that  $\mu_e$  depends on scattering processes.

Ohm's law defining a linear relation can then be rewritten:

$$\sigma = J/\mathcal{E} = n|e|\mu_e$$

### ▼ Electrical resistivity of metals

As we have established previously the resistance can change depending on various factors and therefore we can write the total resistivity as:

$$\rho_{\text{total}} = \rho_{\text{temp}} + \rho_{\text{imp}} + \rho_{\text{disloc}}$$

Temperature variation:

$$\rho_{\text{temp}} = \rho_0 + aT$$

Impurity variation,

Solid state:

$$\rho_{\text{imp}} = A c_i (1 - c_i)$$

$c_i$ , denotes concentration of impurities

Two phase:

$$\rho_{\text{imp}} = V_1 \rho_1 + V_2 \rho_2$$

$V_1, V_2$ , denotes volume fractions  
 $\rho_1, \rho_2$ , resistivity of the two phases

#### ▼ Types of semiconductors

General formula for conductivity

$$\sigma = n|e|\mu_e + p|e|\mu_h$$

$n$ , is denoted by the electron density  
 $p$ , is denoted by the hole density  
 $\mu_e$  is denoted by the electron mobility  
 $\mu_h$  is denoted by the hole mobility

#### ▼ Intrinsic (pure) semiconductors

For every 'hole' (missing electron) in the lattice there exists one free electron so the intrinsic conductivity can be computed:

$$\sigma = n_i |e| (\mu_e + \mu_h)$$

$$n_i = n = p$$

$n_i$ , is denoted by intrinsic carrier concentration

#### ▼ Extrinsic (doped) semiconductors: n-type

For every 'hole' (missing electron) in the lattice there exists more than one free electron so the extrinsic conductivity can be computed:

$$\sigma = n |e| \mu_e$$

$n$ , is denoted by the concentration of donors

#### ▼ Extrinsic (doped) semiconductors: p-type

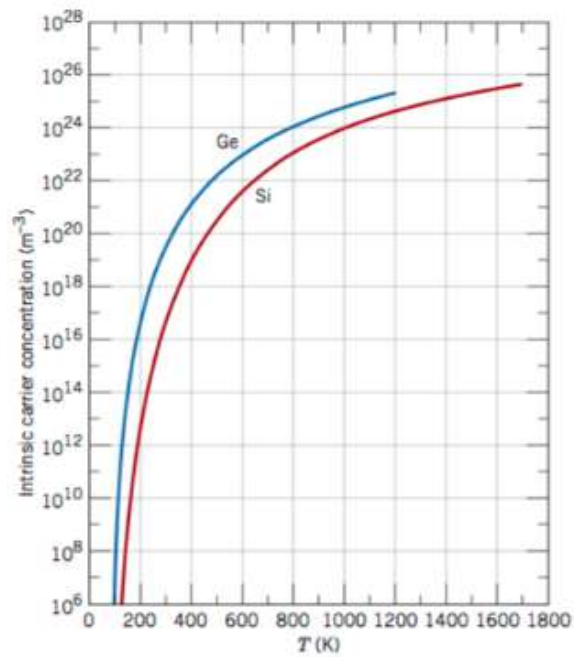
For every 'hole' (missing electron) in the lattice there exists less than one free electron so the extrinsic conductivity can be computed:

$$\sigma = p |e| \mu_h$$

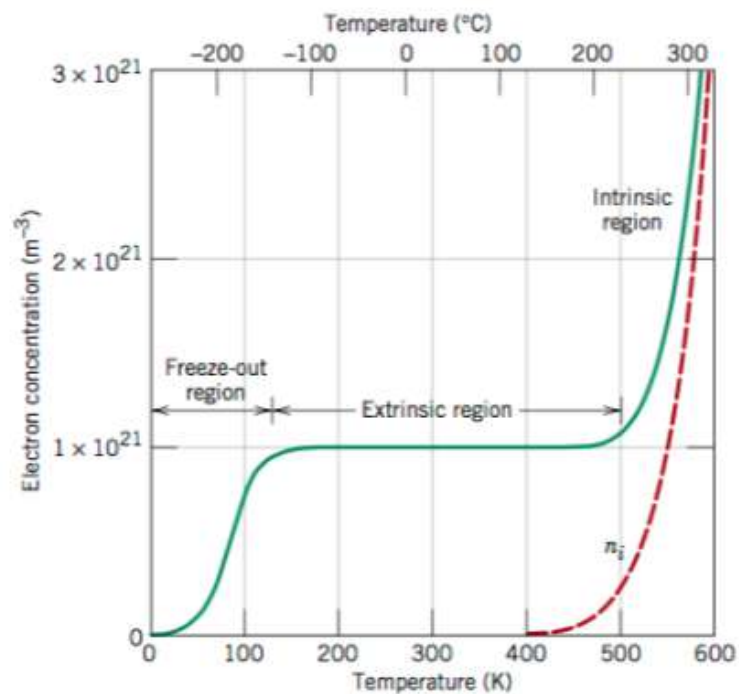
$p$ , is denoted by the concentration of holes (acceptors)

▼ Property correlations

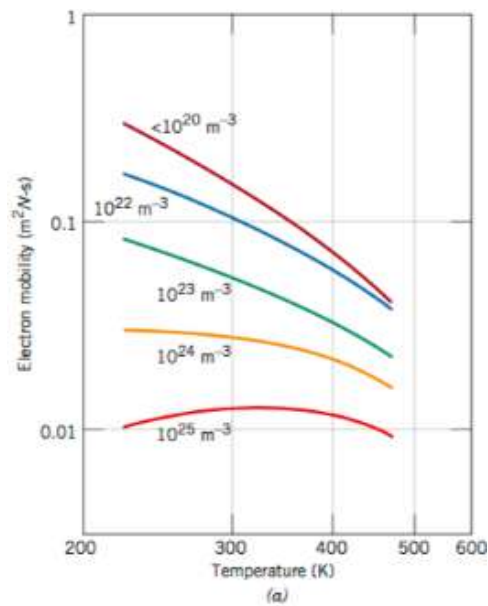
▼ Temperature and intrinsic carrier concentration



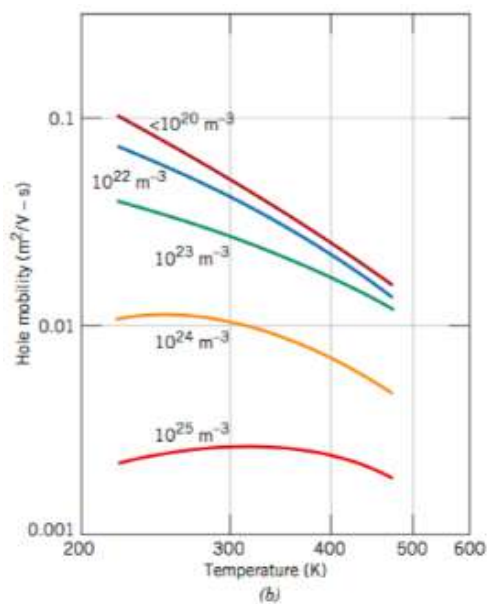
▼ Temperature and extrinsic electron concentration



▼ Temperature and electron mobility



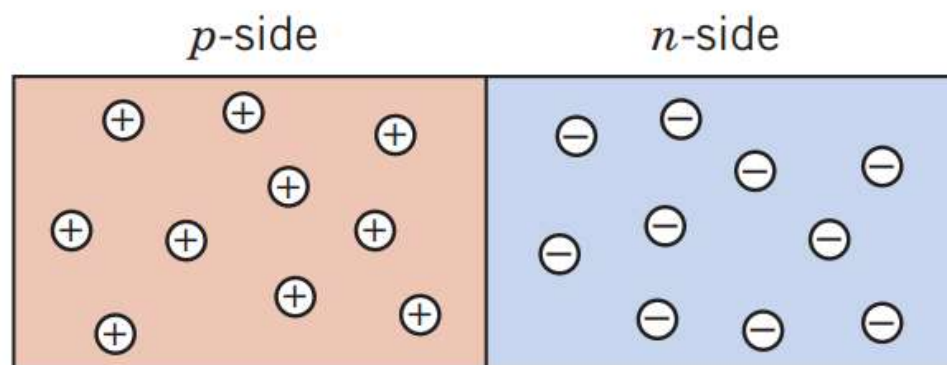
#### ▼ Temperature and hole mobility



#### ▼ Diode (or rectifier)

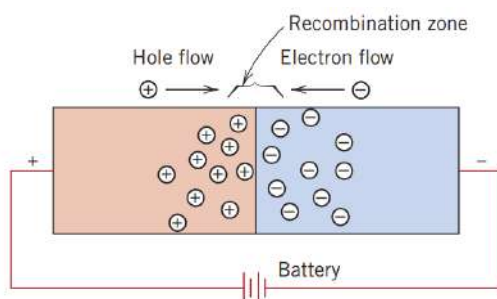
A diode is an electronic device that allows current to flow in only one direction. It's constructed from a single piece of semiconductor that is doped up as to be n-type on one side and p-type on the other.

#### ▼ Outside the circuit, the diode can look like:

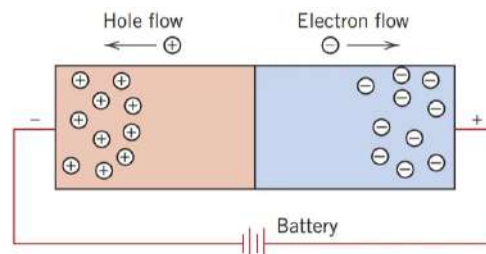


▼ On a circuit, the diode can look like:

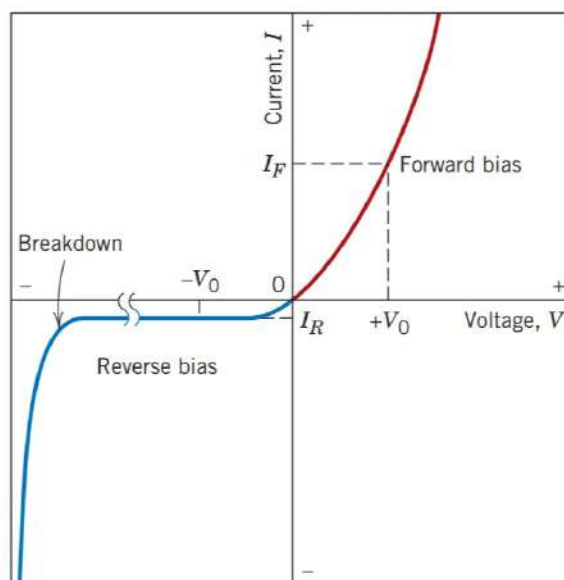
Forward bias, resulting in positive electric potential and electrical current



Reverse bias, resulting in negative electric potential and electrical current

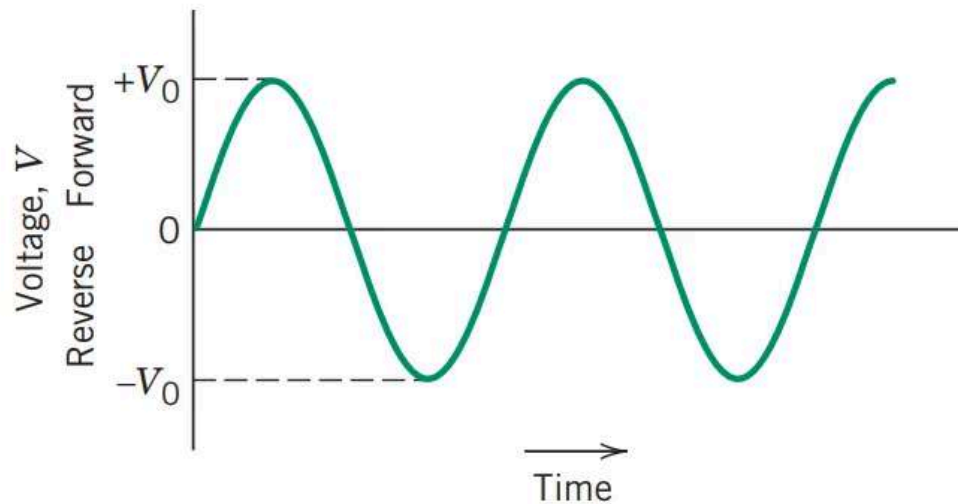


▼ The current-voltage characteristics for forward and reverse bias is:

