

# MLL 100

# Introduction to

# Materials Science and Engineering

***Lecture-18 (February 22, 2022)***

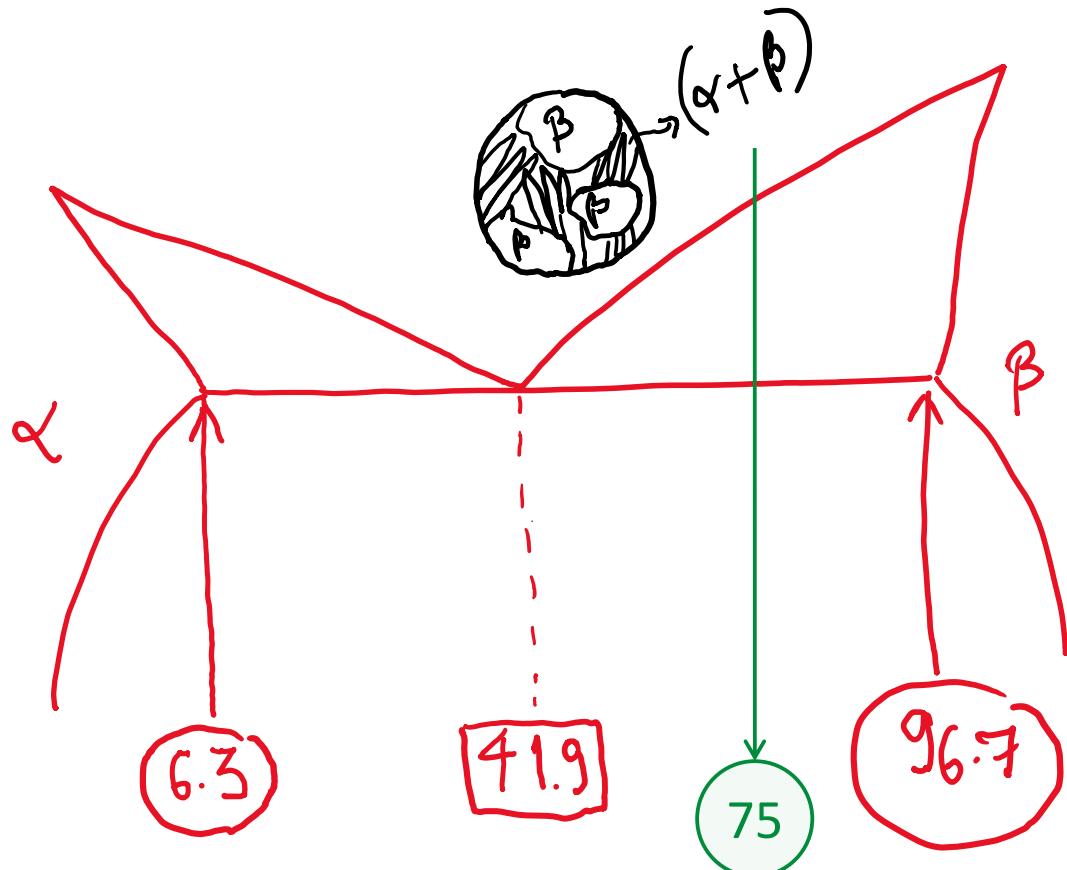
Dr. Sangeeta Santra ([ssantra@mse.iitd.ac.in](mailto:ssantra@mse.iitd.ac.in))



IIT Delhi

Department of Materials Science and Engineering

P-Q forms an eutectic phase diagram with an eutectic composition of 41.9 wt.% Q at an eutectic temperature of 200 °C. The two terminal solid solutions,  $\alpha$  and  $\beta$  have respective compositions of 6.3 wt.% Q and 96.7 wt.% Q at 200 °C. What percentage of the  $\beta$  phase (in %) constitutes the eutectic mixture just at a temperature below 200 °C for an alloy with a composition of 75.0 wt.% Q? Write your answer up to two decimal places and in %.



$$\rightarrow \beta = \left( \frac{75 - 41.9}{96.7 - 41.9} \right) = 60.4 \%$$

$$L = 39.6 \%$$

$$\rightarrow \alpha = \left( \frac{96.7 - 75}{96.7 - 6.3} \right) = 24\%$$

24% of a part of 39.6% L

$$\therefore \begin{cases} 60.6\% \text{ of } \alpha \text{ in E.M} \\ 39.39\% \text{ of } \beta \text{ in E.M} \end{cases}$$

# What have we learnt in Lecture-17?

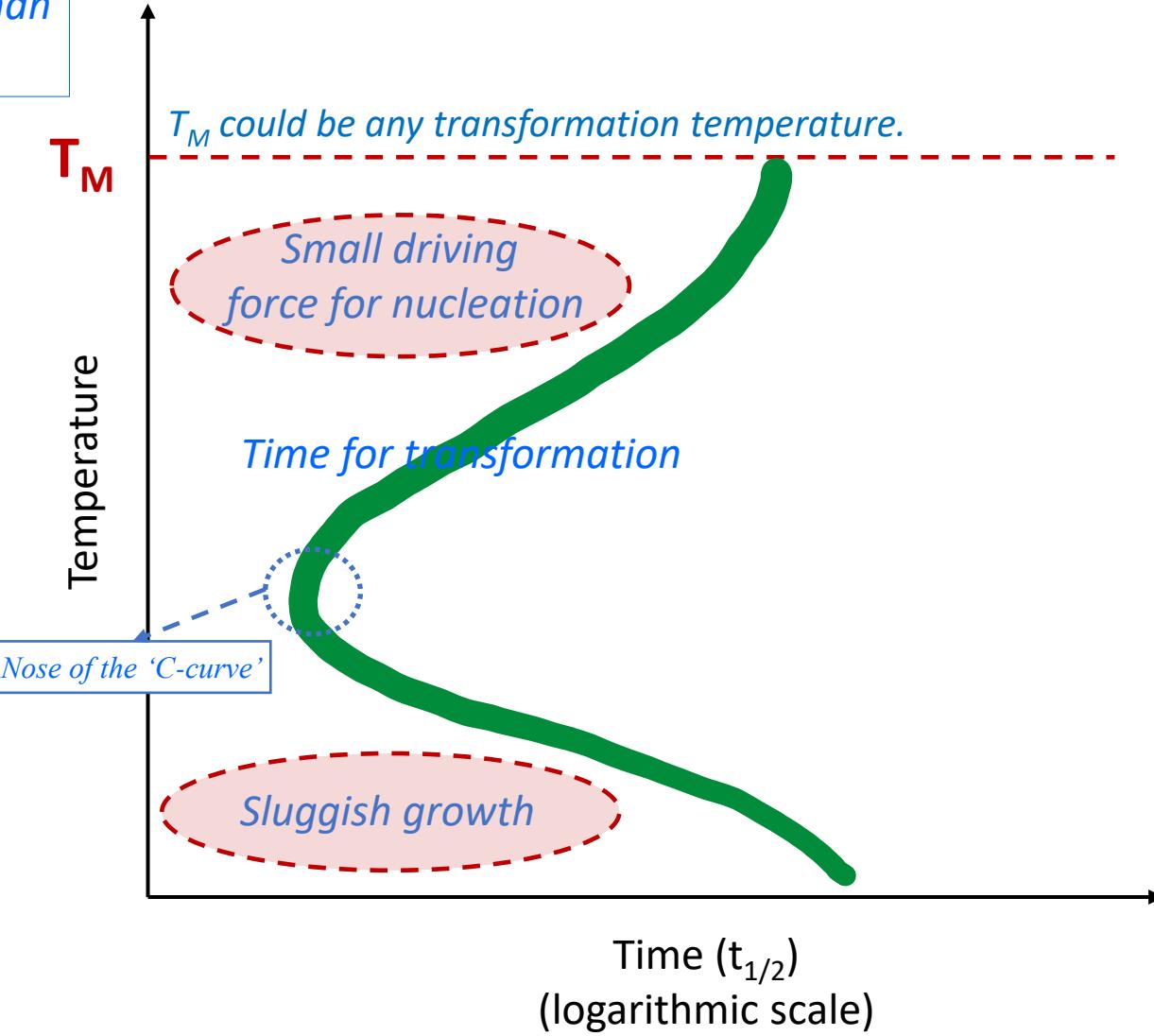
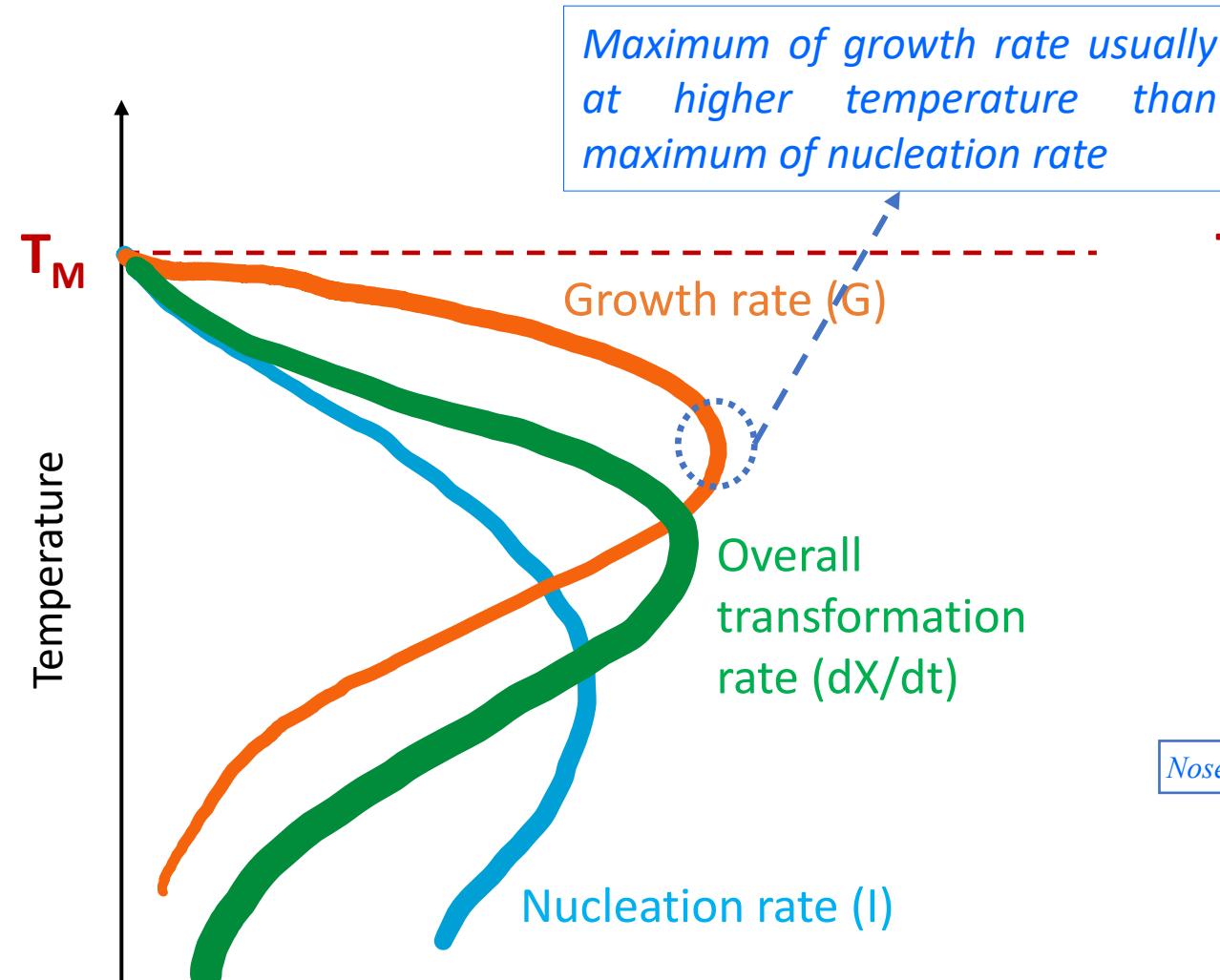
- Nucleation and growth rate
- Transformation rate
- Transformation curve: Start of the curve and nose of the curve

Fri (END)  
Girlfri (END)  
Boyfri (END)  
Bestfri (END)

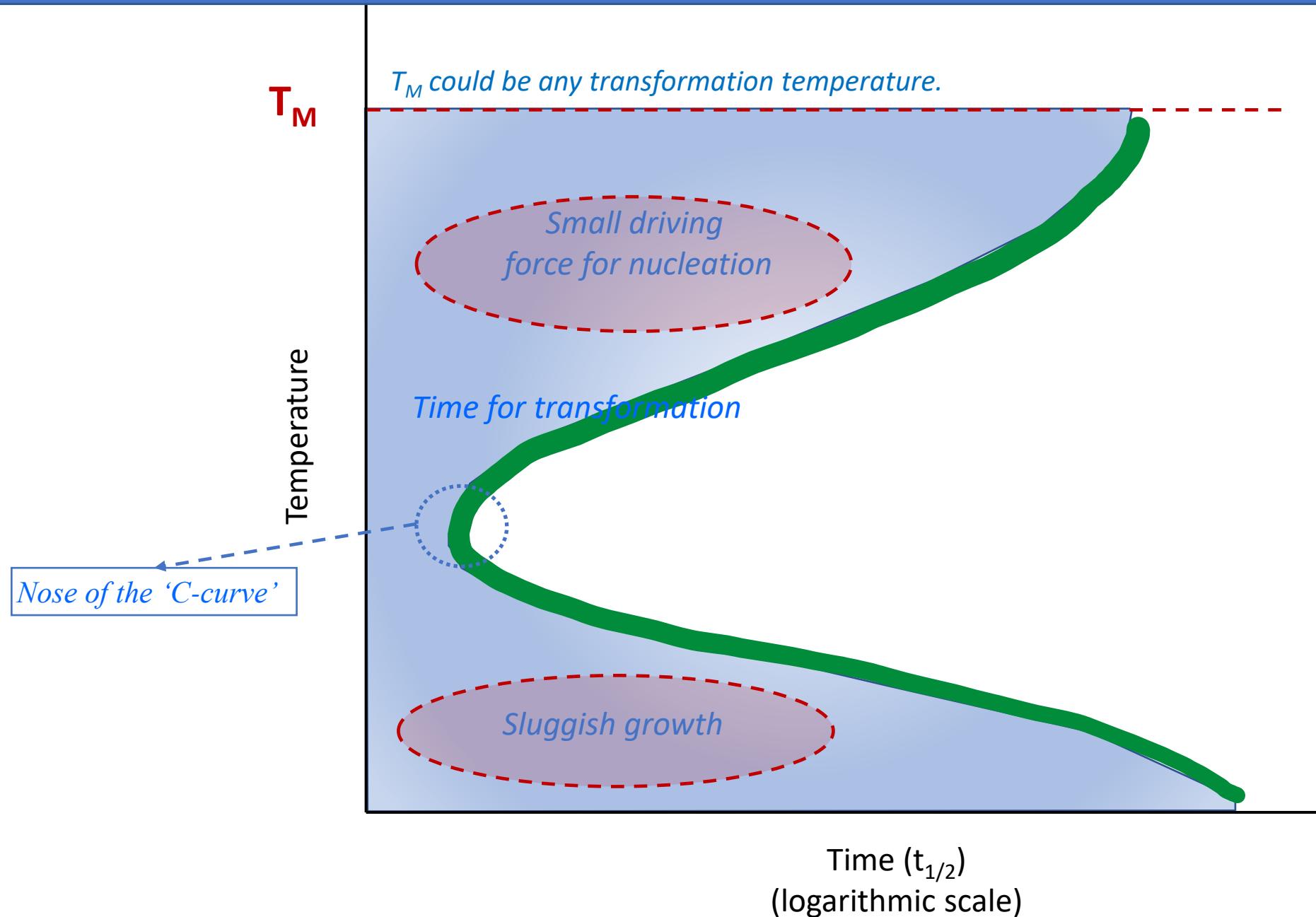
Everything has an end.

*Let us see how a transformation of a material ends!!*

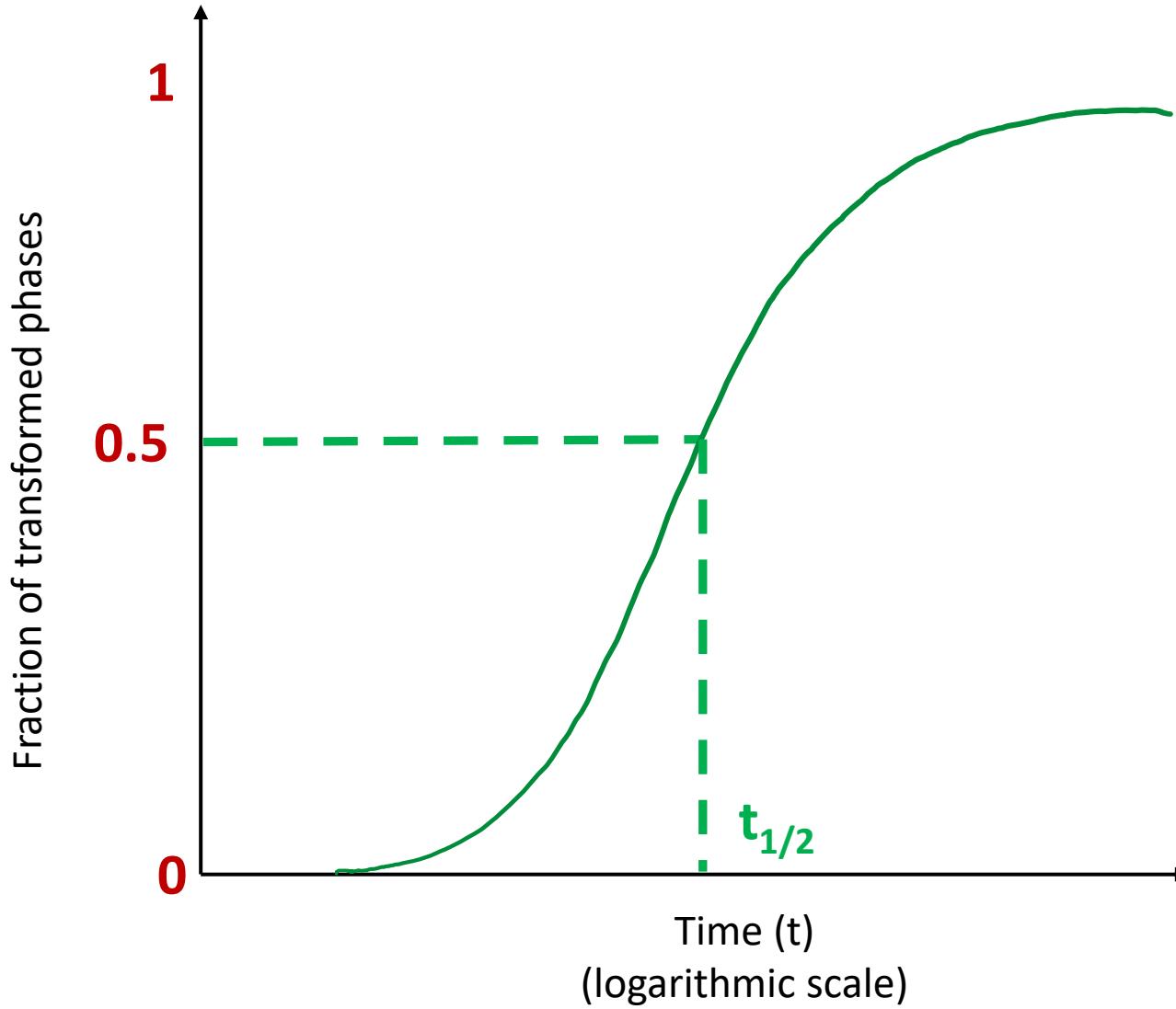
# Transformation rate



# Transformation rate



# Avrami Equation



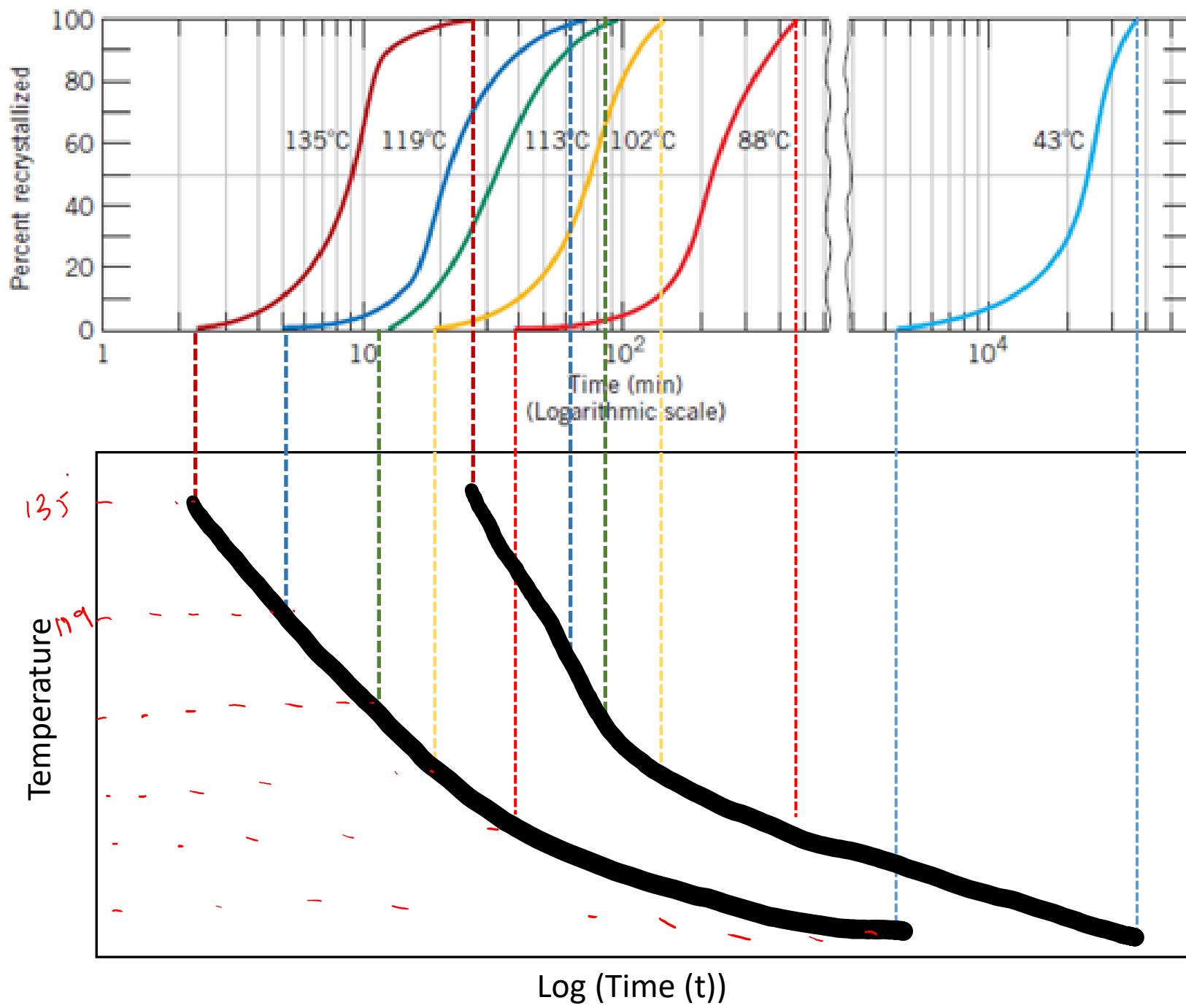
$f \rightarrow \frac{\text{volume fraction of } \alpha \text{ at } t}{\text{final volume of } \alpha}$

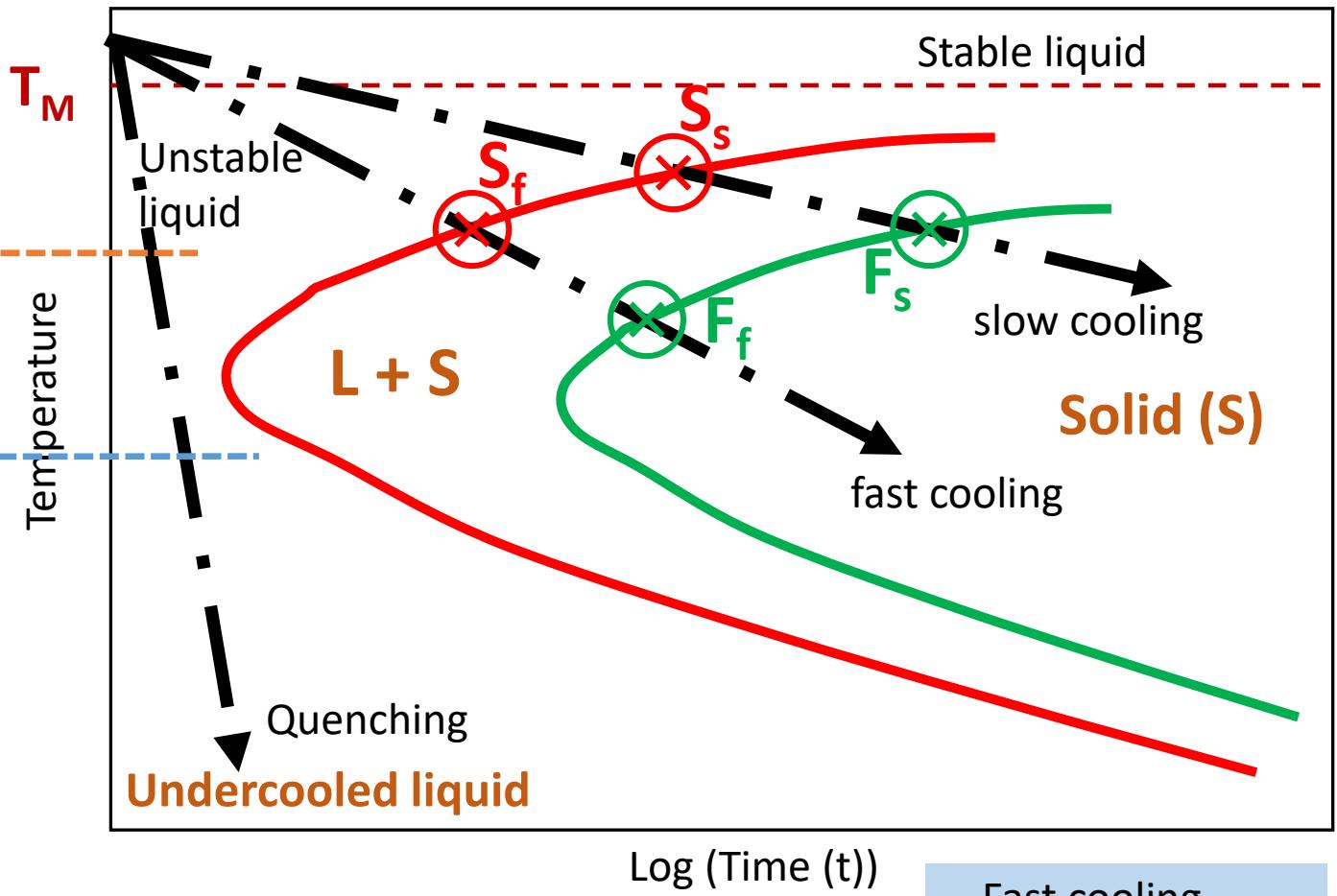
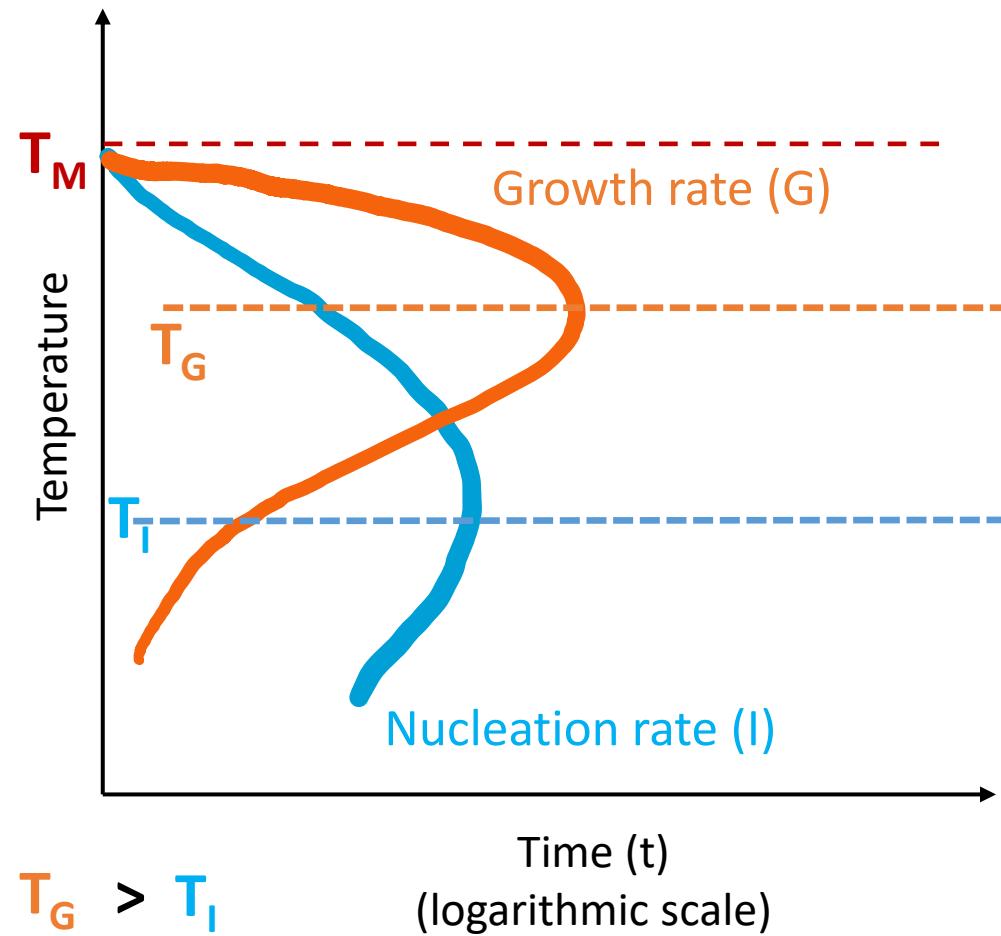
$L \rightarrow \alpha$

$f \rightarrow \text{volume fraction of } \alpha$

Fraction of  
transformed phases:

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





## □ Steel:

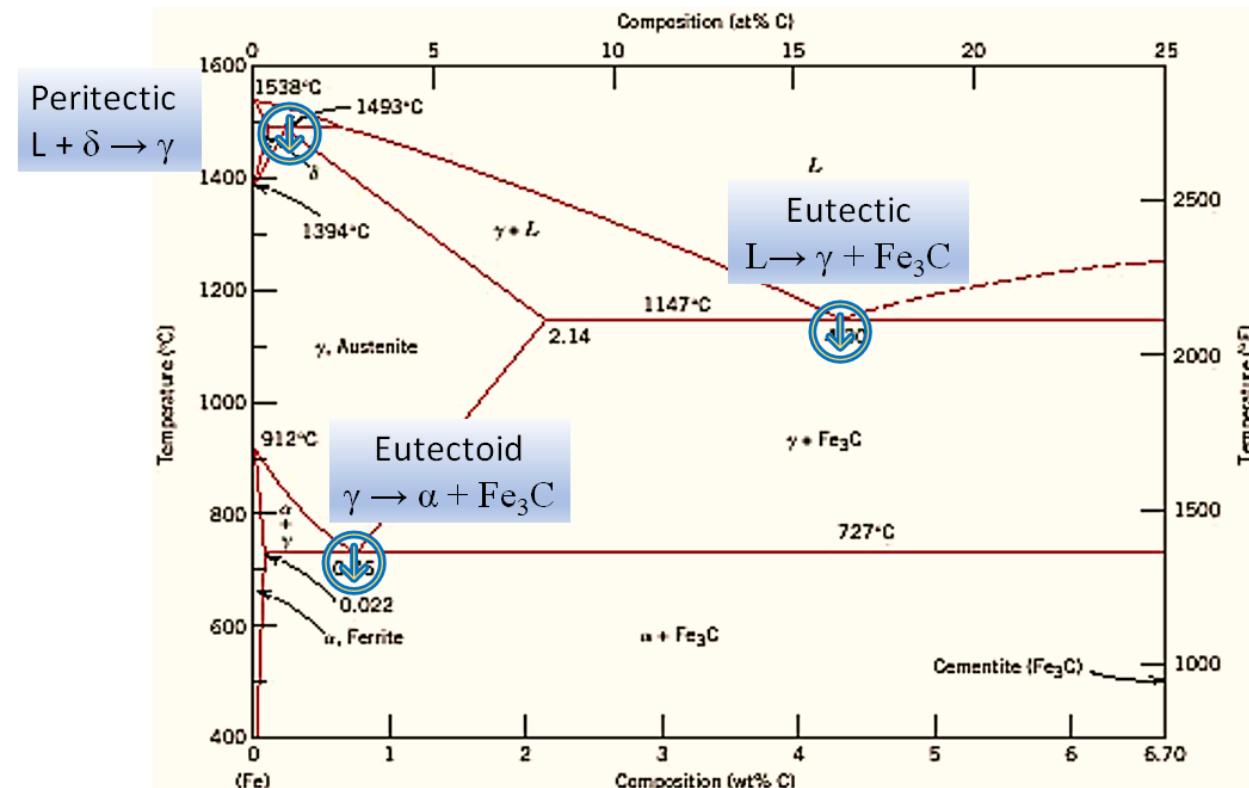
Iron (Fe)-based alloy containing C < 2.14 wt.%)

## □ Broad classification of steel based on the carbon content:

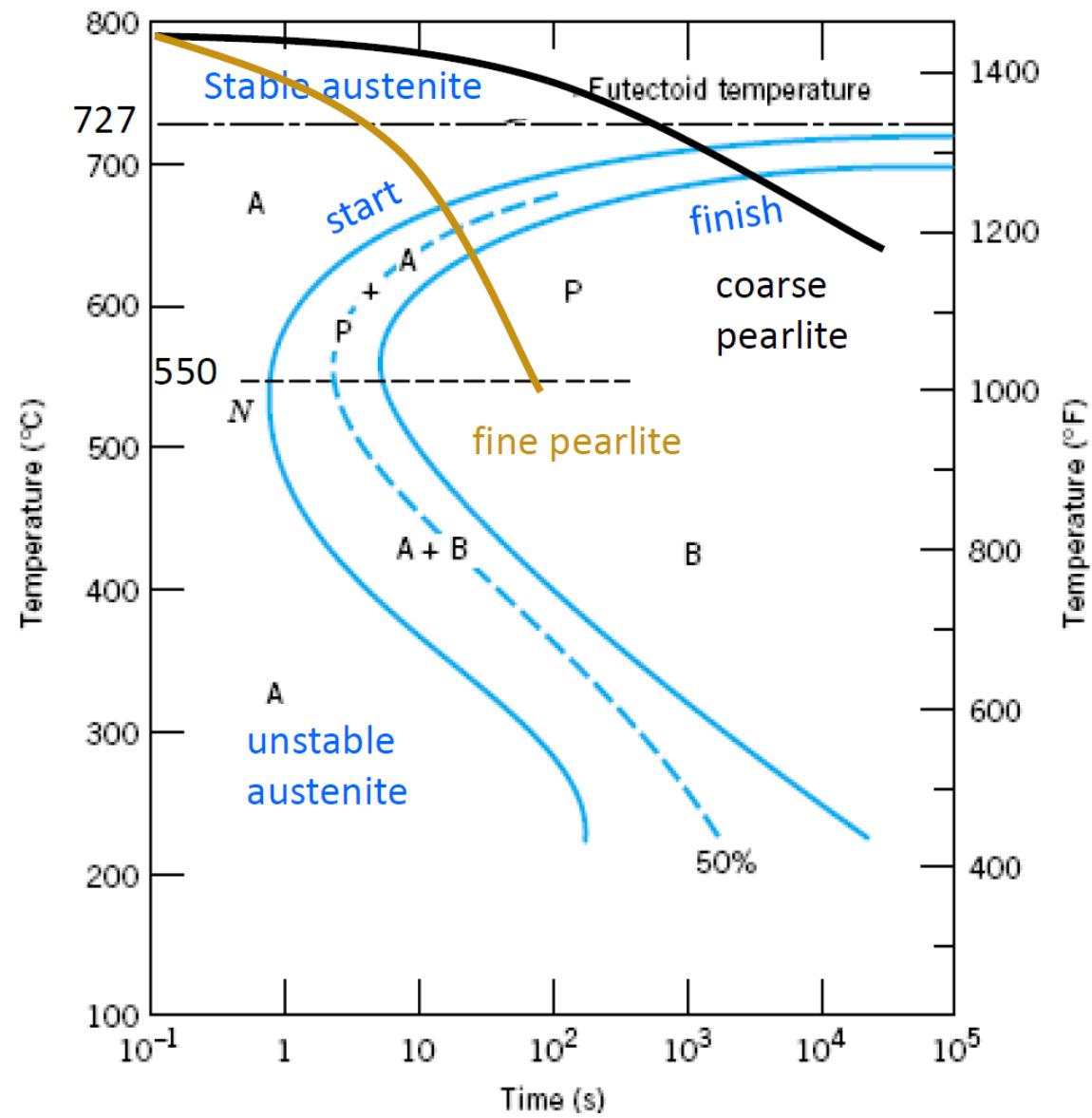
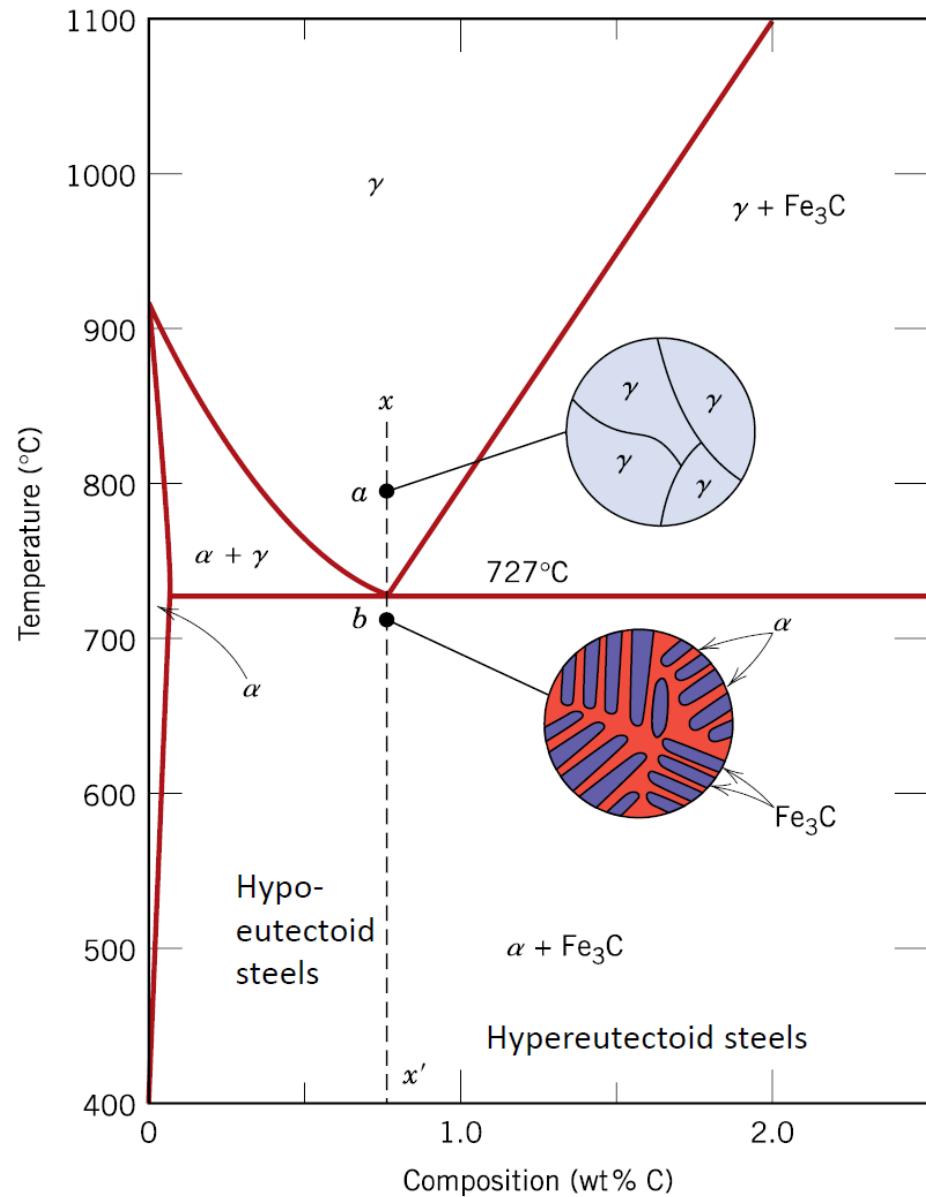
- Eutectoid steel ( C ~ 0.8 wt.% C)
- Hypo-eutectoid steel (C < 0.8 wt.% C)
- Hyper-eutectoid steel (C > 0.8 wt.% C)

## □ What about the alloy with C > 2.14 wt.% C?

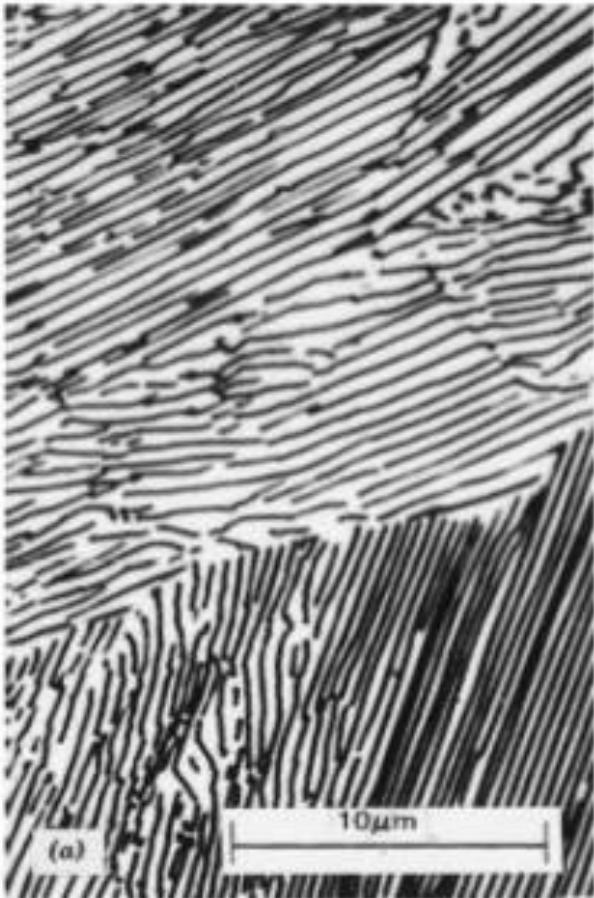
Cast iron



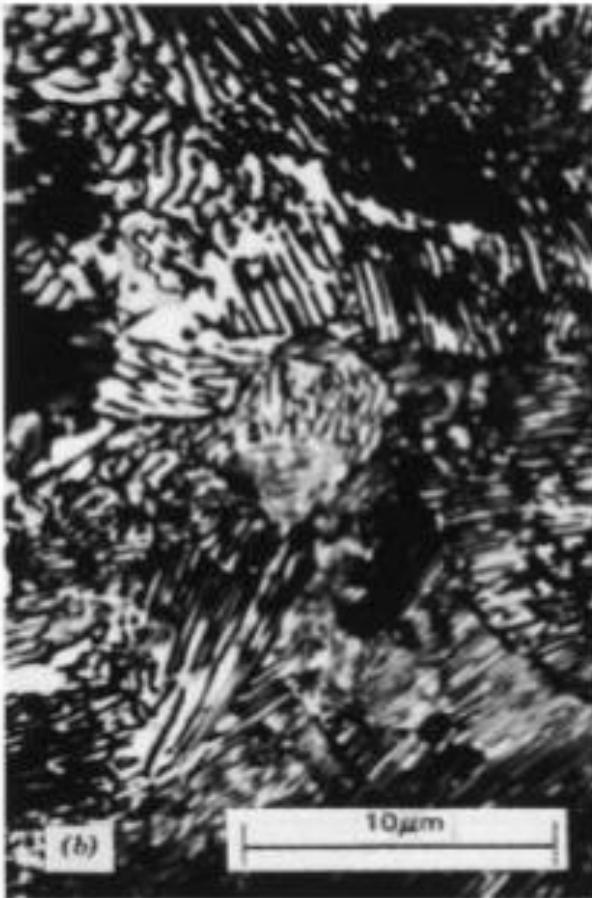
# TTT diagram for Eutectoid steel (0.8 wt.% C)



# Microstructure of Pearlite



Coarse pearlite  
(Slow cooling)



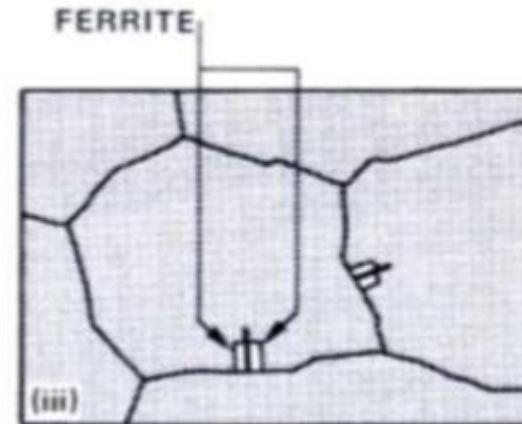
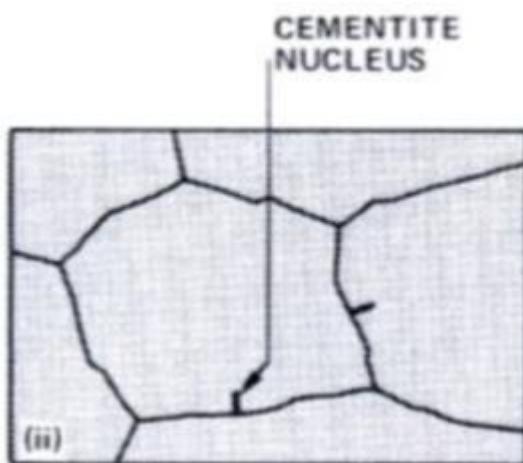
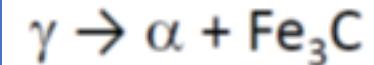
Fine pearlite  
(Fast cooling)

***'Pearlite' is not a phase,  
rather a mixture of phases.***

Coarse pearlite → Annealing → Furnace cooling

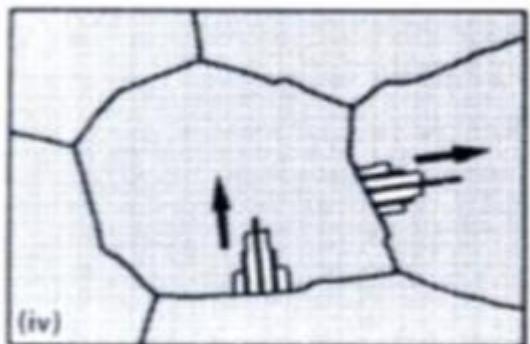
Fine pearlite → Normalizing → Air cooling

# Austenite to pearlite transformation mechanism



*Heterogeneous nucleation at grain boundaries of austenite*

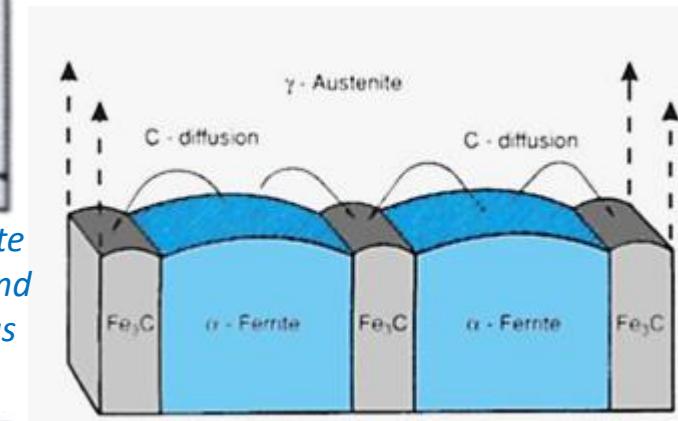
*Heterogeneous nucleation of ferrite at grain boundaries of austenite and in the vicinity of cementite nucleus*



*Ferrite and cementite phases grow inward of the austenite grain*

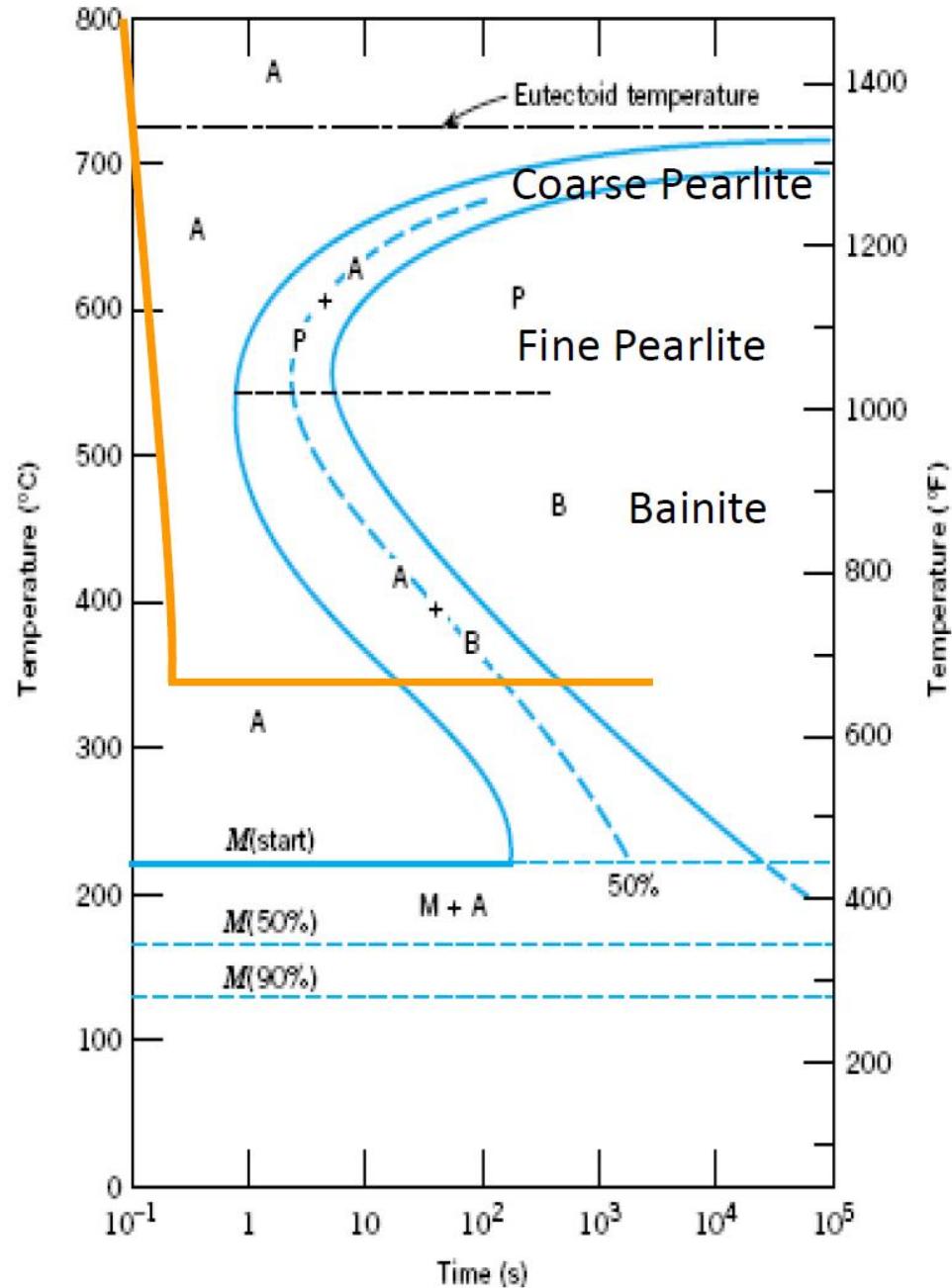


***How does the interlamellar spacing vary with temperature?***



*Interlamellar spacing ( $\lambda$ )*

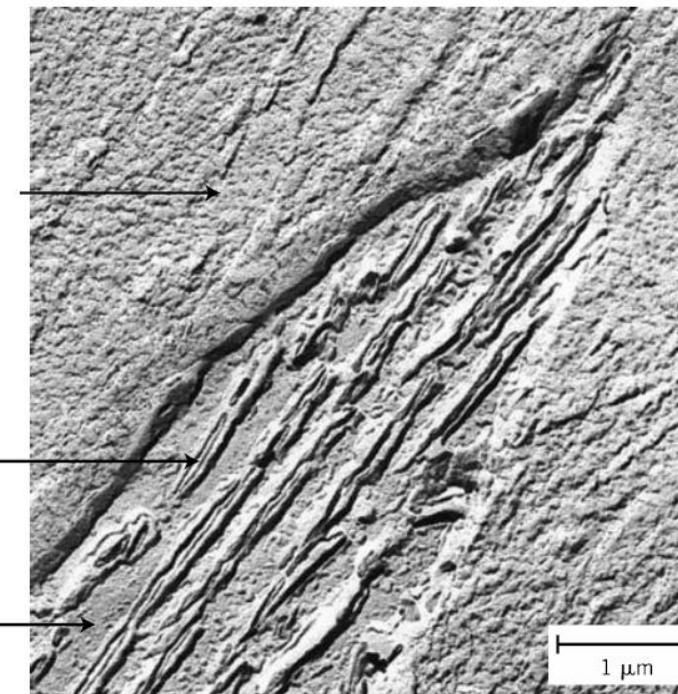
- *Interlamellar spacing is a function of temperature of transformation.*
- *Lower  $T \rightarrow$  nucleation rate higher  $\rightarrow$  finer interlamellar spacing  $\rightarrow$  higher hardness/strength*



## Bainite

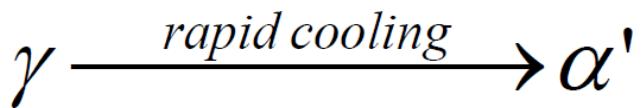
Short needles of  $\text{Fe}_3\text{C}$  embedded in plates of ferrite

C diffuses only to short distances



## Austempering

# QUENCHING



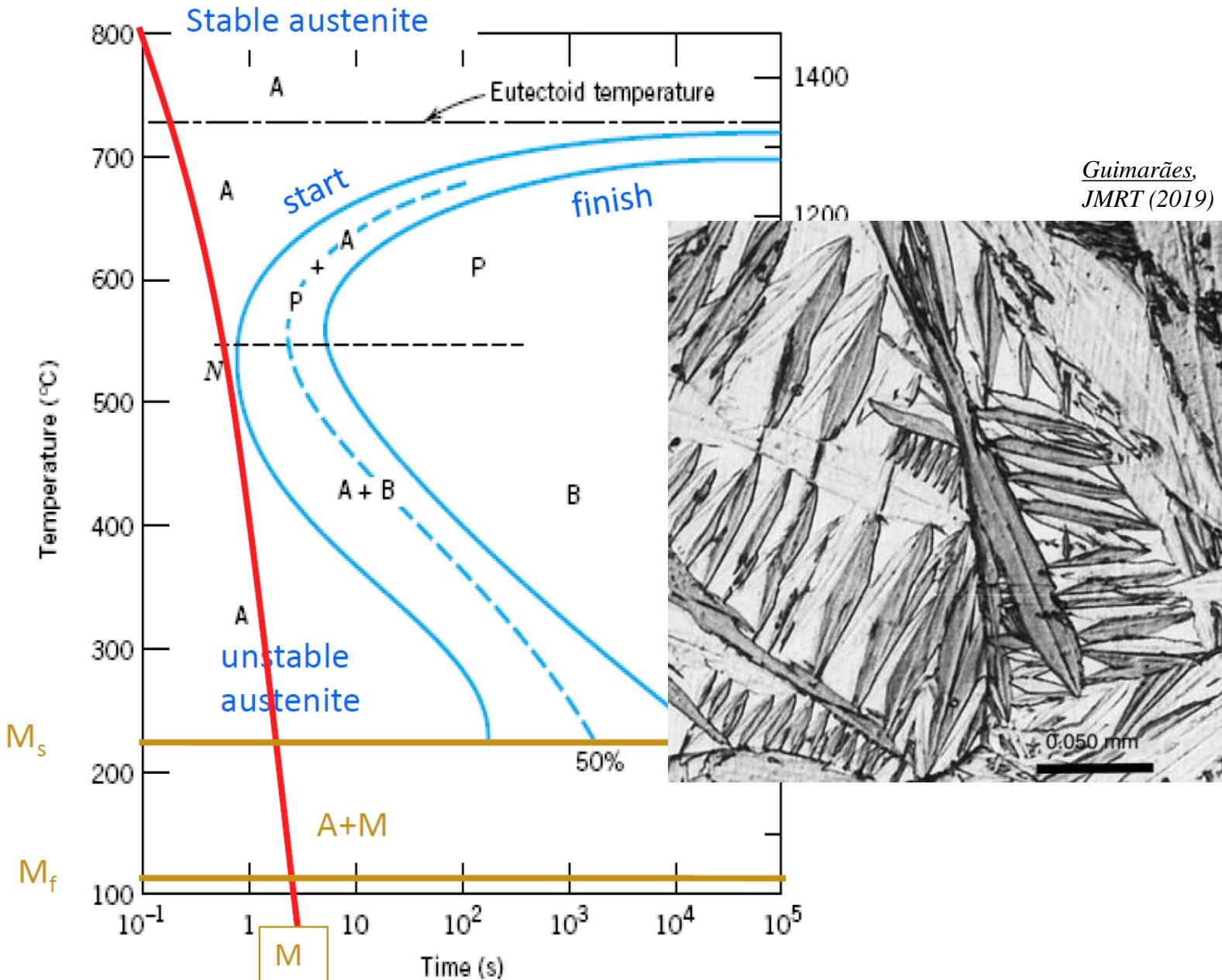
$\alpha'$ : martensite (M)

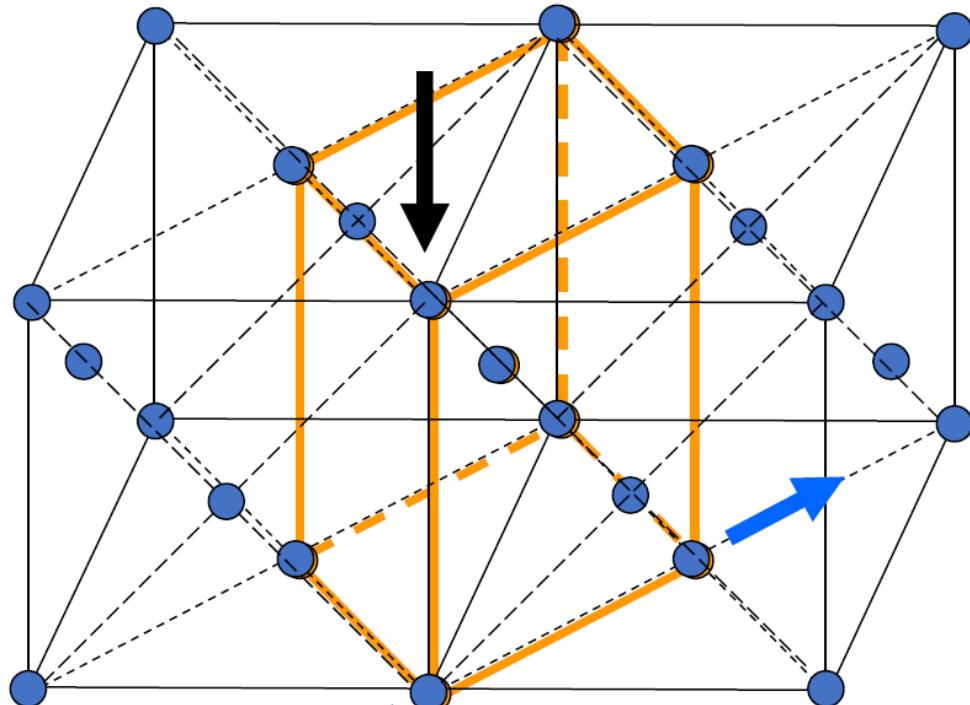
Extremely rapid, no C-curves are present for this phase

$M_s$  : Martensite start temperature

$M_f$  : Martensite finish temperature

TTT diagram for eutectoid steel





BCT unit cell of  $\gamma$  (austenite)

$$\frac{c}{a} = \sqrt{2} = 1.414$$

BCT unit cell of  $\alpha'$  (martensite)

$$\frac{c}{a} = 1.00 - 1.08$$

0% C (BCC)

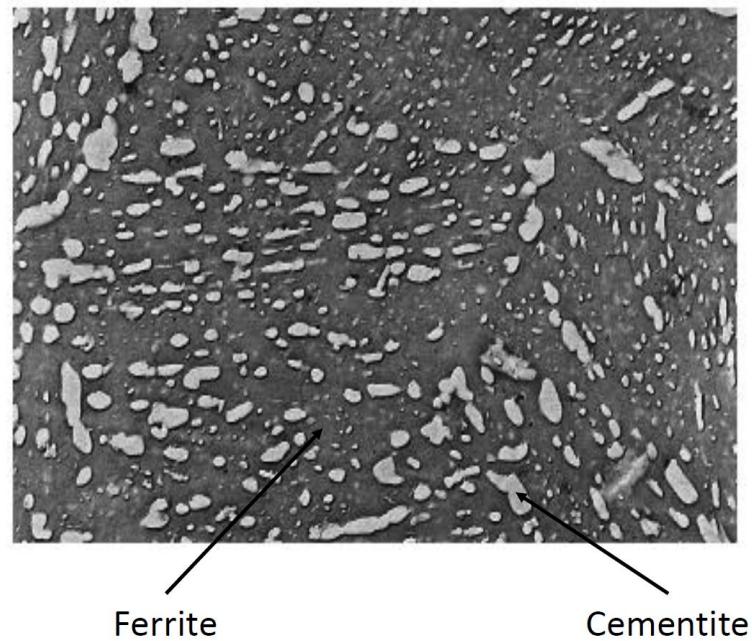
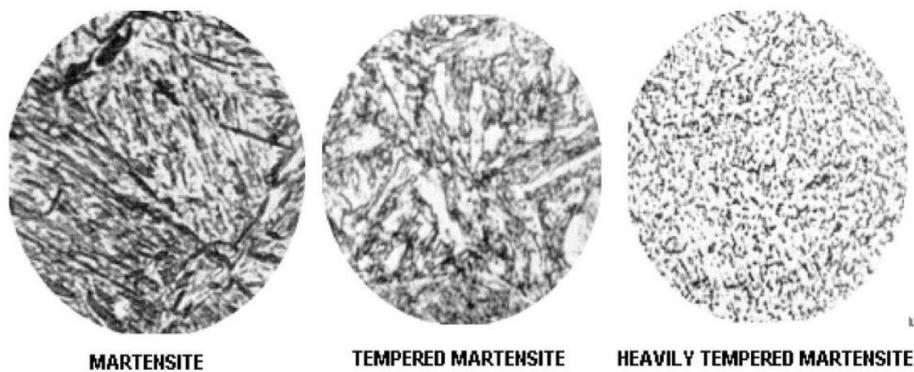
1.2 % C

# Tempering of Martensite

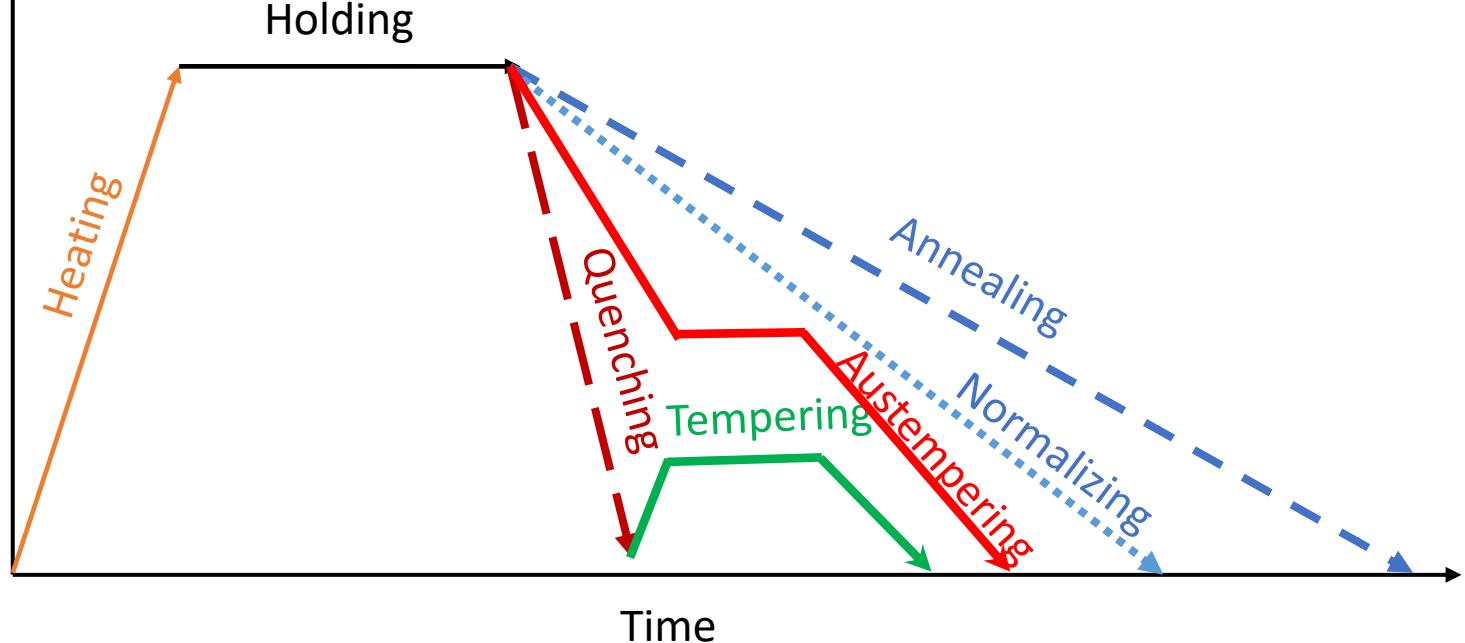
The hard martensite is brittle, so what to do???

## Tempering of martensite

Heating of quenched martensite to some intermediate temperature to allow the trapped C to come out and increase the toughness of steel



Temperature



Annealing

Furnace cooling

Coarse pearlite

Normalizing

Air cooling

Fine pearlite

Quenching

Water cooling

Martensite

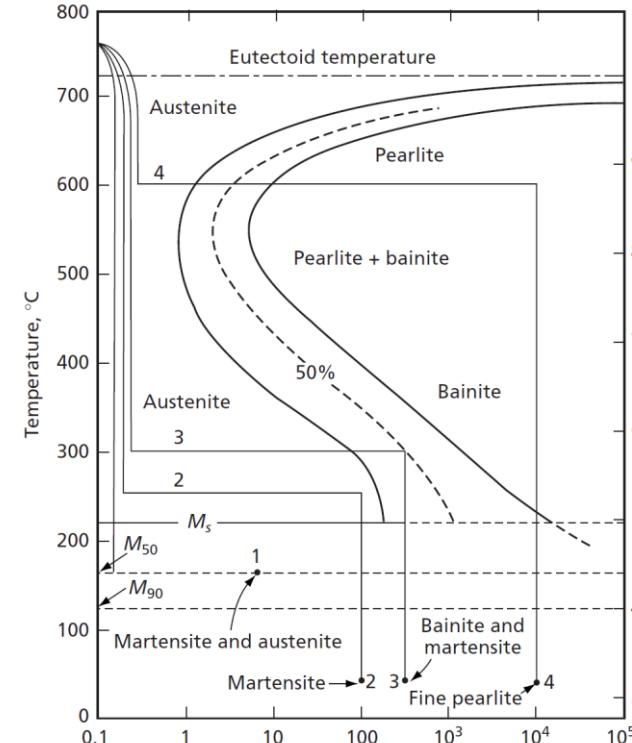
Austempering

Cooling to an intermediate temperature  
hold and again cooling

Bainite

Tempering

Quenching, heating to an intermediate temperature  
and hold and then cooling again



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# MLL 100

# Introduction to

# Materials Science and Engineering

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***Lecture-19 (February 23, 2022)***

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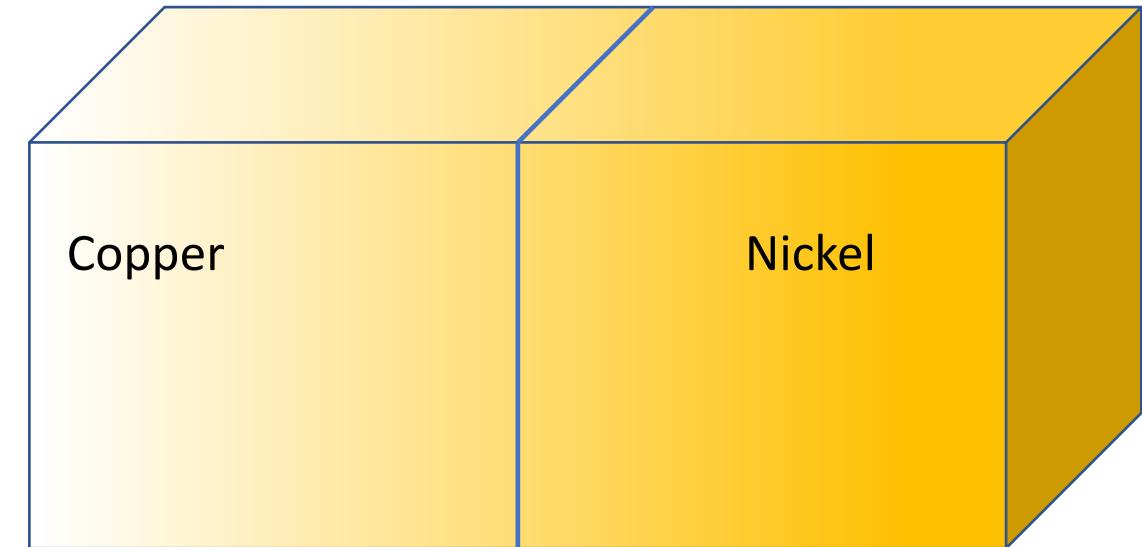
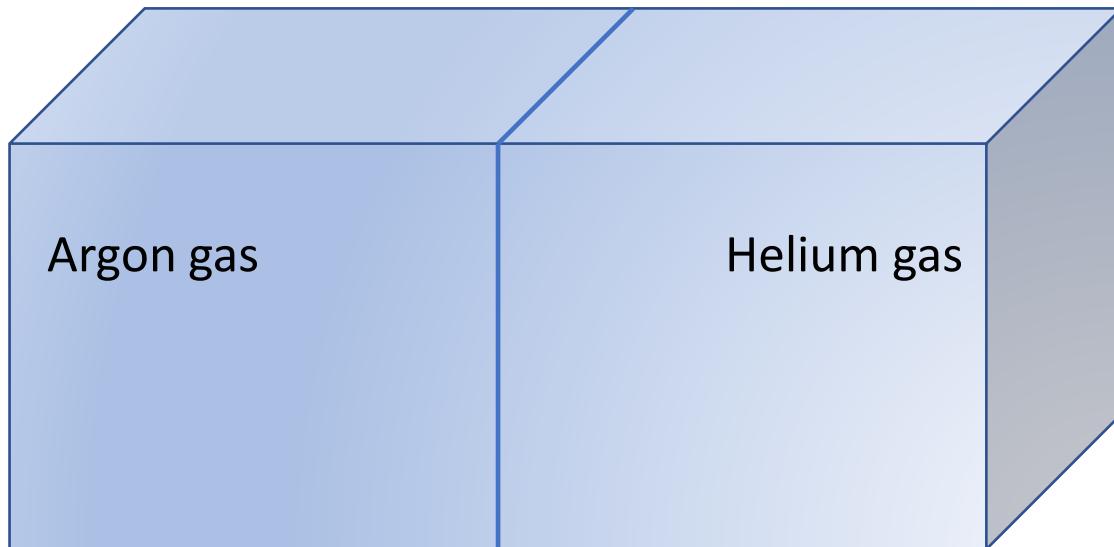
Department of Materials Science and Engineering

# What have we learnt in Lecture-18?

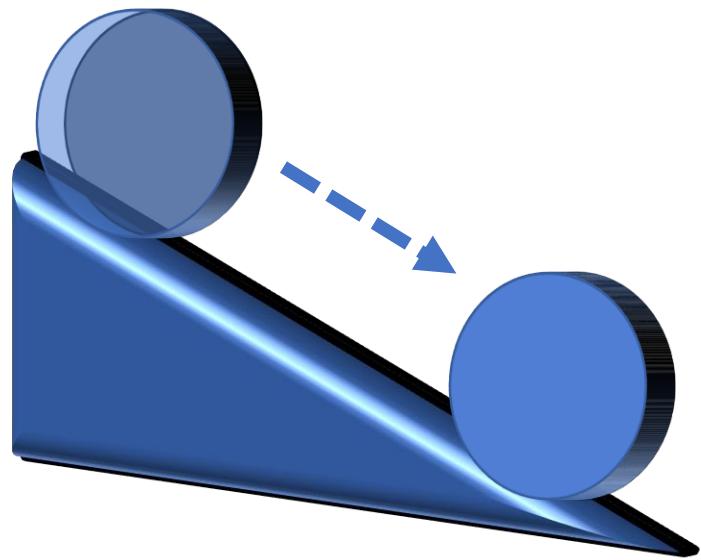
- TTT diagram (Transformation-temperature-time)
- Avrami equation
- Bainite, Martensite
- Different kinds of cooling rates: Annealing, Normalizing, Austempering, Quenching

**Imagine a chamber with a partition in the middle. Either side of the partition contains two different gases, Argon and Helium. What happens if the partition gets removed?**

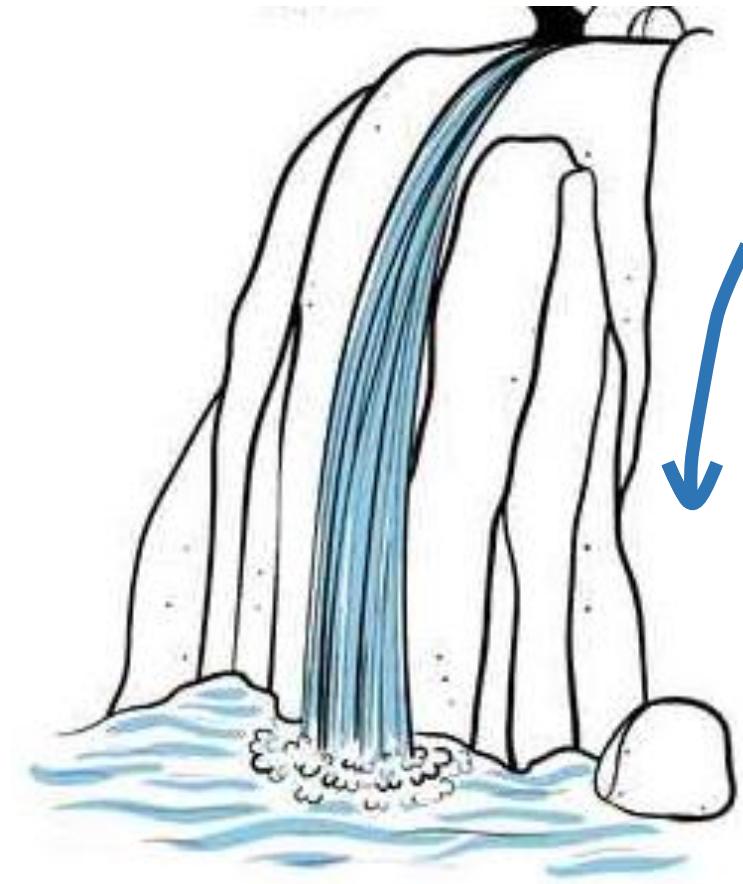
**In the second case, consider two single solid crystals, copper and nickel. What happens after the removal of partition?**



# Diffusion



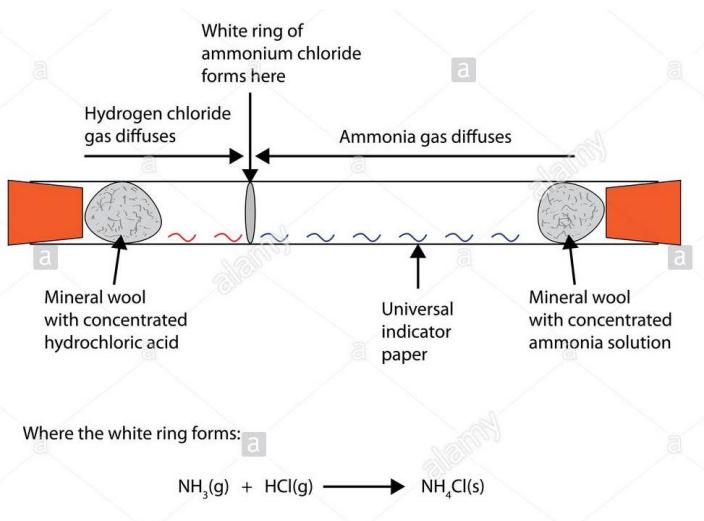
Disc rolling down the slope



Water falling down the hill slope

# What is diffusion?

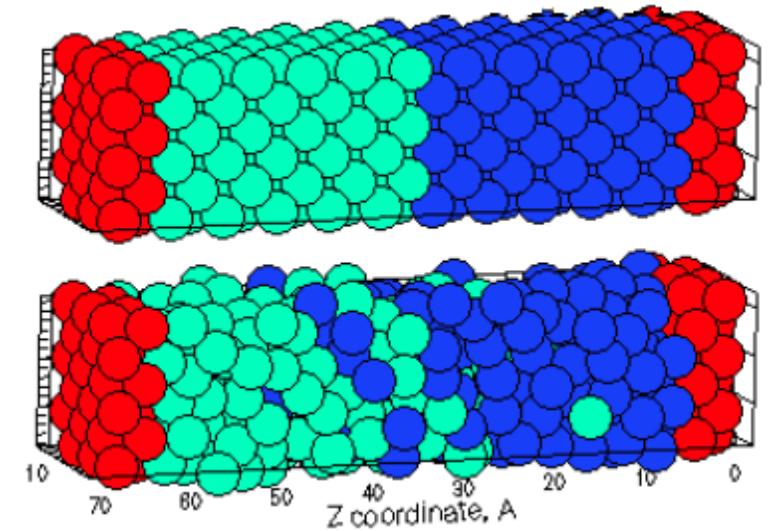
- Flow of atoms under the influence of a gradient, i.e. from a higher potential region to a lower potential region.