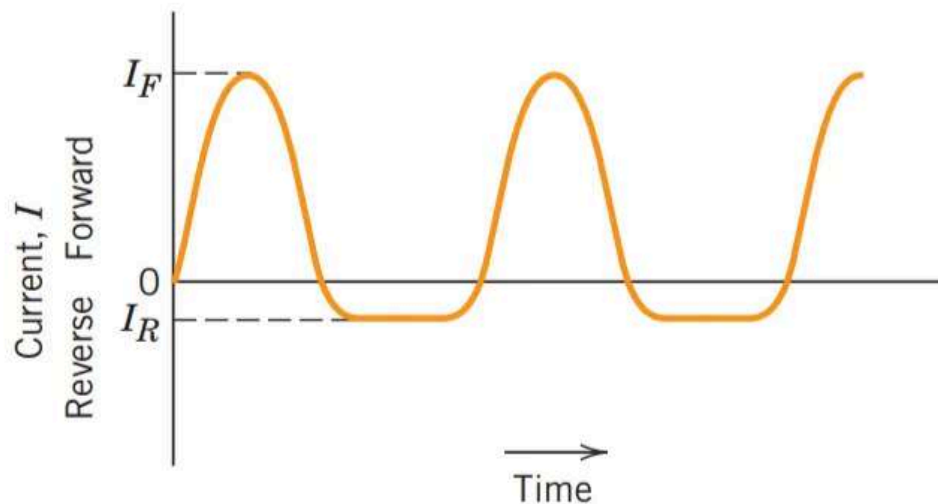


▼ Voltage vs Time





▼ Current vs Time

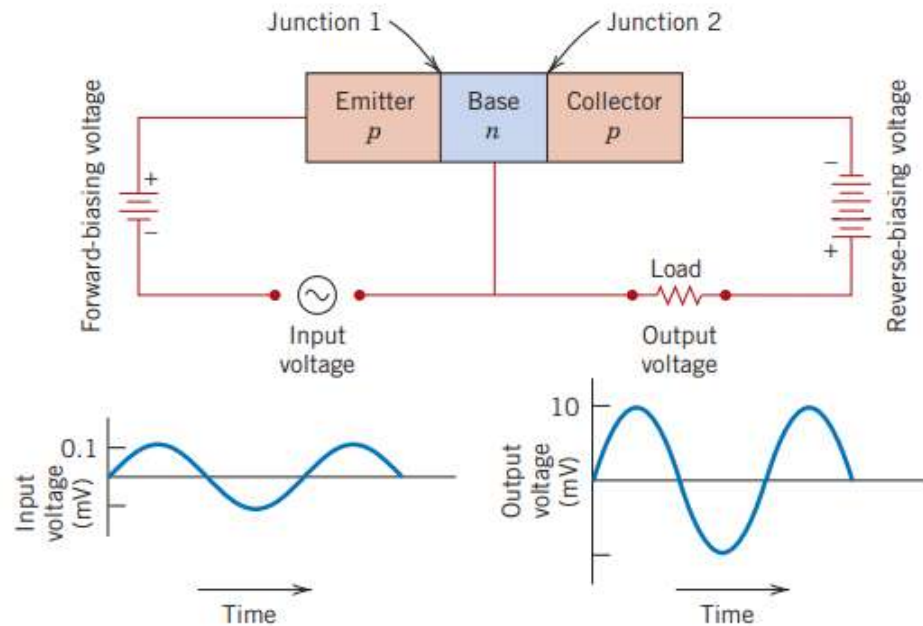


▼ Transistors

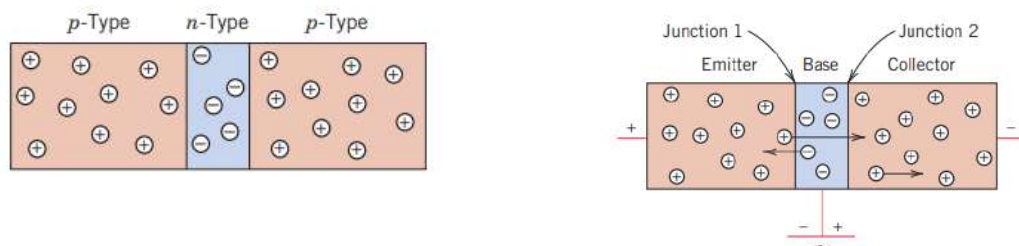
Transistors are very useful semiconducting devices capable of amplifying an electrical signal. In general we will work with *p-n-p* junction transistors.

▼ *p-n-p* junction transistor

Schematic diagram of a *p-n-p* junction transistor and its associated circuitry, including input and output voltage time characteristic showing voltage amplification.



For a junction transistor *p-n-p* type, the distributions and directions of electron and hole motion will look like the figure on the left when no potential is applied, and like the figure on the right with appropriate bias for voltage application.



#### ▼ Basic definitions (thermal)

$$C = \frac{dQ}{dT}$$

Heat capacity,  $C$

Heat,  $Q$

Temperature  $T$

Specific heat  $c_v, c_p$

Units:  $(J/(mol\ K))$

Units: Joule ( $J$ )

Units: Kelvin ( $K$ )

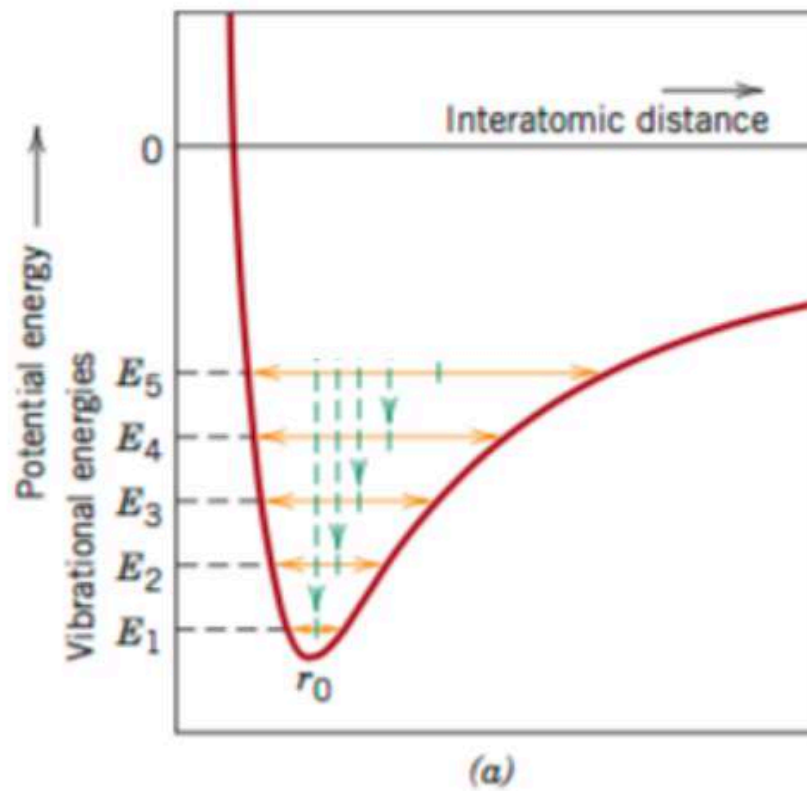
Units:  $(J/(kg\ K))$

Note that specific heat exists for a fixed volume or pressure.

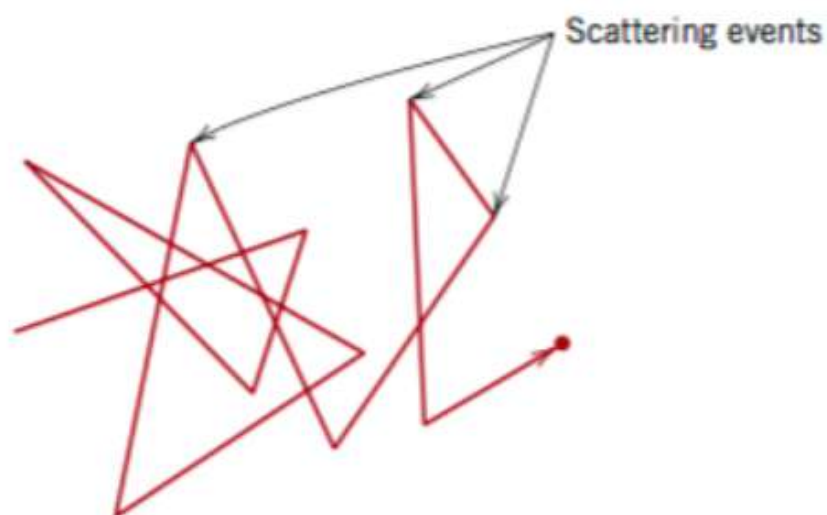
$$\Delta E = mc_p \Delta T$$

#### ▼ Capacitors

▼ Vibrational heat capacity



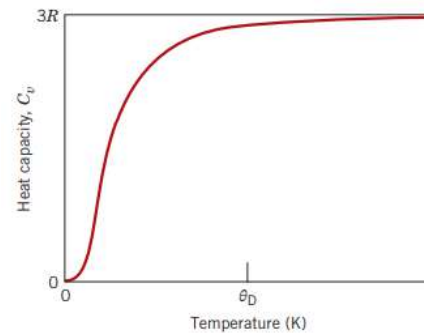
▼ Conduction electron heat capacity (only metals and only minor contribution)



▼ Vibrational heat capacity

According to Debye, the temperature dependence of the heat capacity at constant volume  $\theta_D = T_D$ , which is the Debye temperature. At low temperatures we can use:

$$C_v = AT^3$$



In general, the Heat capacity as a function of temperature is defined as,

$$C_v = 9NkT \left( \frac{T}{T_D} \right)^3 \int_0^{T_D/T} \frac{x^3}{e^x - 1} dx$$

For easier usage two approximations can be made

$$\frac{C_v}{Nk} \sim \frac{12\pi^4}{5} \left( \frac{T}{T_D} \right)^3, \text{ for } T \ll T_D$$

$$C_v \sim 3R, \text{ for } T \gg T_D$$

$R$ , is the gas constant

$$R = 8.31 J/(molK)$$

▼ Debye temperature for various materials

Aluminium	428 K	Manganese	410 K
Beryllium	1440 K	Nickel	450 K
Cadmium	209 K	Platinum	240 K
Caesium	38 K	Sapphire	1047 K
Carbon	2230 K	Silicon	645 K
Chromium	630 K	Silver	215 K
Copper	343.5 K	Tantalum	240 K
Gold	170 K	Tin (white)	200 K
Iron	470 K	Titanium	420 K
Lead	105 K	Tungsten	400 K

▼ Thermal expansion

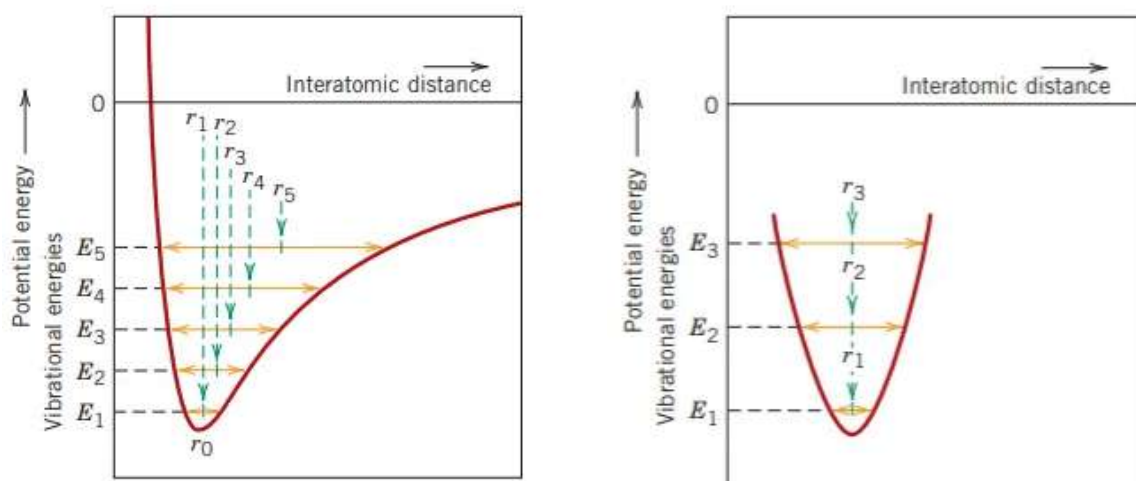
Linear expansion coefficient,  $\alpha_l$  (unit is  $K^{-1}$ ):

$$\frac{\Delta L}{L} = \alpha_l \Delta T$$

Volume expansion coefficient,  $\alpha_V$  (unit is  $K^{-1}$ ):

$$\frac{\Delta V}{V} = \alpha_V \Delta T$$

The figure on the left relates to loose bonds while the figure on the right relates to harder bonds



▼ Range of linear expansion coefficient for metals, ceramic and polymers

	Metals	Ceramics	Polymers
$\alpha_l (K^{-1})$	$5 - 25 \cdot 10^{-6}$	$0.5 - 5 \cdot 10^{-6}$	$50 - 400 \cdot 10^{-6}$

▼ Thermal stress

Thermal stress is computed using the following formula:

$$\sigma = E\alpha_l\Delta T$$

▼ Heat loss

Using the following equation we get heat loss

$$\frac{dQ}{dt} = qAt$$

$\frac{dQ}{dt}$ , denotes the heat loss  
 $q$ , denotes the heat flux  
 $A$ , denotes the cross sectional area

▼ Transport of heat

Using Ficks first law for a steady state heat flow is computed as,

$$q = -k \frac{\Delta T}{\Delta x}$$

Heat flow,  $q$   
 Thermal conductivity,  $k$

Units:  $(W/m^2)$   
 Units:  $(W/(mK))$

Only use the minus when working with vector directions or coordinate systems. The minus sign ensures that heat flows from higher to lower temperature.