*Gas: Diffusion of ammonia*



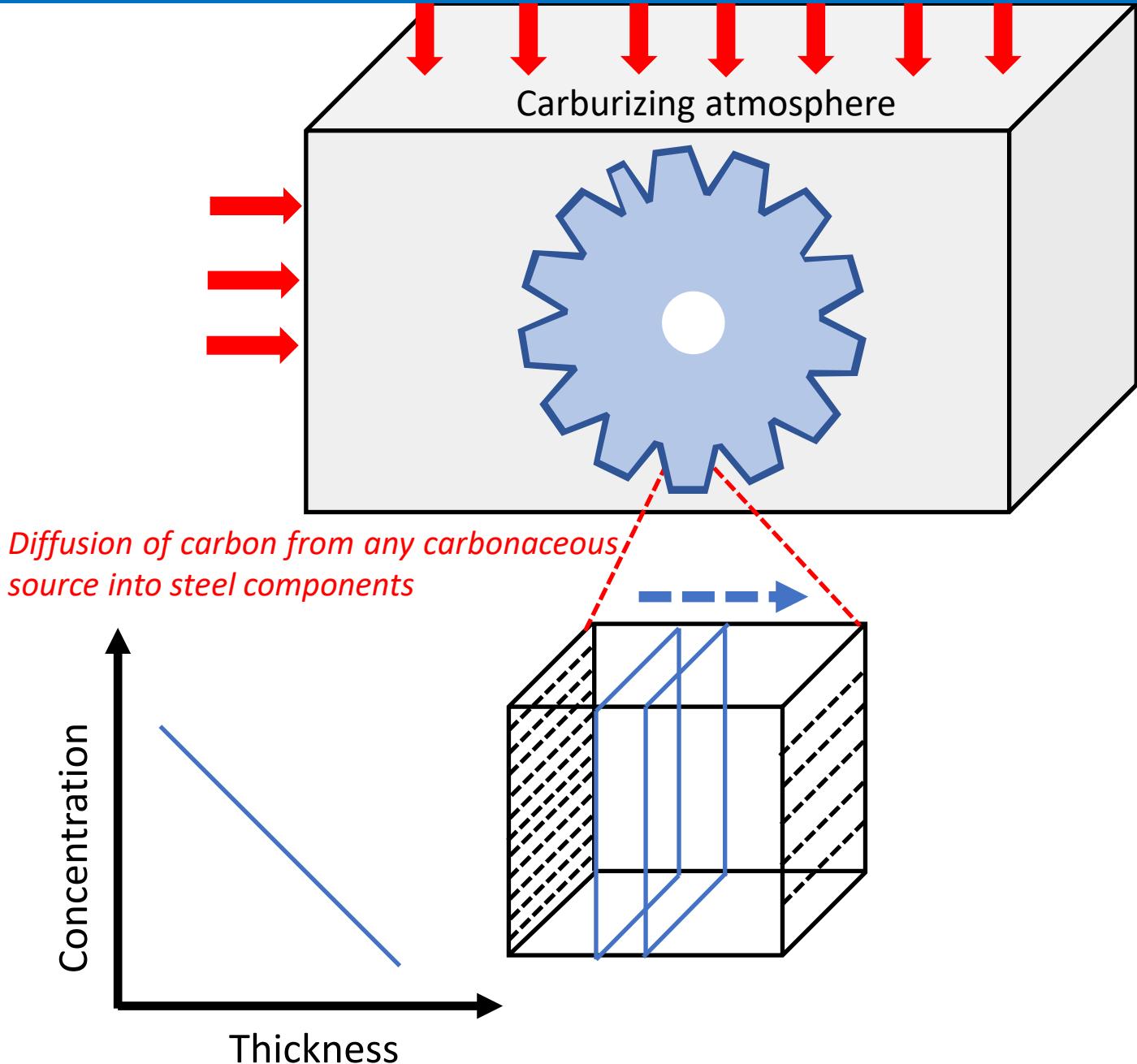
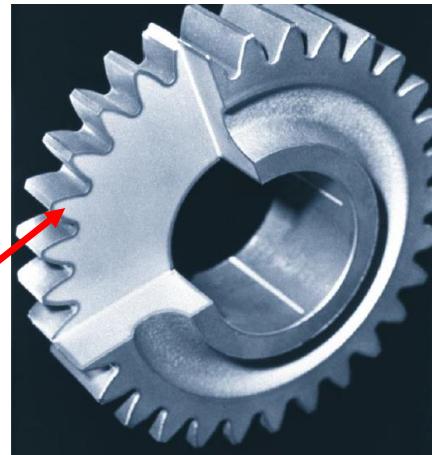
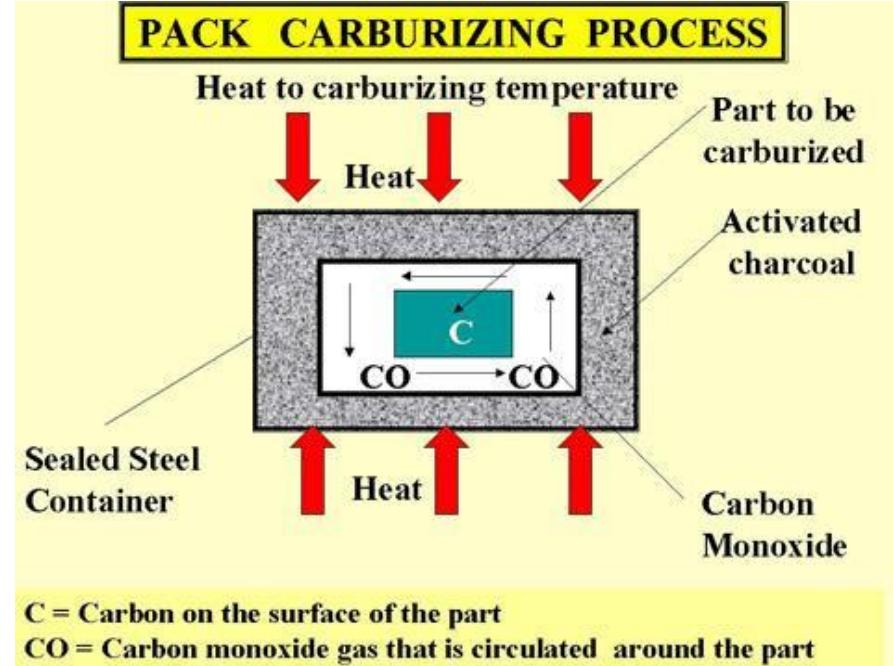
*Liquid: Diffusion of ink in water*



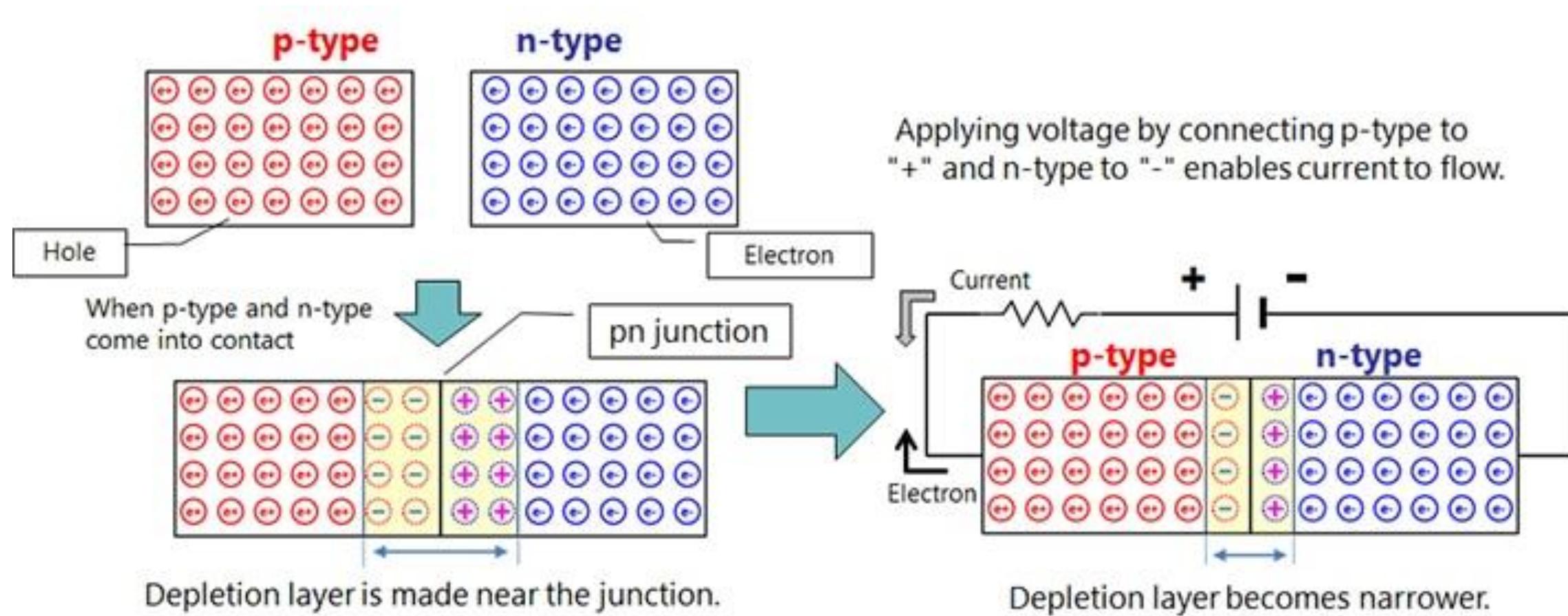
*Solid: Diffusion of atoms in copper and brass*

Diffusion in solids occur very slowly compared to those in liquids and gases, and also, is very restricted.

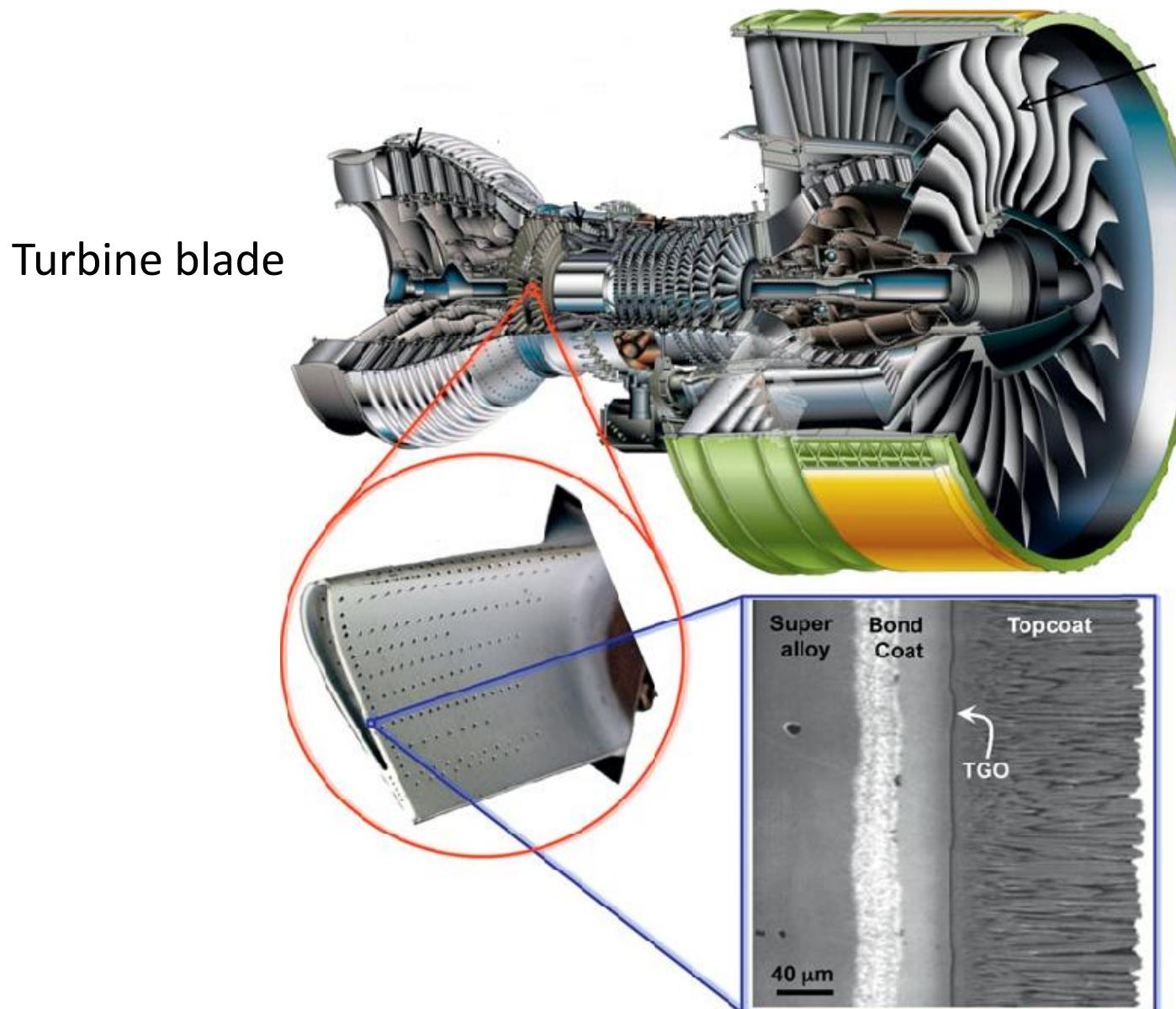
# How was diffusion exploited to engineer gears?



# Diffusion in semiconductor applications

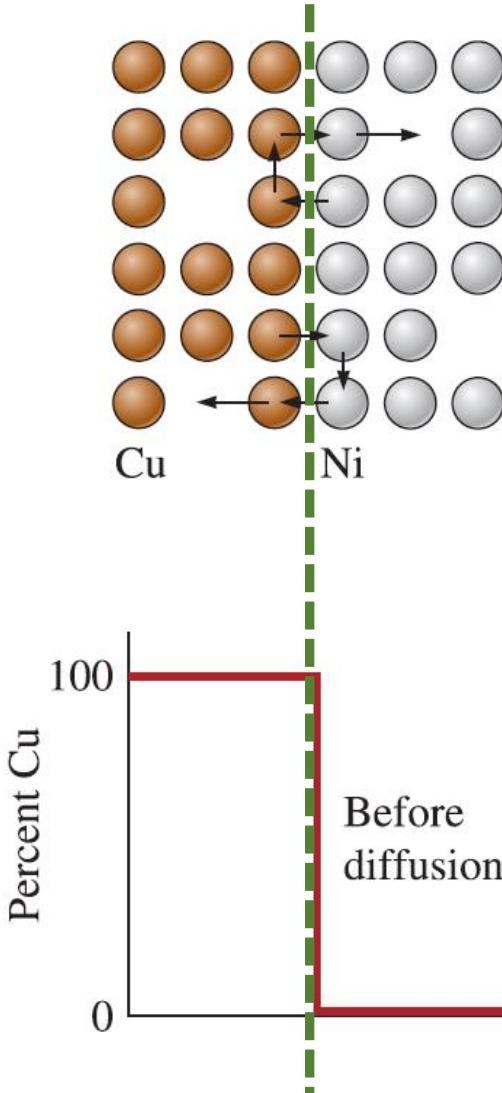


# Aircraft engine

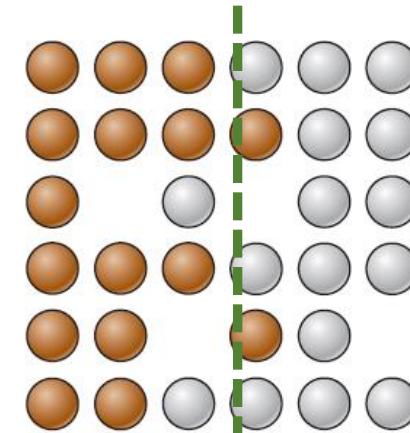


# How was the study of diffusion started off?

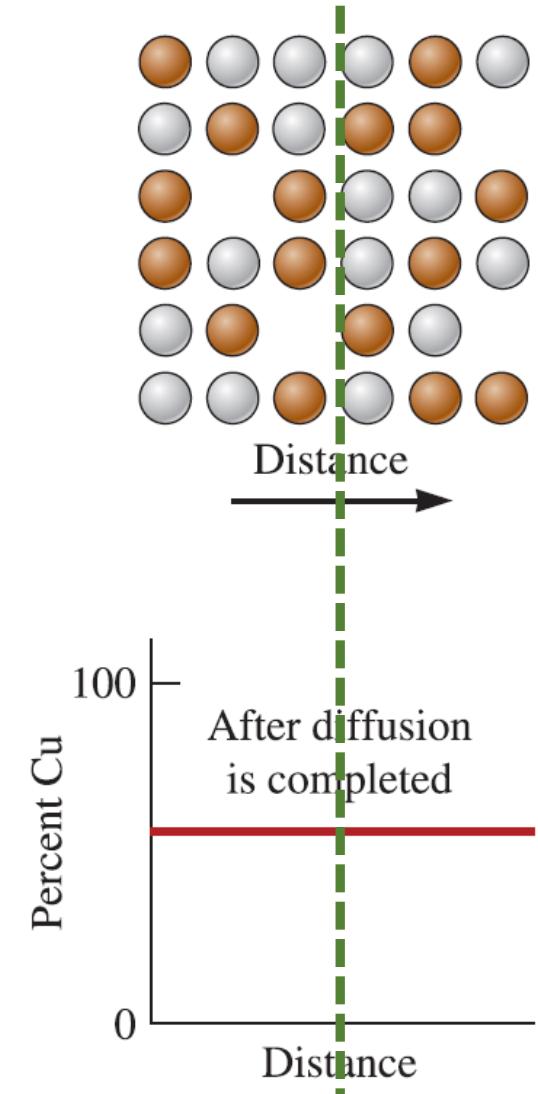
Initial stage



During diffusion



Completion of diffusion



# What drives diffusion?

- Temperature and a chemical potential gradient.
- Thermal energy -----> Atomic vibrations in lattice -----> Atomic jumps
- Gradient: Chemical potential (*What about the concentration gradient??*)

Gibbs free energy (Minimized)

$$(\Delta G = +\Delta H - T\Delta S)$$

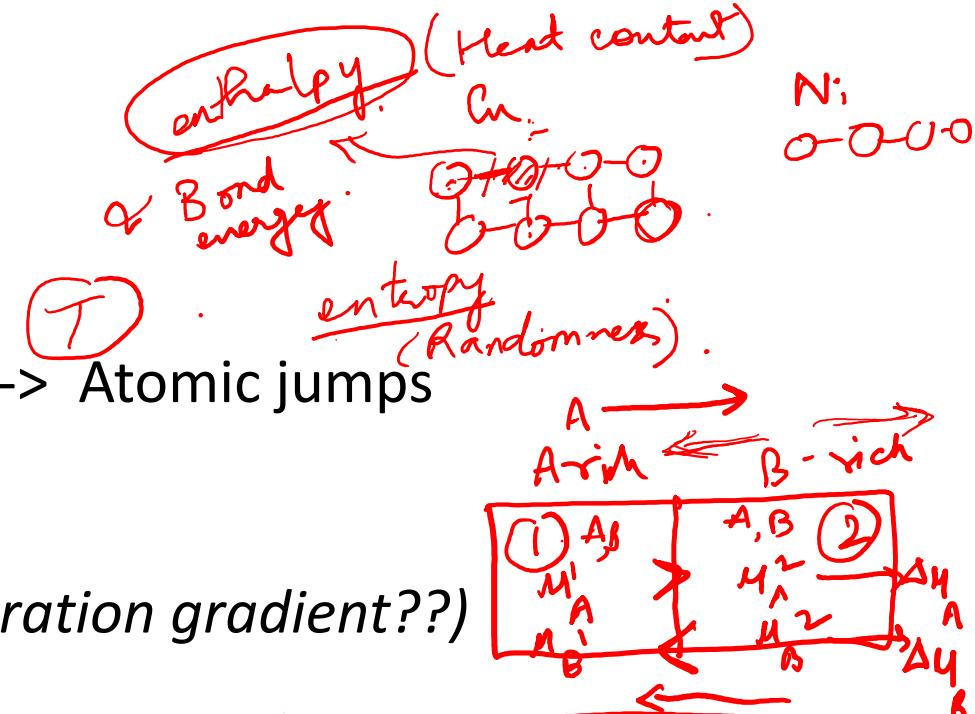
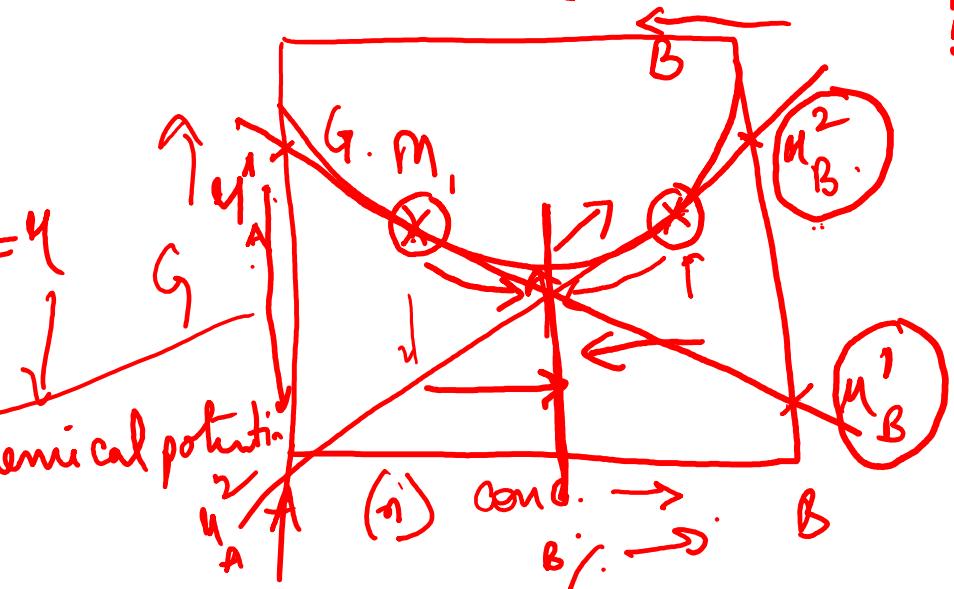
( $G_w$ ,  $G_m$ ,  $G_{mix}$ )

enthalpy

entropy

chemical potential gradient

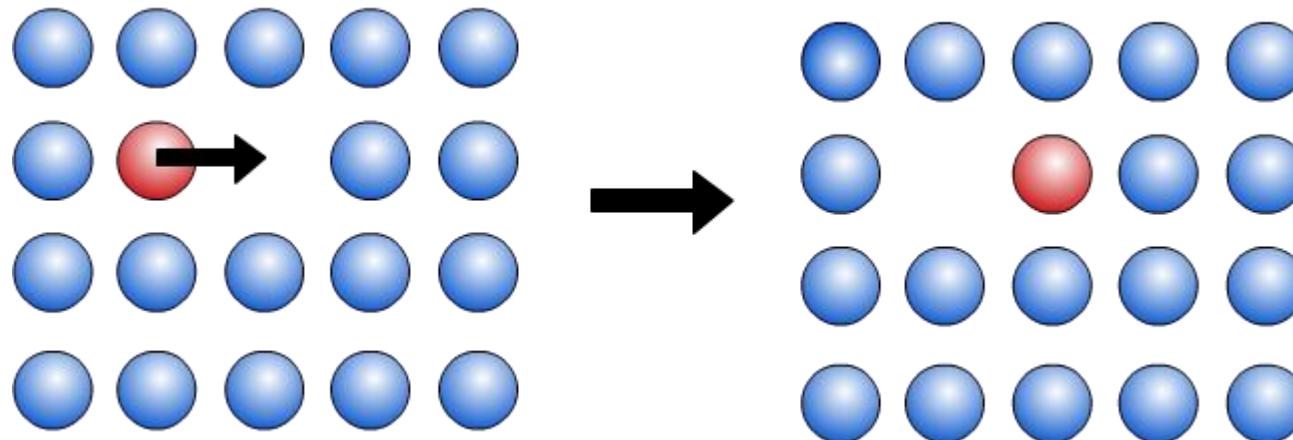
$$\frac{dG}{dn} = \gamma$$



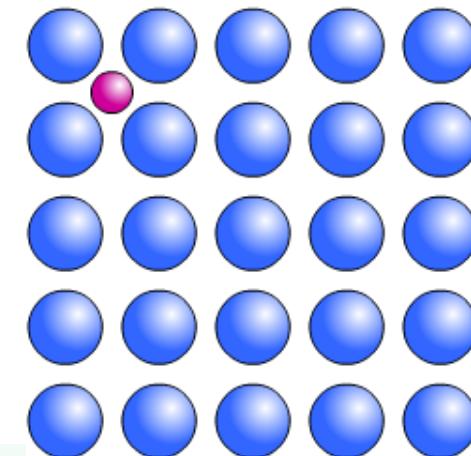
# How does diffusion occur in a solid?

## Substitutional diffusion

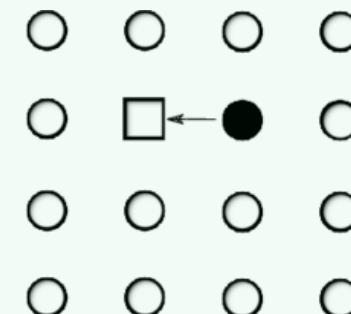
*Motion of atom* →



## Interstitial diffusion



### Vacancy-mediated diffusion



- ❑ Diffusion of an atom via vacancy depends on two factors:
  - How easily vacancies can form in the lattice?
  - How easy it is for an atom to move into a vacancy?
  
- ❑ The dependence upon the presence of vacancies makes substitutional diffusion slower than interstitial diffusion.

# Defects (Imperfections) in crystalline solid

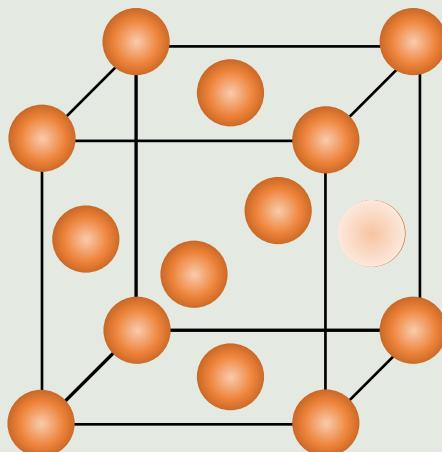
*Disruption in the regular arrangement of internal constituents of a solid.*

Classification based on: (i) Dimensionality, (ii) Thermodynamics, (iii) Sources

## Equilibrium defects

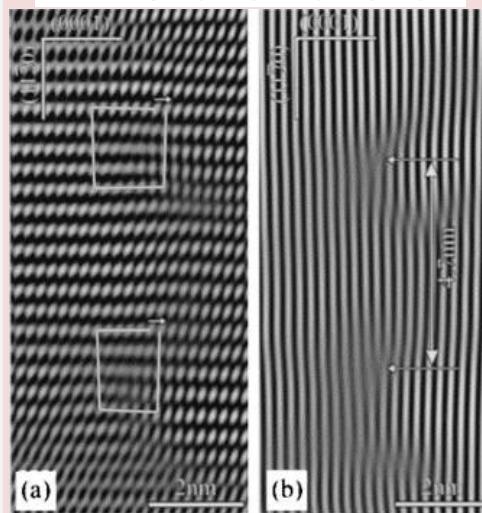
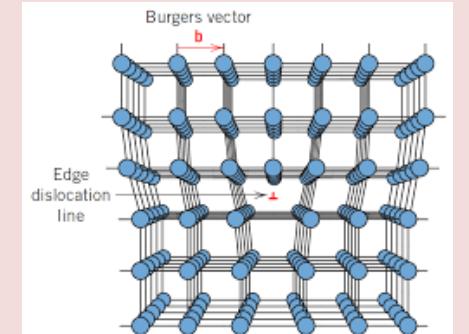
(Decreases free energy  
of the system)

### 0-D: Point defect

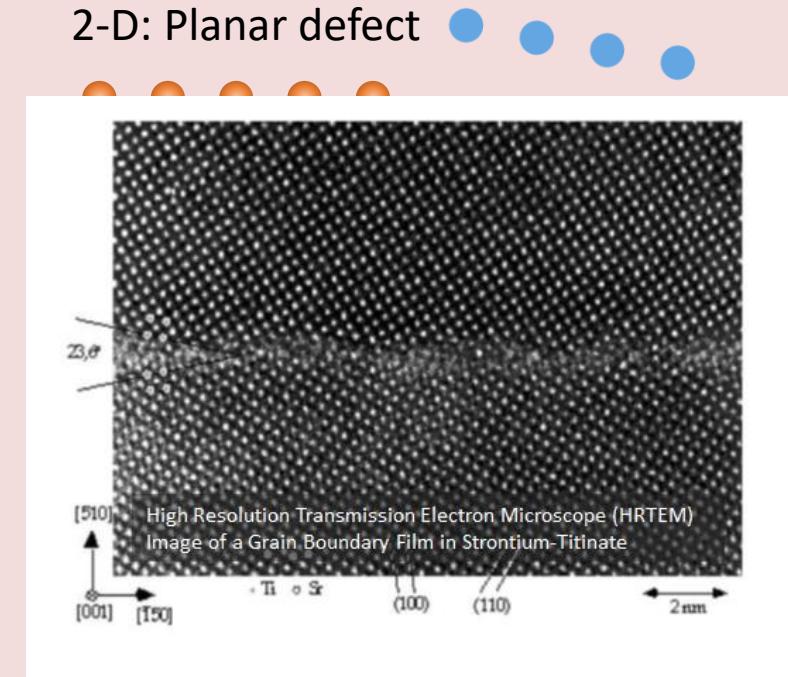


- Vacancies
- Self-interstitials

### 1-D: Line defect



### 2-D: Planar defect

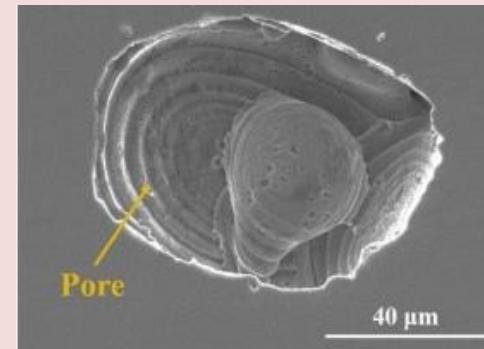


- Dislocations
- Grain boundaries
- Interfaces

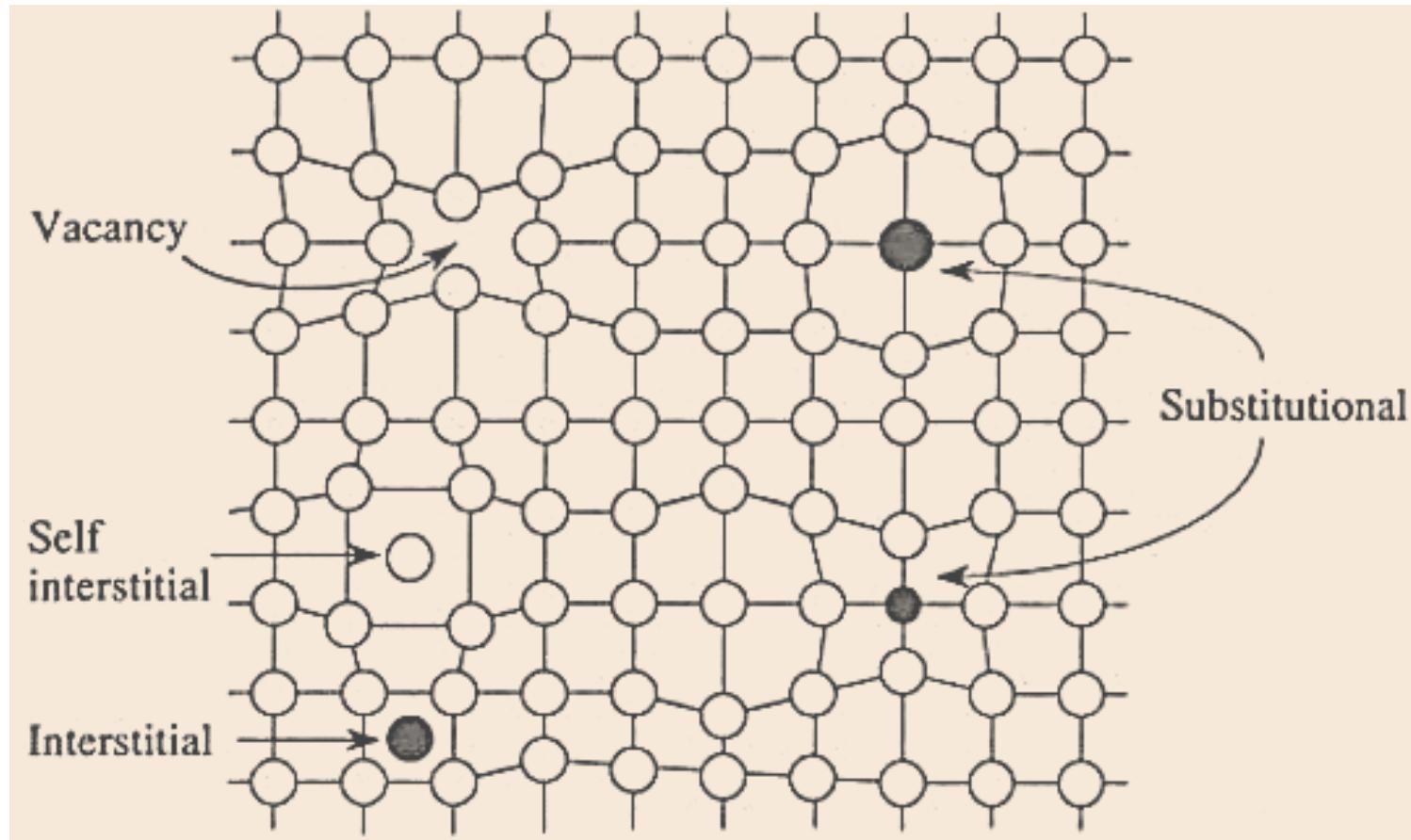
## Non-equilibrium defects

(Increases free energy of the system)

### 3-D: Volumetric defect



- Voids
- Precipitates



## 1. Vacancy

(Entity missing from regular lattice site)

## 2. Self-interstitial

(Lattice atoms present at interstitial sites)

## 3. Substitutional solute

(Foreign atoms occupying regular lattice site)

## 4. Interstitial solute

(Foreign atoms typically with a size much smaller than the regular atoms occupying the interstitial sites)

# Why a vacancy is thermodynamically stable defect?

Stability of a system at a constant pressure:

$$G = H - T \cdot S$$

Let's assume that a system at state '1' has a free energy of ' $G_1$ ' and ' $G_2$ ' at state '2':

$$G_1 = H_1 - T \cdot S_1$$

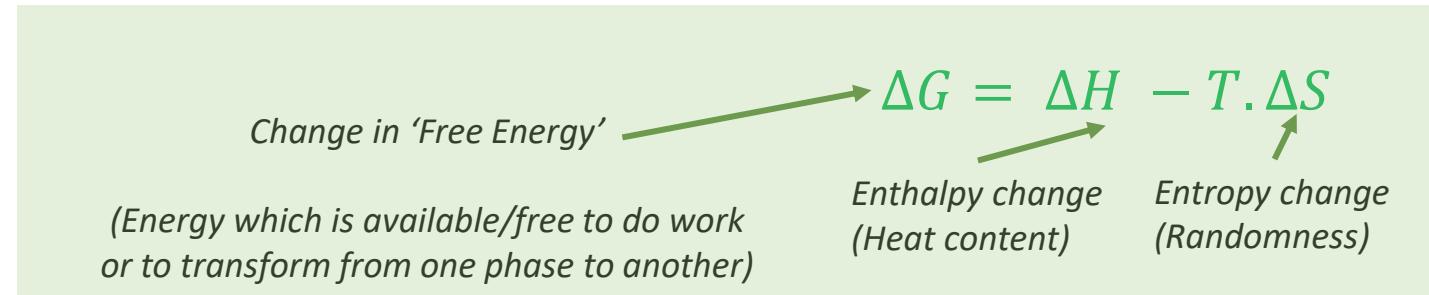
$$G_2 = H_2 - T \cdot S_2$$

The system would like to attain state '2' only if:

**Perfect crystal**

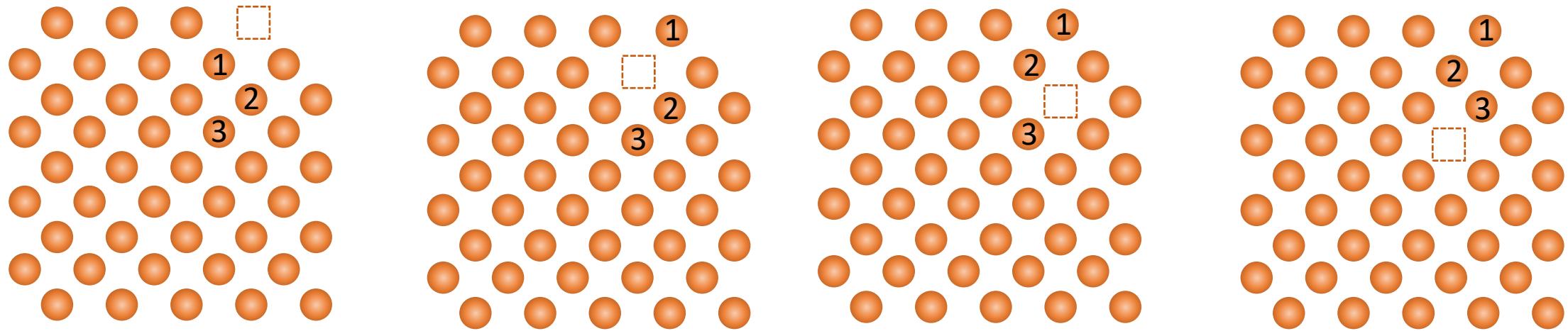


*Remove balls from random positions  
(vacancies)*



*Remove balls from a line  
(dislocations)*

## Formation of a vacancy

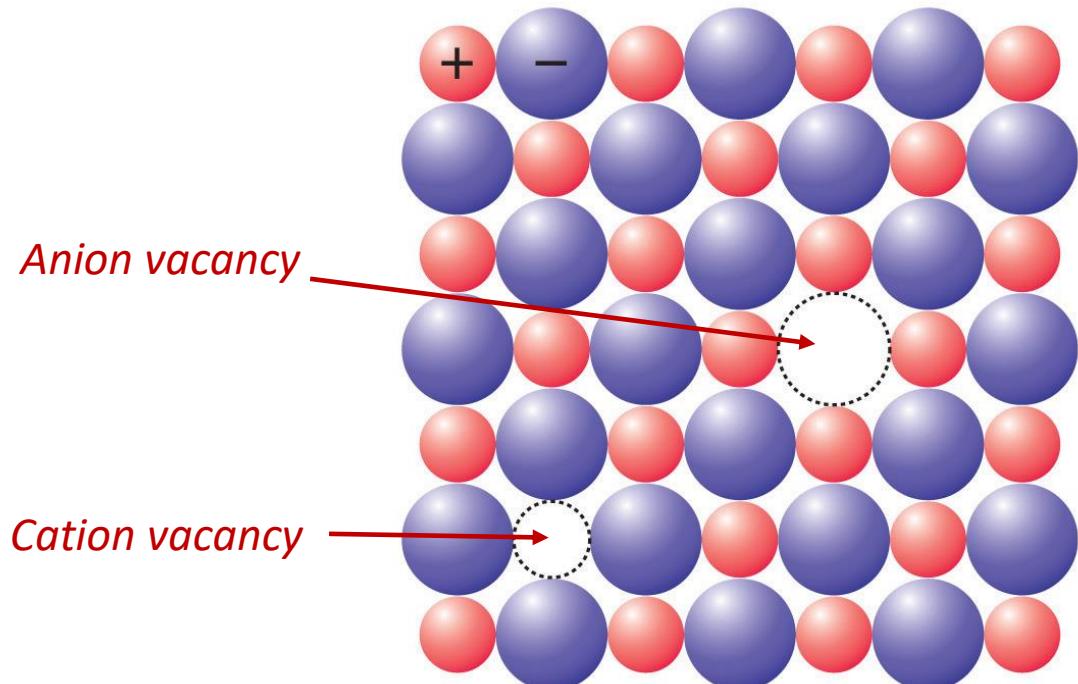


- When atoms diffuse from the interior of a crystal to the free surface, thermal vacancies get created.
- Bonds are broken because of the creation of vacancies → Increase in enthalpy, (+ve  $H_v$ ) → Unfavourable for the system.
- Increase in entropy → irregular vibration of atoms surrounding the vacancies and entropy of mixing (configurational entropy), i.e., different possibilities of mixing arrangements of components and vacancies.

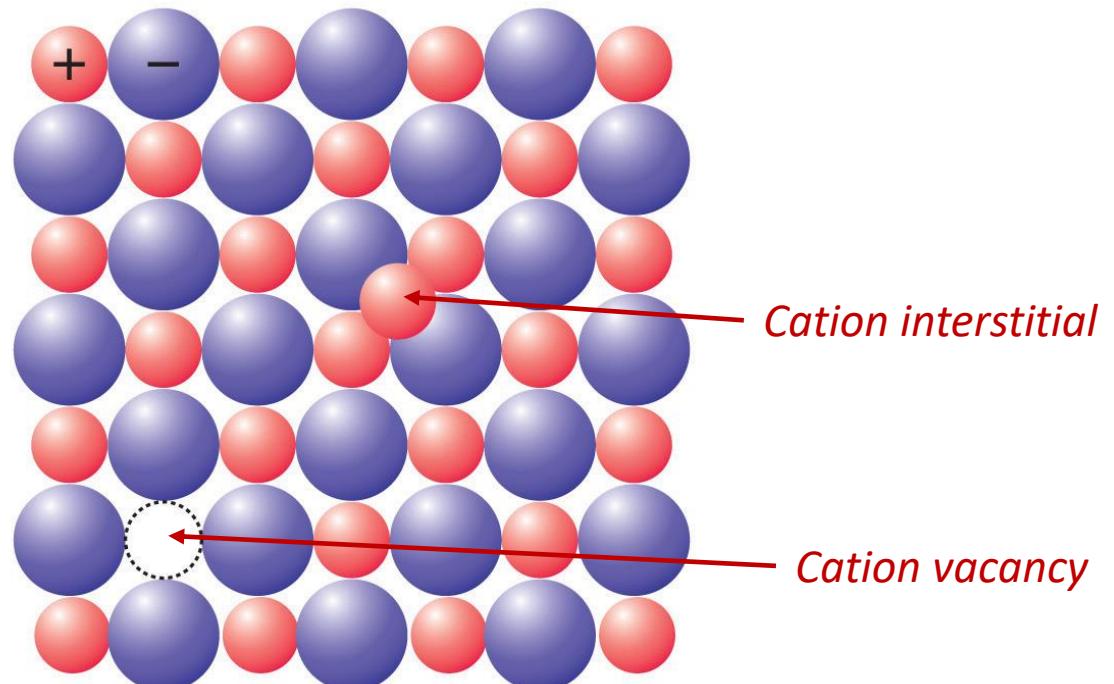
# Point defects in ionic solids

Defects in semiconductors:

- (i) Intrinsic defects (Present in a pure material at equilibrium)
- (ii) Extrinsic defects (Defects resulting because of doping/alloying)



**(a) Schottky defect**



**(b) Frenkel defect**

Creation of a vacancy in an ionic solid: Charge neutrality ----> anion vacancy + cation vacancy (Schottky defect)

----> Cation vacancy + interstitial (Frenkel defect)

# Laws of diffusion



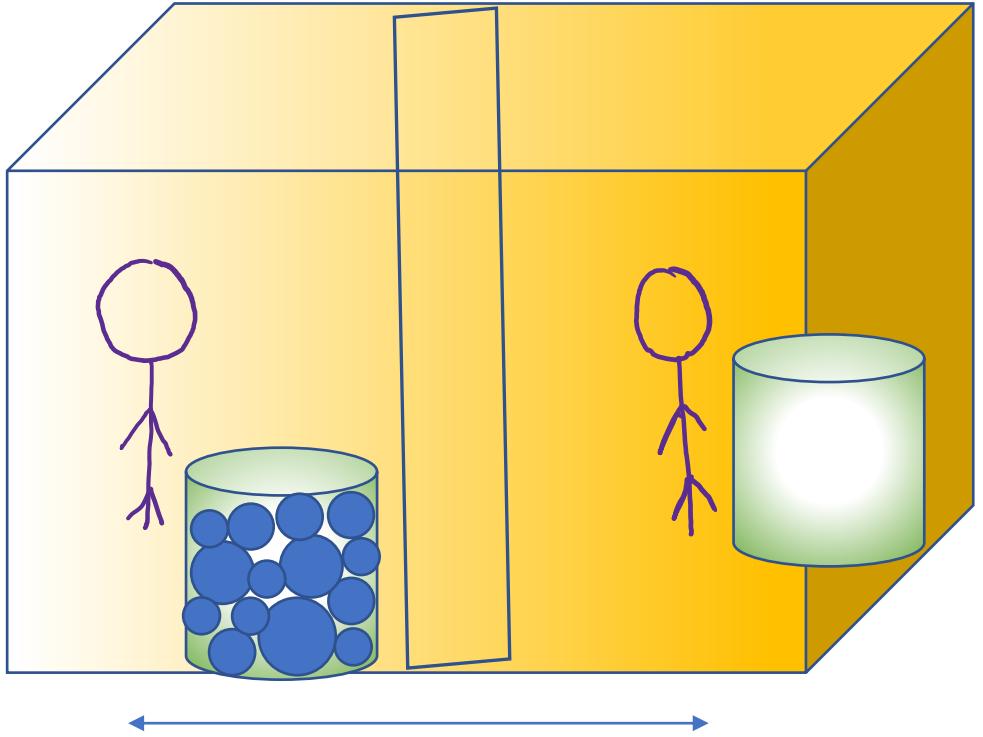
Fick's first law of diffusion

*(Empirical law)*



Fick's second law of diffusion

*(First Law + Mass balance)*



- Area of window (A) ↑
- Distance between two persons (x) ↓
- Time (t) ↑
- No. of balls (B) ↑

Number of balls reaching to your friend  $\propto \frac{(B_1 - B_2) \cdot A \cdot t}{\Delta x}$

$$\frac{(\text{Number of balls reaching to your friend })}{A \cdot t} \propto \frac{(B_1 - B_2)}{\Delta x}$$

$$\frac{(\text{Number of balls reaching to your friend })}{A \cdot t} = (\text{property of a ball}) \cdot \frac{(B_1 - B_2)}{\Delta x}$$

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# MLL 100

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# Materials Science and Engineering

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***Lecture-20 (February 25, 2022)***

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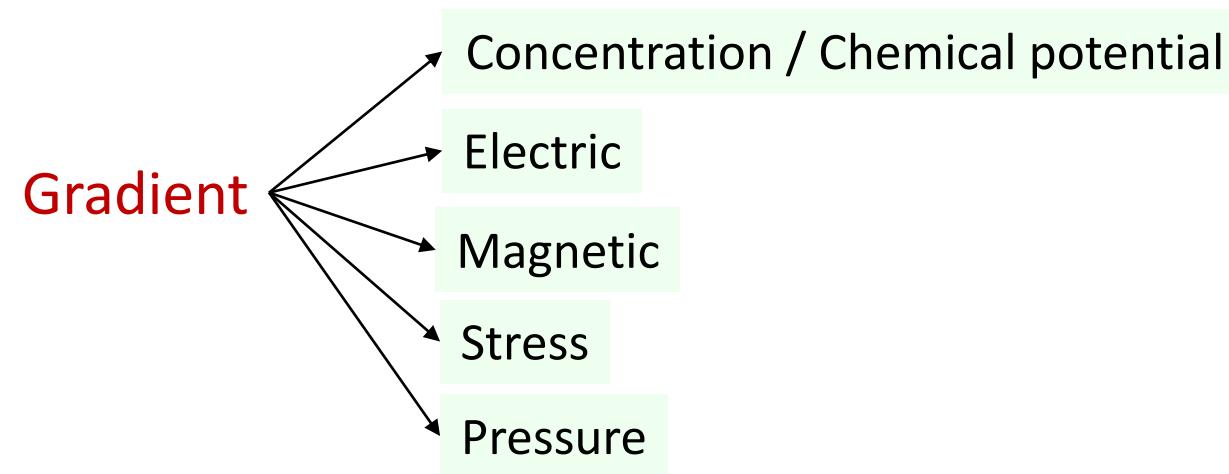


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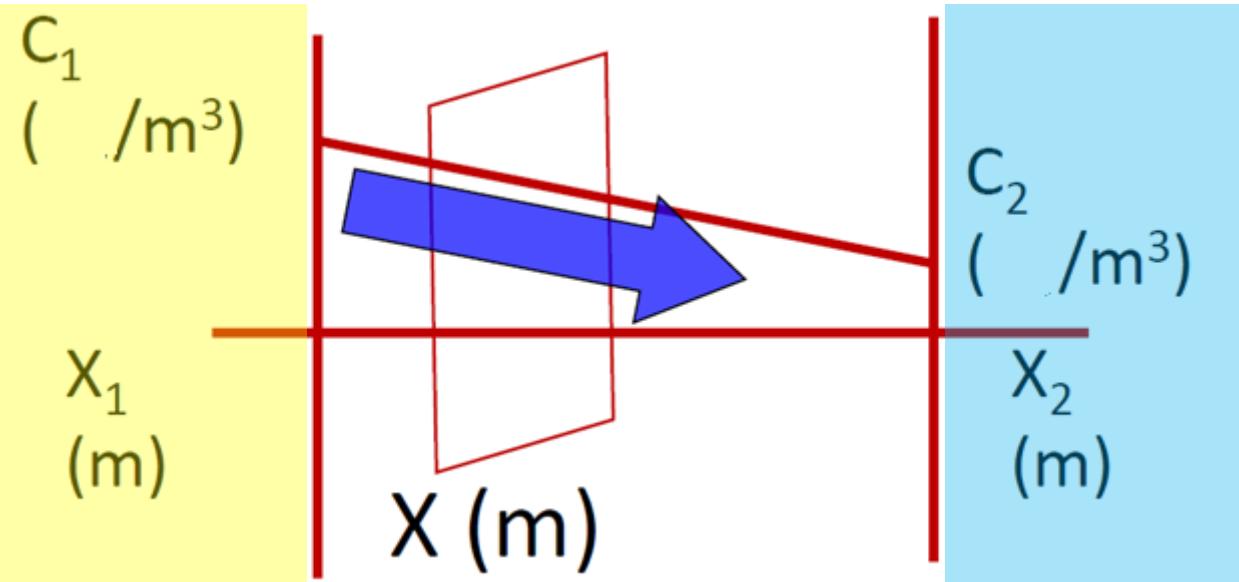
# What have we learnt in Lecture-19?

- ❑ Diffusion
- ❑ Driving force of diffusion: chemical potential gradient

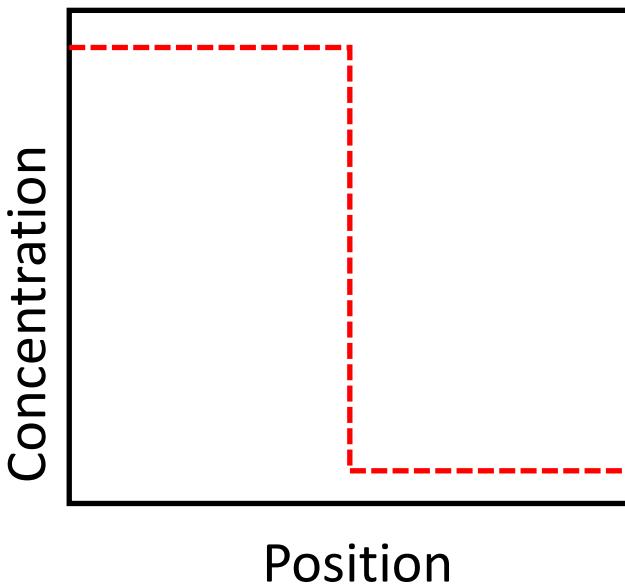


- ❑ Analogy to Fick's first law

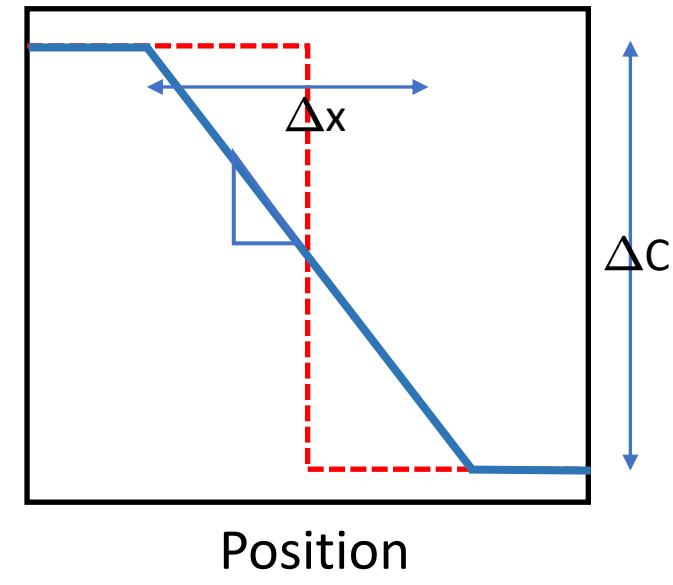
# Fick's first law of diffusion



$t = t_o$



$t = t_1$



For one-dimensional:

(-ve) sign implies flow of atoms down the concentration gradient

Flux of atoms per unit area per unit time

$J_i = -D \left( \frac{dC_i}{dx} \right)$

Material property

Gradient

How the composition of a material varies with the distance?

What is the unit of diffusion coefficient (D)?

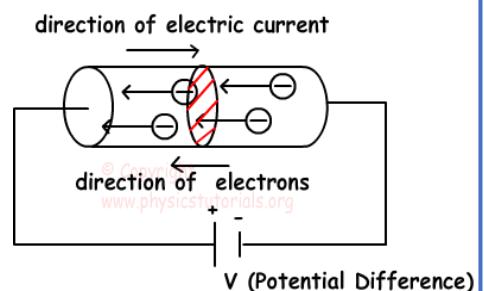
$$J = -D \frac{(C_2 - C_1)_{\text{atoms/m}^3}}{(x_2 - x_1) \text{ m}}$$

atoms/m<sup>2</sup>.s       $m^2/s$

## Charge flow (electrical conduction)

□ What quantity flows?

Electrons



□ What is the gradient?

Potential drop

$$j_e \propto -\frac{dV}{dx}$$

## Electrical conductivity

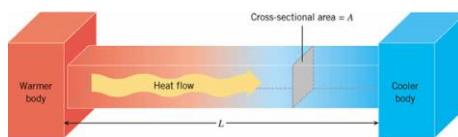
$$j_e = -\sigma \frac{dV}{dx}$$

□ What is the law describing this behaviour?

Ohm's law

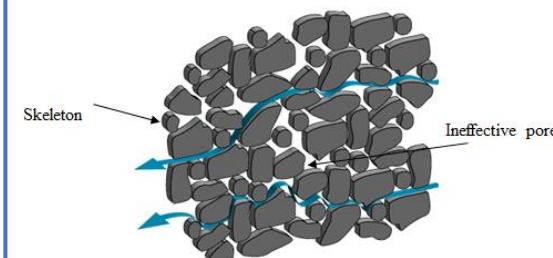
## Phonon flow (thermal conduction)

phonons



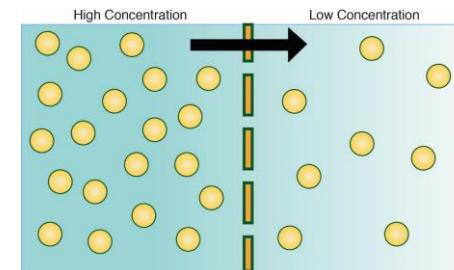
## Fluid flow in porous medium

fluid



## Atomic flow (diffusion)

atoms



Pressure difference

$$j_f \propto -\frac{dP}{dx}$$

## Hydraulic permeability

$$j_f = -K \frac{dP}{dx}$$

## Diffusivity

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

Darcy's law

Fick's law

Temperature difference

$$j_q \propto -\frac{dT}{dx}$$

Fourier's law

□ What material property gets represented?

Ohm's law

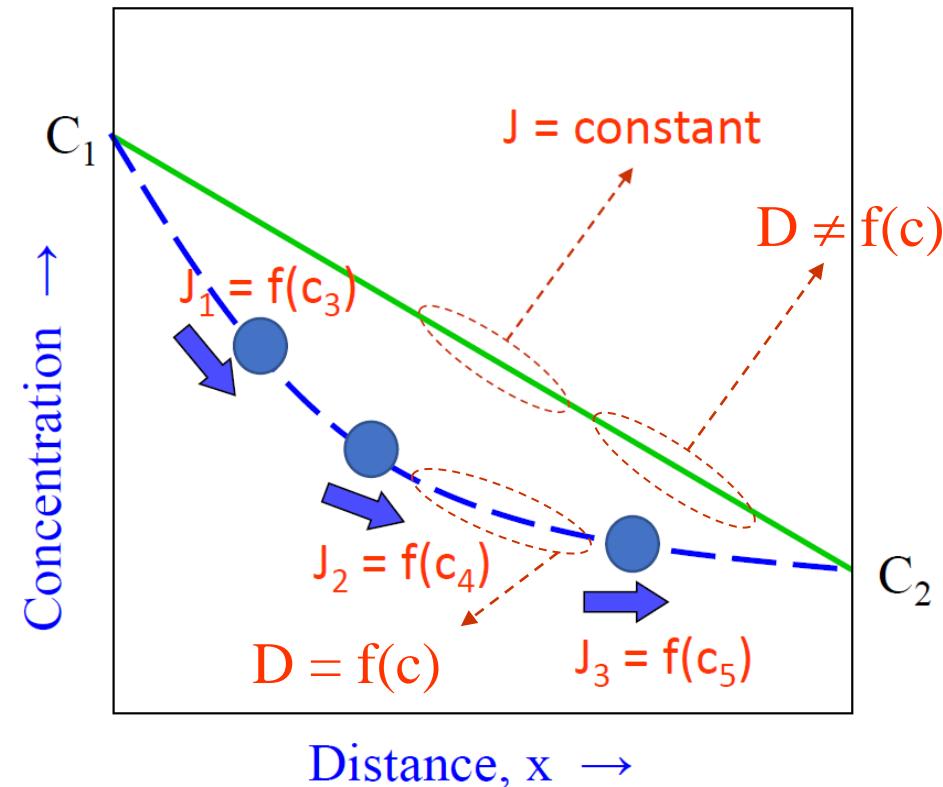
Fourier's law

# Steady-state of diffusion

In steady state diffusion there is neither accumulation nor depletion of the diffusing species anywhere in the medium at any time and Fick's first law is easily applicable

$$J = -D \frac{dc}{dx}$$

Constant



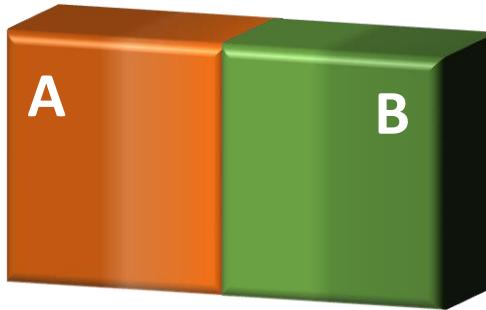
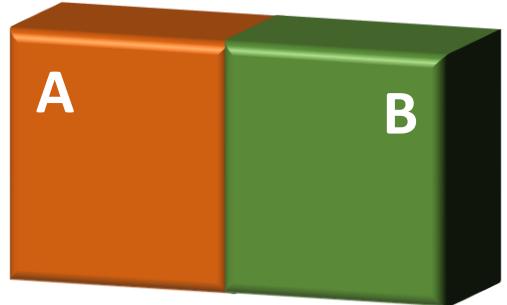
## Steady-state

Concentration  $\neq f(\text{time}, t)$

$$\frac{dC}{dx} = \text{constant}; \quad \frac{dC}{dt} = 0$$

$J \neq f(x, t)$  (No accumulation of matter)

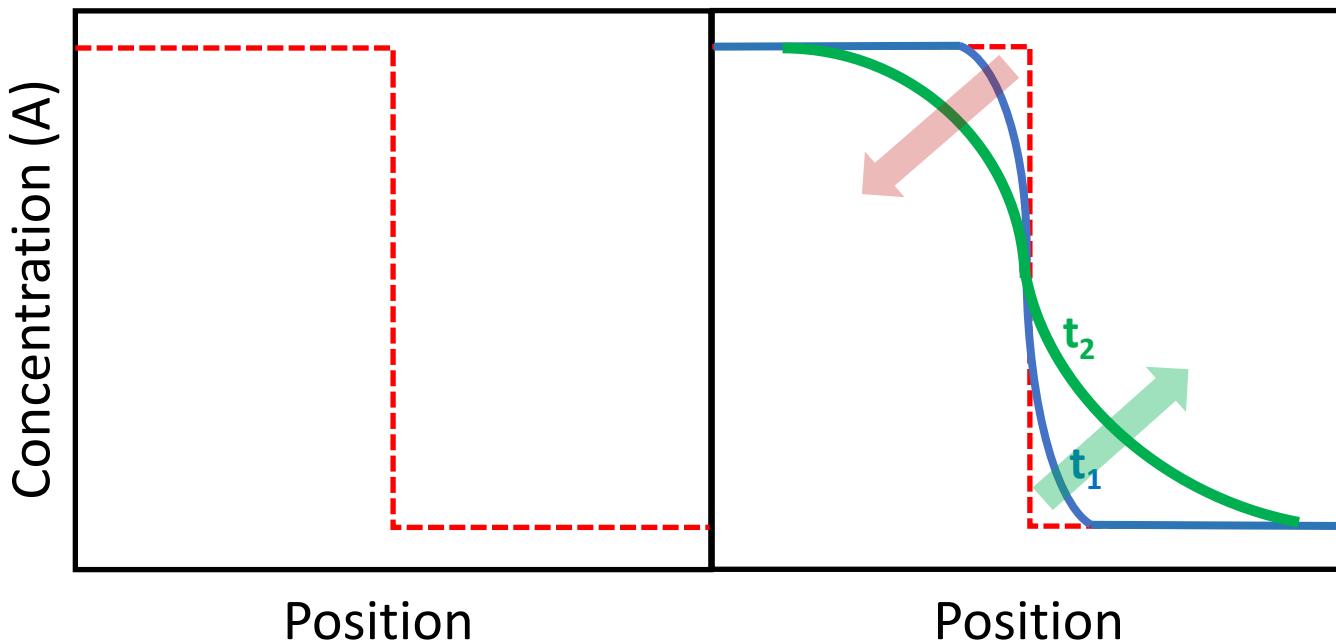
## Fick's second law: for non-steady state



$t = t_0$

$t = t_1$

$t = t_2$



Concentration =  $f$  (position, time)

$$\frac{dC}{dx} \neq \text{constant}; \quad \frac{dC}{dt} \neq 0$$

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2}$$

# Fick's second law

$J_x$  is the flux arriving at plane A and  $J_{x+\Delta x}$  is the flux leaving plane B. Then the Accumulation of matter is given by:  $(J_x - J_{x+\Delta x})$ .

- How many atoms got accumulated in  $\Delta x$  in time  $\Delta t$ ?

$$\text{Atoms crossing plane A} - \text{Atoms crossing plane B} = (N_x) - (N_{x+\Delta x})$$

$$\text{Flux, } J = (\text{No. of atoms}) / (A.t) = (J_x \cdot A.t) - (J_{x+\Delta x} \cdot A.t)$$

$$\left[ \left( \frac{\text{Atoms}}{m^3} \cdot \frac{1}{s} \right) \cdot m \right] = \left[ \frac{\text{Atoms}}{m^2 s} \right] \equiv [J]$$

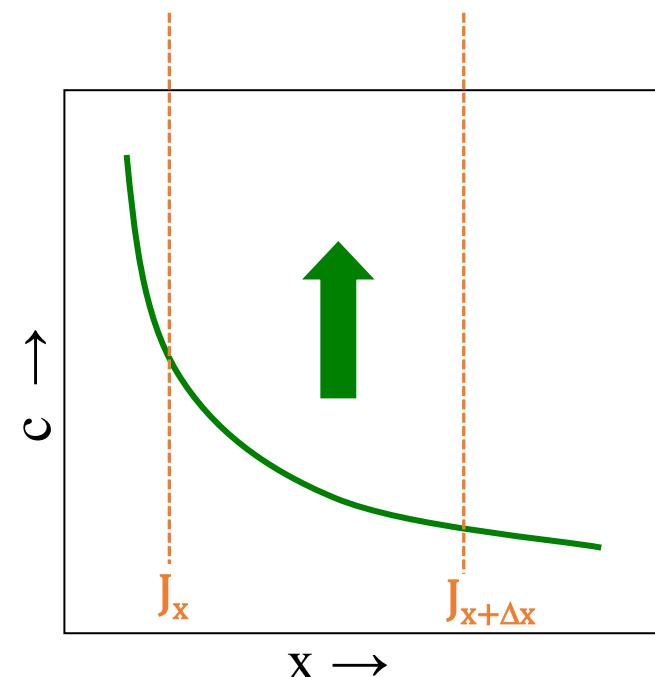
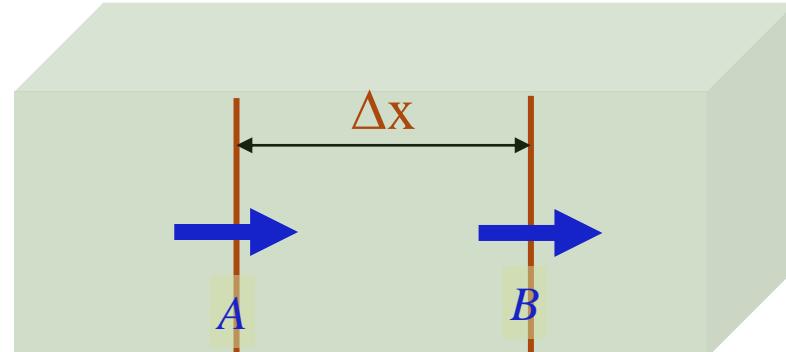
$$(N_x) - (N_{x+\Delta x}) = (J_x - J_{x+\Delta x}) \cdot A \cdot t$$

$$(\Delta N_x) = (\Delta J_x) \cdot A \cdot \Delta t$$

$$\text{Concentration, } C = (\text{No. of atoms}) / (V)$$

$$(\Delta C_x) \cdot V = (\Delta J_x) \cdot A \cdot \Delta t$$

$$(\Delta C_x) \cdot A \cdot \Delta x = (\Delta J_x) \cdot A \cdot \Delta t$$



- Rearrangement of terms:

$$\left( \frac{\Delta c_x}{\Delta t} \right) = - \frac{\Delta J_x}{\Delta x}$$

- Applying limits on both the sides of the equation:

$$\lim_{t \rightarrow 0} \left( \frac{\Delta c_x}{\Delta t} \right) = \lim_{x \rightarrow 0} \left( - \frac{\Delta J_x}{\Delta x} \right)$$

- On substituting the Fick's first law:

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

- Assuming that the diffusion coefficient  $D$  is not a function of location  $x$  and the concentration ( $c$ ) of diffusing species, a simplified version of Fick's second law as:

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

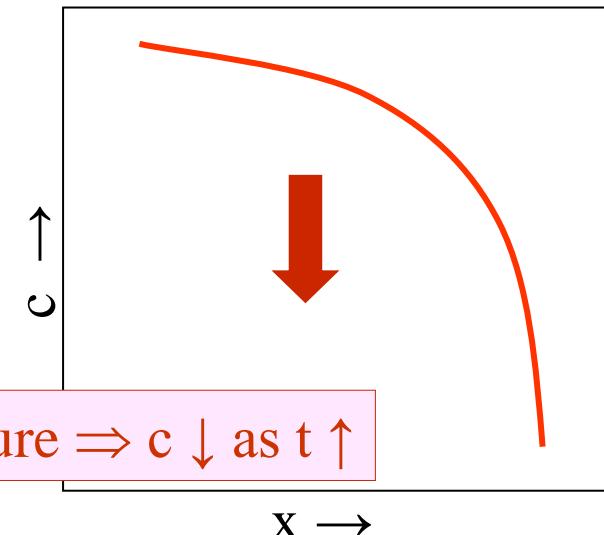
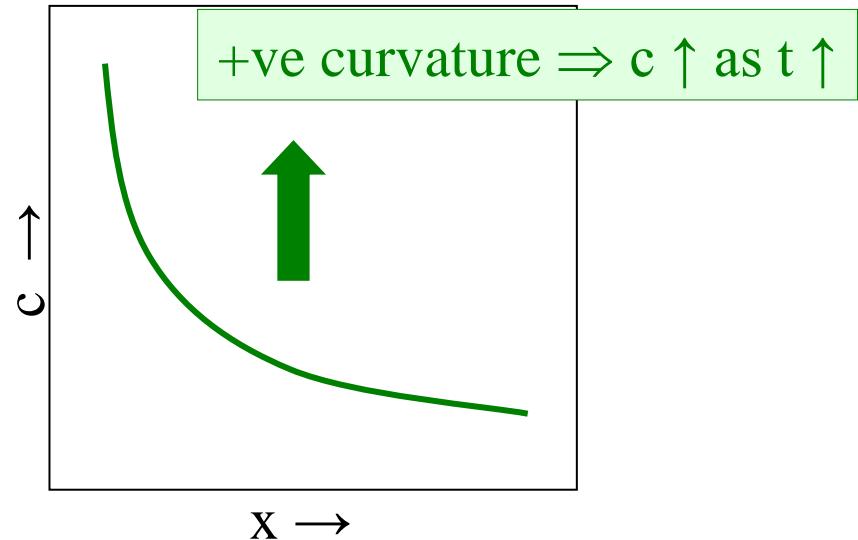
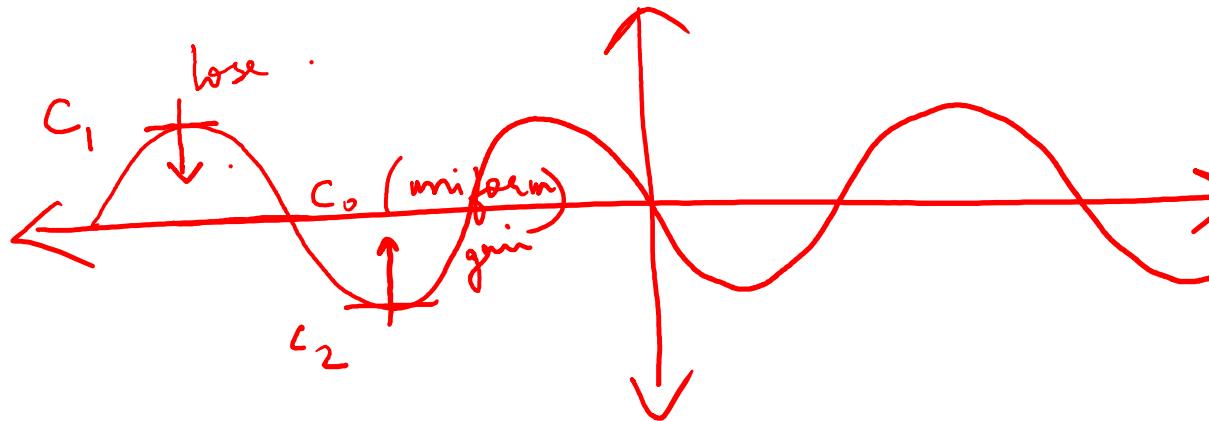
$$\left( \frac{\partial c}{\partial t} \right) = D \frac{\partial^2 c}{\partial x^2}$$

# Homogenization

*RHS: Curvature of  
the  $c$  vs  $x$  curve*

$$\left( \frac{\partial c}{\partial t} \right) = D \frac{\partial^2 c}{\partial x^2}$$

*LHS: change is  
concentration with time*



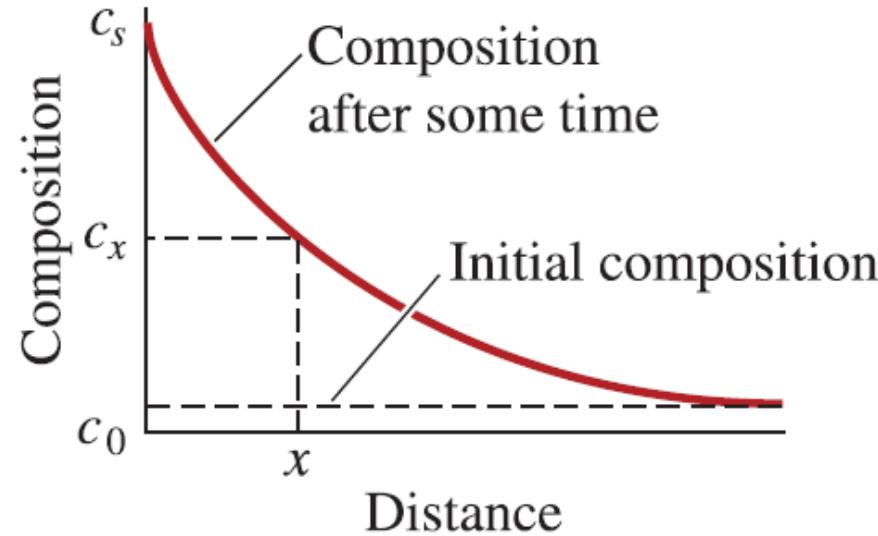
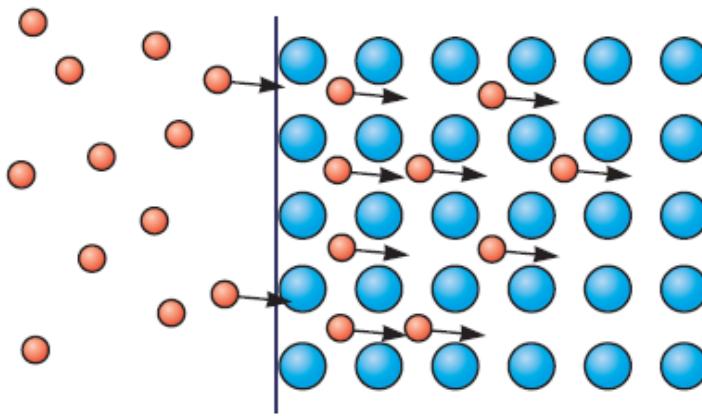
$$\left( \frac{\partial c}{\partial t} \right) = D \frac{\partial^2 c}{\partial x^2} \rightarrow c(x, t) = A - B \operatorname{erf} \left( \frac{x}{2\sqrt{Dt}} \right)$$

*Solution with 2 constants  
determined from Boundary Conditions and Initial Condition*

**Tabulation of Error Function Values**

<b><i>z</i></b>	<b><i>erf(z)</i></b>	<b><i>z</i></b>	<b><i>erf(z)</i></b>	<b><i>z</i></b>	<b><i>erf(z)</i></b>
0	0	0.55	0.5633	1.3	0.9340
0.025	0.0282	0.60	0.6039	1.4	0.9523
0.05	0.0564	0.65	0.6420	1.5	0.9661
0.10	0.1125	0.70	0.6778	1.6	0.9763
0.15	0.1680	0.75	0.7112	1.7	0.9838
0.20	0.2227	0.80	0.7421	1.8	0.9891
0.25	0.2763	0.85	0.7707	1.9	0.9928
0.30	0.3286	0.90	0.7970	2.0	0.9953
0.35	0.3794	0.95	0.8209	2.2	0.9981
0.40	0.4284	1.0	0.8427	2.4	0.9993
0.45	0.4755	1.1	0.8802	2.6	0.9998
0.50	0.5205	1.2	0.9103	2.8	0.9999

- $\operatorname{erf}(\infty) = 1$
- $\operatorname{erf}(-\infty) = -1$
- $\operatorname{erf}(0) = 0$
- $\operatorname{erf}(-x) = -\operatorname{erf}(x)$



- Solution to the equation depends on the boundary conditions for a particular situation

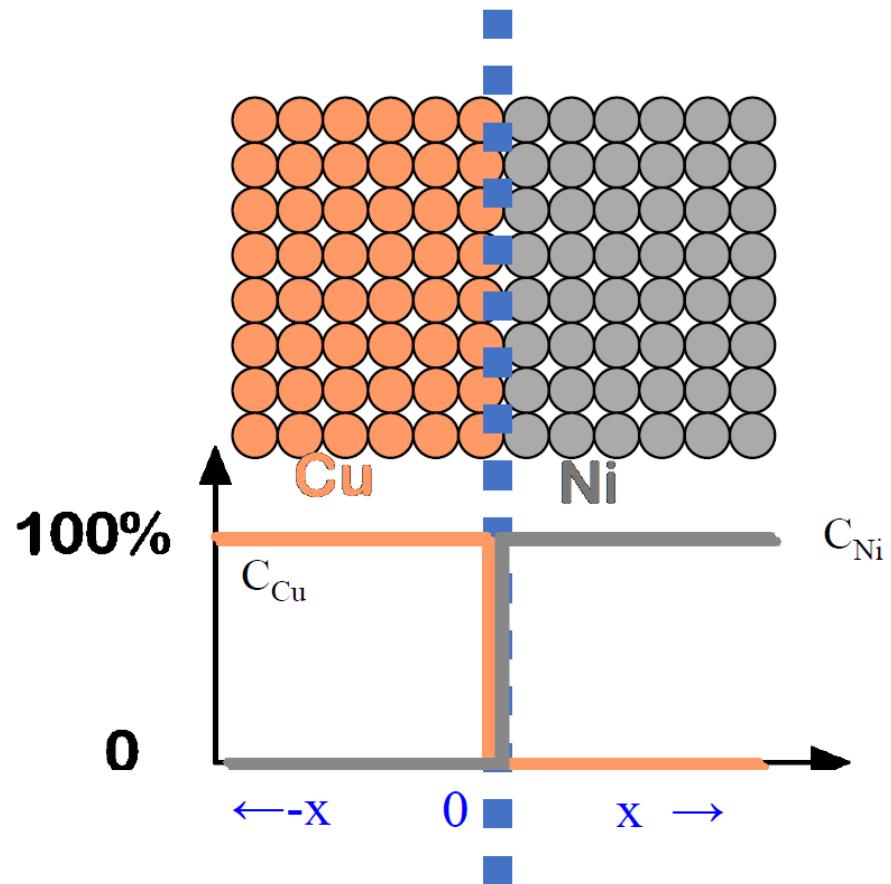
$$\frac{c_s - c_x}{c_s - c_0} = \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$c_s$ : a constant concentration of the diffusing atoms at the surface of the material,

$c_0$ : initial uniform concentration of the diffusing atoms in the material

$c_x$ : concentration of the diffusing atom at location  $x$  below the surface after time  $t$ .