For several carriers of heat the thermal conductivity is computed as,

$$k = k_{\text{lattice}} + k_{\text{electron}} \quad (\text{plus convection and radiation})$$

### ▼ Thermal properties

#### ▼ Table of thermal properties

	Lorenz number			
Material	$c_p$ (J/kg·K) <sup>a</sup>	$\alpha_l$ [(°C) <sup>-1</sup> × 10 <sup>-6</sup> ] <sup>b</sup>	$k$ (W/m·K) <sup>c</sup>	$L$ [Ω·W/(K) <sup>2</sup> × 10 <sup>-8</sup> ]
Metals				
Aluminum	900	23.6	247	2.20
Copper	386	17.0	398	2.25
Gold	128	14.2	315	2.50
Iron	448	11.8	80	2.71
Nickel	443	13.3	90	2.08
Silver	235	19.7	428	2.13
Tungsten	138	4.5	178	3.20
1025 Steel	486	12.0	51.9	—
316 Stainless steel	502	16.0	15.9	—
Brass (70Cu–30Zn)	375	20.0	120	—
Kovar (54Fe–29Ni–17Co)	460	5.1	17	2.80
Invar (64Fe–36Ni)	500	1.6	10	2.75
Super Invar (63Fe–32Ni–5Co)	500	0.72	10	2.68
Ceramics				
Alumina (Al <sub>2</sub> O <sub>3</sub> )	775	7.6	39	—
Magnesia (MgO)	940	13.5 <sup>d</sup>	37.7	—
Spinel (MgAl <sub>2</sub> O <sub>4</sub> )	790	7.6 <sup>d</sup>	15.0 <sup>e</sup>	—
Fused silica (SiO <sub>2</sub> )	740	0.4	1.4	—
Soda-lime glass	840	9.0	1.7	—
Borosilicate (Pyrex™) glass	850	3.3	1.4	—

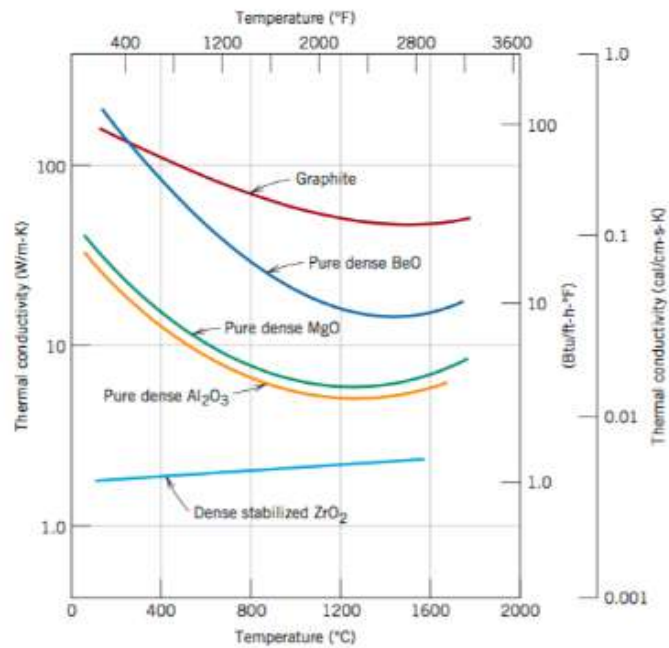
#### ▼ Thermal properties for metals

Since in metals they have the same carrier for both heat and electricity, the following ratio is constant.

$$L = \frac{k}{\sigma T}$$

#### ▼ Thermal properties for ceramics

Since in ceramics, only phonons are carriers we can see a very different graph of thermal conductivity and temperature



It's important to note that porosity in ceramic materials may have a dramatic effect on thermal conductivity. Under most circumstances, increasing the pore volume results in a reduction of the thermal conductivity.

▼ General table with both electrical and thermal properties

	ELECTRICAL CONDUCTIVITY $\Omega^{-1} \text{ m}^{-1}$	SPECIFIC HEAT $\text{J}/(\text{kg K})$	THERMAL CONDUCTIVITY $\text{W}/(\text{mK})$
<b>METALS</b>	$2 \cdot 10^6 - 10^8$	$10^2 - 10^3$	10-400
<b>CERAMICS</b>	$10^{-9} - 10^{-15}$	$6 \cdot 10^2 - 10^3$	1-50
<b>SEMICONDUCTORS</b>	$10^{-4} - 10^4$	$10^2 - 10^3$	100
<b>POLYMERS</b>	$10^{-10} - 10^{-15}$	$10^3 - 2 \cdot 10^3$	0.1-0.2

Role	Electrons	Phonons
Transport charge?	Yes	No
Transport heat?	Yes (in metals)	Yes (mainly in insulators)
Cause resistance?	No	Yes scatter electrons

## Phase diagrams

▼ Phases and solubility



Phase is defined as the homogeneous part of a system, i.e., having equal and unique chemical and physical properties.

- Gas  $\rightarrow$  Liquid  $\rightarrow$  Crystalline or Amorphous solid
- Single solid phase materials (Isomorphism)
- Several solid phase materials (Allotropy, Polymorphism)

The solubility limit is the maximum concentration of A in B

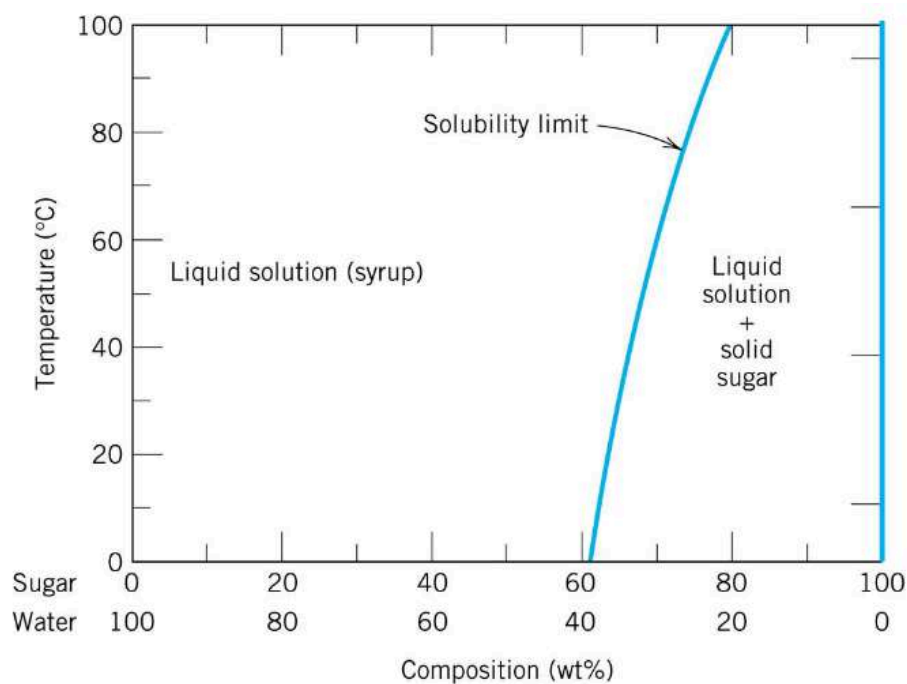
#### ▼ Material properties

- Number of phases
- Chemical composition and crystal structure of each phase
- Phase fraction (mass or volume fraction)
- Size and spatial arrangement of phases

#### ▼ Phase diagrams

Graphical representation of phases as a function of the temperature and chemical composition.

##### ▼ Sugar-Water phase diagram example



##### ▼ Characteristics of equilibrium phase diagrams

- Represent the state of lowest energy (Gibbs energy  $G$ )
- Show phases in equilibrium

- Do not show how much time is required for attaining equilibrium

Note: in the case where equilibrium is never obtained (for assessable time) we refer to this as the Metastable state (non-equilibrium)

#### ▼ Lever rule for mass fractions

Sum of mass fractions:

$$1 = W_{\alpha} + W_L$$

Average composition (with conservation of mass):

$$c_0 = c_{\alpha}W_{\alpha} + c_LW_L$$

Lever rule:

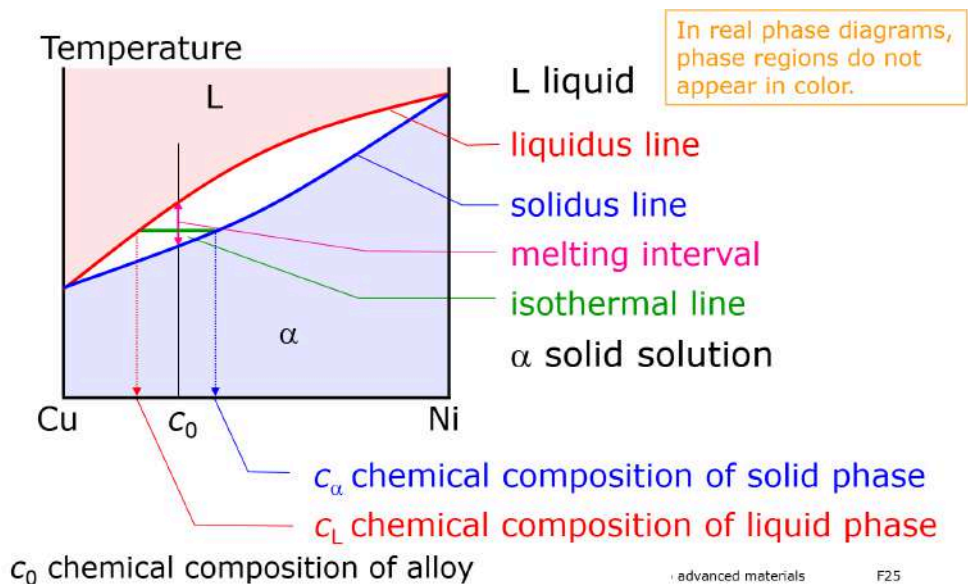
$$W_{\alpha} = \frac{c_0 - c_L}{c_{\alpha} - c_L} = \frac{R}{S + R}$$

$$W_L = \frac{c_{\alpha} - c_0}{c_{\alpha} - c_L} = \frac{S}{S + R}$$

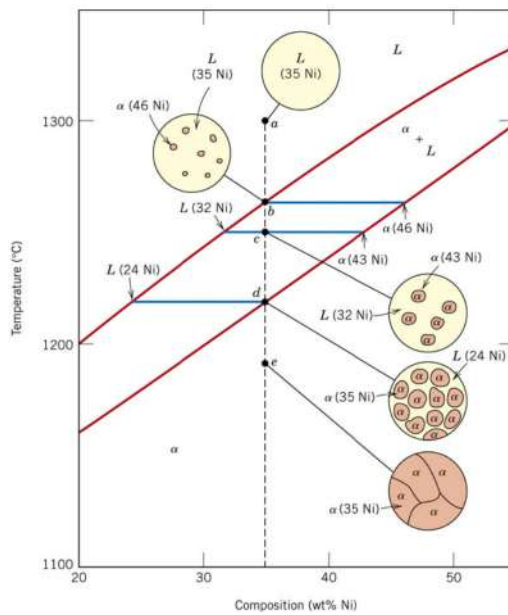
$$W_LR = W_{\alpha}S$$

#### ▼ Isomorphous binary system (complete solubility)

##### ▼ Example of phase diagram



##### ▼ Microstructure - equilibrium cooling



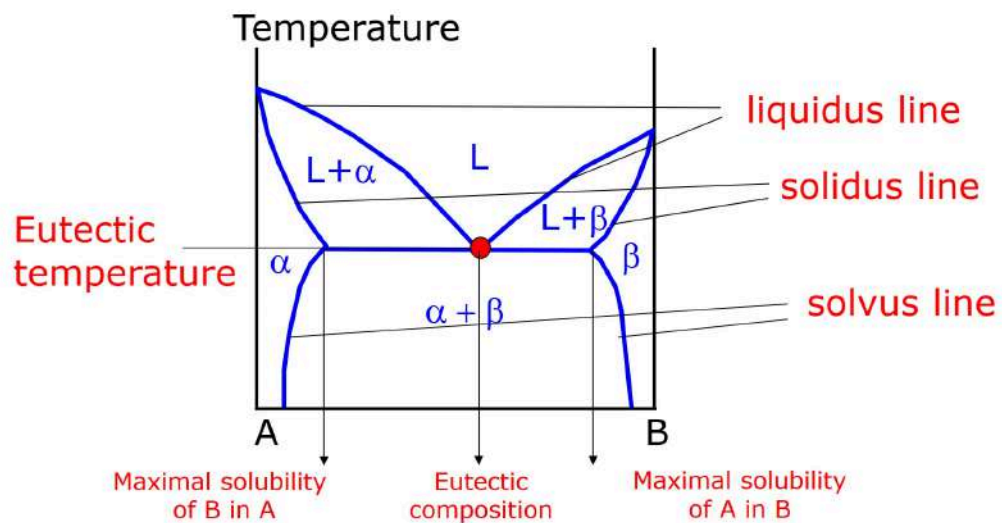
Extremely slow cooling of the material

During solidification, there is a change of composition of the phases by atomic motion (diffusion)

Diffusion depends on time and temperature (faster at higher temperatures)

▼ Binary eutectic systems (limited solubility in the solid state)

▼ Example of phase diagram



▼ Gibbs phase rule

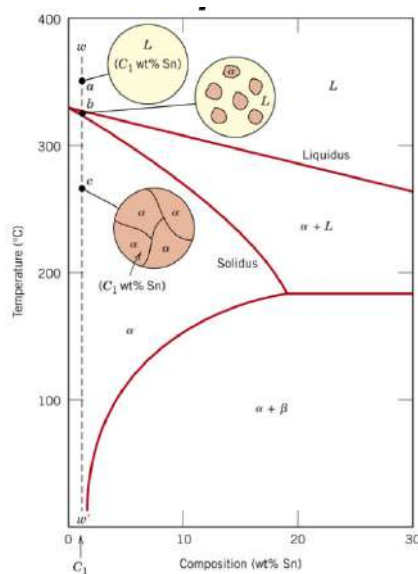
$$df + pe = nc + 1$$

df, is defined as the number of degrees of freedom

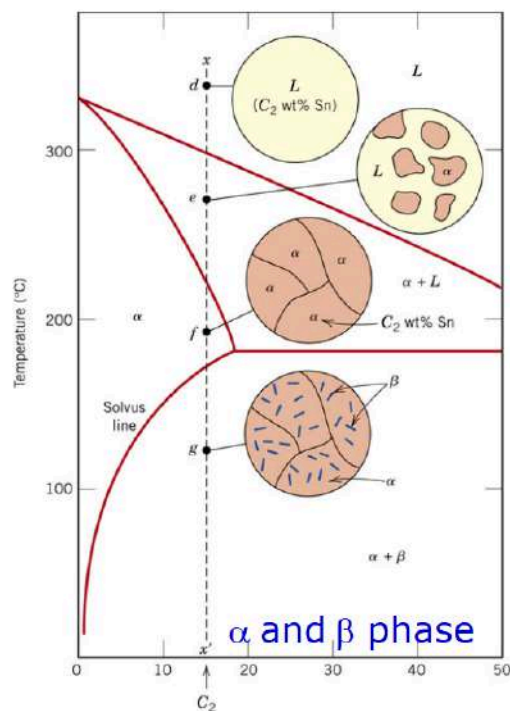
pe, is defined as the number of phases in equilibrium

nc, is defined as the number of constituents

▼ Microstructure

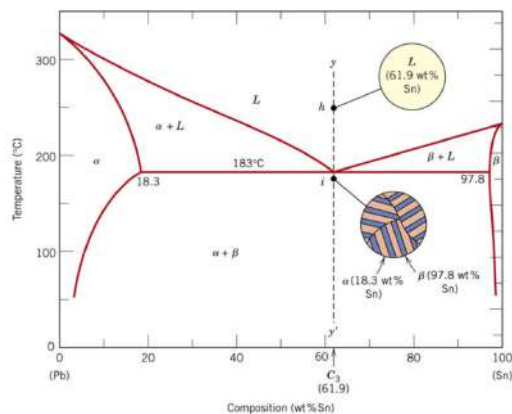


The entire content of B is soluble in  $\alpha$   
Single phase  $\alpha$  or (A) as in an isomorphous system.



The entire content of element B is soluble in  $\alpha$  at a higher temperature, but not at RT.

Precipitates of  $\beta$  phase in  $\alpha$  matrix at RT.



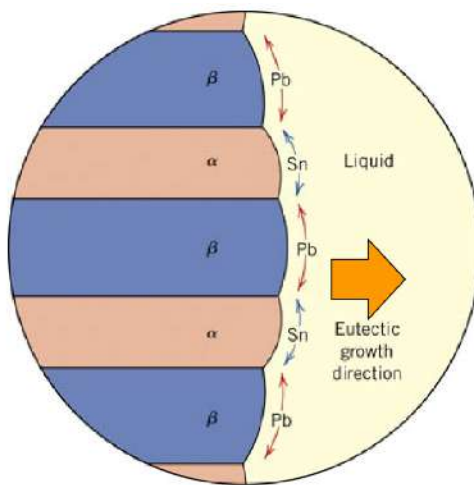
Lamellar structure: alternating layers of  $\alpha$  and  $\beta$ .

The distance between lamellae depends on the cooling rate.

Properties depend on the distance between lamellae.

Slow solidification - wide lamellae

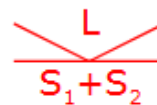
Fast solidification - thin lamellae



### ▼ Characteristic points

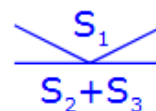
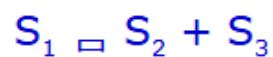
#### ▼ Eutectic

eutectic

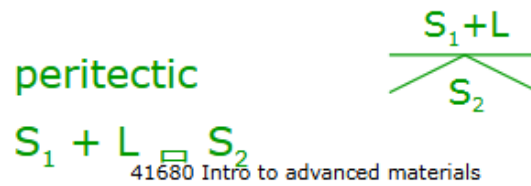


#### ▼ Eutectoid

eutectoid



#### ▼ Peritectic



## Simulation

### ▼ Reasoning behind modeling and simulation

- Avoiding trial and error,

Since creating the object could be expensive, predicting failure in rare events (Like earthquakes or typhoons) helps reduce trial and error.

- Optimizing design parameters,

In the case that the material is expensive, reducing it while keeping the safety standards is optimal

### ▼ Components of a simulation

- Geometry (Tetrahedral mesh, grid)
- Material properties (Thermal conductivity, density)
- Physics models (mathematics, partial differential equations)
- Boundary conditions (limiting ourselves to a certain domain, consequences of the material at the boundaries)
- Solver (How to solve the equations on the model)

### ▼ Heat equation

Describes how the distribution of heat changes in a solid medium with time

$$\frac{\partial u}{\partial t} = \alpha \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right)$$

### ▼ Heat equation notation

$u$ , is defined as the temperature

$t$ , defined as time

$(x, y, z)$ , defined as spatial coordinates

$\frac{\partial u}{\partial t}$ , defined as the change in temperature with time

$\alpha$ , is a material parameter defined as the thermal diffusivity

$$\alpha = \frac{k}{c\rho}$$

$k$ , is defined as the thermal conductivity

$c$ , is the specific heat capacity

$\rho$ , is the density of the material

Whenever the second derivative is non-zero the temperature changes ( $\frac{\partial u}{\partial t}$  is non-zero). i.e. where the curvature of the temperature with space is large.

In a steady state solution (no change with time), the right-hand side is zero everywhere.

If the average temperature in the surroundings is higher, then the material heats up.

If the average temperature is lower, then the material cools down.

Alternatively, the Laplacian differential operator ( $\nabla^2 u$ ) is used for compact notation (can be used as a generalization of the second derivative to  $n$  dimensions).

$$\left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right) = \nabla^2 u$$

#### ▼ Solutions to the heat equation

In partial differential equations, infinitely many solutions exist, to arrive at the wanted solution, we use constraints such as,

- The initial state of the system
- The boundary conditions (what happens at the edges of the simulation domain)
- Dirichlet boundary conditions,  $u = f$  (set a boundary to have a constant value temperature)
- Neumann boundary conditions,  $\frac{\partial u}{\partial n} = f$  (set a boundary to have a specific temperature gradient, the  $n$  means that it's the gradient normal to the boundary)

#### ▼ Modeling the real world

The mathematical values have direct real-world interpretations,

- In the case of Dirichlet boundary conditions,  $u = f$

Model a part of the boundary as having a set temperature that never changes. The system is in contact with something that can be considered to have a constant temperature.

- In the case of Neumann boundary conditions,  $\frac{\partial u}{\partial n} = f$

$$\frac{\partial u}{\partial n} = 0$$

We consider an ideal insulating surface to have these conditions since no heat can be transferred.

$$\frac{\partial u}{\partial n} > 0$$

We consider the surface to have these conditions when heat is introduced into the system.

$$\frac{\partial u}{\partial n} < 0$$

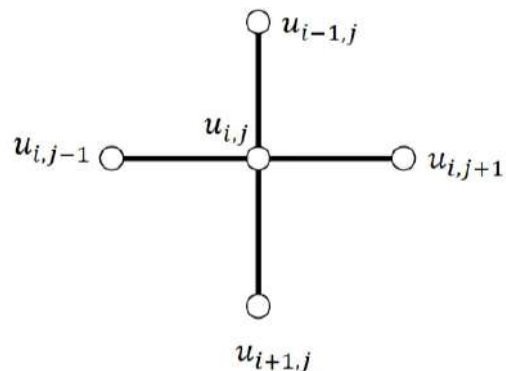
We consider the surface to have these conditions when heat is removed from the system.

#### ▼ Finite difference method

We use nomenclature for working on a grid with discrete time steps.

- Spatial discretization

To start, we define the temperature  $u_{ij}$  at all grid points  $(i, j)$ , the neighboring grid points are defined as relative to the  $u_{ij}$  depending on the boundary conditions.



- Temporal discretization

$u^n$  is the temperature at the current time step, and  $u^{n+1}$  is the temperature at the next time step.

- Spatial and temporal discretization

$u_{ij}^n$  is the temperature at the current time at the grid point  $(i, j)$ .

With this the forward differences in time is calculated as,

$$\frac{\partial u}{\partial t} \approx \frac{u_{i,j}^{n+1} - u_{i,j}^n}{\Delta t}$$

And the central differences in space as,



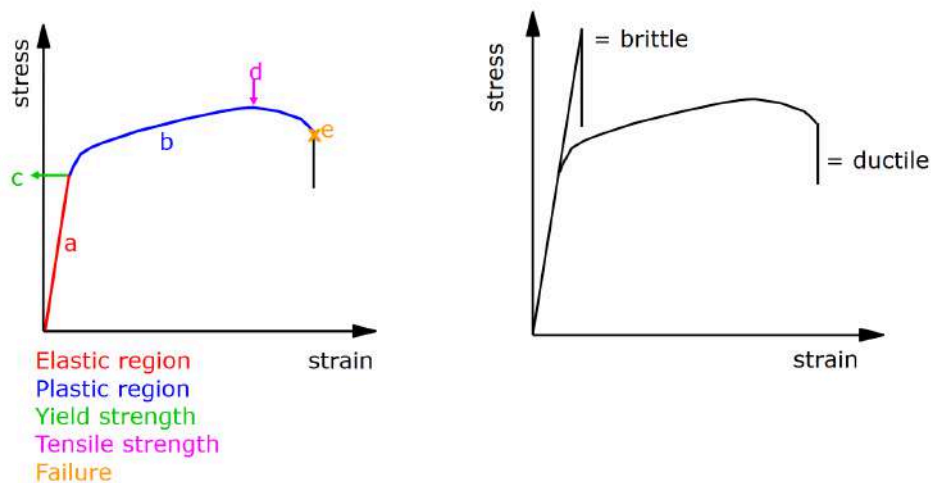
$$\begin{aligned}\frac{\partial u}{\partial x} &\approx \frac{u_{i+1,j}^n - u_{i,j}^n}{\Delta x} \\ \frac{\partial^2 u}{\partial x^2} &\approx \frac{u_{i+1,j}^n - 2u_{i,j}^n + u_{i-1,j}^n}{(\Delta x)^2} \\ \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} &\approx \\ &\approx \frac{u_{i+1,j}^n - 2u_{i,j}^n + u_{i-1,j}^n}{(\Delta x)^2} + \frac{u_{i,j+1}^n - 2u_{i,j}^n + u_{i,j-1}^n}{(\Delta y)^2}\end{aligned}$$

Putting everything together we get,

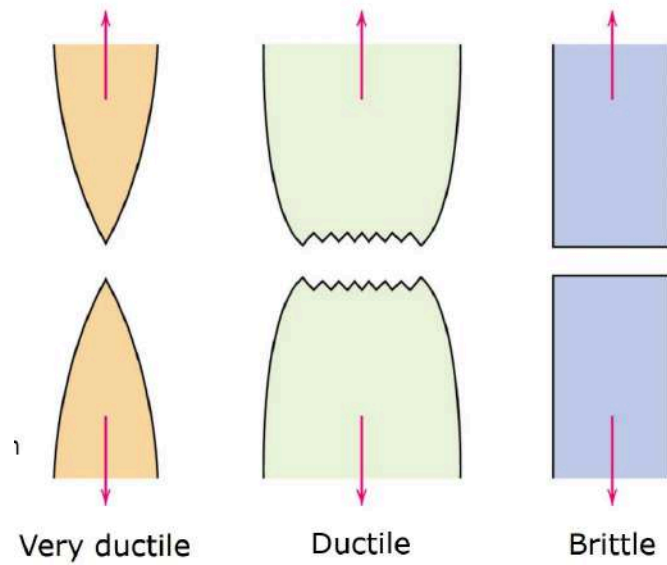
$$\begin{aligned}\frac{u_{i,j}^{n+1} - u_{i,j}^n}{\Delta t} &= \\ &= \alpha \left( \frac{u_{i+1,j}^n - 2u_{i,j}^n + u_{i-1,j}^n}{(\Delta x)^2} + \frac{u_{i,j+1}^n - 2u_{i,j}^n + u_{i,j-1}^n}{(\Delta y)^2} \right) \Leftrightarrow \\ &\Leftrightarrow u_{i,j}^{n+1} = \\ &u_{i,j}^n + \alpha \left( \frac{u_{i+1,j}^n - 2u_{i,j}^n + u_{i-1,j}^n}{(\Delta x)^2} + \frac{u_{i,j+1}^n - 2u_{i,j}^n + u_{i,j-1}^n}{(\Delta y)^2} \right)\end{aligned}$$