# Calculating values of A and B



- $c(+x, t=0) = C_{Ni}$
- $c(-x, t=0) = C_{Cu}$

- $Erf(\infty) = 1$
- $Erf(-\infty) = -1$
- $Erf(0) = 0$
- $Erf(-\gamma) = -Erf(\gamma)$

$$c(x, t) = A - B \operatorname{erf} \left( \frac{x}{2\sqrt{Dt}} \right)$$

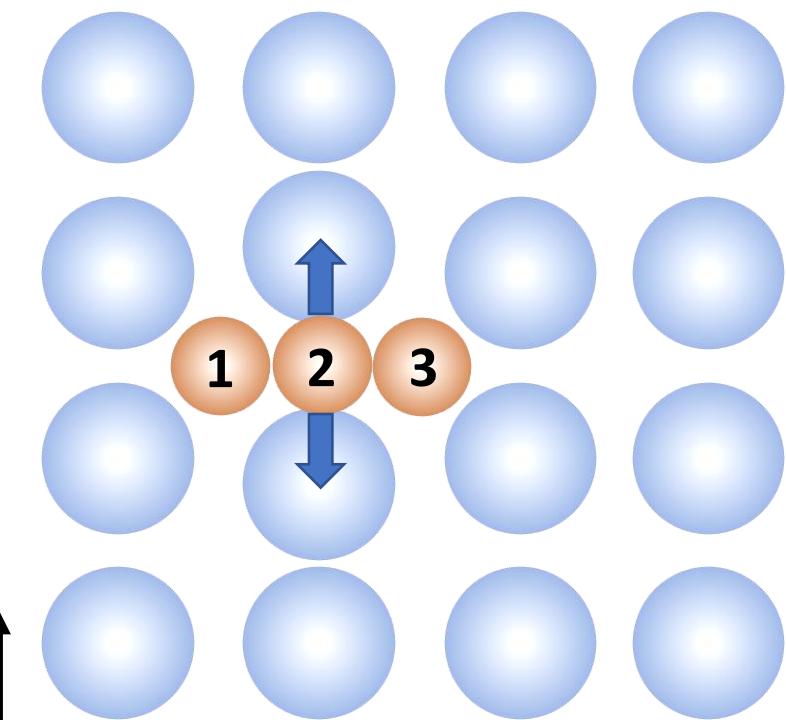
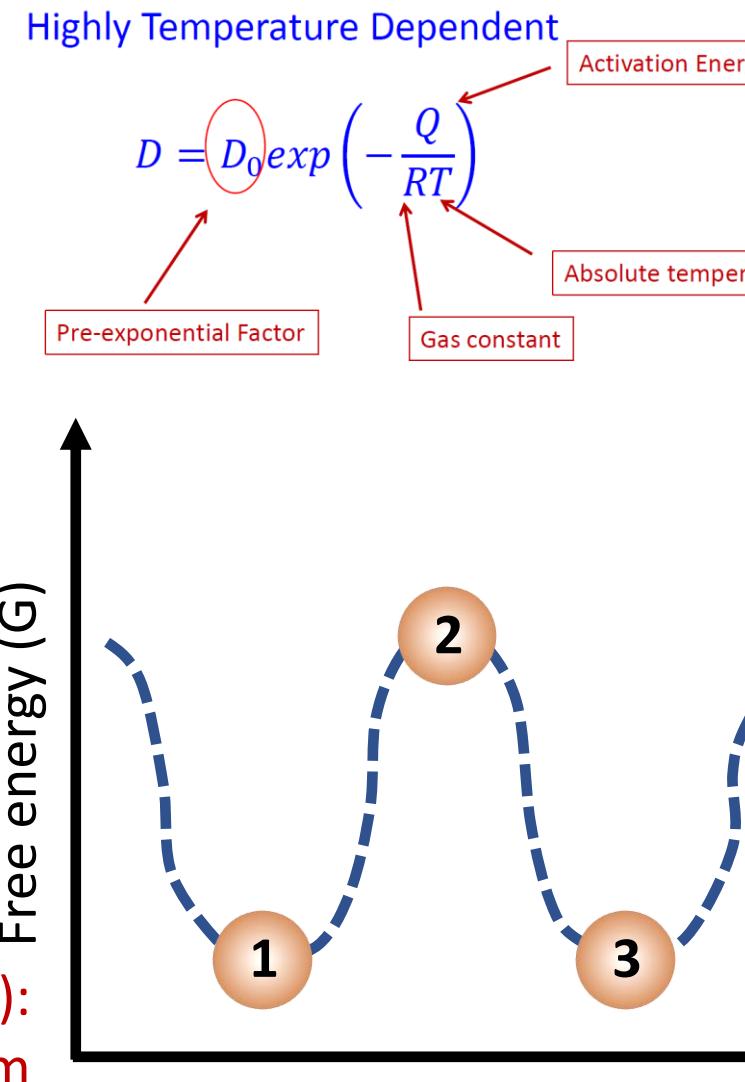
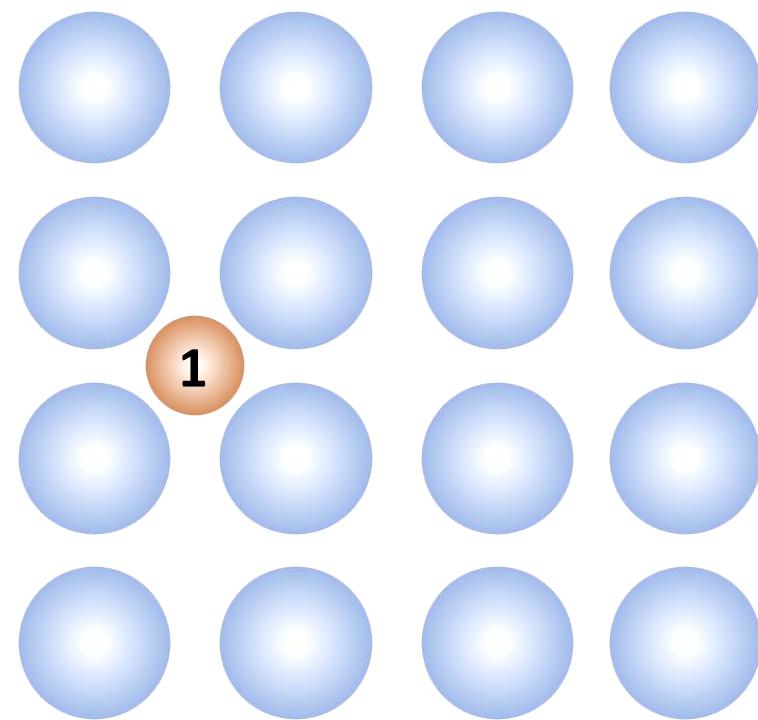
▪ Substituting these values and erf values

$$\blacksquare C_{Ni} = A - B \operatorname{erf}(\infty) = A - B$$

$$\blacksquare C_{Cu} = A - B \operatorname{erf}(-\infty) = A + B$$

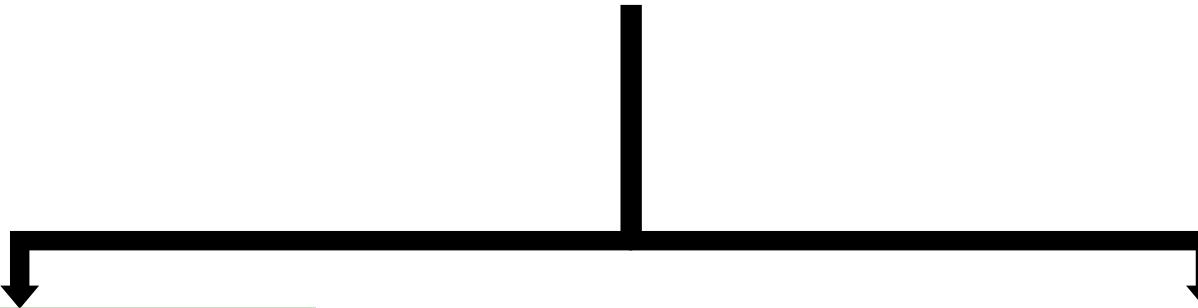
$$A = (C_{Ni} + C_{Cu})/2$$
$$B = (C_{Cu} - C_{Ni})/2$$

# How does 'temperature' influence atomic movement?



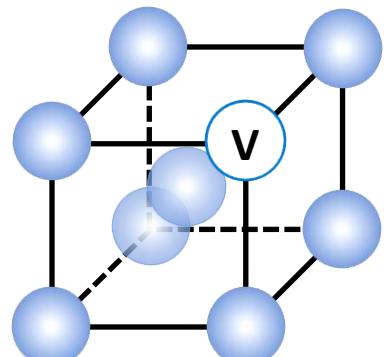
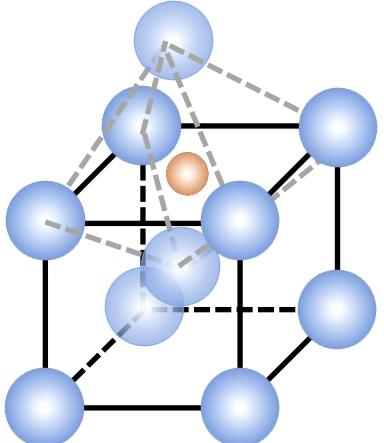
Activation energy barrier ( $\Delta G_m$ ):  
Difference in energy of the atom before its jump and at its position halfway.

# How does an atom diffuse in a solid?



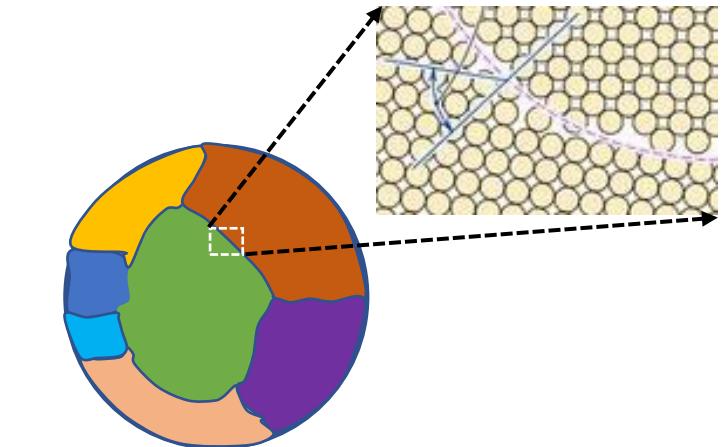
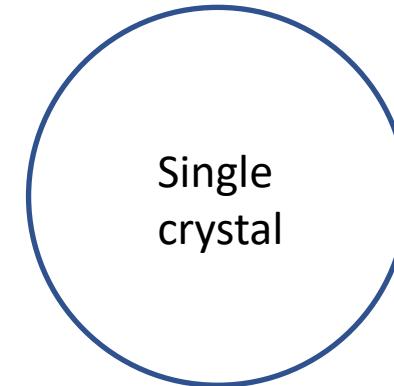
## Crystal structure

- Interstitial
- Substitutional
  - ⇒ Vacancy



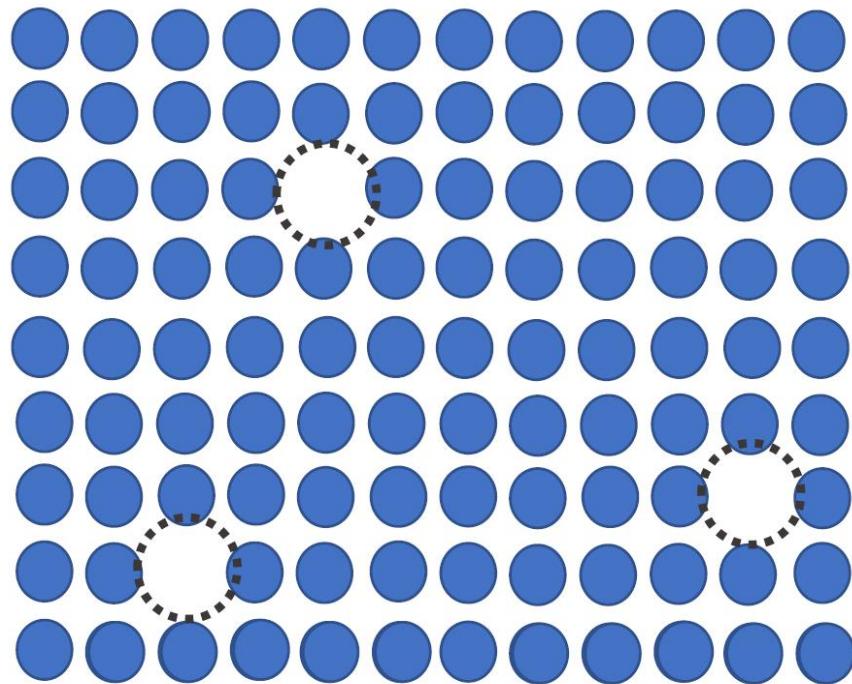
## Grain structure

- Lattice
- Grain boundary

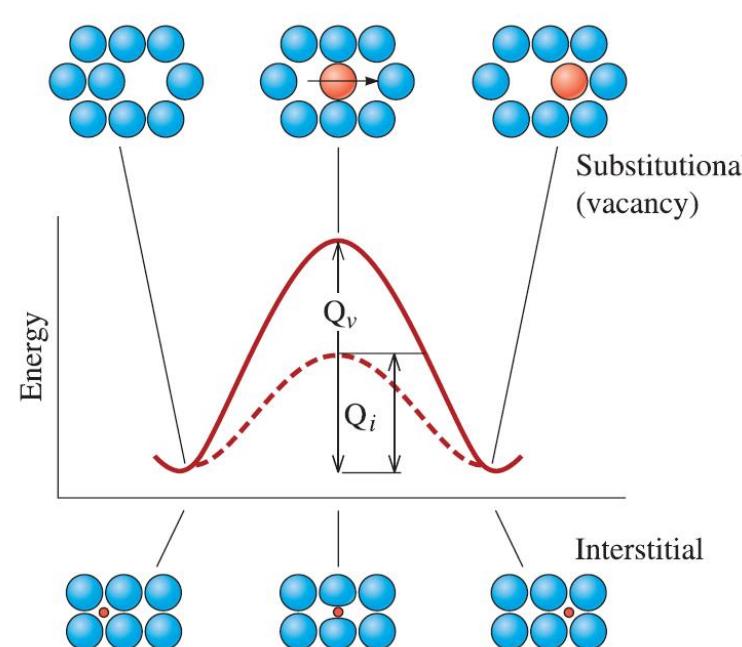


# Vacancy diffusion requires high content of vacancies

Probability for an atomic jump  $\propto$   
(probability that the atom has sufficient energy)  
 $\times$ (probability that the nearby site is vacant)



$$D_{sub} = p \delta^2 \vartheta \exp\left(-\frac{\Delta H_m}{RT}\right) \exp\left(-\frac{\Delta H_f}{RT}\right)$$



$$Q_{vacancy} = \Delta H_m + \Delta H_J$$

$$Q_{interstitial} = \Delta H_m$$

$$Q_{vacancy} > Q_{interstitial}$$

# Lecture 22

## Chemical Bonding and Intermolecular forces- Part 2

### Textbooks:

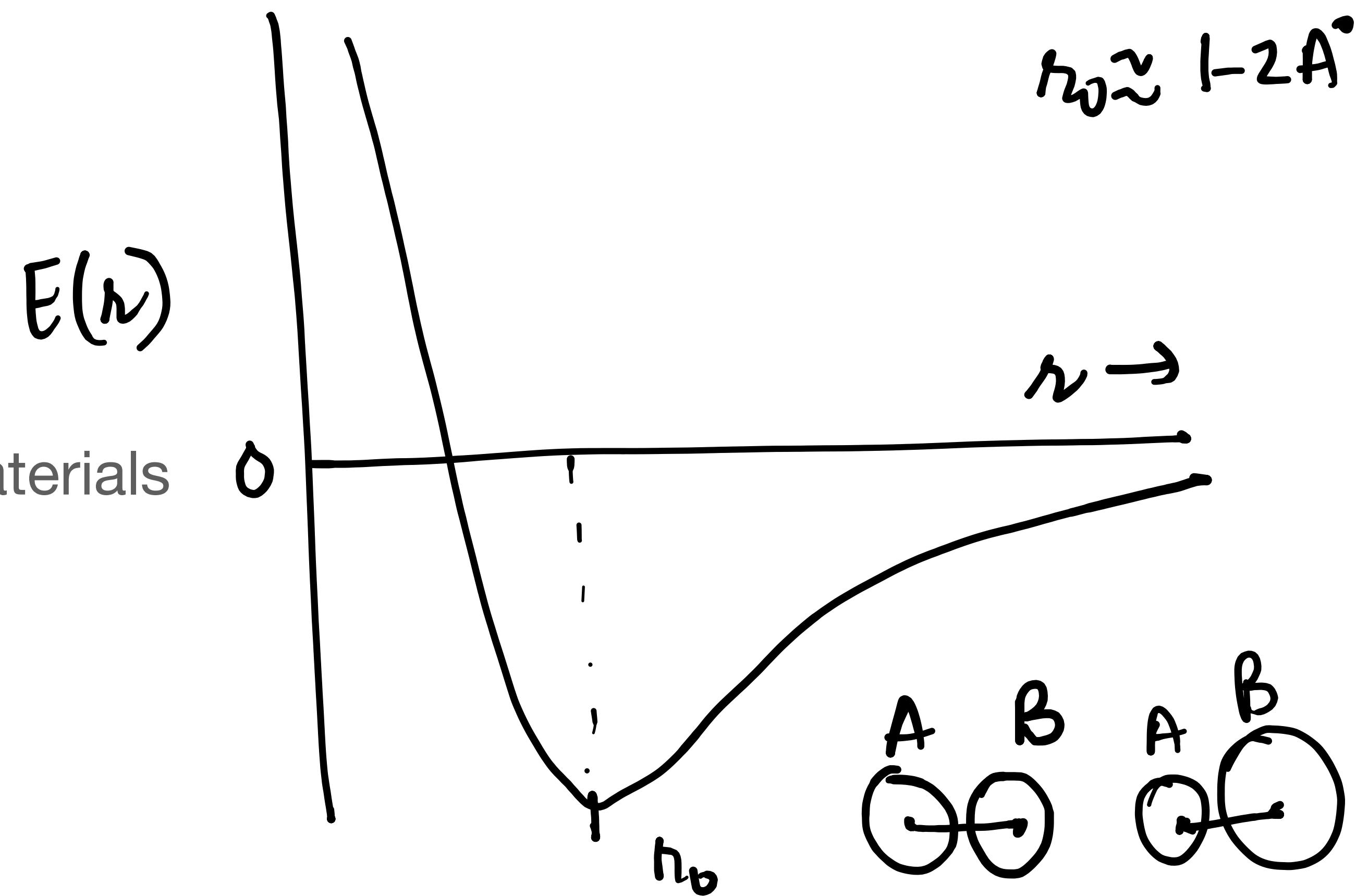
- Introduction to materials science and Engineering: V. Raghavan
- Materials Science and Engineering: Callister and Rethwisch

# Recap

- Why intermolecular forces/chemical bonding are important to understand?
- Differences between chemical bonding and intermolecular forces
- The net force and net energy of interaction between atoms: attraction and repulsion

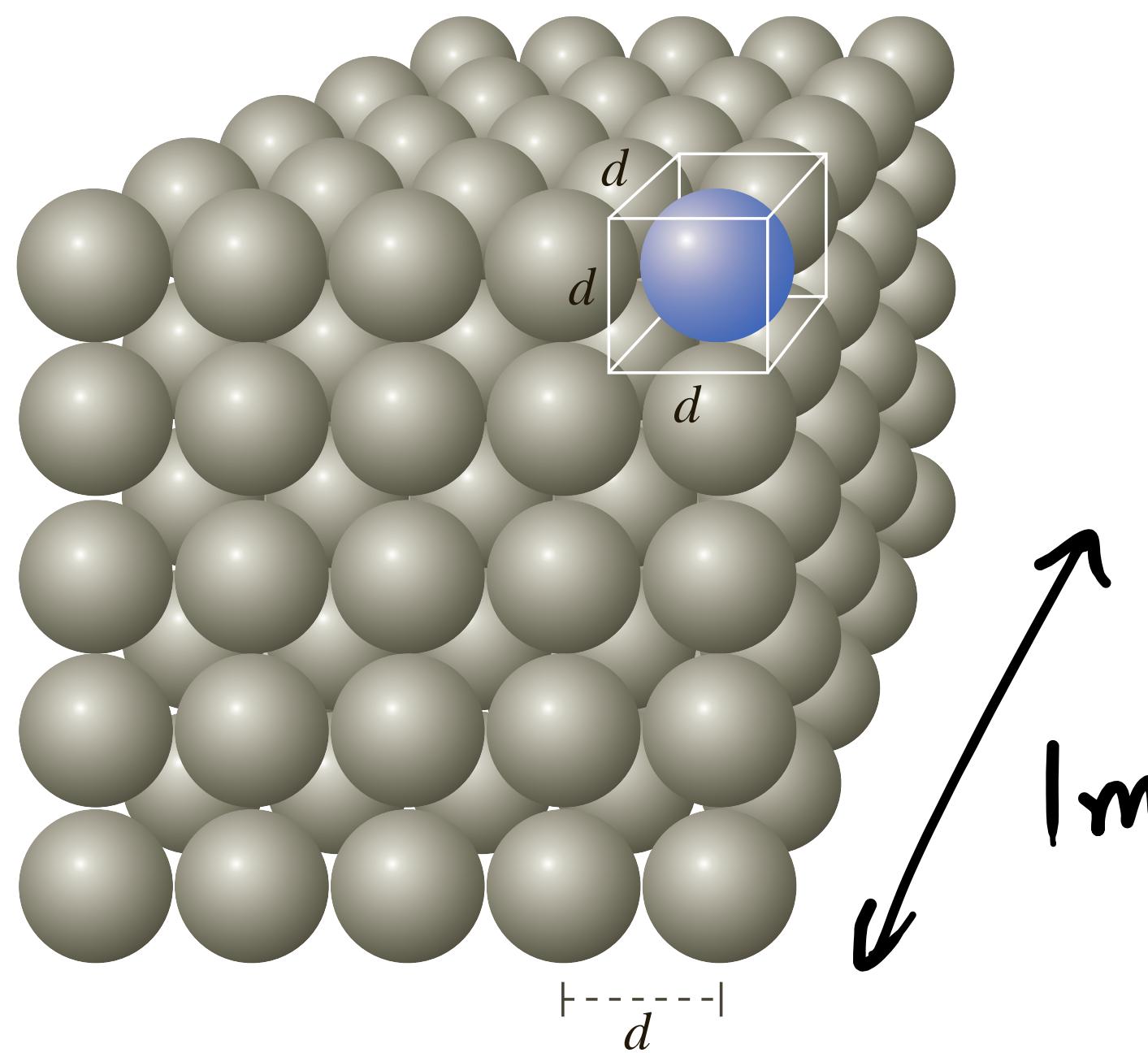
# Pre-cap

- Different types of chemical bonding
- Different types of intermolecular forces
- Effect of these forces on properties of materials



## Problem: Computing the diameter of a Copper Atom (Length of a Bond in Copper)

One mole of copper ( $6.02 \times 10^{23}$  atoms) has a mass of 64 g. The density of copper is  $8.94 \text{ g/cm}^3$ . What is the approximate diameter, in meters, of a copper atom in solid copper?

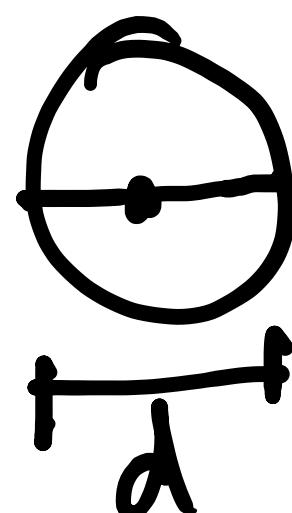


$$\text{Density} = 8.94 \text{ g cm}^{-3} = 8.94 \times 10^3 \text{ kg m}^{-3}$$

In a cube of edge length 1m, the no. of Cu atoms is,

$$8.94 \times 10^3 \frac{\text{kg}}{\text{m}^3} \times \frac{1 \text{ mol}}{0.064 \text{ kg}} \times \frac{6.023 \times 10^{23} \text{ atoms}}{1 \text{ mol}}$$
$$= 8.41 \times 10^{28} \text{ atoms in } 1\text{m}^3$$

In 1 m length, no. of Cu atoms =  $(8.41 \times 10^{28})$   
=  $4.38 \times 10^9$  atoms

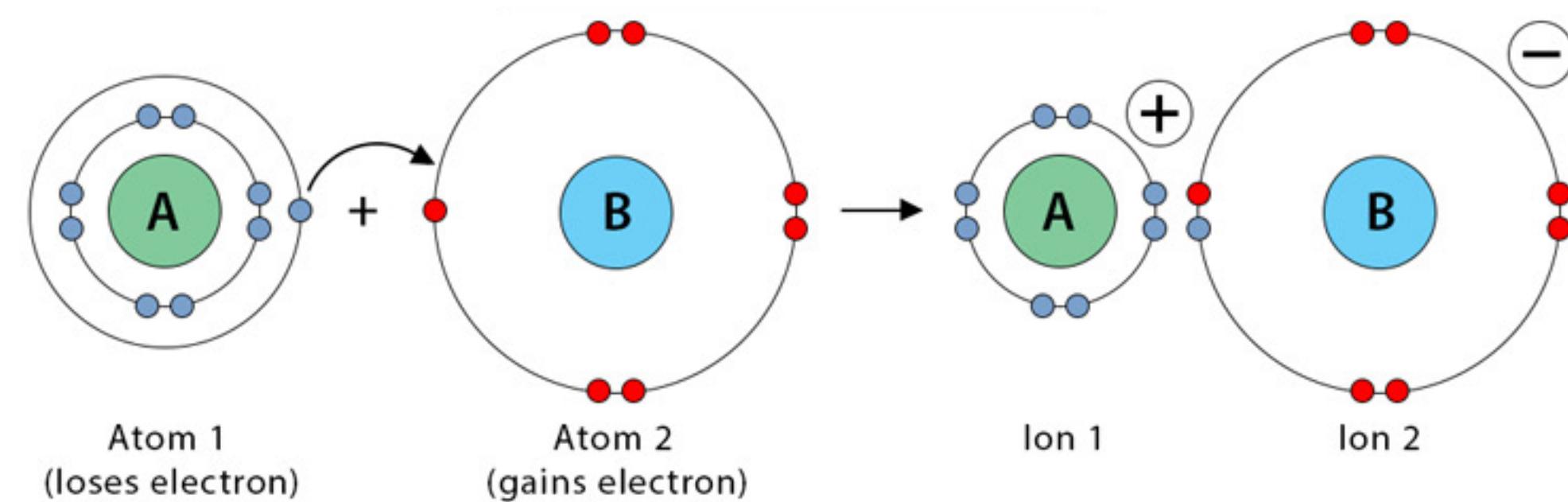
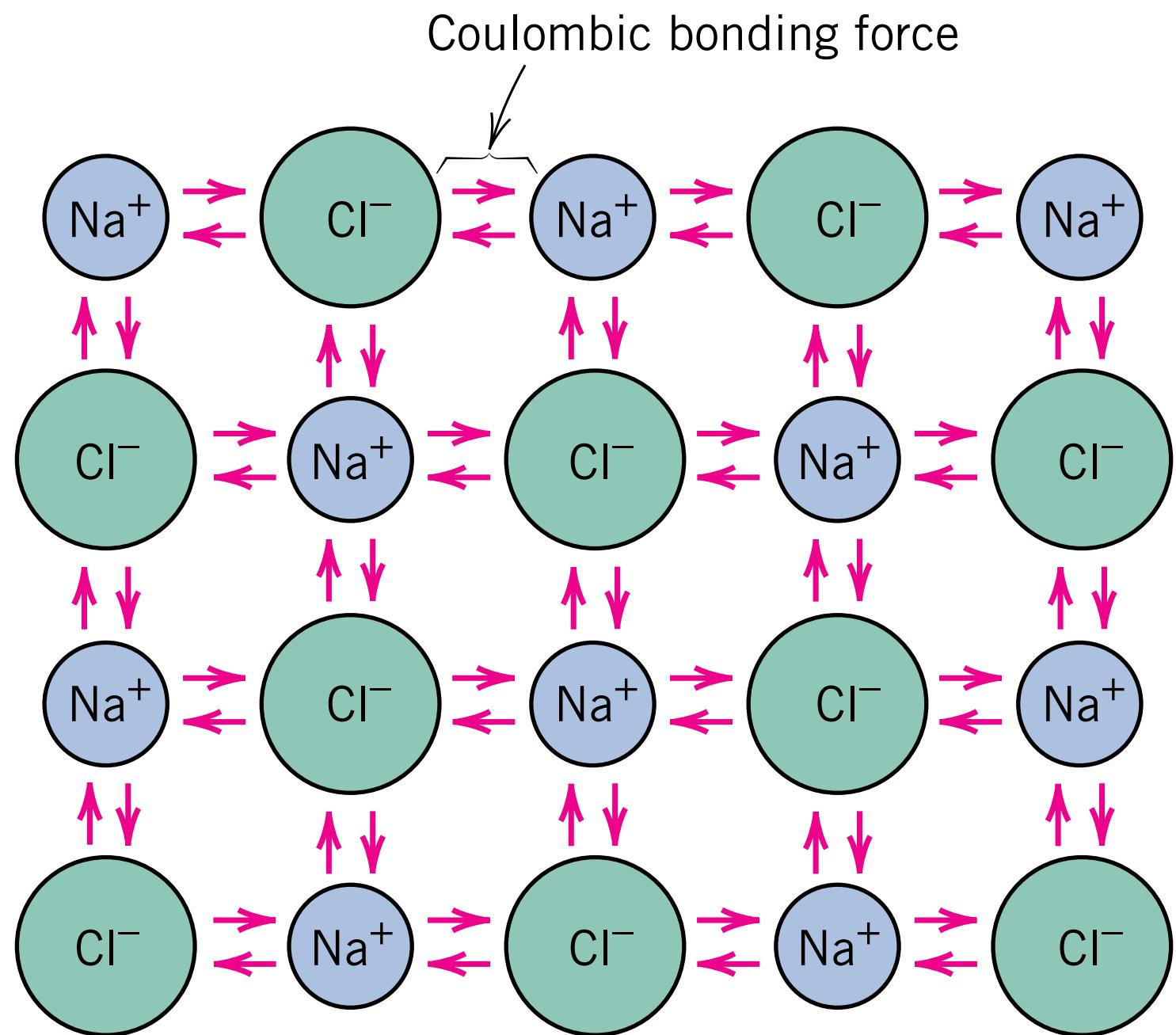


$$\therefore d = \text{Diameter of 1 Cu atom} = \frac{1 \text{ m}}{4.38 \times 10^9} = 2.28 \times 10^{-10} \text{ m}$$
$$= 2.28 \text{ Å}$$

# **Ionization potential, electronegativity and electron affinity**

- **Ionization potential:** the energy required to remove an electron from its outer orbital
- **Electron affinity:** the work done by the system when the extra electron is attracted from infinity to the outer orbital of the neutral atom
- **Electronegativity:** the tendency of the atom to attract electrons to itself during the formation of bonds with other atoms is measured by electronegativity.