## Failure

### ▼ Stress-strain curve

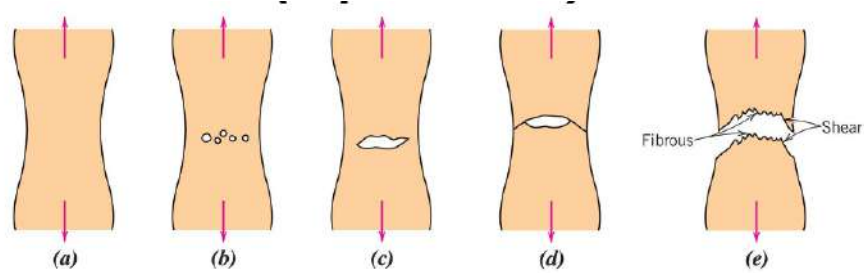


### ▼ How ductile a material is and how it will look after failure



▼ Ductile failure (cup and cone)

Different stages of failure in ductile materials

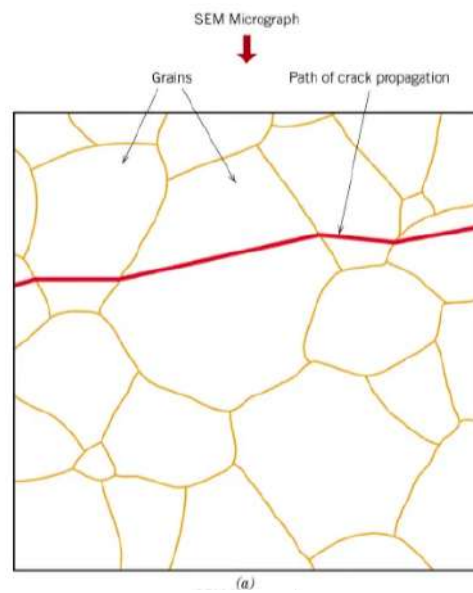


- Necking
- Small voids
- Crack formation by coalescence of voids
- Crack growth
- Shear failure at the end

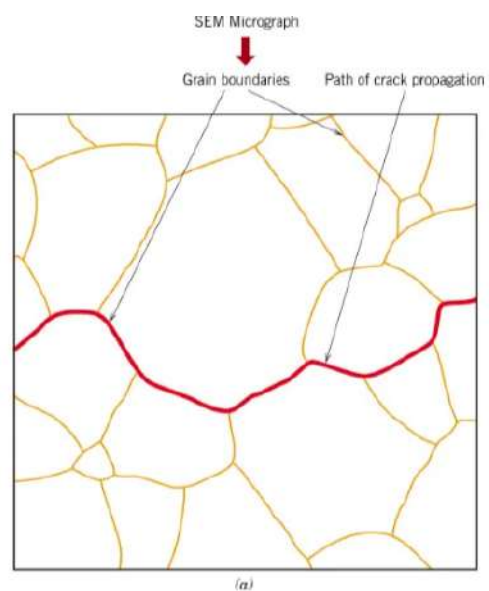
▼ Cracks

Crack formation during manufacturing or during service can either be:

- Transcrystalline crack (=across grains), due to heterogeneous dislocation motion/activity



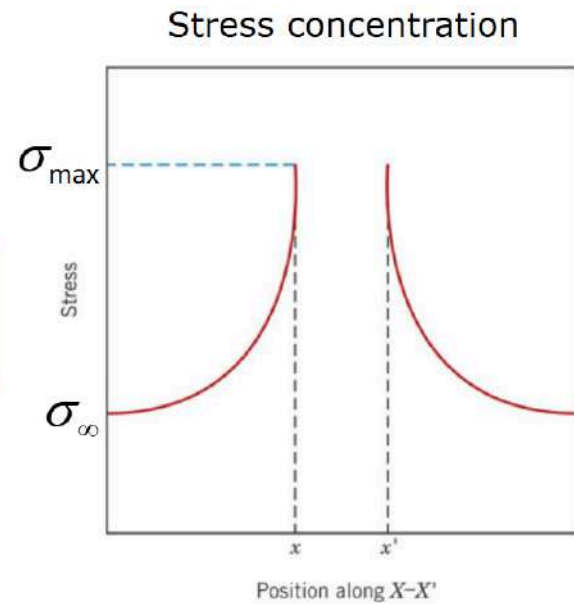
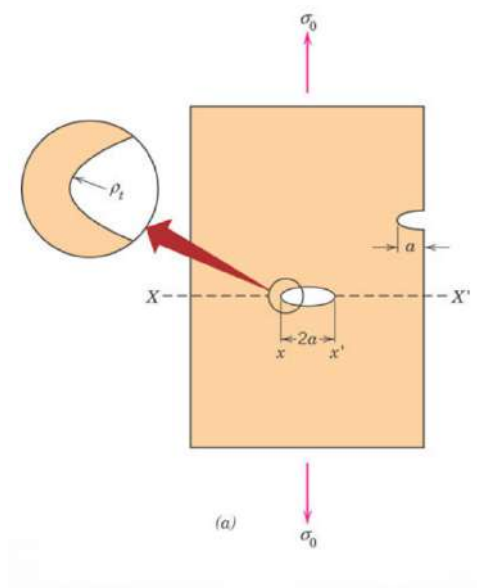
- Intercrystalline crack (=between grains), due to grain boundary sliding



It's important to note that cracks are not necessarily dangerous, only if they grow in an unstable manner

▼ Stress concentration at cracks

Stress vs position along  $X - X'$

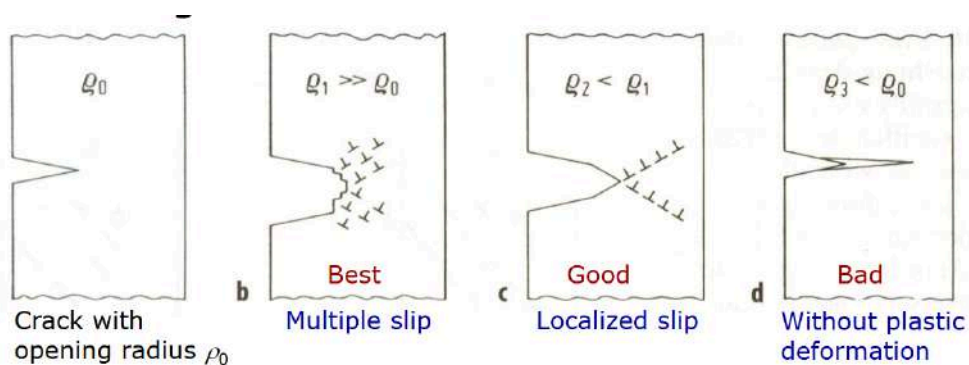


$$\sigma_{\max} = \sigma_0 \left( 1 + 2\sqrt{\frac{a}{\rho_t}} \right) \approx 2\sigma_0 \sqrt{\frac{a}{\rho_t}}$$

$\sigma_0$ , is defined as the applied stress  
 $a$ , is defined as half the crack length  
 $\rho_t$ , is defined as the curvature radius

It is often preferred to avoid edges since these have very small radii and therefore a large maximal stress

#### ▼ Crack growth



Plastic deformation ahead of crack tip

- Blunts crack tip
- Reduces stress concentration
- Initially stable crack growth, before unstable crack growth starts

- Finally catastrophic crack growth failure

#### ▼ Fracture toughness

Critical stress for crack growth in brittle material,

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

$\gamma_s$ , is defined as the surface energy

$E$ , is defined as the elastic modulus

$a$ , is defined as half the crack length

Fracture toughness  $K_{Ic}$  is a parameter unique to each material. Its unit is  $MPa\sqrt{m}$  and its computed using,

$$K_{Ic} = Y\sigma_c\sqrt{\pi a} = Y\sqrt{2E\gamma_s}$$

$Y$ , is a geometry factor independent of crack length

and usually for thick specimens  $Y \approx 1$

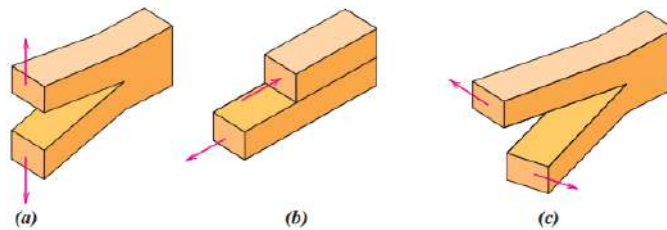
$K_{Ic}$ , is small for brittle material and large for tough material

The stress intensity factor  $K_I$  is computed using,

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

If the stress intensity factor is larger than the fracture toughness, then it's considered a catastrophic crack growth.

**Figure 8.10** The three modes of crack surface displacement. (a) Mode I, opening or tensile mode; (b) mode II, sliding mode; and (c) mode III, tearing mode.



#### ▼ Ductile failure vs Brittle failure

Depends on:

- Material (microstructure, crystal structure, chemical composition)
- Conditions (atmosphere, temperature, load,...)

Brittle failures occur suddenly and fast, like the speed of sound, as an example is steel  $1000m/s$

Ductile to brittle transition temperature DBTT

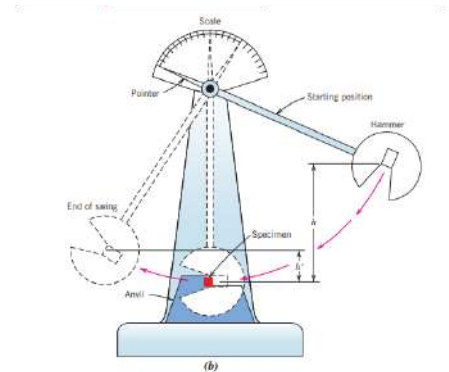
- Some metals (fcc: Al, Cu, Ni, stainless steel) remain ductile at low temperatures.

- bcc metals fail ductile at high temperatures and brittle at low temperatures
- hcp metals show different types of behaviors

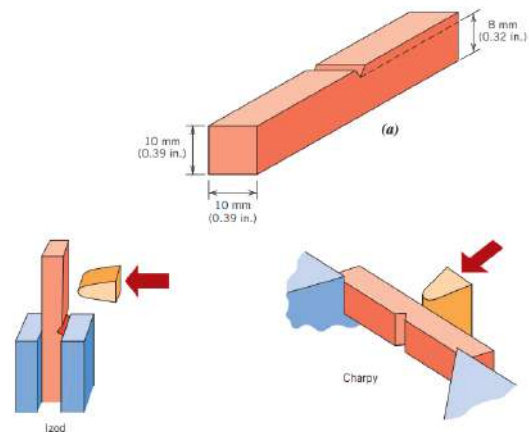
#### ▼ Toughness testing, Impact testing

Impact testing using the apparatus on the right, the hammer is released from a fixed height  $h$  and strikes the specimen. The energy extended in the fracture is reflected in the difference between  $h$  and the swing height  $h'$ . Energy loss is calculated as,

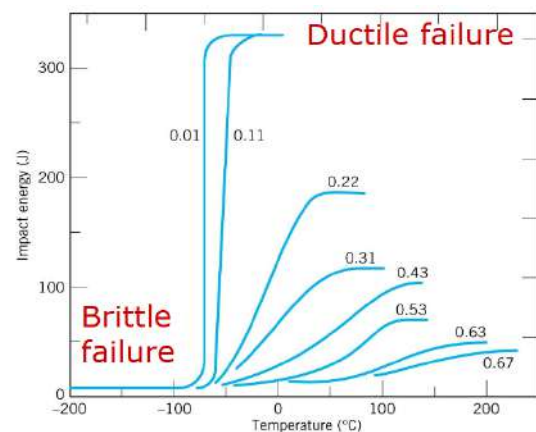
$$J = mg(h - h')$$



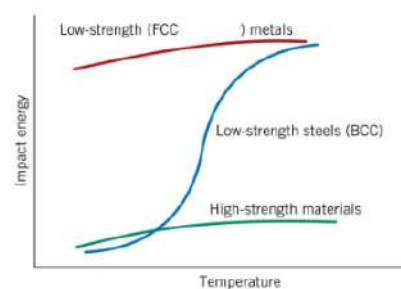
Specimen used for Charpy and Izod impact tests



Charpy impact test example of steel with different carbon content



## General Charpy impact test



- Hexagonal metals
  - with DBTT: Zn, Mg
  - without DBTT: Zr, Ti

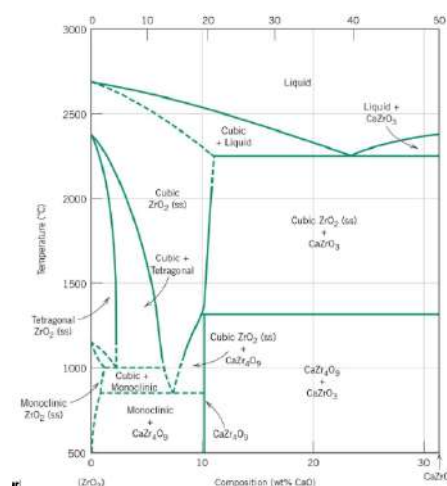
41680 Intro advanced materials

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# Mechanical properties of ceramics and polymers

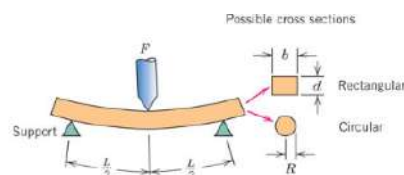
## ▼ Phase diagrams of ceramics

With ceramics instead of elements as terminals, we have chemical compounds, as seen in the phase diagram on the right. Phase diagrams of ceramics are known to have several solid phase materials (polymorphism).