# Ionic bonding



- Atoms of metallic elements give up their valence electrons to non-metallic atoms - e.g. Na Cl

Coulombic energy:

$$E_A = -\frac{A}{r} \quad \text{and} \quad E_R = \frac{B}{r^n}$$

A, B are constants,  $n=8$

$$A = \frac{(z_1 e)(z_2 e)}{4\pi\epsilon_0} ; z_i = \text{valency of ion}$$

$e = \text{electronic charge}$

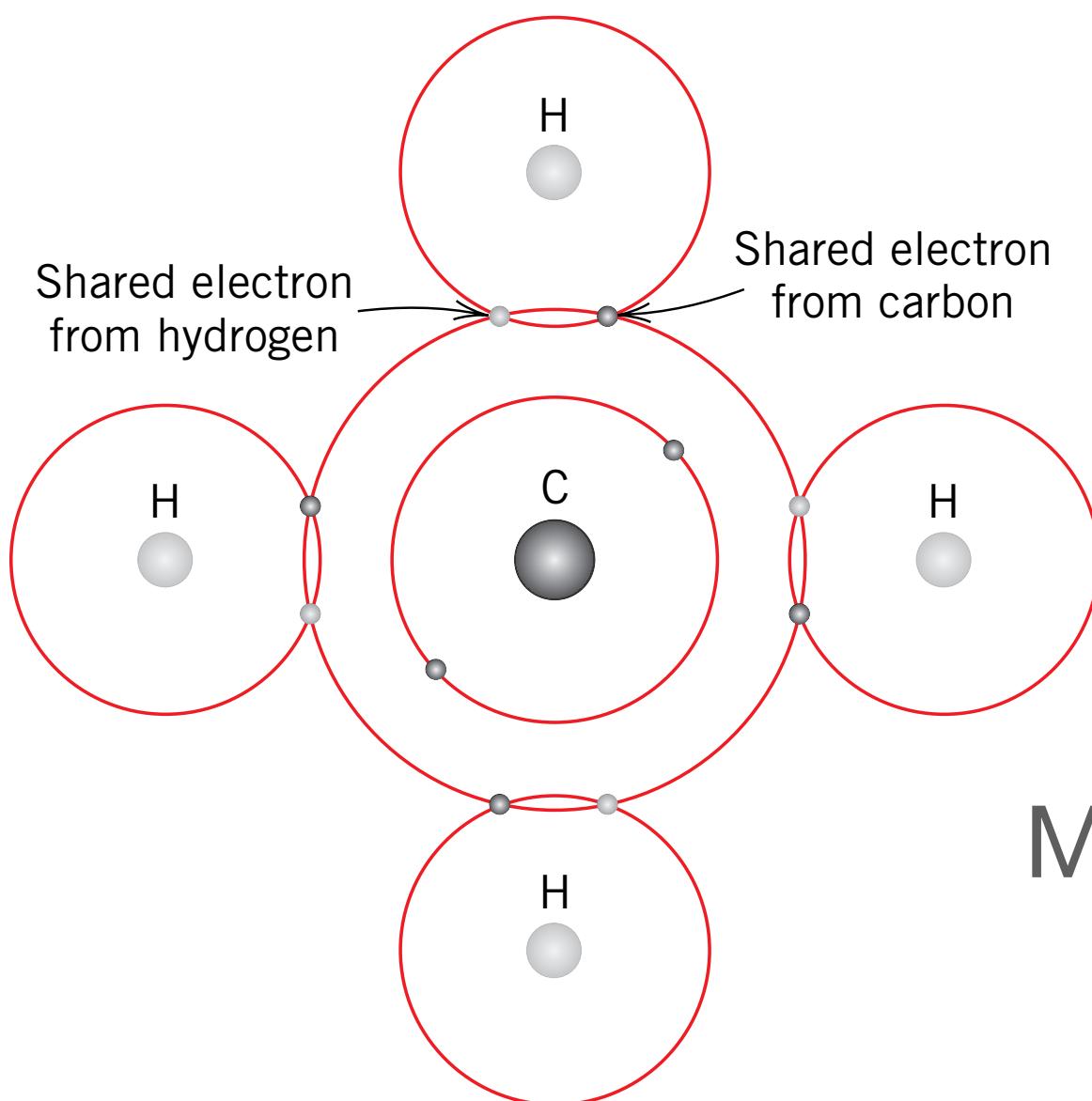
( $1.602 \times 10^{-19} \text{ C}$ )

$\epsilon_0 = \text{permittivity of vacuum}$

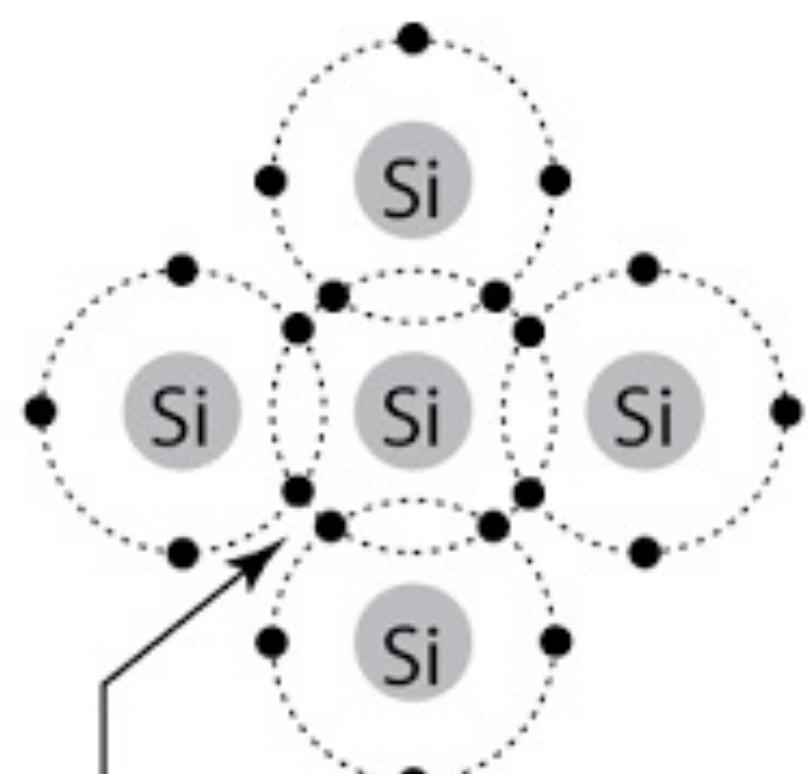
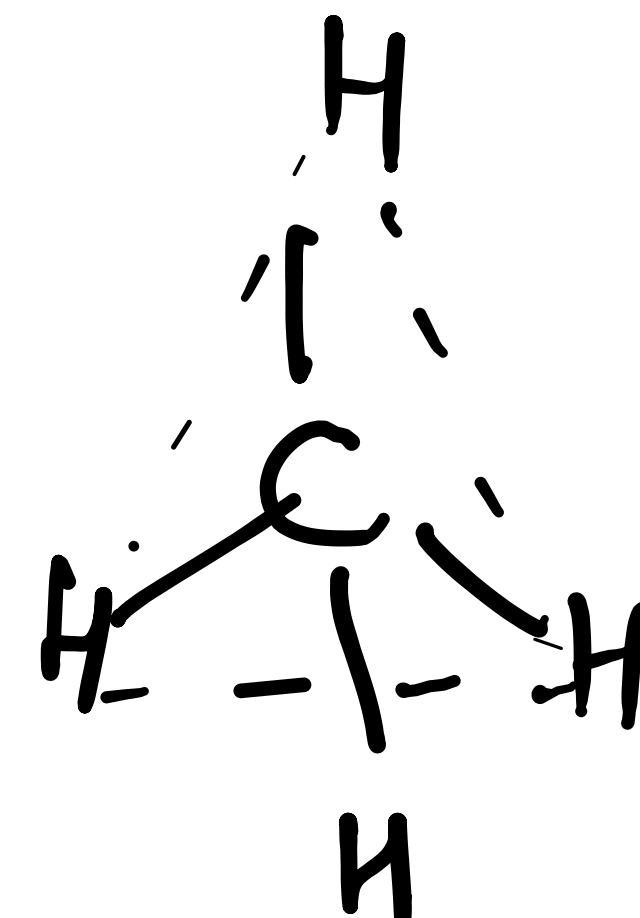
$$E \propto \frac{1}{r}$$

- long-range interaction
- Non-directional

# Covalent bonding



Methane



Silicon

- electrons are shared between the atoms

- Directional bonding

- Polar covalent bonding :



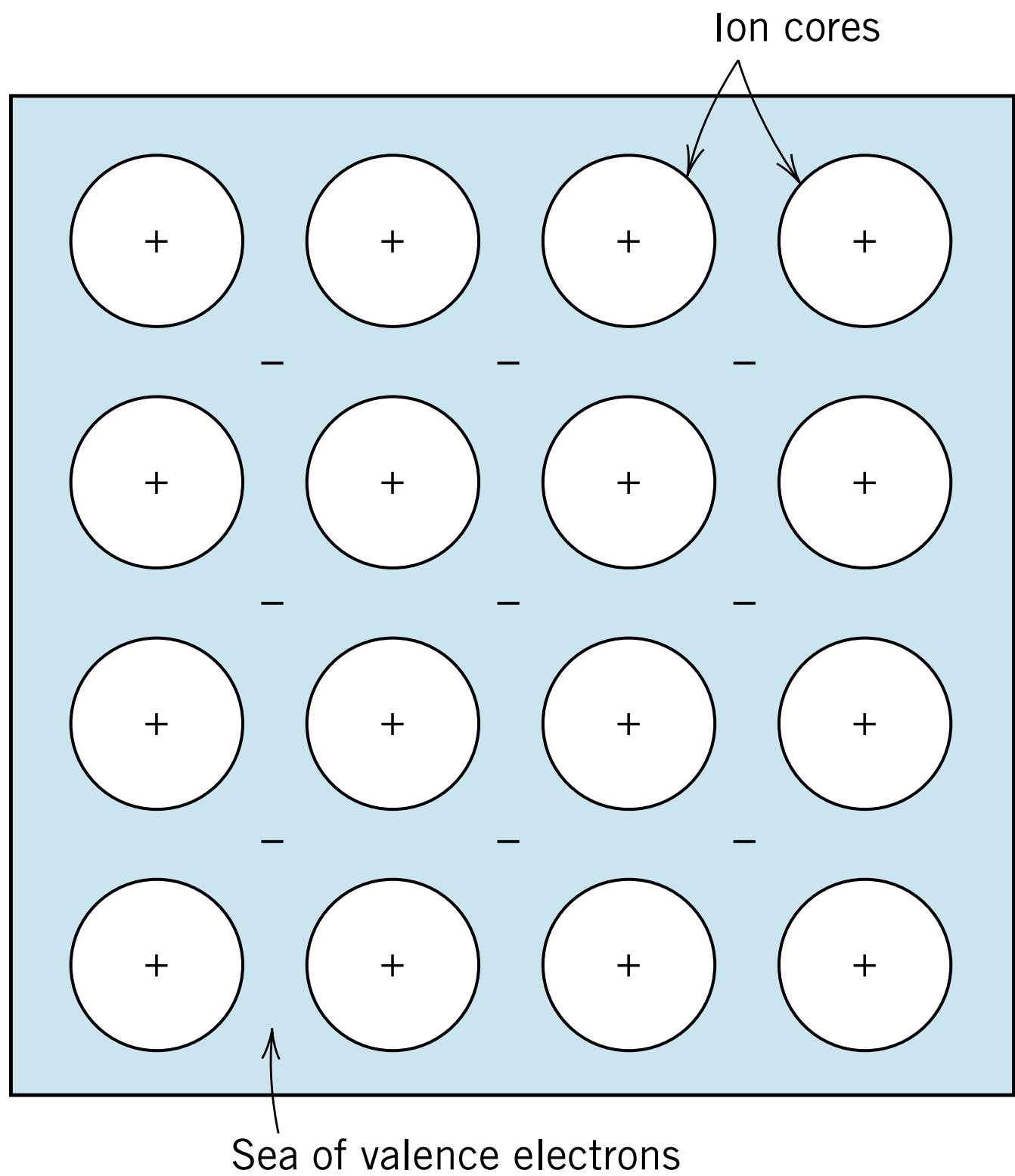
electronic charge distribution is unequal between the atoms

- Non-polar covalent bonding :

electronic charge dist. is equal b/w atoms



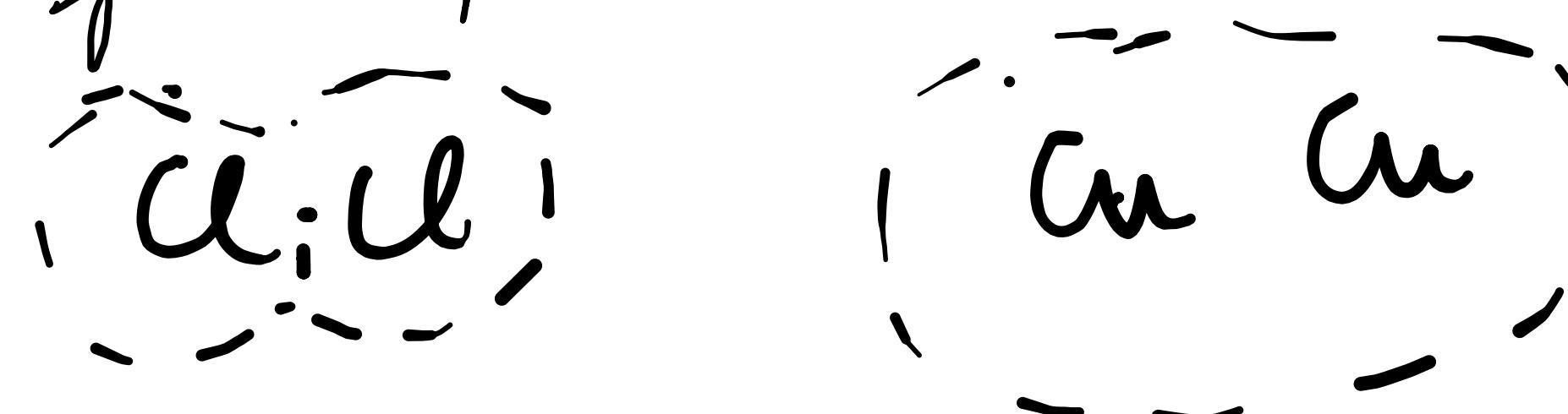
# Metallic Bonding



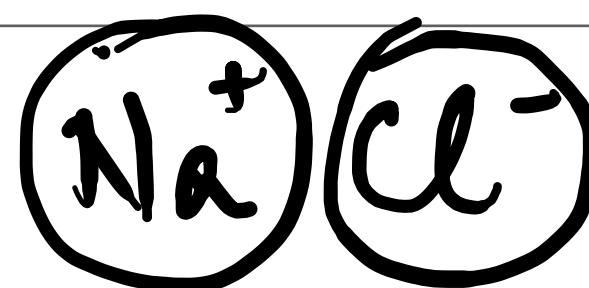
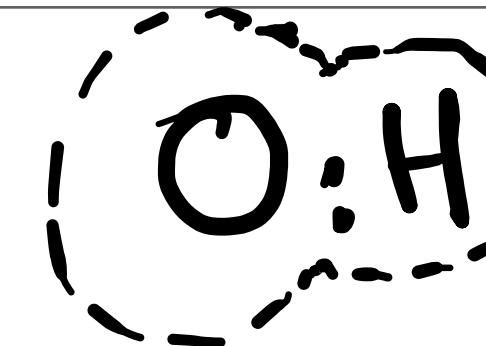
Cu, Fe, Zn

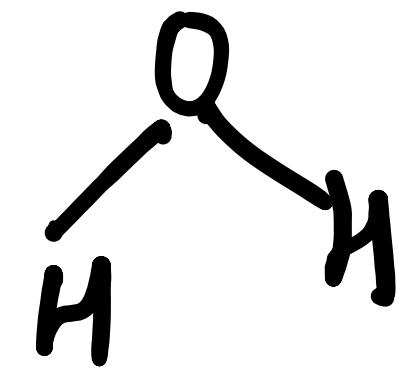
- Metals have a large no. of valence electrons that are delocalized over the atom. These  $e^-$  do not bound to any atom
- Non-directional bonding
- The  $e^-$  cloud shields positively charged nuclei from repulsion and act as glue to hold the nuclei together -

eg: Group I, II metals



# Chemical Bonding- A summary

Bond	Attraction	Energy (kJ/mol)	Example	Model
Ionic	Cation-anion	400-4000	Na-Cl	
Non-polar covalent	Sharing of electrons	150-1000	Cl-Cl	
Polar covalent	Sharing of electrons	150-1000	H-Cl	

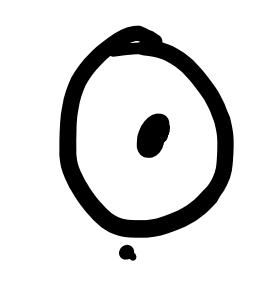


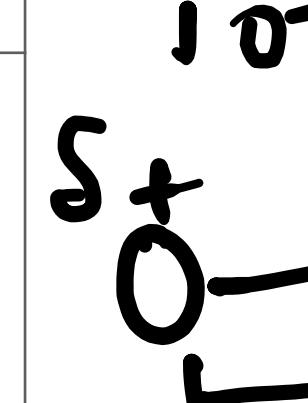
# “Non-bonding” Intermolecular forces

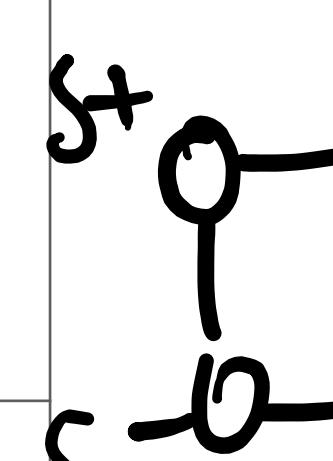
**Electrostatic**

Bond	Attraction	Energy (kJ/mol)	Example	Model
Ion-dipole	Ion-dipole	40-600	$\text{Na}^+ \cdots \text{H-Cl}$	
Dipole-dipole	Dipole-dipole	5-25	$\text{H-Cl} \cdots \text{H-Cl}$	
Induction	ion-induced dipole	3-15	$\text{Na}^+ \cdots \text{H-H}$	
Dipole-induced dipole	Dipole-polarizable electron cloud	2-10	$\text{H-Cl} \cdots \text{Cl-Cl}$	
✓ London dispersion forces	Polarizable electron cloud	0.05-40	$\text{Cl-Cl} \cdots \text{Cl-Cl}$	

Multipoles: Set of partial charges arranged in a symmetric manner.

 : Monopole eg:  $\text{Na}^+$ ,  $\text{Cl}^-$

 : dipole eg:  $\text{H-Cl}$

 : Quadrupole eg:  $\text{CO}_2$

 : Octopole eg:  $\text{CH}_4$

(8 charges) 

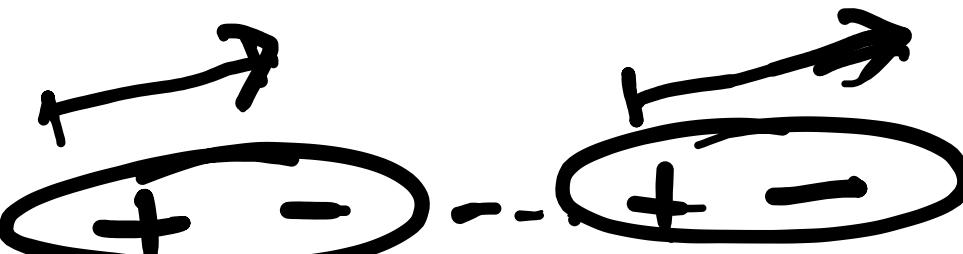
Ion-dipole:



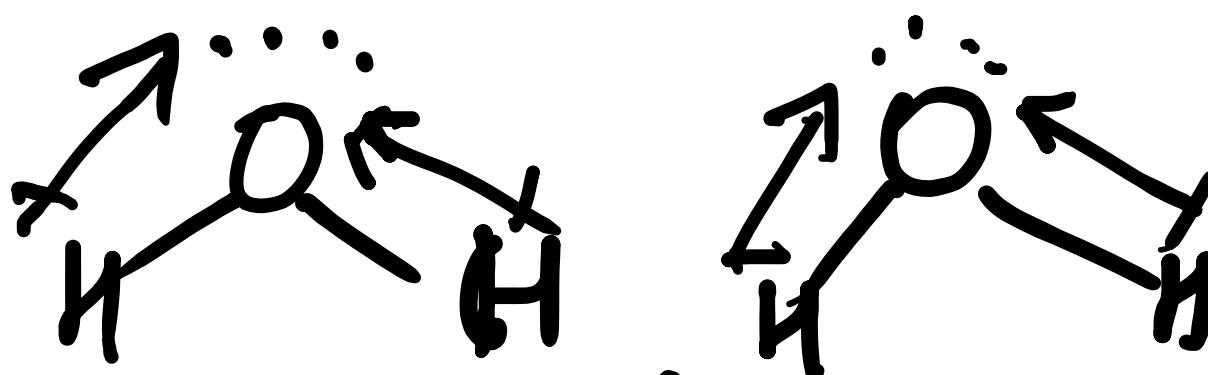
$$E \propto -\frac{1}{r^2}$$



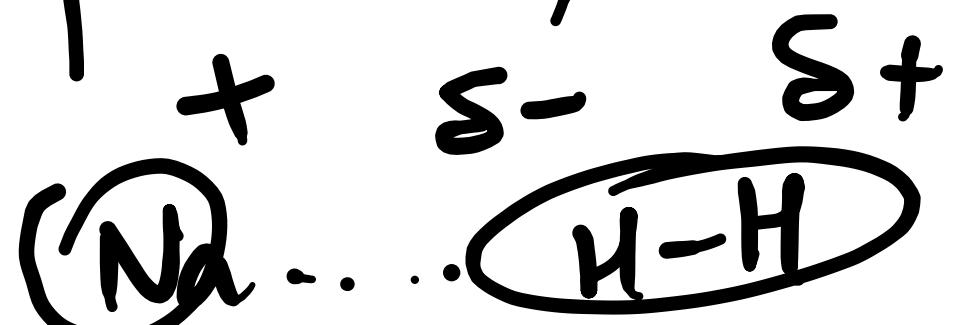
Dipole-Dipole:



$$E \propto -\frac{1}{r^3}$$



Induction interaction: multipole  
another molecule depending on  
molecule.



$$E \propto -\frac{1}{r^6}$$

Ion-induced dipole:



Dipole-induced dipole:

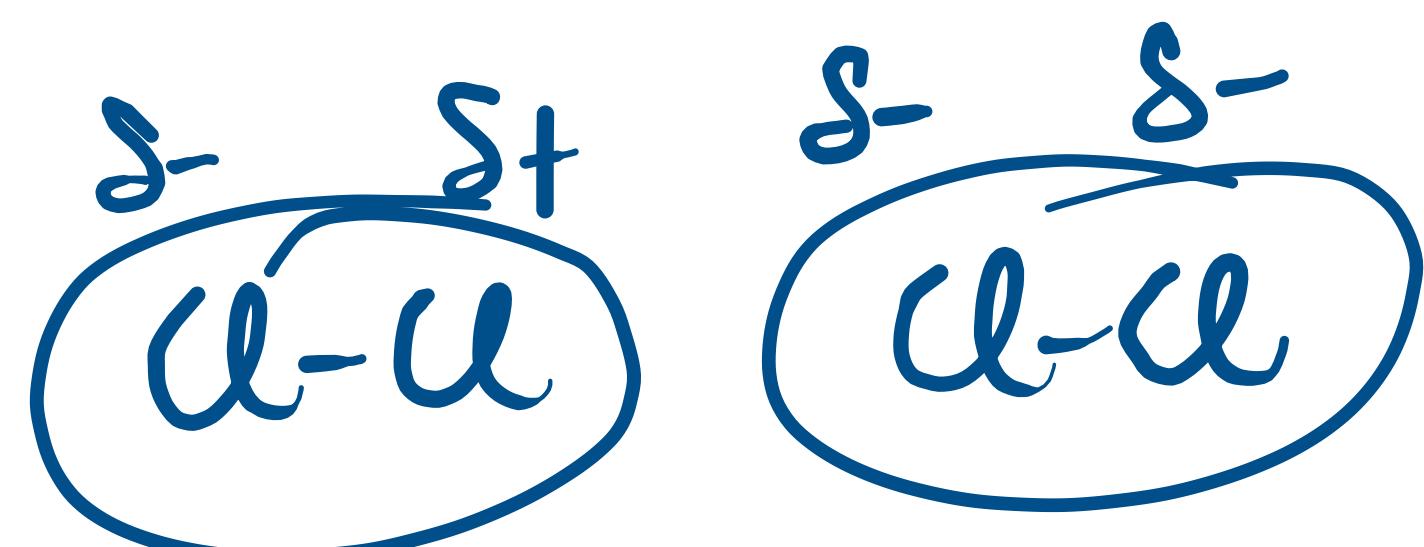


induces interaction in  
polarizability of that  
transient dipole  
"Distortion in  
e<sup>-</sup> charge distribution"

Dispersion interaction:  
(van der Waals)



$$\epsilon(r) = 4\epsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$



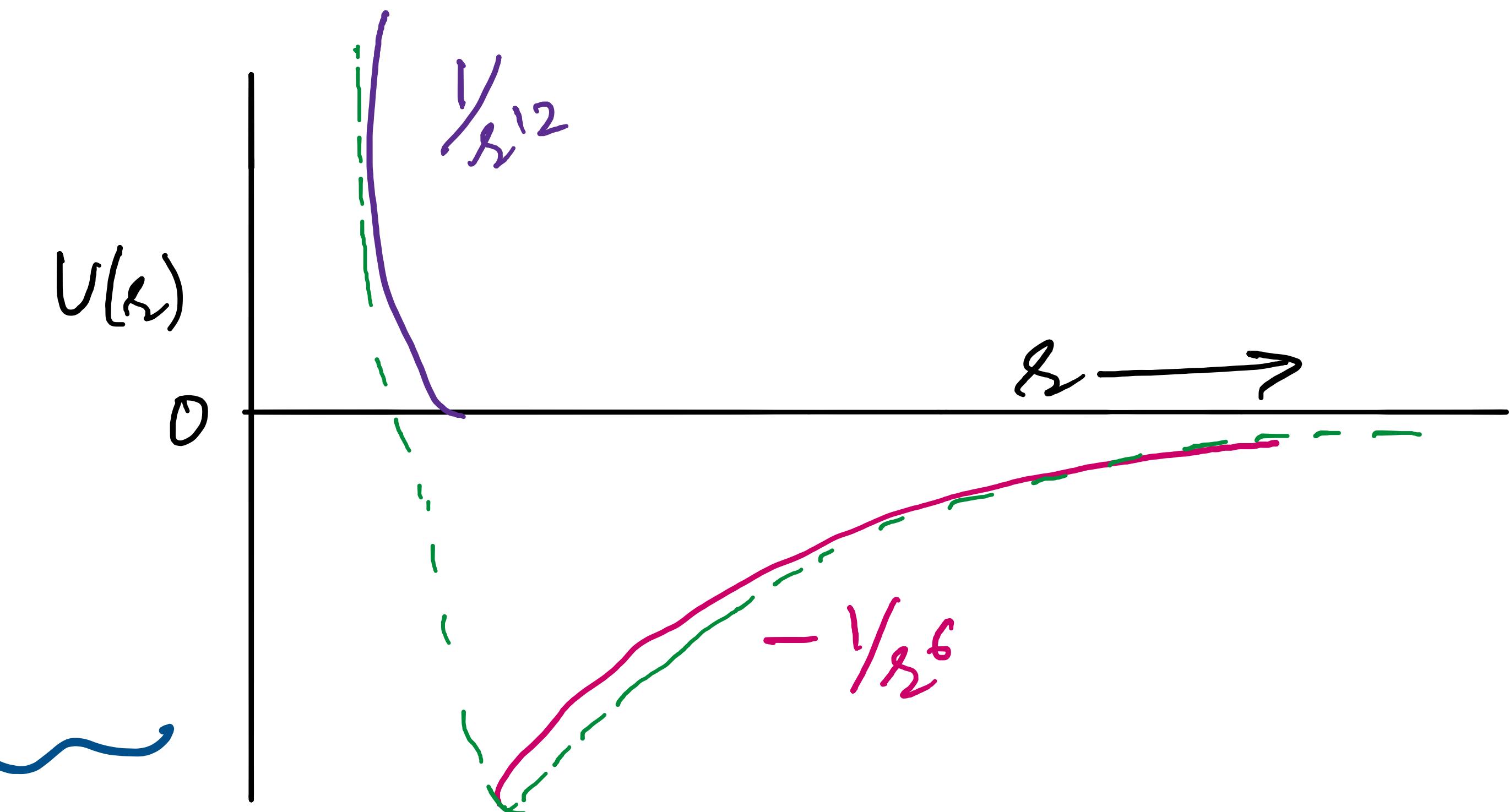
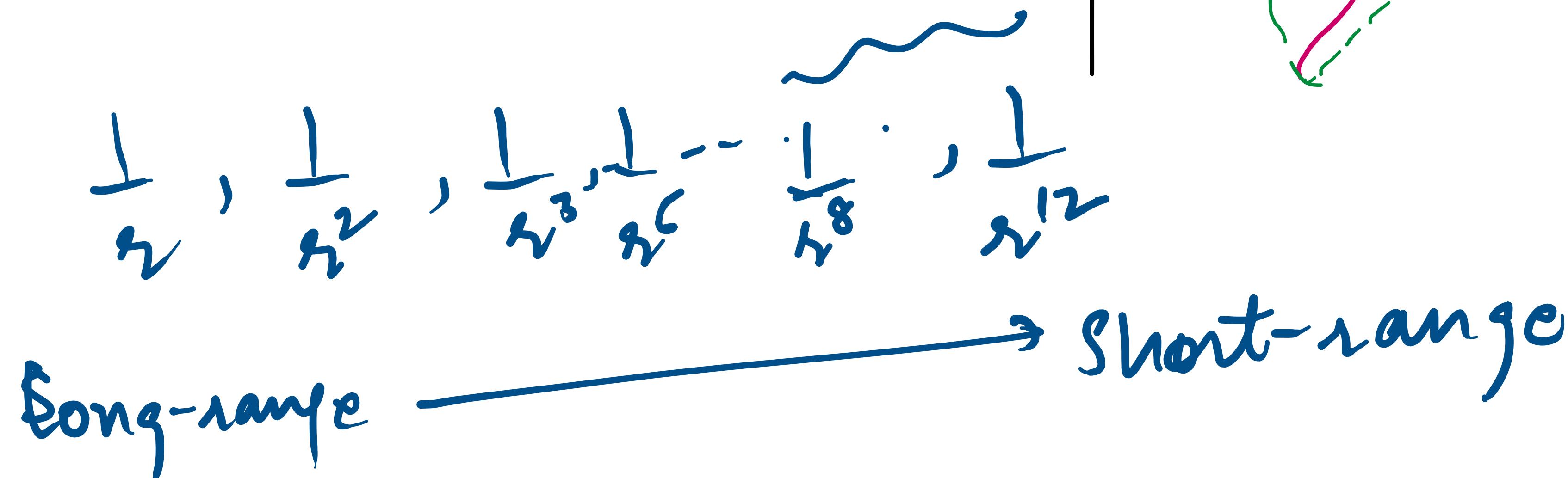
"Fluctuation" in charge distribution  
repulsion attraction

# General functional form of the van der Waals energy

$$U(r) = 4\epsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$

Lennard-Jones Potential

- Weak interactions
- Ubiquitous in nature
- Non-directional bonding





# Lecture 23

## Materials and their structure

### Textbooks:

- Introduction to materials science and Engineering: V. Raghavan
- Materials Science and Engineering: Callister and Rethwisch

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Department of Materials Science and Engineering  
[divyanayar@mse.iitd.ac.in](mailto:divyanayar@mse.iitd.ac.in)

# Recap

- Types of chemical bonding (Primary bonding)
  1. Ionic bonding: ion-ion (Coulombic attraction and repulsion)
  2. Covalent bonding (polar covalent and non-polar covalent bond)
  3. Metallic bonding
- Non-bonding intermolecular forces (Secondary bonding):
  1. Electrostatic interactions (multipoles): ion-dipole, dipole-dipole
  2. Induction interactions
  3. Dispersion interactions
  4. Hydrogen bonding
  5. Hydrophobic interactions

# Non-bonding Intermolecular forces

- **Electrostatic interactions:** originate from interactions between molecular multipoles. The strength depends on  $1/r^n$   
e.g. ion-ion, ion-dipole, dipole-dipole, dipole-quadrupole etc.
- **Induction interactions:** that arise from interaction between a static multipole moment of one molecule and polarizability of the other molecule. *Arise from distortion in charge distribution.*  
E.g. ion-induced dipole, dipole-induced dipole
- **London or dispersion forces:** originates from correlations between instantaneous dipoles of neighboring atoms. *Arise from fluctuations in charge distribution.*

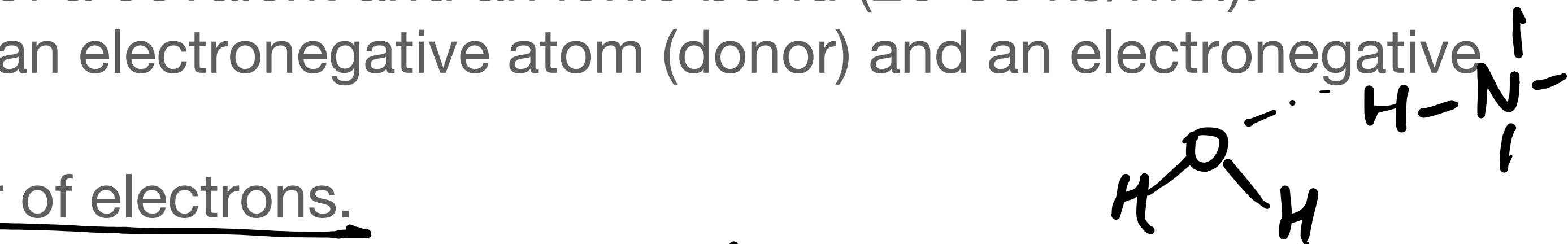
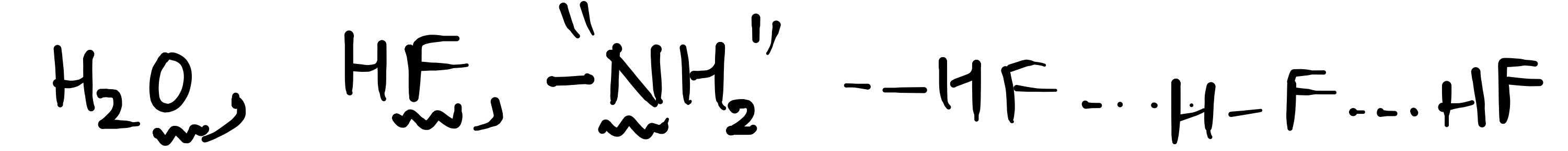
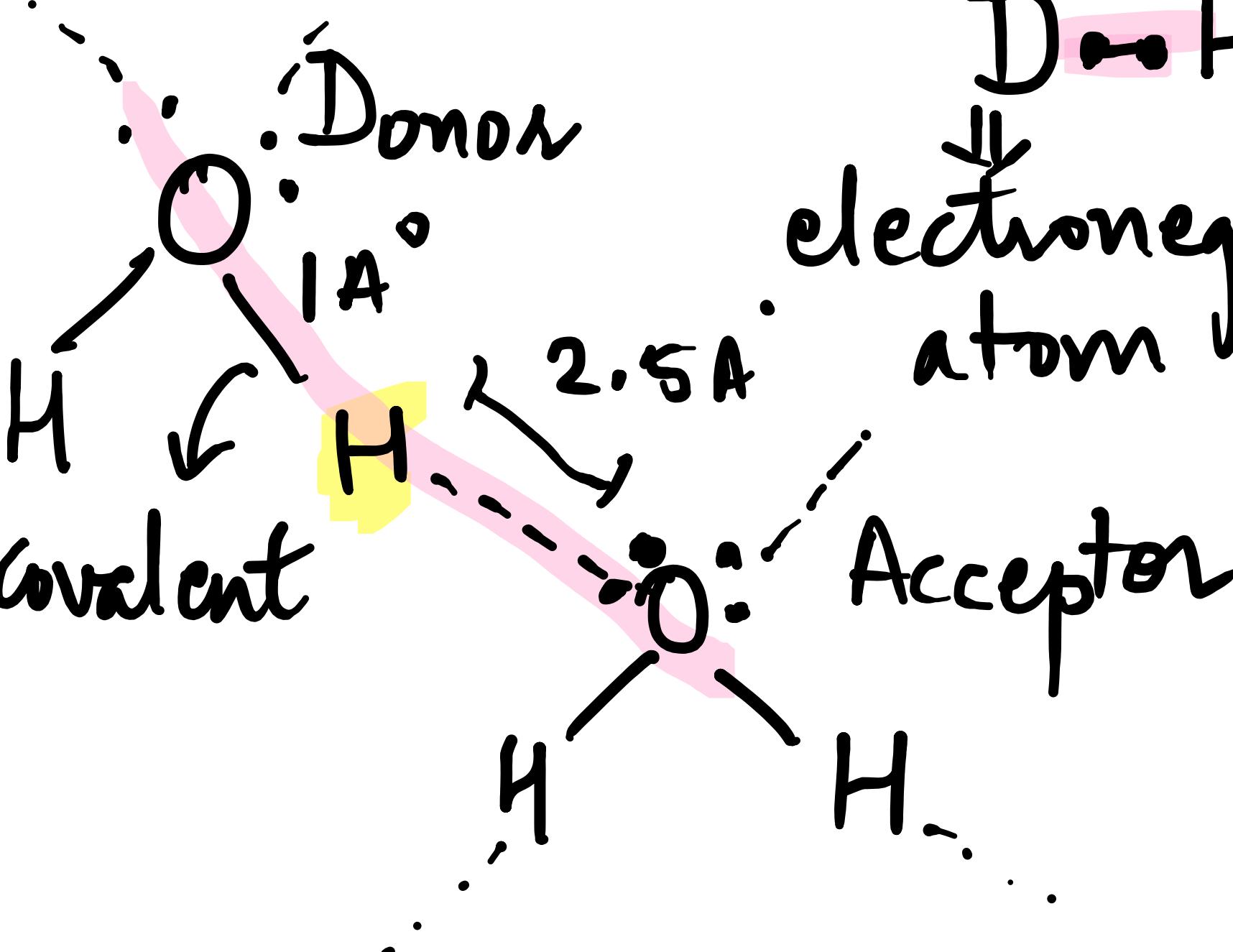
$$\downarrow E_{vdw} = \frac{4\epsilon}{r^6} \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$

$\mu$  = dipole moment  
 $\alpha$  = polarizability

$$E_{ind} = - \frac{2\mu^2 \alpha}{4\pi \epsilon_0 r^6}$$

# Hydrogen bonding

- It is intermediate between electrostatic interactions and a true chemical bond
- The energy of interaction lies between that of a covalent and an ionic bond (20-30 kJ/mol).
- Formed between a H covalently bonded to an electronegative atom (donor) and an electronegative atom (acceptor)
- Interaction of a bonded pair with a lone pair of electrons.
- Directional bonding



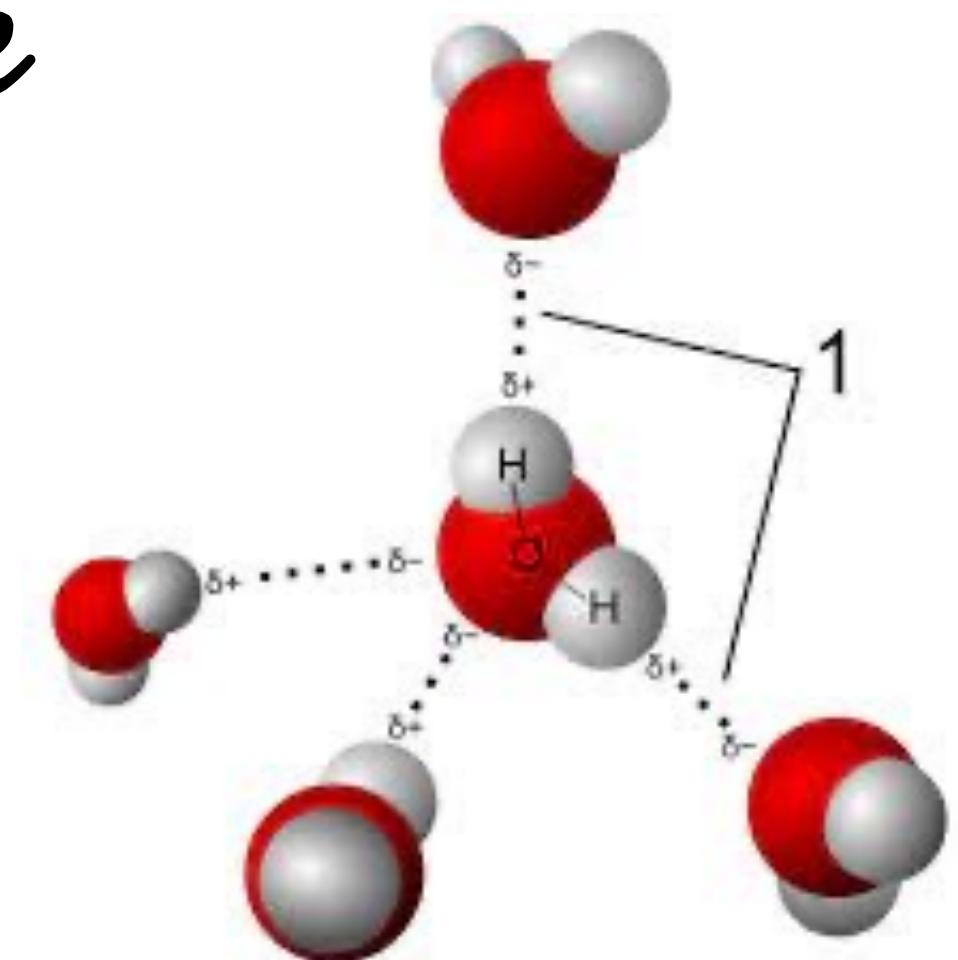
covalent  
D  $\leftrightarrow$  H  $\cdots \cdots \cdots$  :A  
lone pair of  $e^-$

electronegative atom  
H-bond

Distance :  $\text{H}-\text{A} = 2.5 \text{\AA}$

$\text{D}-\text{A} \approx 3.5 \text{\AA}$

Orientation :  $\angle \text{AHD} > 150^\circ$



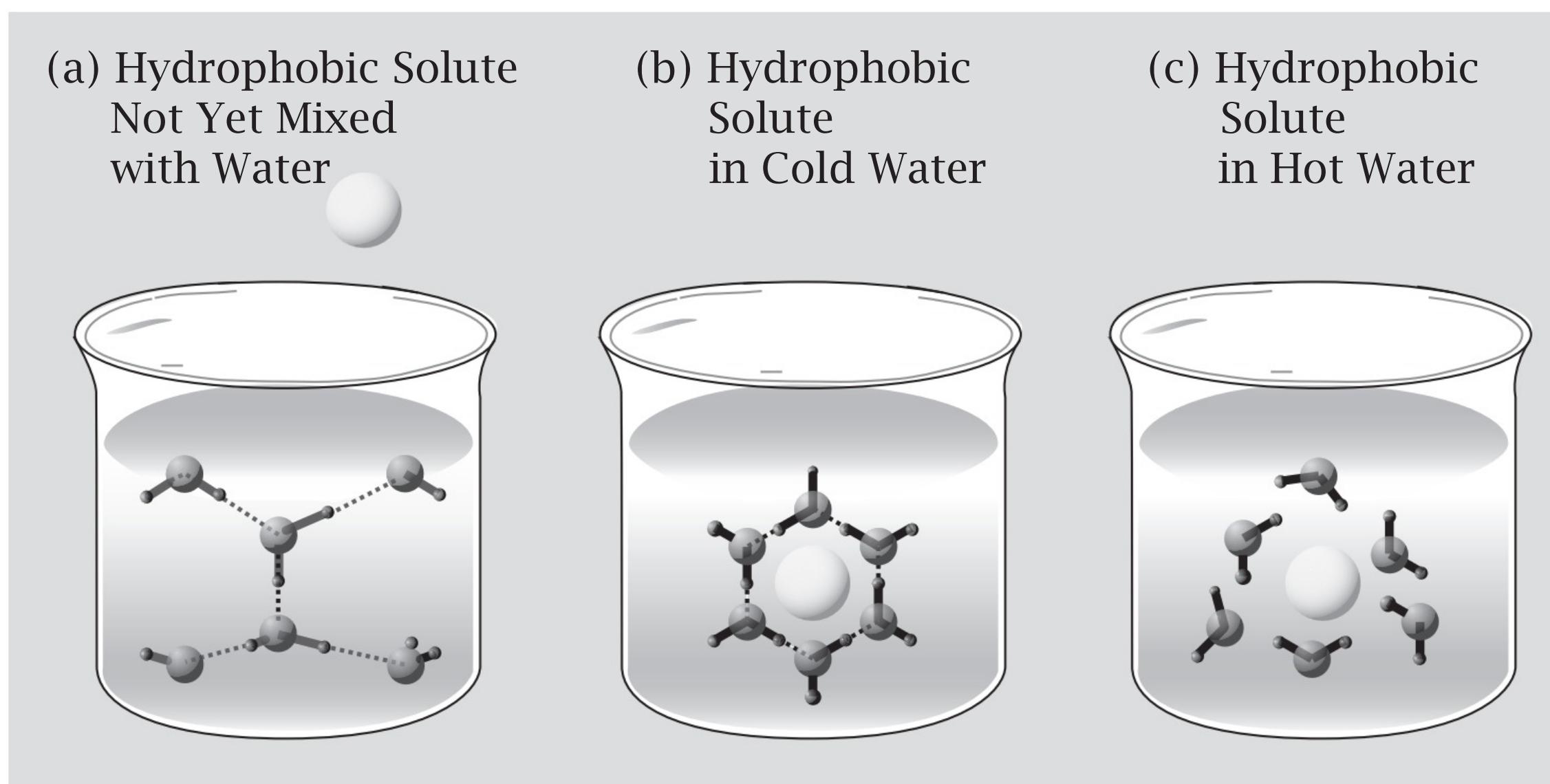
# Hydrophobic interactions

- Interactions between non-polar solutes (hydrophobes) in water.
- Water molecules reorganize around the hydrophobe in an ordered manner that is entropically favourable.
- At high temperatures, the ordering of water is broken and enthalpically it is favourable to solvate the hydrophobe.
- Often found in biomaterials.