## ▼ Mechanical testing of ceramics

When mechanical testing ceramics, the three-point bending test is used.



The Flexural strength for a rectangular cross-section is then calculated as,

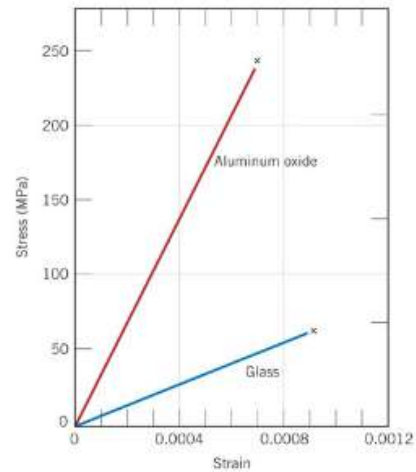
$$\sigma_{fs} = \frac{3FL}{2bd^2}$$

The Flexural strength for a circular cross-section is then calculated as,

$$\sigma_{fs} = \frac{FL}{\pi R^2}$$

$F$  is the applied force at fracture.

Since ceramics are brittle, they have elastic behavior until fracture, and their yield strength is equal to their tensile strength ( $\sigma_y = \sigma_{UTS}$ )



#### ▼ Mechanical properties of crystalline ceramics

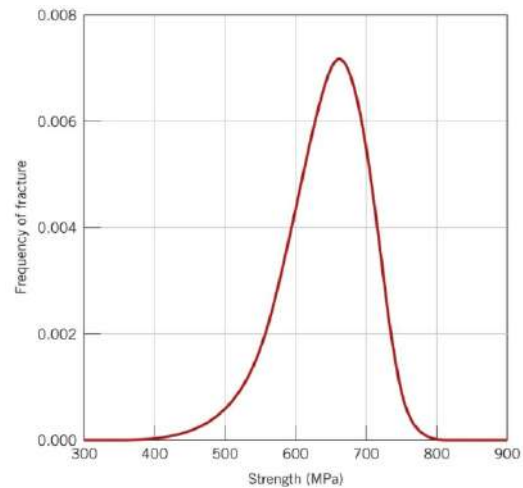
They are generally very brittle

Dislocations

- Motion may not lead neighbors with the same charge
- Low number of slip systems
- Limited deformability
- Low ductility
- Large specimen variation (Weibull distribution)

Micro cracks

- Also in amorphous ceramics, Stress concentrations from manufacturing can be removed from the surface



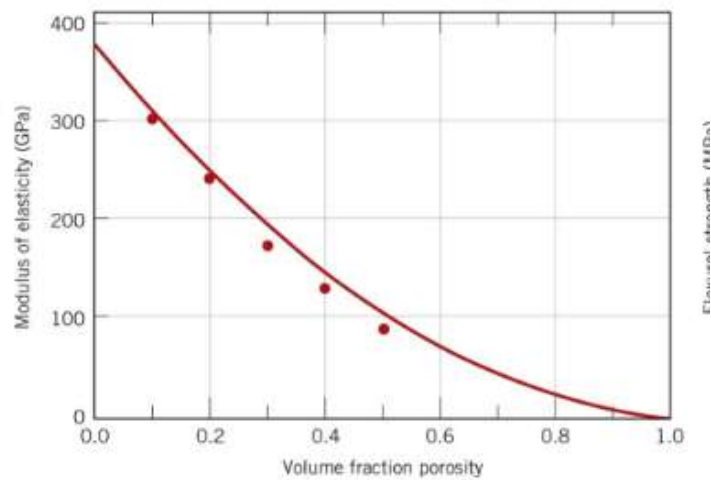
#### ▼ Effect of porosity

Pores in materials due to powder sintering cause a variation in the modulus of elasticity and the flexural strength. We define Porosity  $P$  as the volume fraction of pores.

$$E = E_0(1 - 1.9P + 0.9P^2)$$



### ▼ Modulus of elasticity and the volume fraction porosity

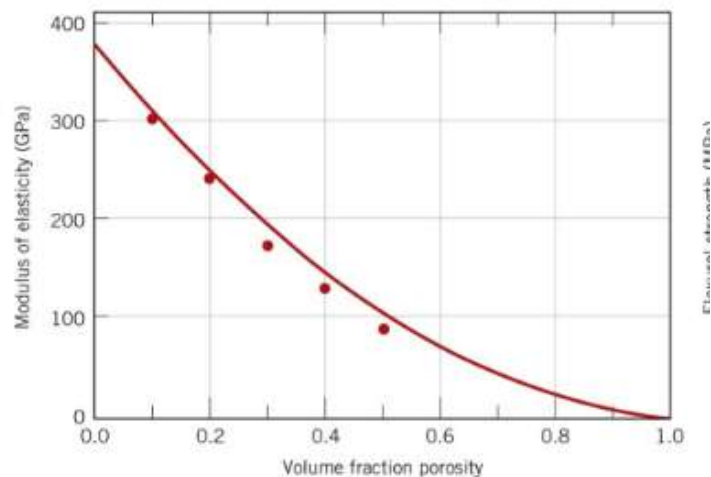


Porosity reduces flexural strength for two reasons: pores reduce the cross-sectional area across which a load is applied, and they also act as stress concentrators.

$$\sigma_{fs} = \sigma_{fs,0} e^{-nP}$$

$n$ , is an experimental constant

### ▼ Flexural strength and the volume fraction porosity



### ▼ Mechanical properties of amorphous ceramics

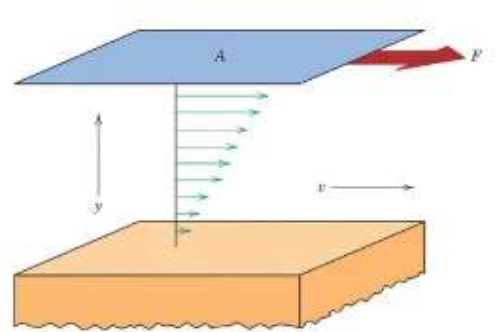
Plastic deformation occurs due to atomic jumps (viscous flow) since there are no crystalline lattices and therefore no dislocations.

Viscous behaviour is explained by the shear stress  $\tau$  as,

$$\tau = \eta \gamma$$

Which is computed using shear test,

$$\tau = F/A$$



The units for viscosity  $\eta$  are poise  $P$  and pascal-seconds  $Pa \cdot s$

$$10P = 1Pa \cdot s$$

It's good to note that Viscosity depends on a lot of things, including temperature, as temperature heightens the viscosity lowers.

Material	Viscosity $Pa \cdot s$
Water	$1 \cdot 10^{-3}$
Olive oil	0.08
Honey	2 - 10

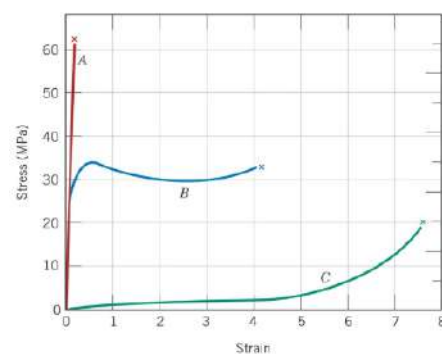
#### ▼ Mechanical properties of polymers

It's important to understand that there are multiple types of polymers with varying behaviors,

A - shows a brittle polymer

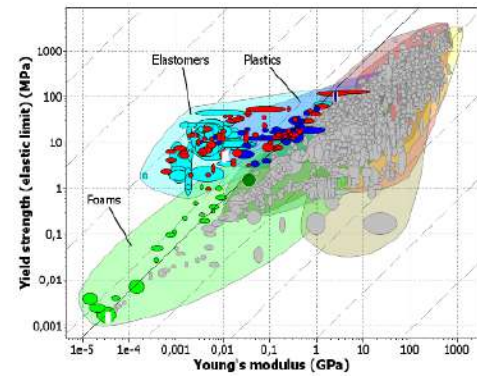
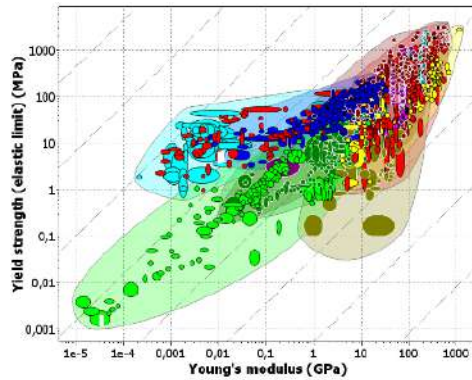
B - shows an elastoplastic polymer

C - shows a purely elastic polymer (elastomers)



Yield strength and Young's modulus

Theoretical yield strength (defect-free material)



Elastomers have  $\sigma > \sigma_{th}$ , which leads to chains and entropy

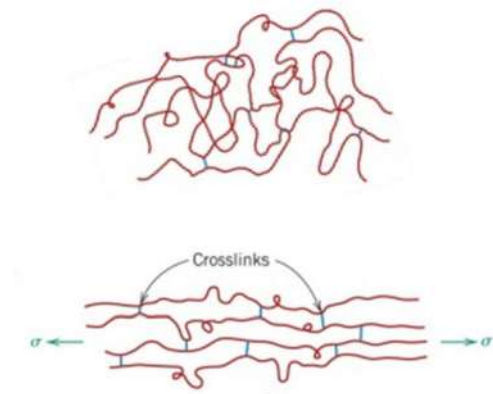
General polymers  $\sigma \ll \sigma_{th}$ , which lead to defects

### ▼ Elastomers

Their compliance is determined by the entropy

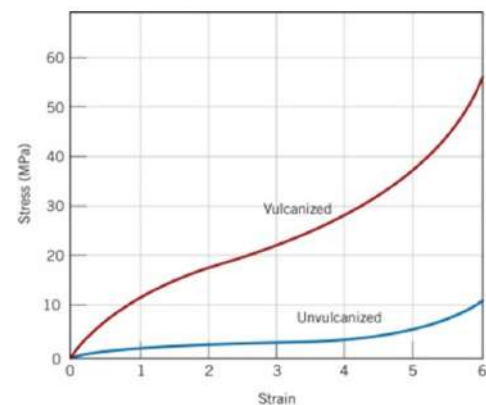
#### ▼ Elastic properties

- Covalent cross bonds
- When a load is removed, curly conformation is reestablished and disorder is increased (entropy)
- Low modulus of elasticity
- Young's modulus increases with increasing temperature
- Rubber becomes warm when stretched



#### ▼ Vulcanization

Sulfur increases the number of cross bonds. The Effects of cross bonds are reduction in flexible chain length.

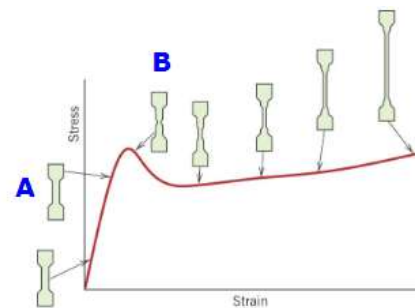


### ▼ Mechanical properties of semi-crystalline polymers

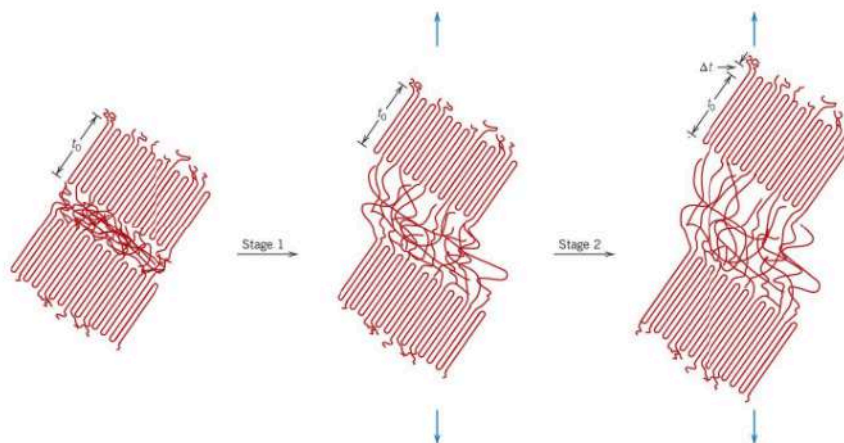
When applying strain to a semi-crystalline polymer the following occurs:

Stretching of chains, a reorientation of crystalline blocks, alignment with tensile axis and finally hardening suppresses further necking

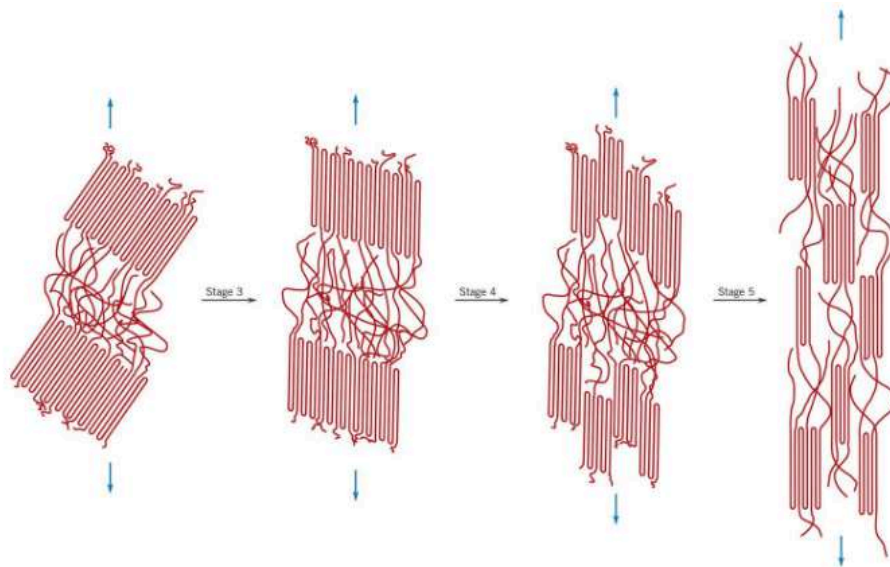
Stress-strain curve of semi-crystalline polymers is shown on the right. Region **A** shows elastic deformation, while region **B** shows plastic deformation (chains align with the tensile axis).



### ▼ Figure of what's happening in region **A**

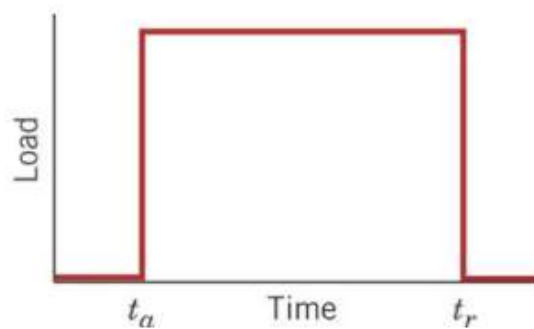


### ▼ Figure of what's happening in region **B**



▼ Mechanical properties of amorphous polymers (Time-dependent behavior)

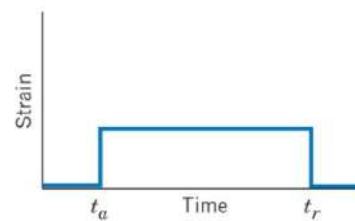
▼ Stress (imposed, action)



▼ Strain (reaction)

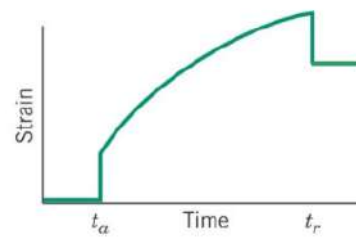
Elastic

$$\tau = G\gamma$$



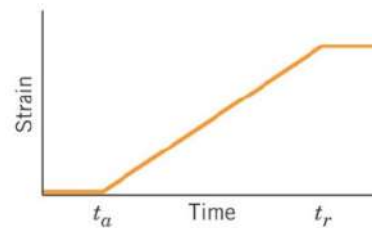
Viscoelastic

Look lower

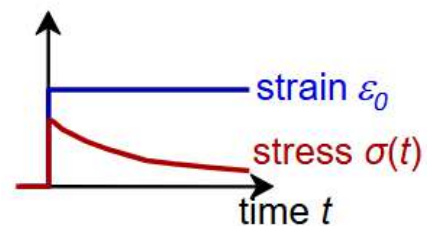


Viscous (low  $E$ )

$$\tau = \eta\gamma$$



With a small strain, stress decreases with time (stress relaxation)



Time-dependent elastic modulus is computed as,

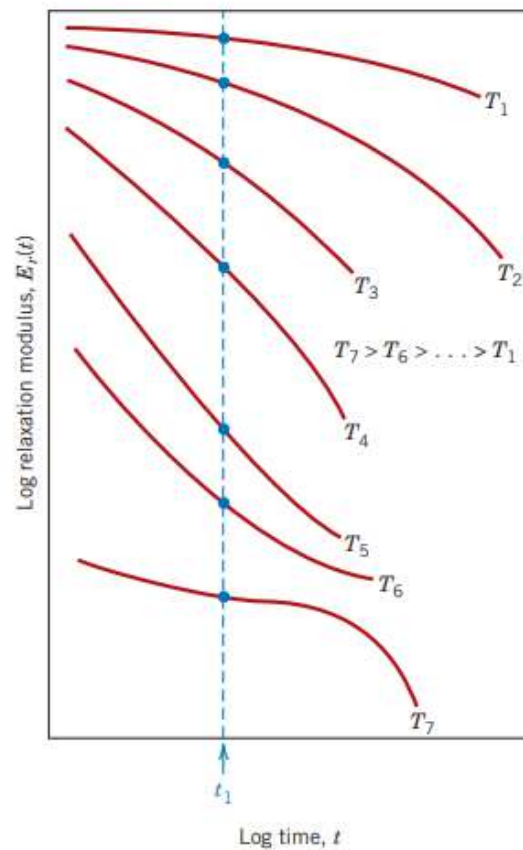
$$E_r(t) = \frac{\sigma(t)}{\epsilon}$$

$\epsilon$ , is the strain level which is constant  
 $\sigma(t)$ , is the measured time-dependent stress

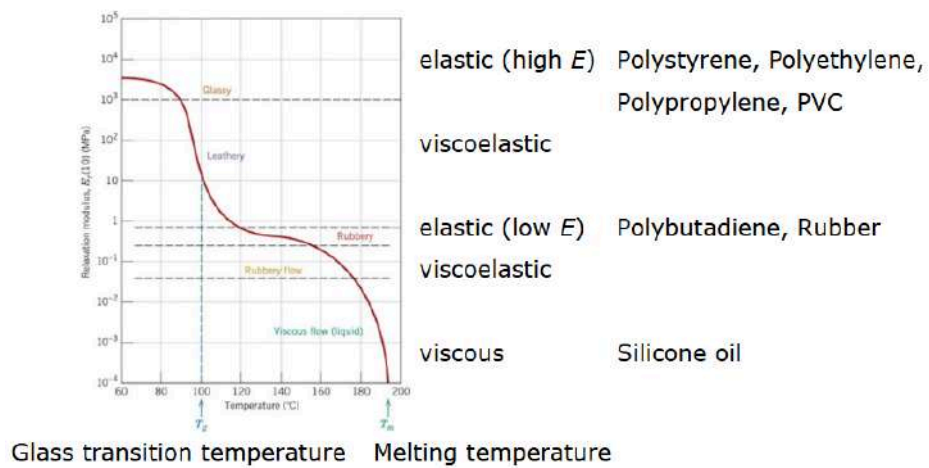
Relaxation modulus is defined as  $E_r(10s)$

Note that the relaxation modulus is temperature sensitive.

▼ Relaxation modulus vs time

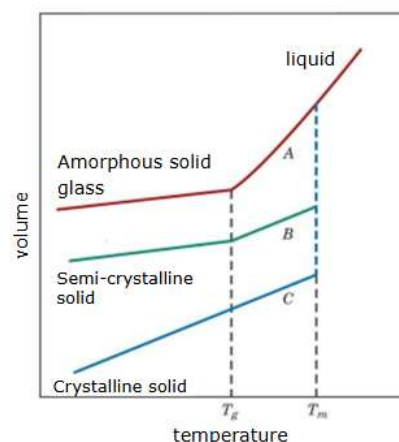


### ▼ Relaxation modulus vs temperature



### ▼ Glass transition

- Normally, a discontinuous phase transition from liquid to crystalline solid.
- Glass transition is a continuous phase transition from liquid to amorphous solid.
- Glass transition temperature is defined as  $T_g$



The glass transition temperature  $T_g$  between rubber and glass depends on chain flexibility. A higher  $T_g$  for stiffer chains is associated with,

- Large side groups
- Strong secondary bonds
- Double bonds in chains
- Many side branches (however, few branches only lower  $T_g$ )
- High molar mass

▼ Table of glass transition temperature and melting temperature for various polymers

<i>Material</i>	<i>Glass Transition Temperature (°C)</i>	<i>Melting Temperature (°C)</i>
Polyethylene (low density)	-110	115
Polytetrafluoroethylene	-97	327
Polyethylene (high density)	-90	137
Polypropylene	-18	175
Nylon 6,6	57	265
Poly(ethylene terephthalate) (PET)	69	265
Poly(vinyl chloride)	87	212
Polystyrene	100	240
Polycarbonate	150	265

Melting temperature follows same trends. We use the following as rule of thumb except in case of branching as side branches always lower  $T_m$ .

$$T_g \propto (0.5 - 0.8)T_m$$

## Composites



### ▼ Basic definitions

Composites are a combination of two or more materials to achieve desired properties.  
(Immiscible mixture)

#### 1. Artificial multiphase materials

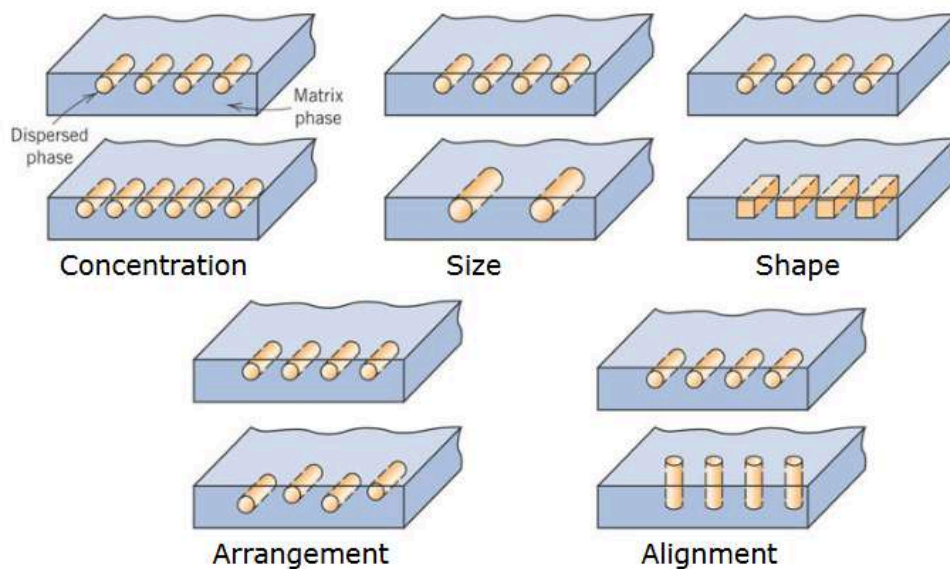
- Phase 1: continuous matrix
- Phase 2: discontinuously distributed in the matrix
- Types:

MMC	PMC	CMC
Metal	Polymer	Ceramic
Matrix Composite		

#### 2. Natural multiphase material, like eutectics

### ▼ Composition of composites

Composites' properties vary with volume fraction; however, there are multiple ways of maintaining the volume fraction constant and still somewhat varying the properties of it.

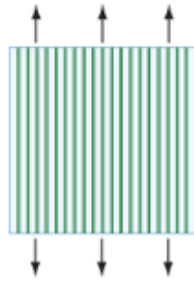


### ▼ Elastic properties of laminar and fiber composites

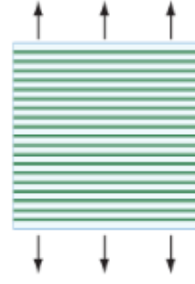
The Elastic properties of laminar and fiber composites have the same formula.

Longitudinal lamellae (iso-strain)

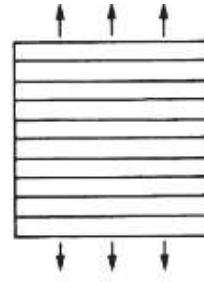
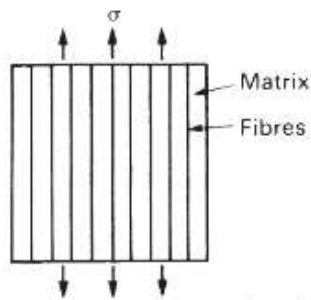
Transversal lamellae (iso-stress)



Longitudinal fibers (iso-strain)



Transversal fibers (iso-stress)



▼ For Longitudinal (Voigt model):

$$\begin{aligned}\varepsilon_c &= \varepsilon_m = \varepsilon_f \\ \sigma_{c\parallel} &= f_m \sigma_m + f_f \sigma_f\end{aligned}$$

Rule of mixture for stress

$$E_{c\parallel} = f_m E_m + f_f E_f$$

Where  $f_m$  and  $f_f$  are the volume fractions.