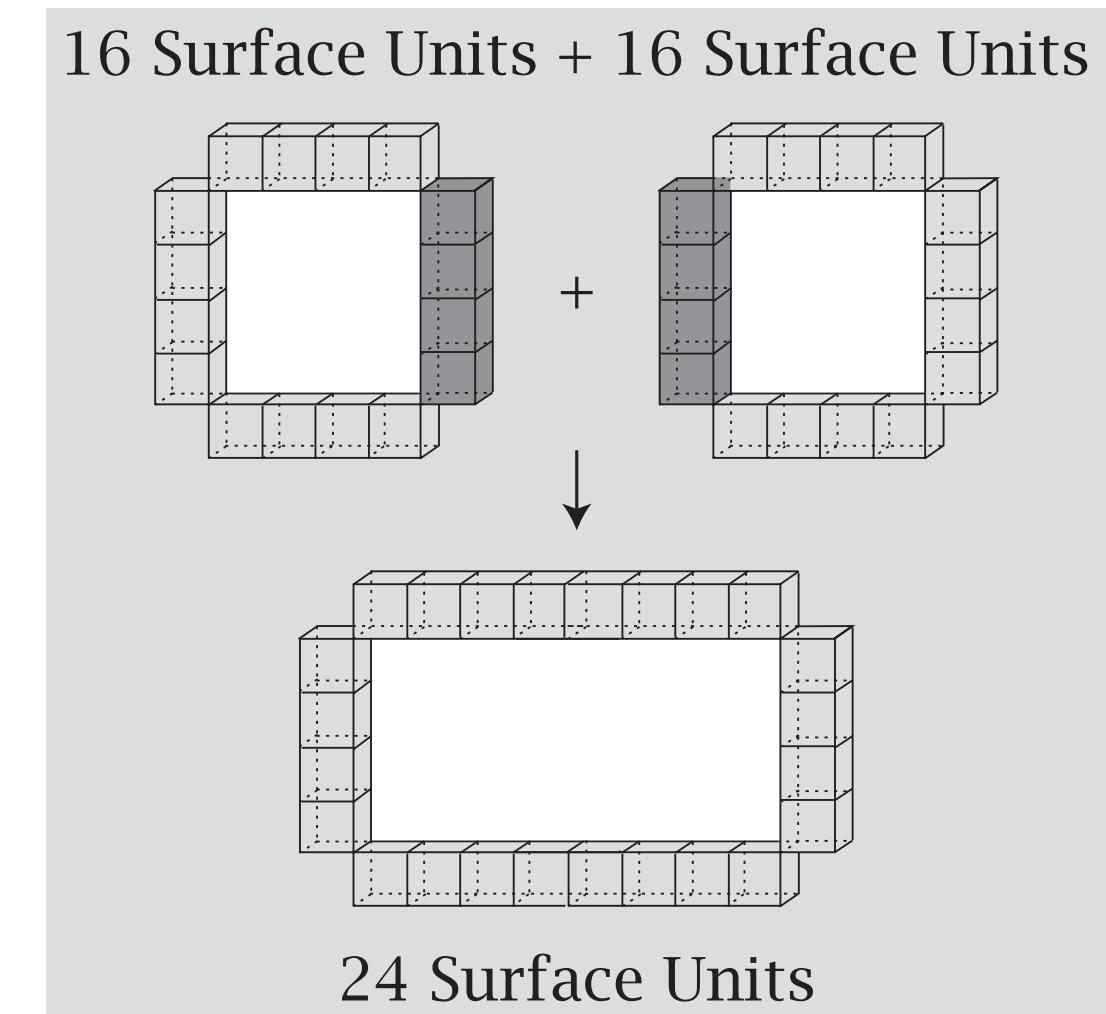
Oil in water

## Hydrophobic solvation

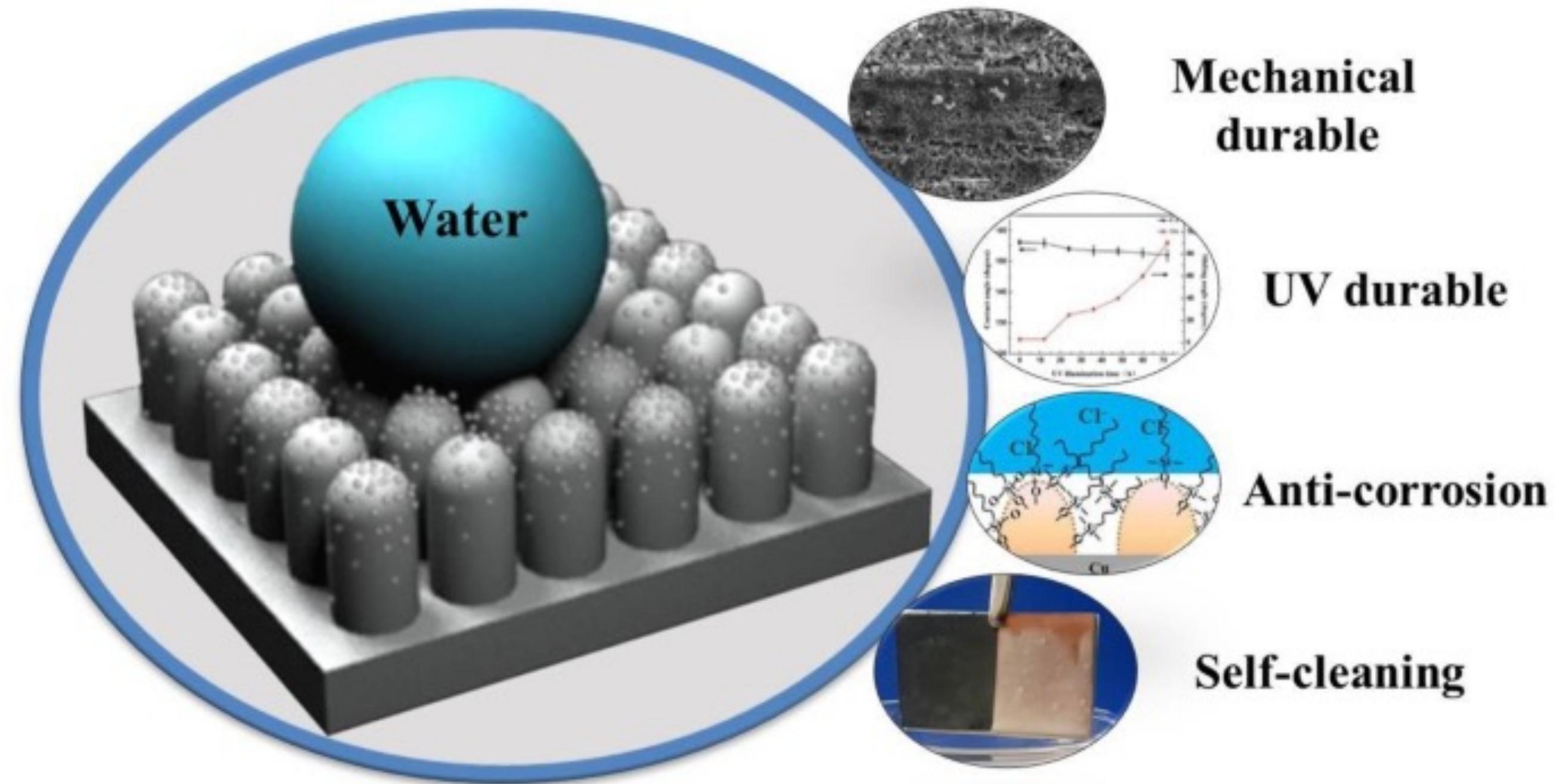


## Hydrophobic association

**Figure 31.8** Why do nonpolar solutes associate in water? Association reduces the total surface area of contact between solute molecules and the surrounding water. When the two solutes are separated, they have, in total, 32 units of surface contact with the solvent. But when the solutes contact each other, they have only 24 units of surface contact with water.

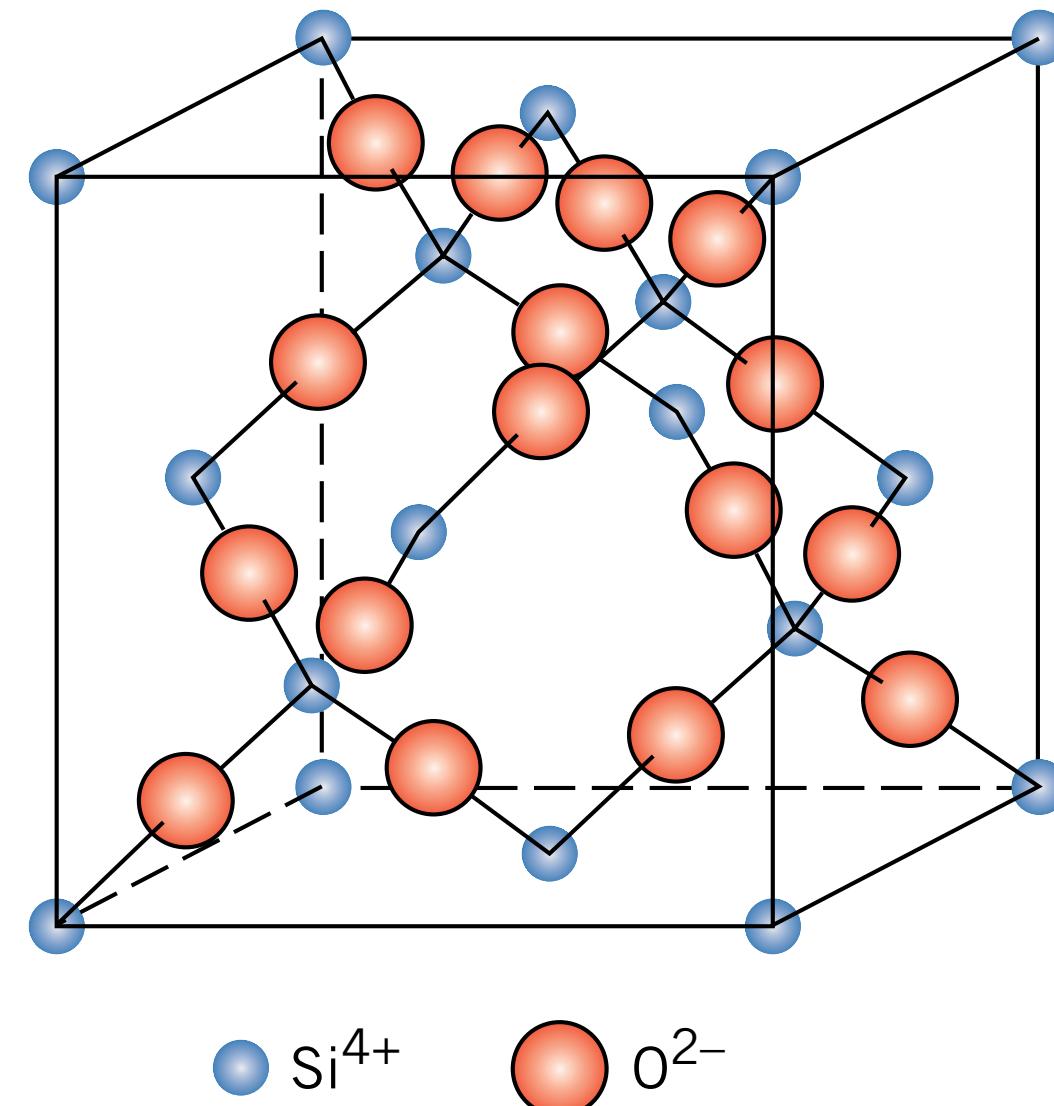


# Superhydrophobic surface

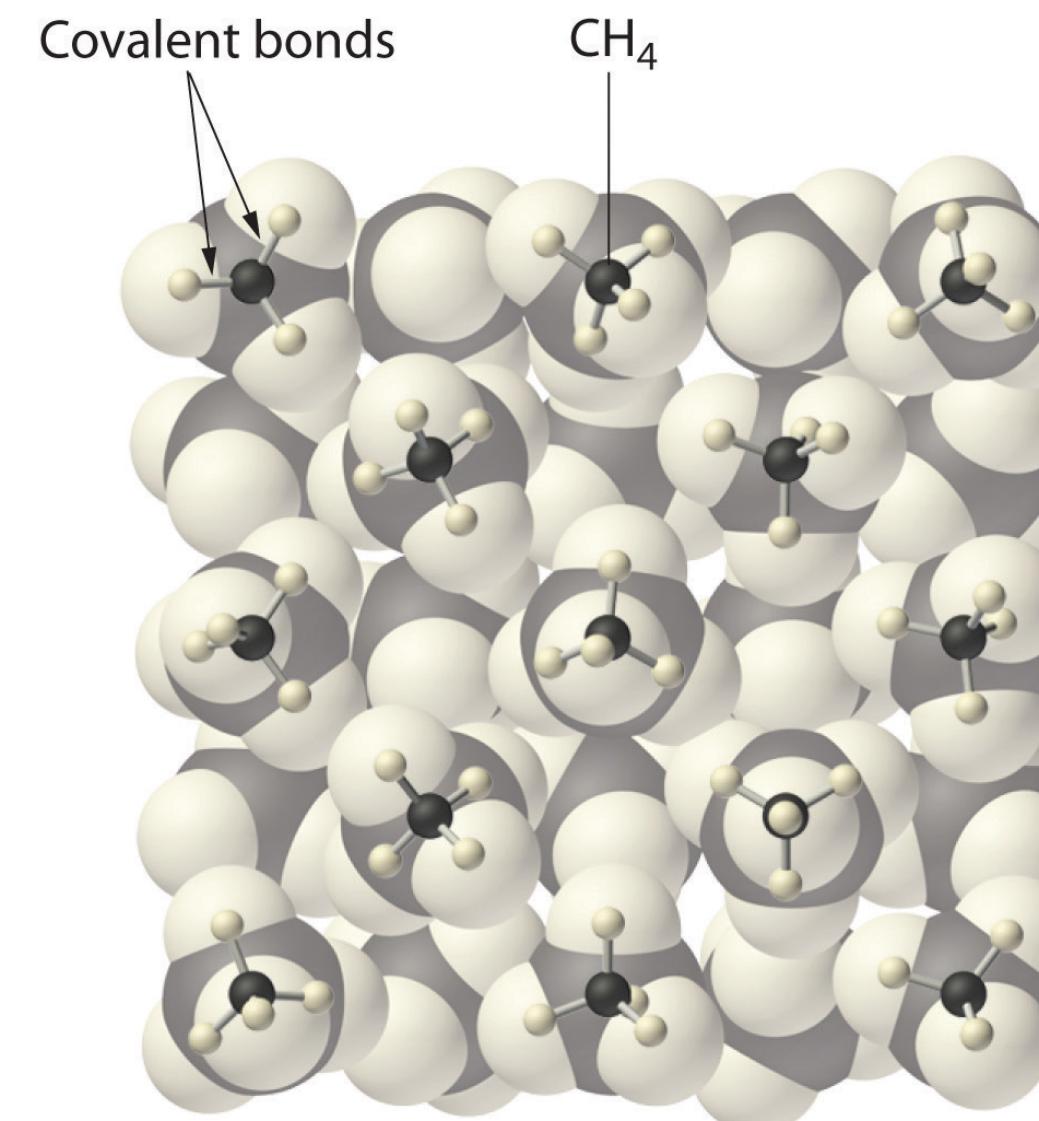


# Bonding character and properties

- **Melting and boiling temperatures:** covalent and ionic solids have higher melting and boiling points.
- When a solid consists of molecules held together by secondary bonds, the melting and boiling points of the solid reflect only the strength of the secondary bonds between the molecules, and not the strength of the primary bonds within the molecule.



- 3-D network of Si-O bonds
- No secondary bonding
- Melting point of 1723 °C
- During melting Si-O bonds are broken



- Secondary bonding: van der Waals forces between CH<sub>4</sub> molecules (strength 1.36 kJ/mol)
  - Melting point of -182 °C
  - C-H bond strength is 413 kJ/mol > Si-O strength of 375 kJ/mol
  - During melting van der Waals forces are weakened

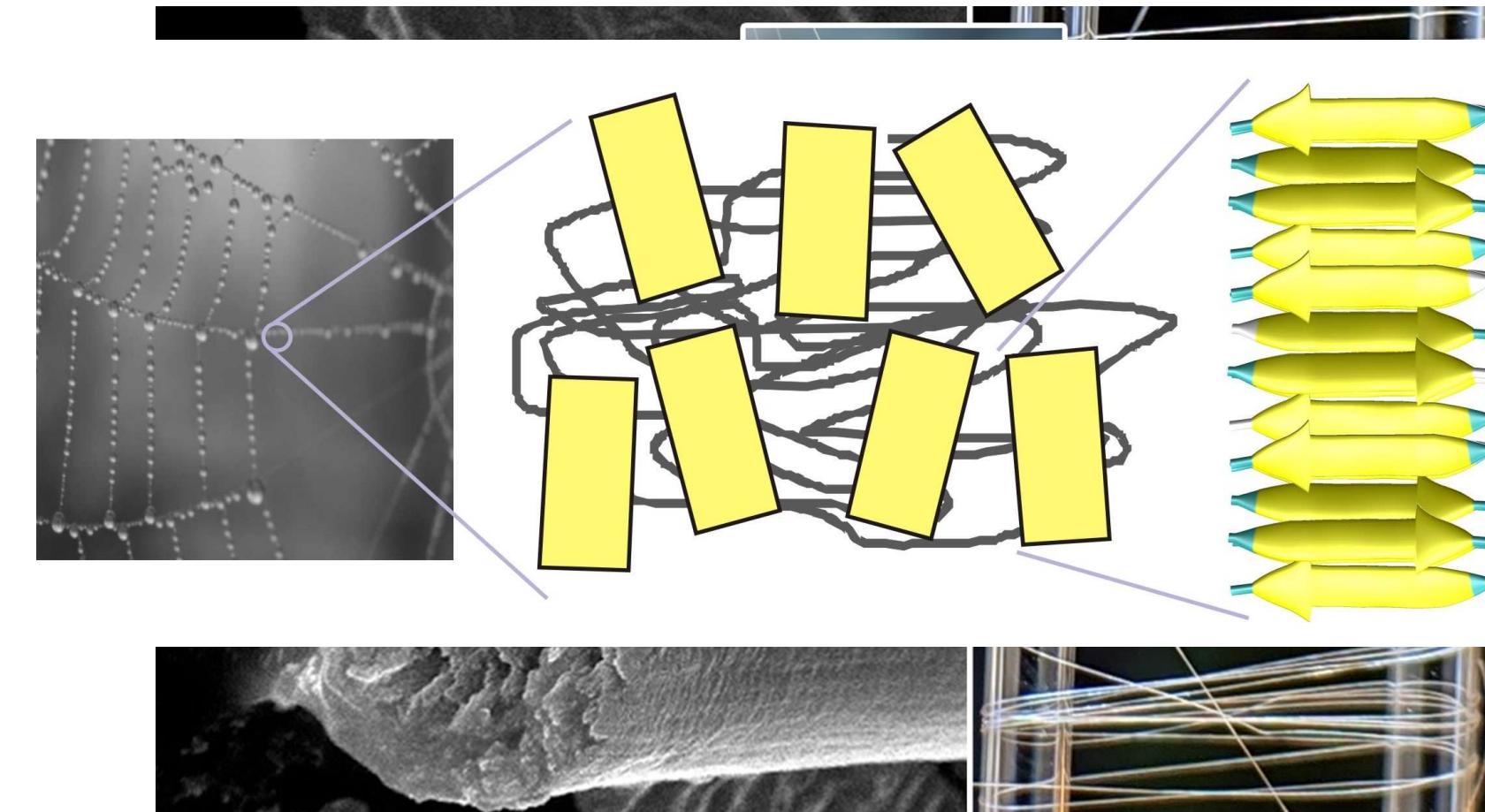
- ***Thermal expansion:*** asymmetry of the potential energy versus distance curve
  - Thermal expansion at a given temperature tends to be less for strongly bonded materials than for weakly bonded materials.
  - Deep potential wells are more symmetrical about the equilibrium position  $r_0$  than shallow potential wells.
- 
- ***Mechanical Properties*** of solids are dependent on the strength of the bonds as well as the directional nature of bonding.
  - Solids with strong and directional bonds tend to be brittle
  - Diamond: *covalently bonded* → hard and brittle
  - *Metallic bonds* are relatively weak and nondirectional, metals are soft, ductile and malleable.
  - *Ionic solids* fall in between covalent and metallic solids in that they may exhibit a very limited amount of ductility.

# Why do we need to understand the intermolecular forces?



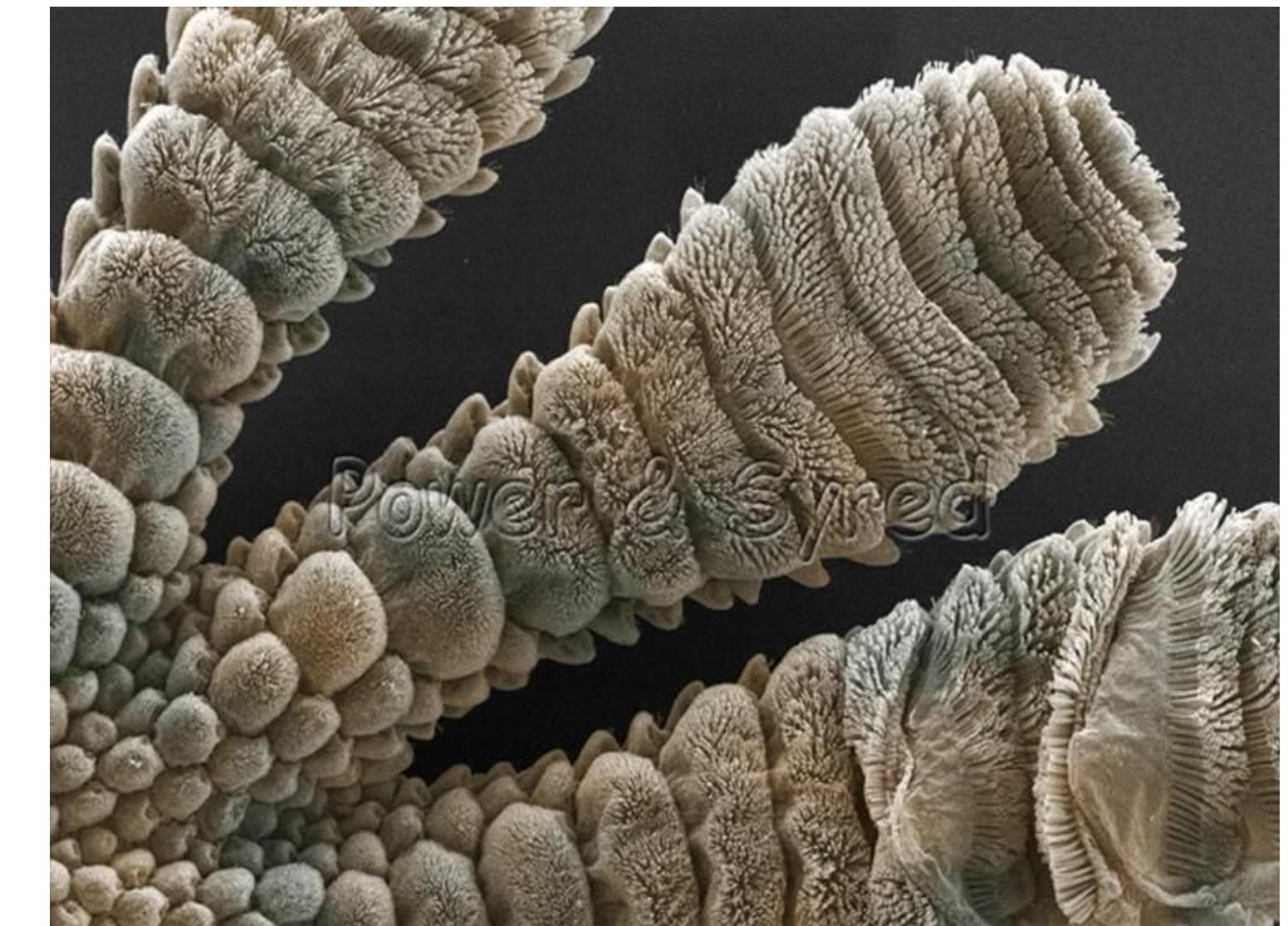
Designing superhydrophobic surfaces, self-cleaning applications

***Hydrophobic interactions***



Designing materials stronger than Kevlar  
**SEM image of spider silk fiber**

***Hydrogen bonding***



Designing materials with adhesive properties  
**SEM image of Gecko feet**

***Van der Waals forces***

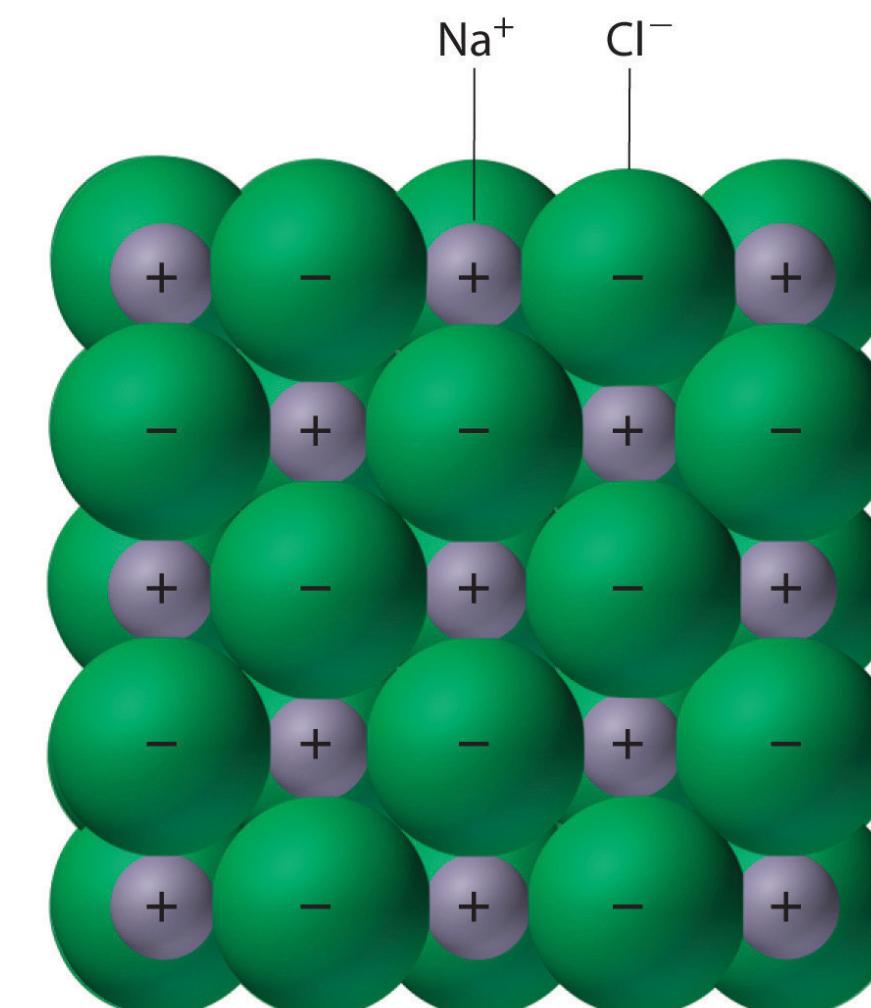
# Structure of solids

*Food for thought... (partially answered)*

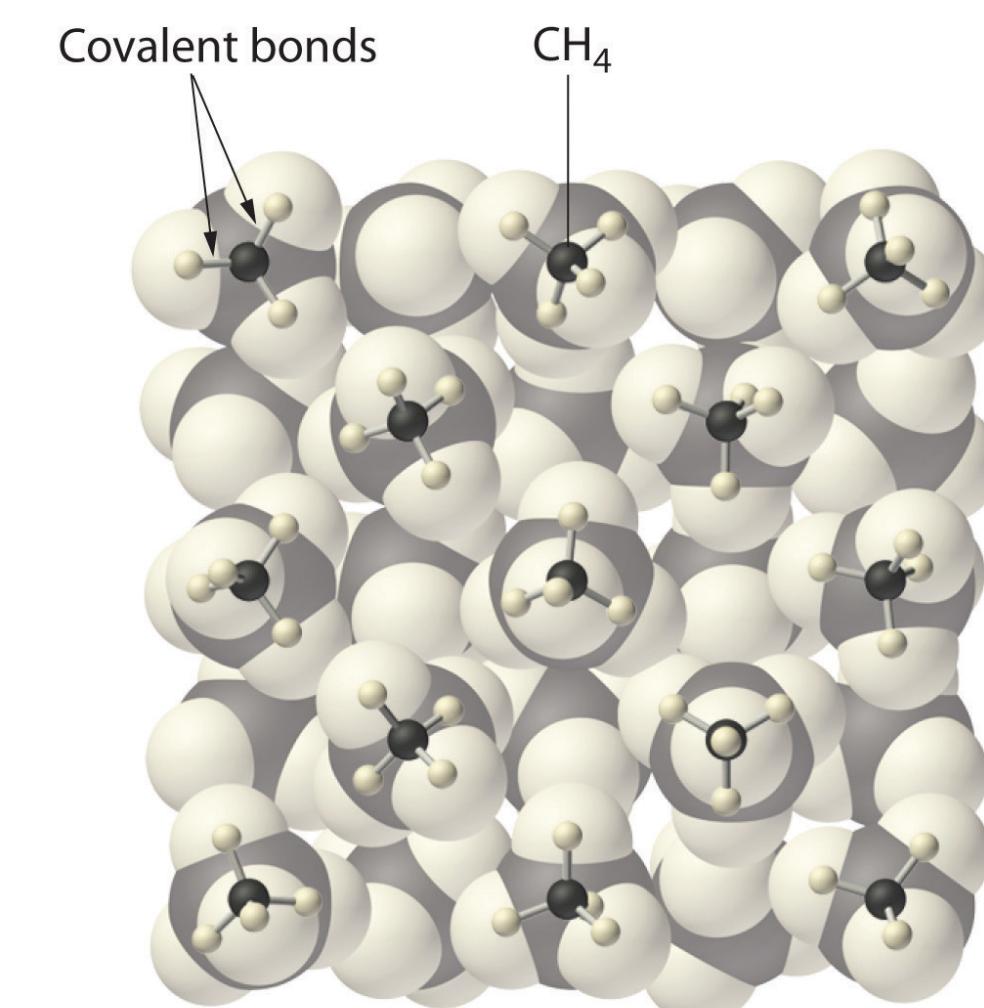
- *Why don't all solids have same strength?*
- *Why do they have any strength at all?*
- *Why aren't they much stronger?*
- *When do we call them strong?*

# Classification of solids

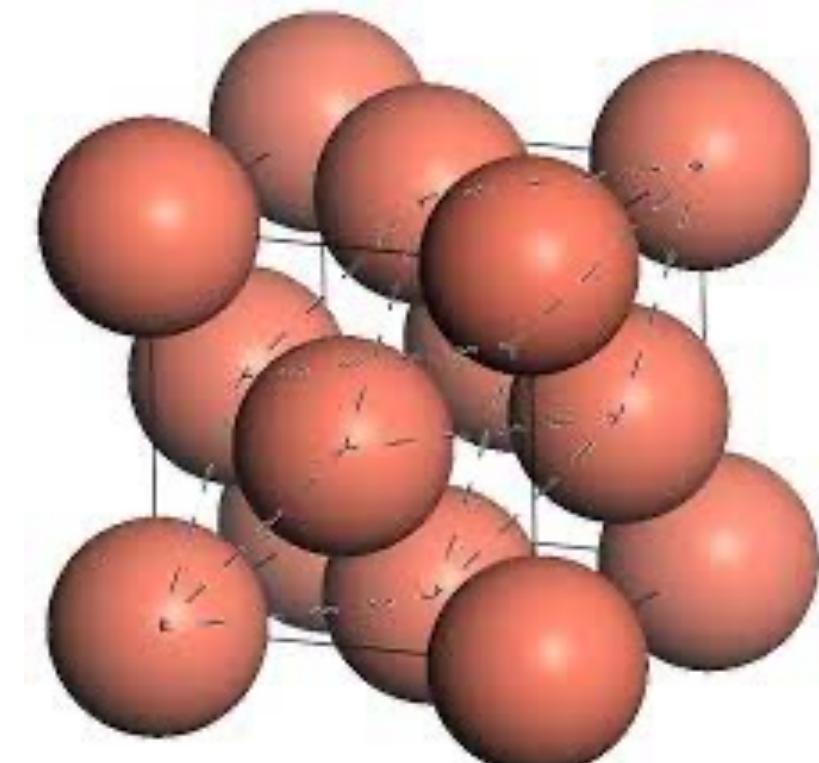
- Ionic solids
- Metallic solids
- Covalent network solids
- Molecular solids



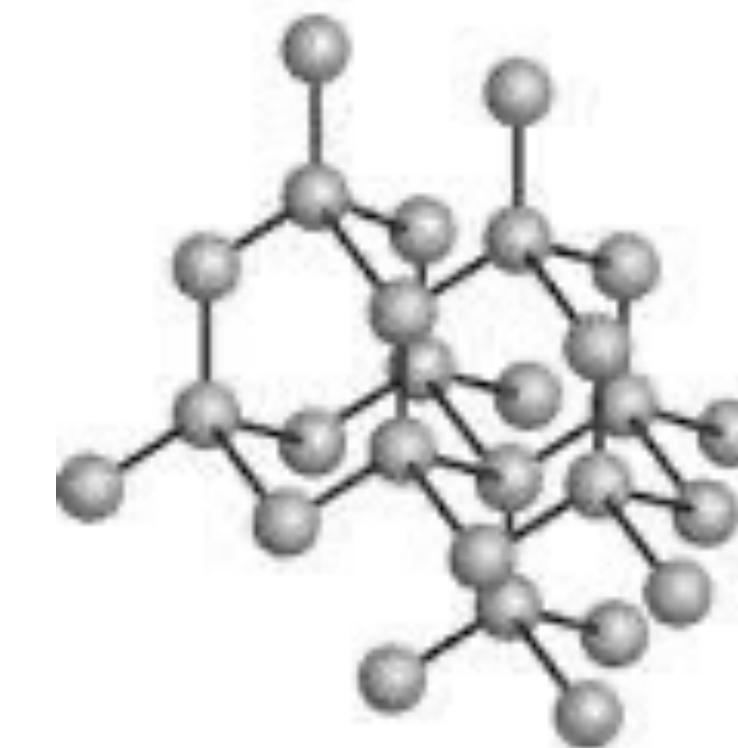
(a) Ionic solid: strong electrostatic interactions



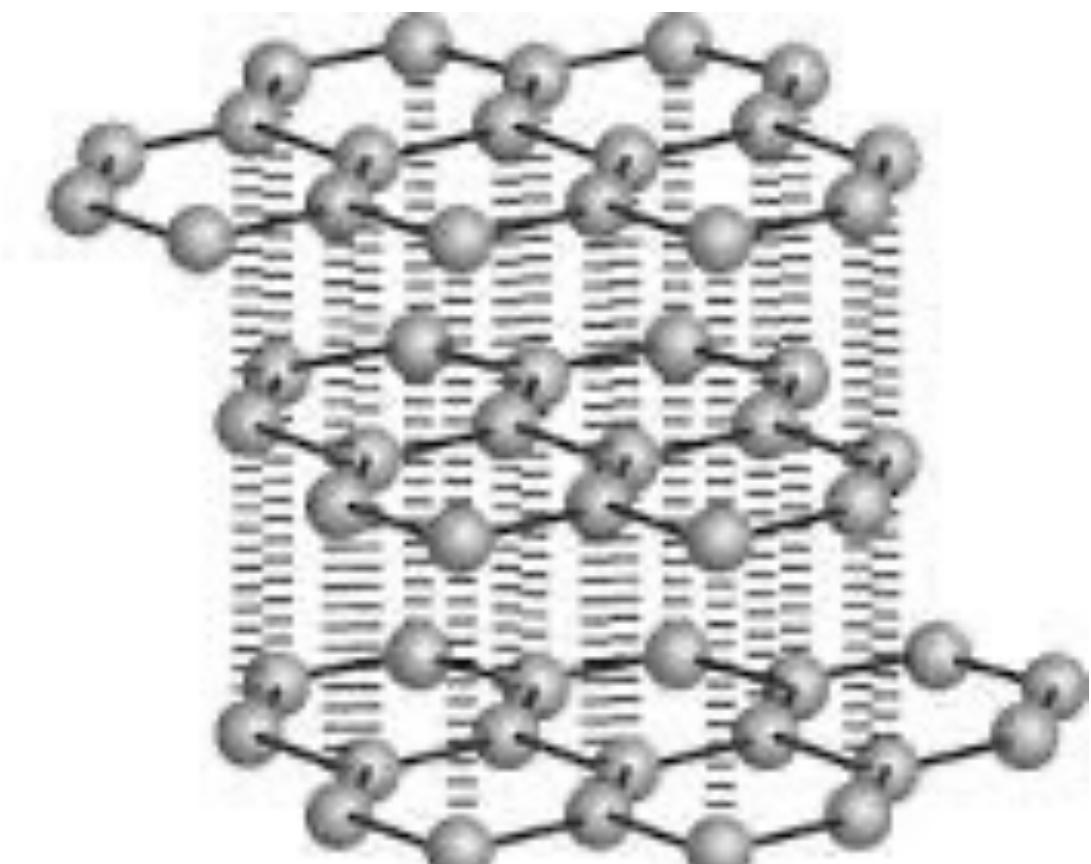
(b) Molecular solid: weak intermolecular forces