▼ For Transversal (Reuss model):

$$\begin{aligned}\sigma_c &= \sigma_m = \sigma_f \\ \varepsilon_{c\perp} &= f_m \varepsilon_m + f_f \varepsilon_f\end{aligned}$$

Rule of mixture for strain

$$\frac{1}{E_{c\perp}} = f_m \frac{1}{E_m} + f_f \frac{1}{E_f}$$

Where  $f_m$  and  $f_f$  are the volume fractions.

The elastic modulus of the composite is found in between  $E_{c\parallel}$  and  $E_{c\perp}$ .

$$E_c \in [E_{c\perp}, E_{c\parallel}]$$

### ▼ Properties of particulate composites

For composites composed of a dispersion of particles (p) in a matrix (m)

We have the volume fractions,

$$f_m + f_p = 1$$

Rule of mixture,

$$x_c = f_m x_m + f_p x_p$$

Mass density,

$$\rho_c = f_m \rho_m + f_p \rho_p$$

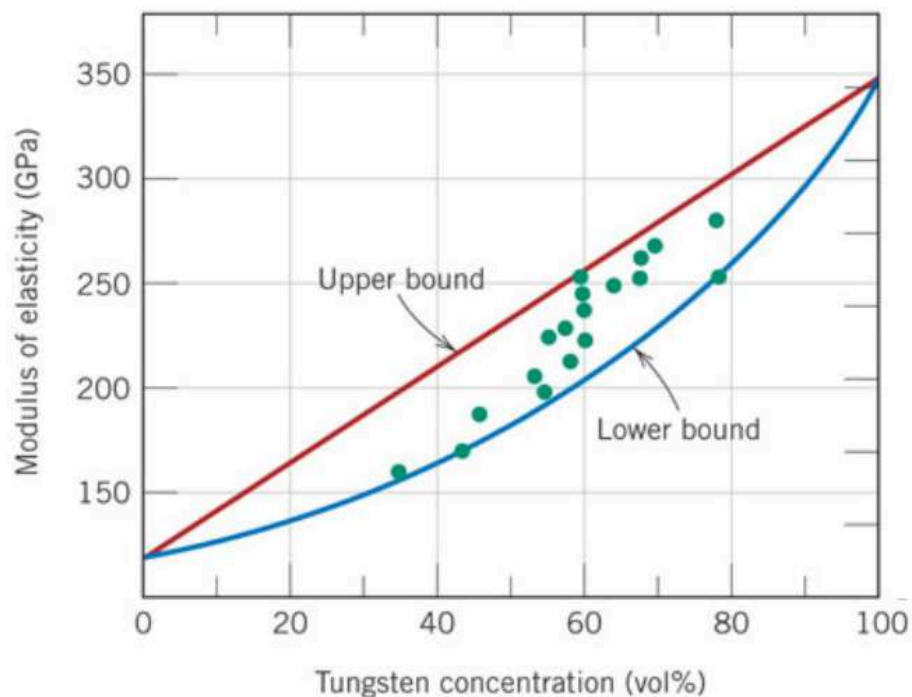
### ▼ Elastic properties of particulate composites

The Young's modulus of particulate composites is found with the Voigt and Reuss models, where the limits where it's found is computed as,

$$E_c = f_m E_m + f_p E_p \text{ upper limit}$$

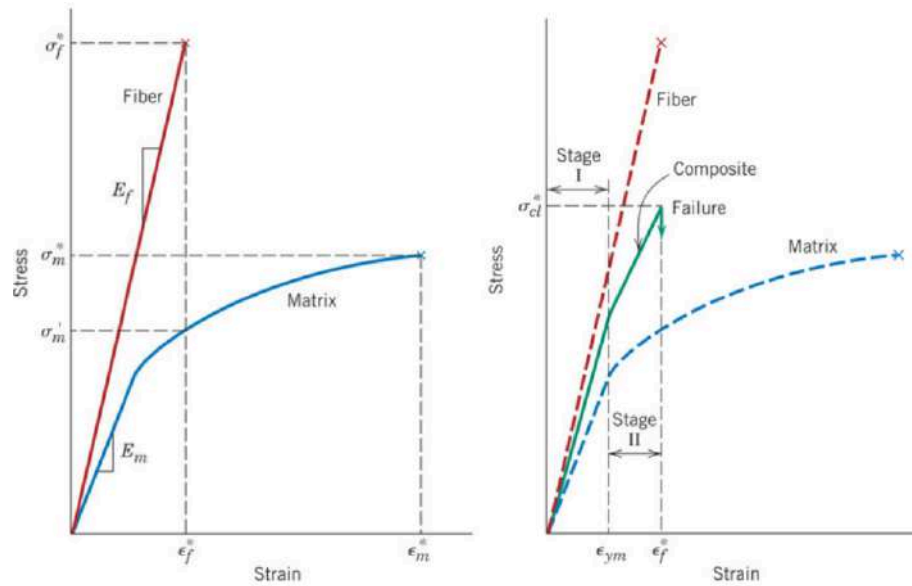
$$\frac{1}{E_c} = f_m \frac{1}{E_m} + f_p \frac{1}{E_p} \text{ lower limit}$$

### ▼ Example of graph modulus of elasticity vs volume fraction



### ▼ Mechanical properties of fiber composites (continuous aligned fibers)

▼ Example of stress-strain curve (only fiber fracture)



Yield strength,

$$\sigma_{y,c} = f_m \sigma_{y,m} + f_f E_f \epsilon_{y,m}$$

Tensile strength,

$$\sigma^* = f_m \sigma_m(\epsilon_f^*) + f_f \sigma_f^* = f_m \sigma_m' + f_f \sigma_f^*$$

$\sigma_f^*$ , is the fracture strength of fibers  
 $\epsilon_f^* < \epsilon_m^*$ , is the strain to failure of fibers

Tensile stress (iso-strain),

$$\sigma(\epsilon) = f_m \sigma_m(\epsilon) + f_f \sigma_f(\epsilon) = f_m \sigma_m(\epsilon) + f_f E_f \epsilon$$

▼ After the fracture of fibers

Fibers are no longer under stress,

Deformation continues in the matrix,

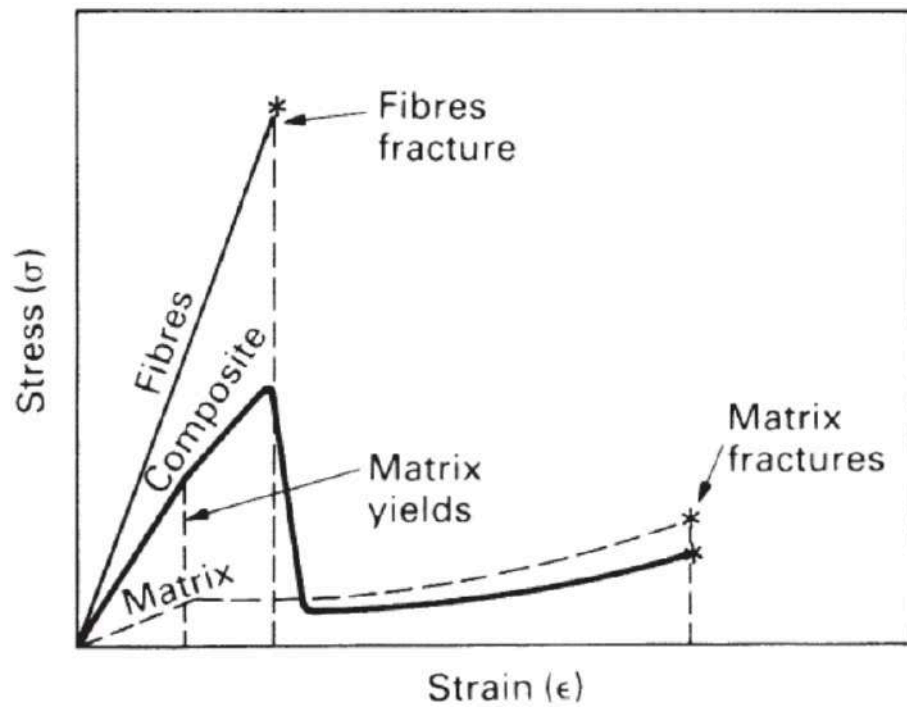
Stress in matrix when carbon fibers crack are stress of the flow curve of the matrix at the strain to failure of fibers,

Strain at the matrix fracture  $\epsilon_m^*$

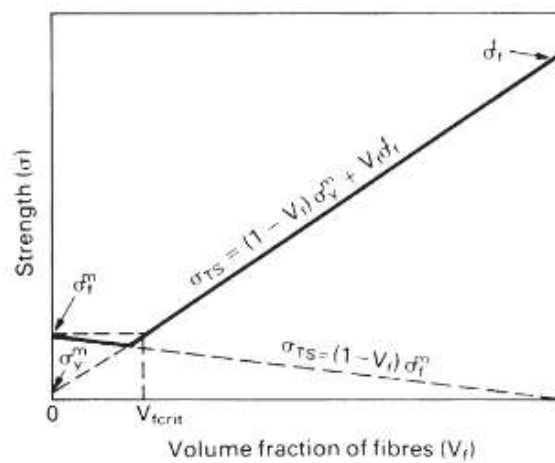
Reduced tensile strength computed as,

$$\sigma = f_m \sigma_m(\epsilon_m^*) = f_m \sigma_m^*$$

▼ Strain-stress curve (all fracture, fibers and matrix)



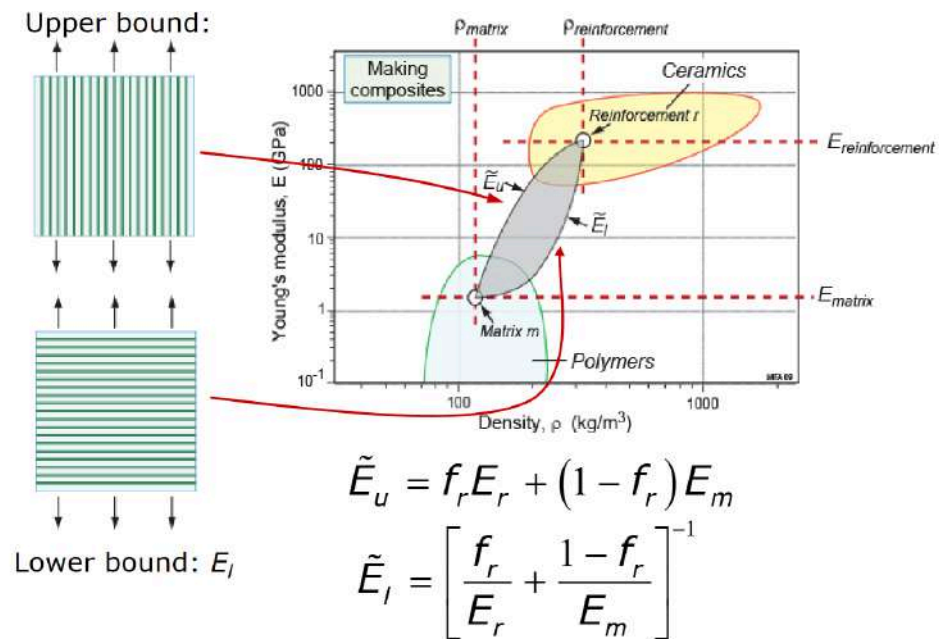
▼ Strength vs volume fraction of fibers ( $V_f$ )



▼ General composites: reinforcement in a matrix

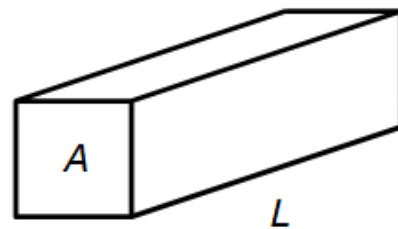
Composite density,

$$\rho_c = f_r \rho_r + (1 - f_r) \rho_m$$



▼ Design: minimize the weight of a light, stiff member

For a specific object with a required  
specified stiffness  $S$  and fixed length  $L$   
that may look like,



Force,

$$F = \sigma A$$

Elongation,

$$\Delta L = \varepsilon L$$

Elastic behavior,

$$\sigma = E\varepsilon$$

Stiffness of a member,

$$S = \frac{F}{\Delta L} = \frac{\sigma A}{\varepsilon L} = \frac{EA}{L}$$

Mass,

$$m = \rho AL = \frac{\rho}{E} SL^2$$

Minimizing mass means maximizing the ratio  $E/\rho$

We can do this for a lot of other parameters, not just  $E$ , like  $\sigma_y$ ,  $\sigma_{UTS}$ , and other stuff.