Metallic solids like Cu, Fe



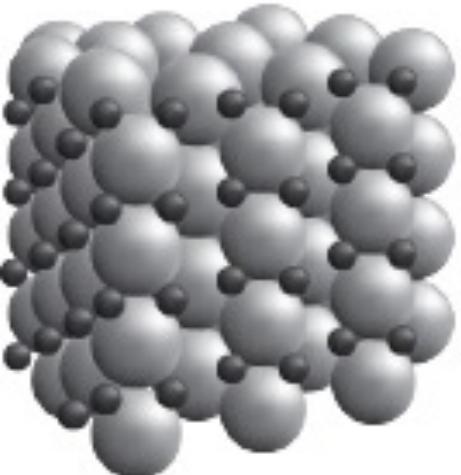
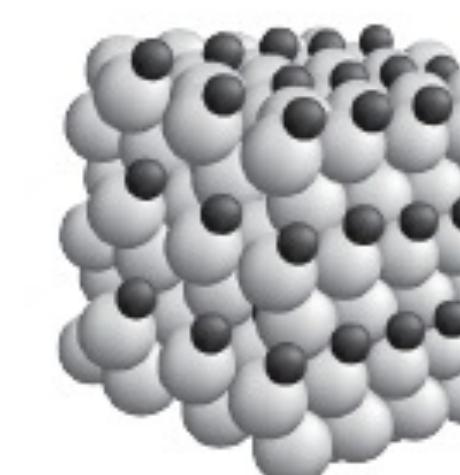
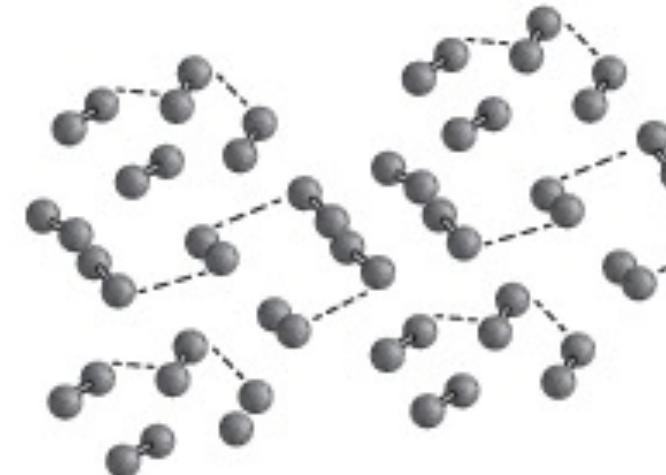
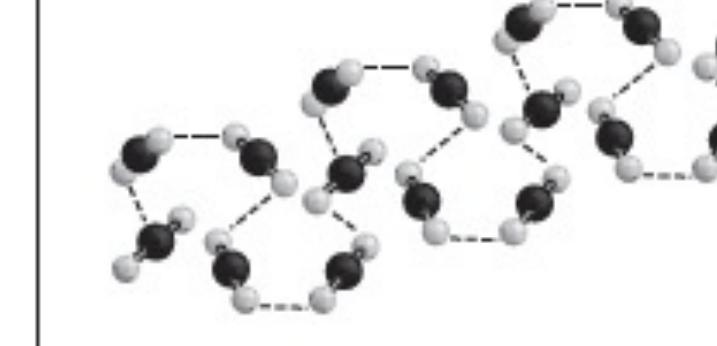
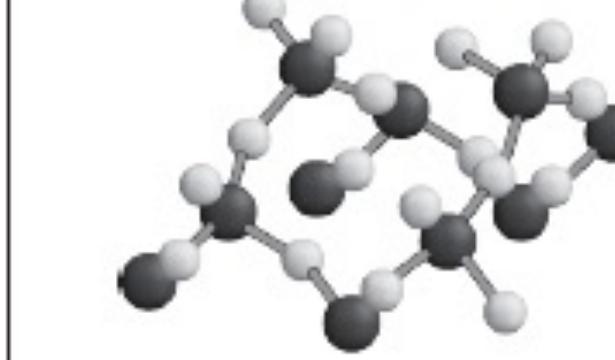
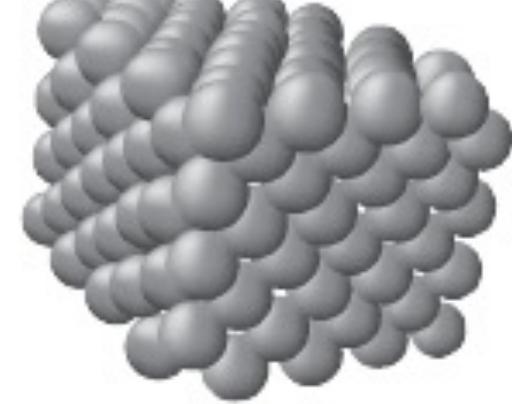
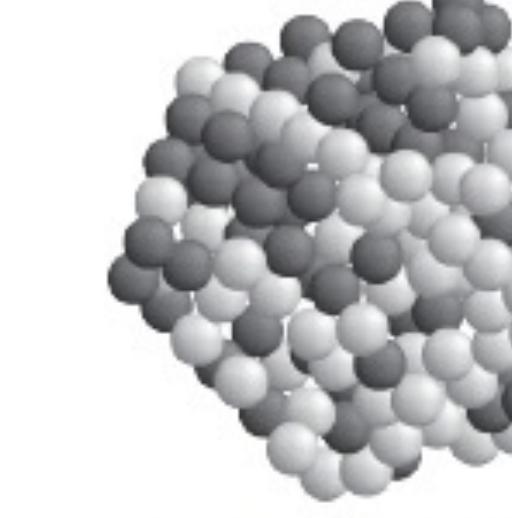
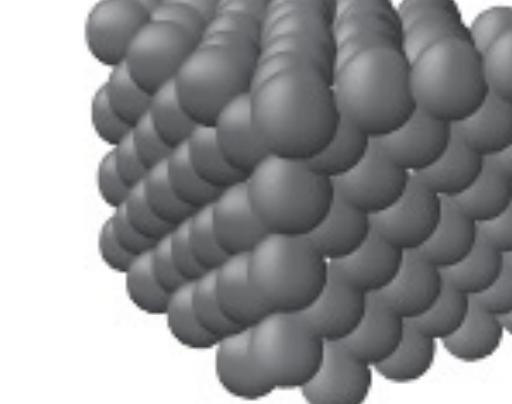
Diamond



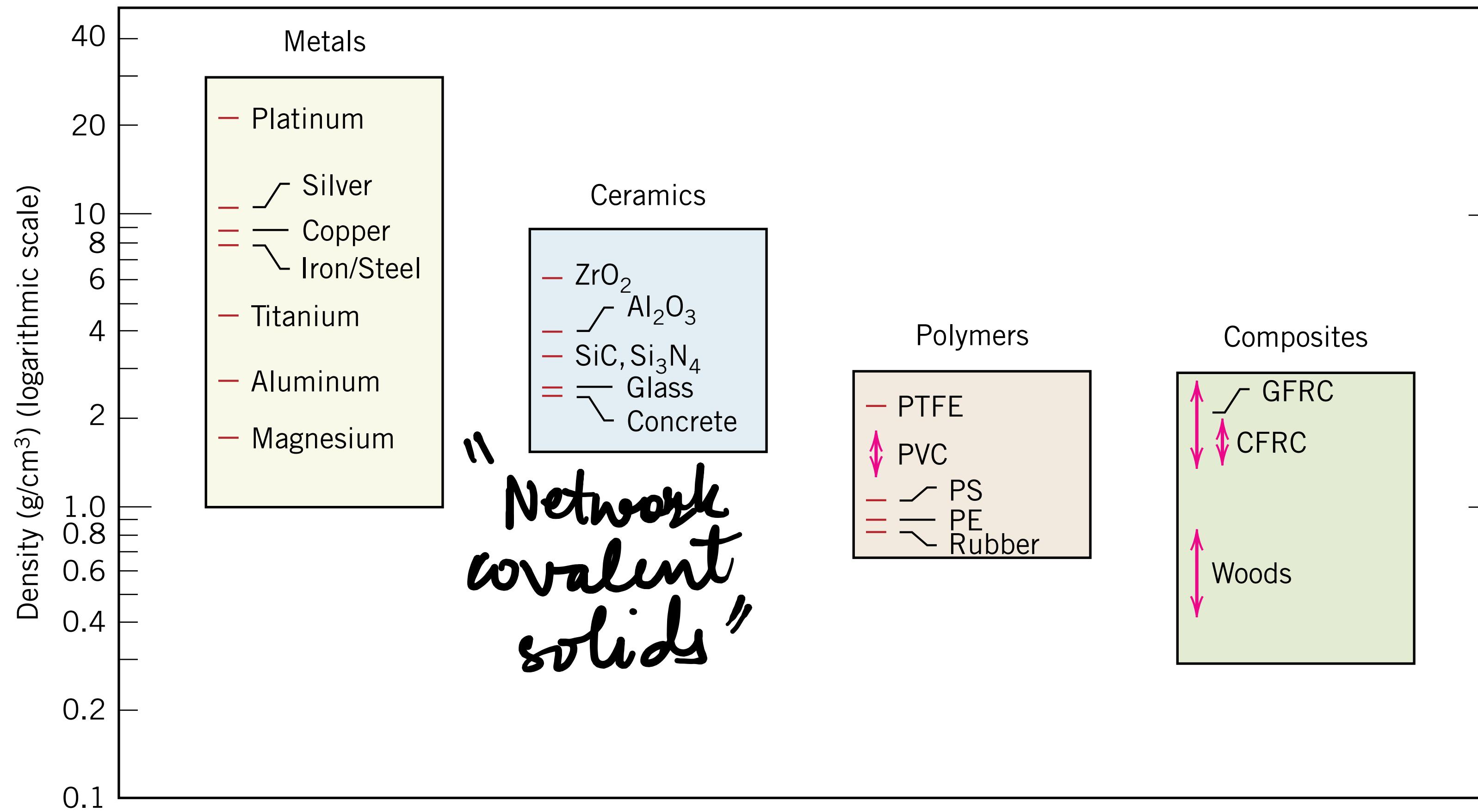
Graphite

Extended networks of atoms held by covalent bonds eg.  $\text{SiO}_2$ , C allotropes

# Some examples

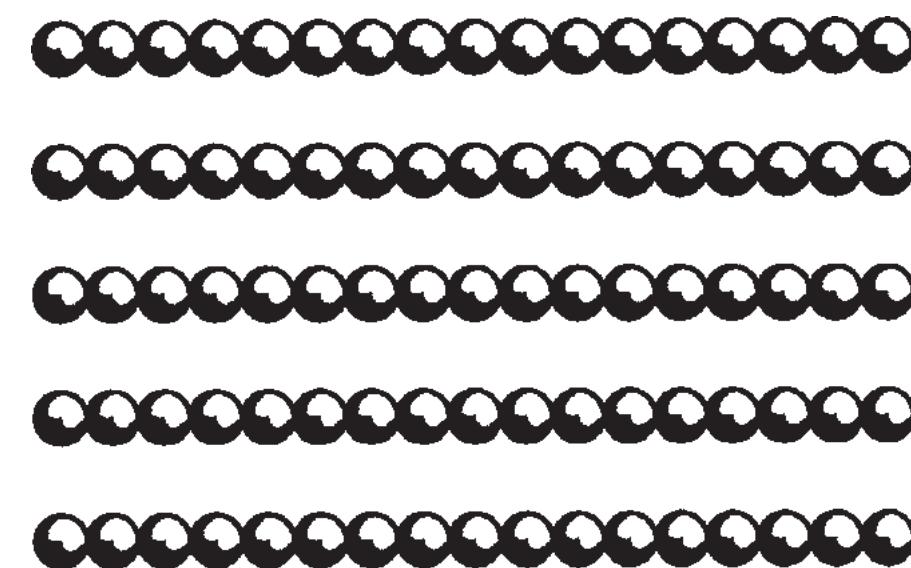
Ionic Solids			
Molecular Solids			
Network Covalent Solids			
Metallic Solids			

# Classification of materials

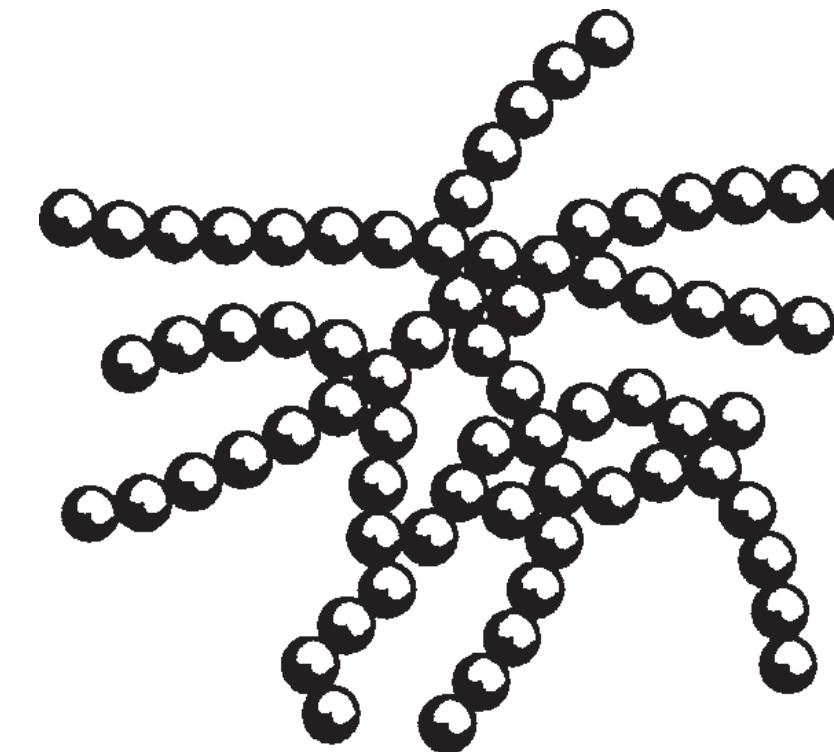


# Crystalline and non-crystalline states

Crystalline state



Molten or glassy state



When primary bonds do not extend in all directions, one-dimensional chain molecules or two-dimensional sheet molecules are formed. Such units have to be aided by secondary bonding forces to form a three-dimensional crystal.



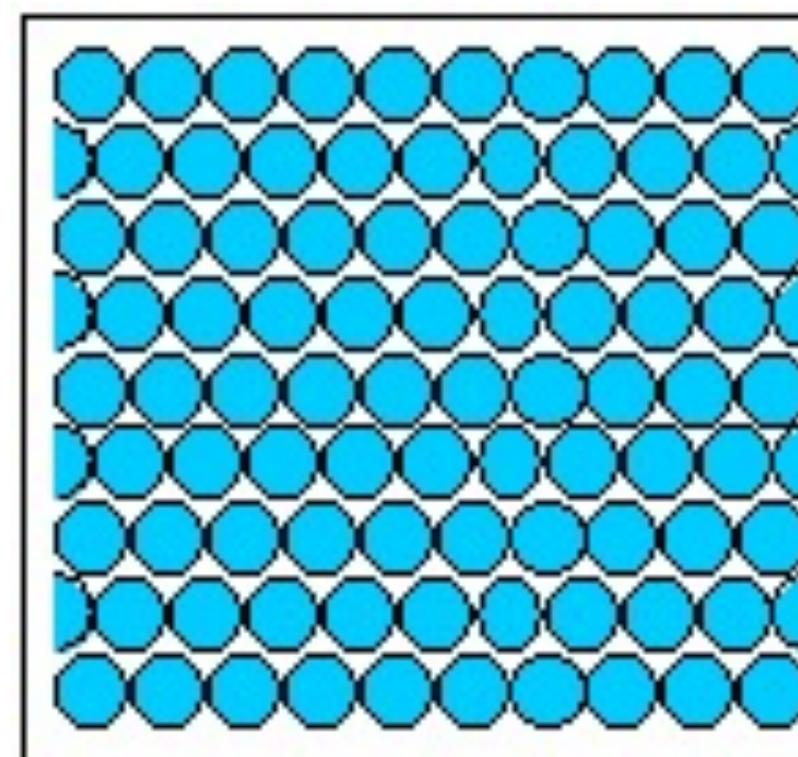
# Crystalline and non-crystalline states

## Crystalline solids

- Long-range order (translational periodicity)
- Defects (vacancy, dislocations etc)
- Atomic arrangement is ordered
- Sharp melting point
- Need slow cooling rates
- Free energy is lowest
- Grain boundaries
- Example: metallic Cu, NaCl

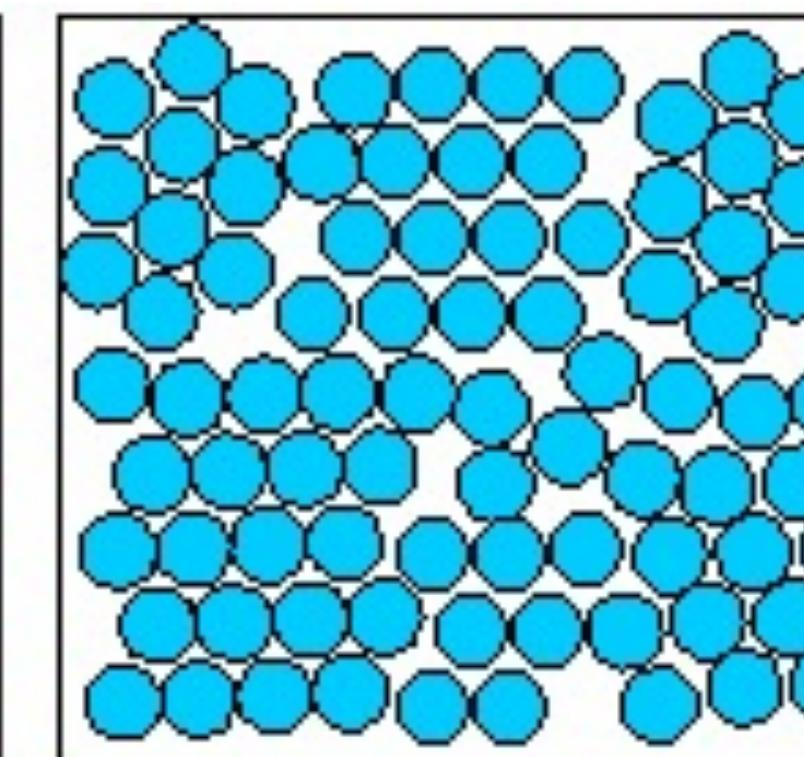
## Amorphous solids

- No long-range translational order i.e. short-range order (not totally random)
- Disordered or random arrangements of atoms
- Gradually softens over a range of temperature.
- Fast cooling rates.
- Free energy is high
- No grain boundaries
- Example: glassy solids (silicates)



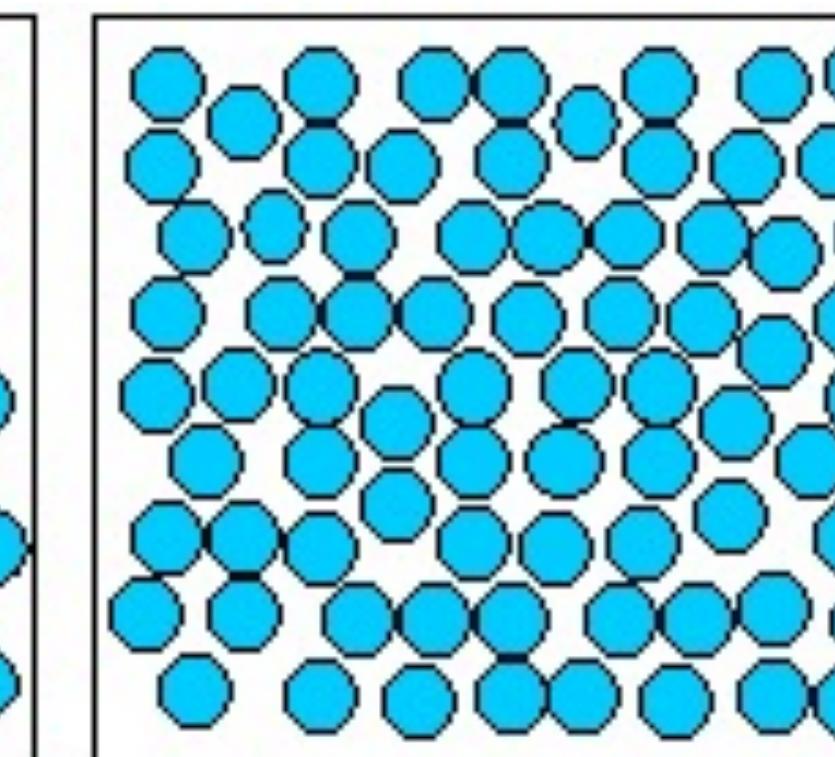
Single crystal

Periodic across the  
whole volume.



Polycrystal

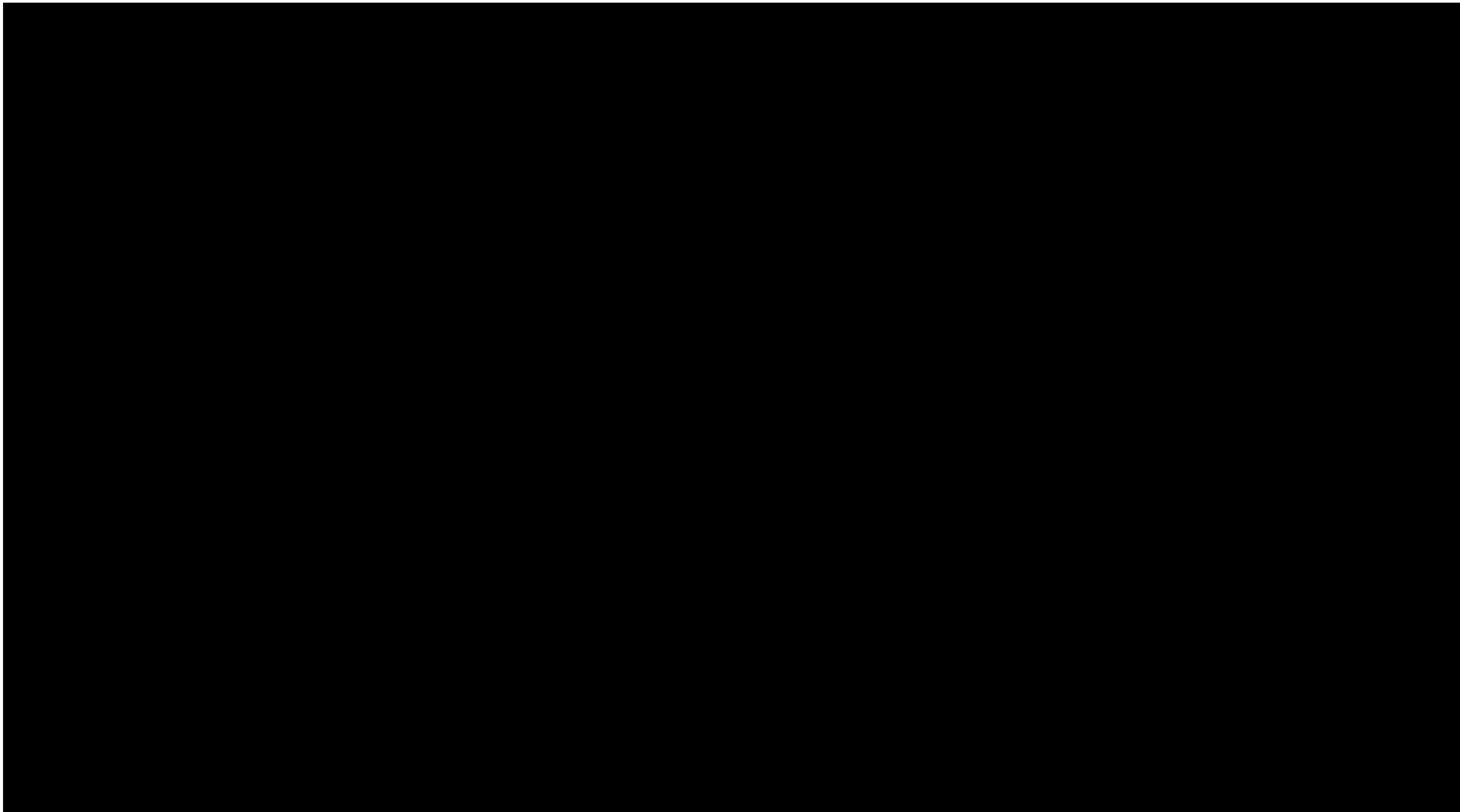
Periodic across  
each grain.



Amorphous solid

Not periodic.

# Is glass a solid or a liquid?



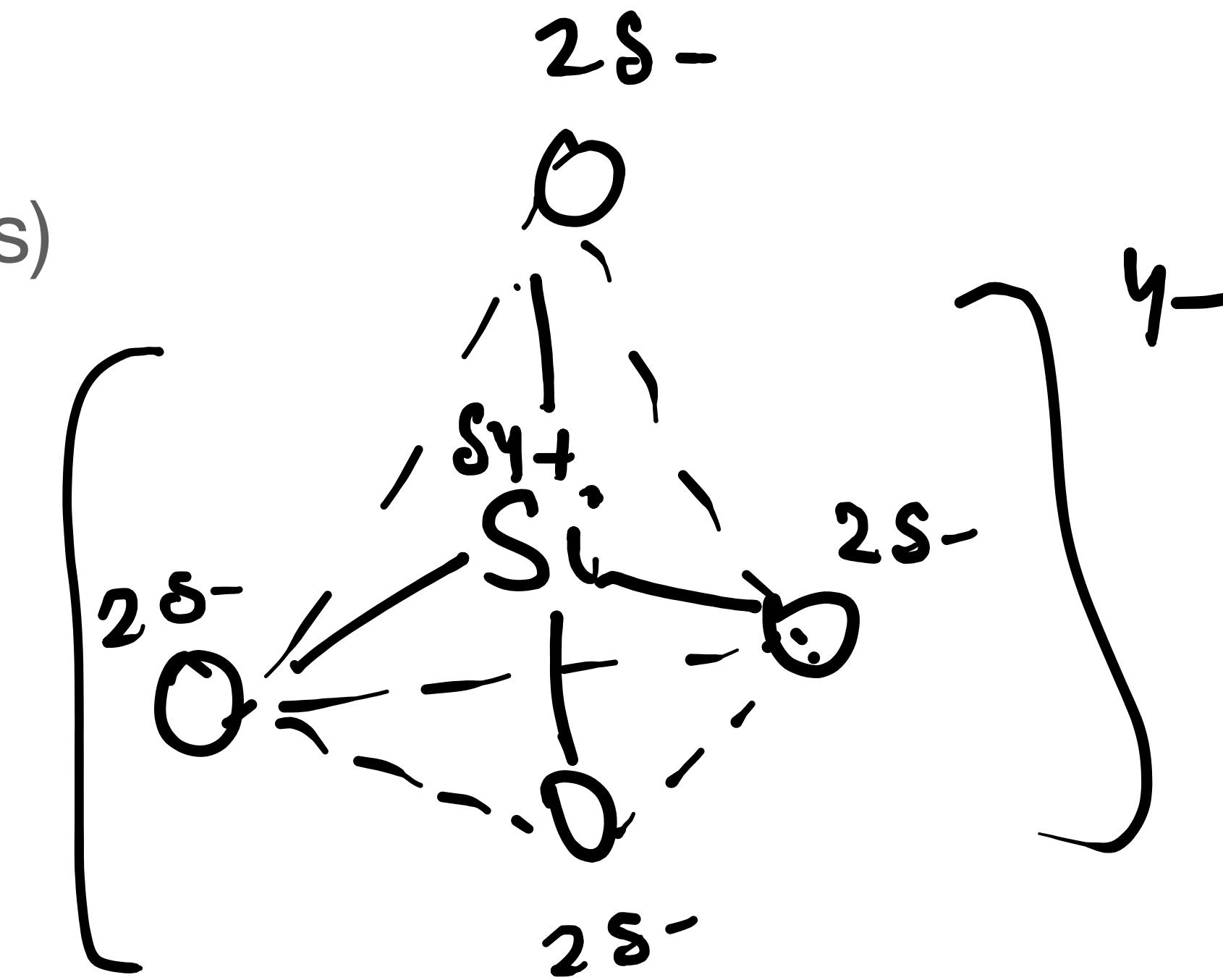
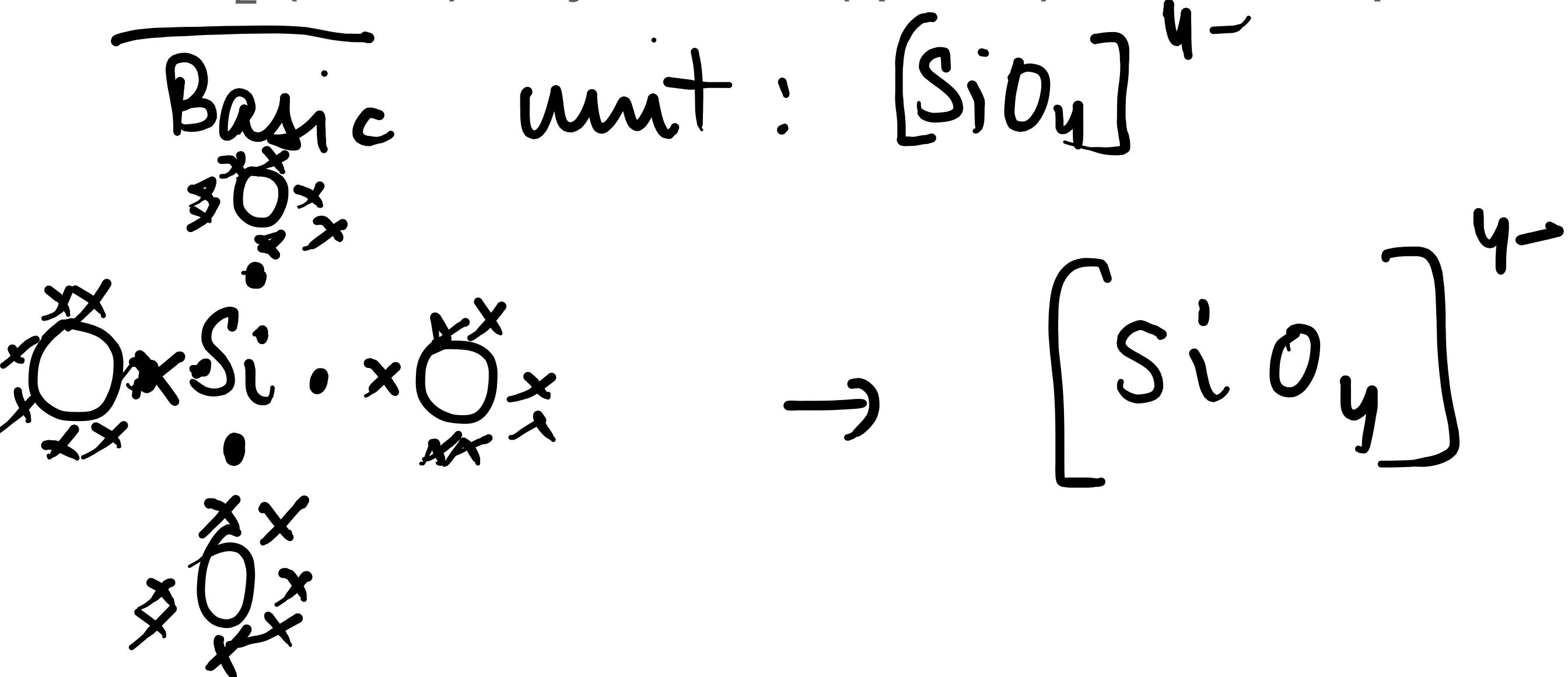
# Amorphous solids (Ceramics: glass)

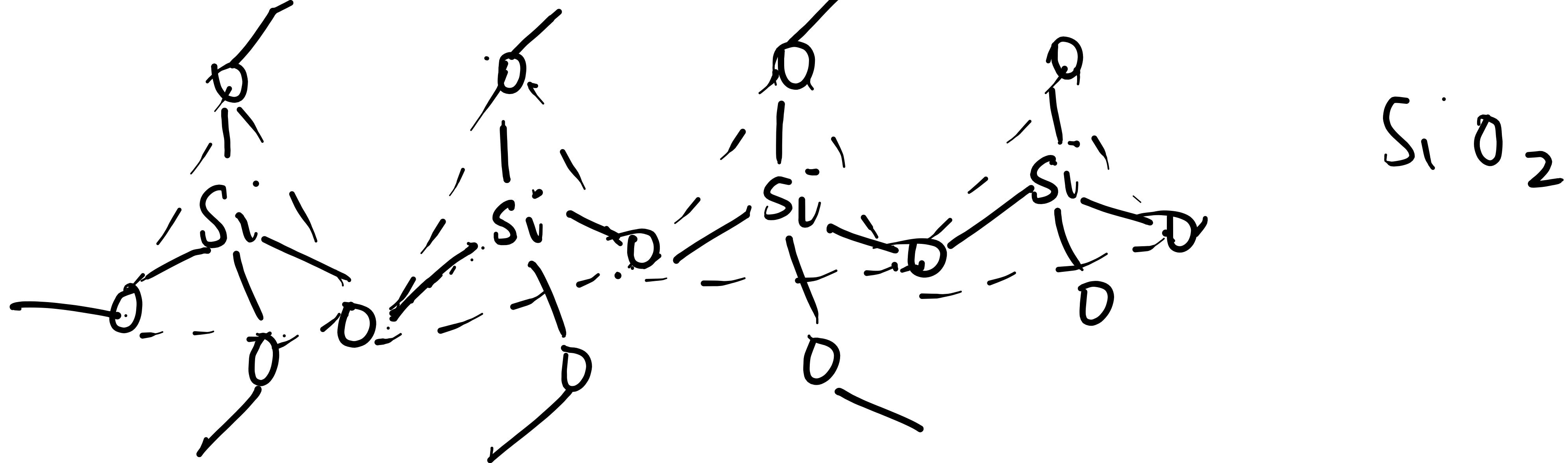
## Silicates: Glassy solids

Ceramics: composed of clay minerals (i.e., porcelain), as well as cement, and glass e.g. aluminum oxide (or alumina,  $\text{Al}_2\text{O}_3$ ), silicon dioxide (or *silica*,  $\text{SiO}_2$ ), silicon carbide ( $\text{SiC}$ ), silicon nitride ( $\text{Si}_3\text{N}_4$ )

- stiff and strong
- Brittle (less ductile)
- Susceptible to fracture
- Low heat and electrical conductivities

$\text{SiO}_2$  (silica): crystalline (quartz) and amorphous (glass)



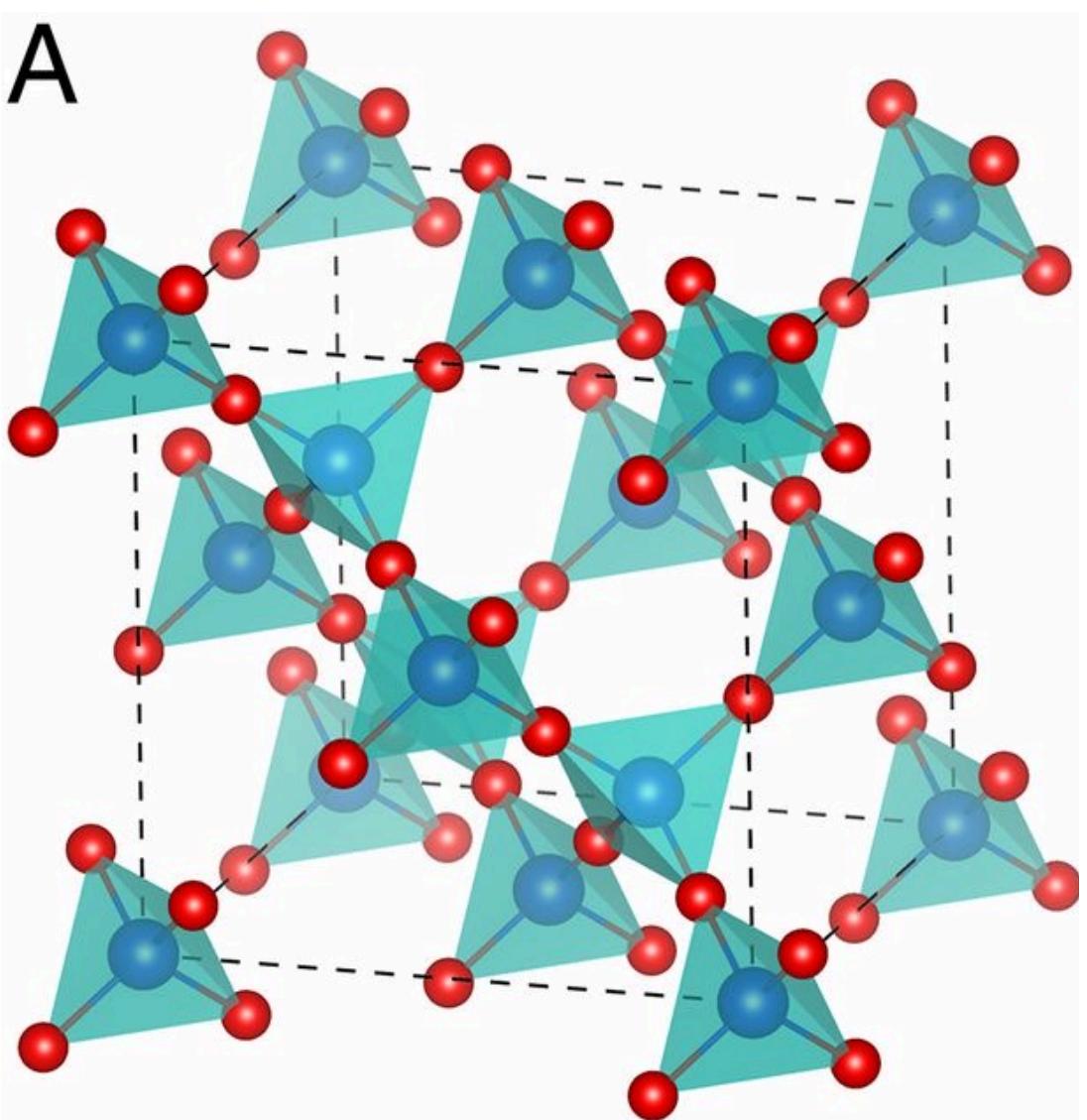


$\frac{1}{2} \times 40$  per tetrahedron  $\rightarrow$  1 Si per TH }  $\text{SiO}_2$   
 $\frac{1}{2} \times 40$  per tetrahedron  $\rightarrow$  20 per TH

- Composition is maintained
- Electro neutrality is "

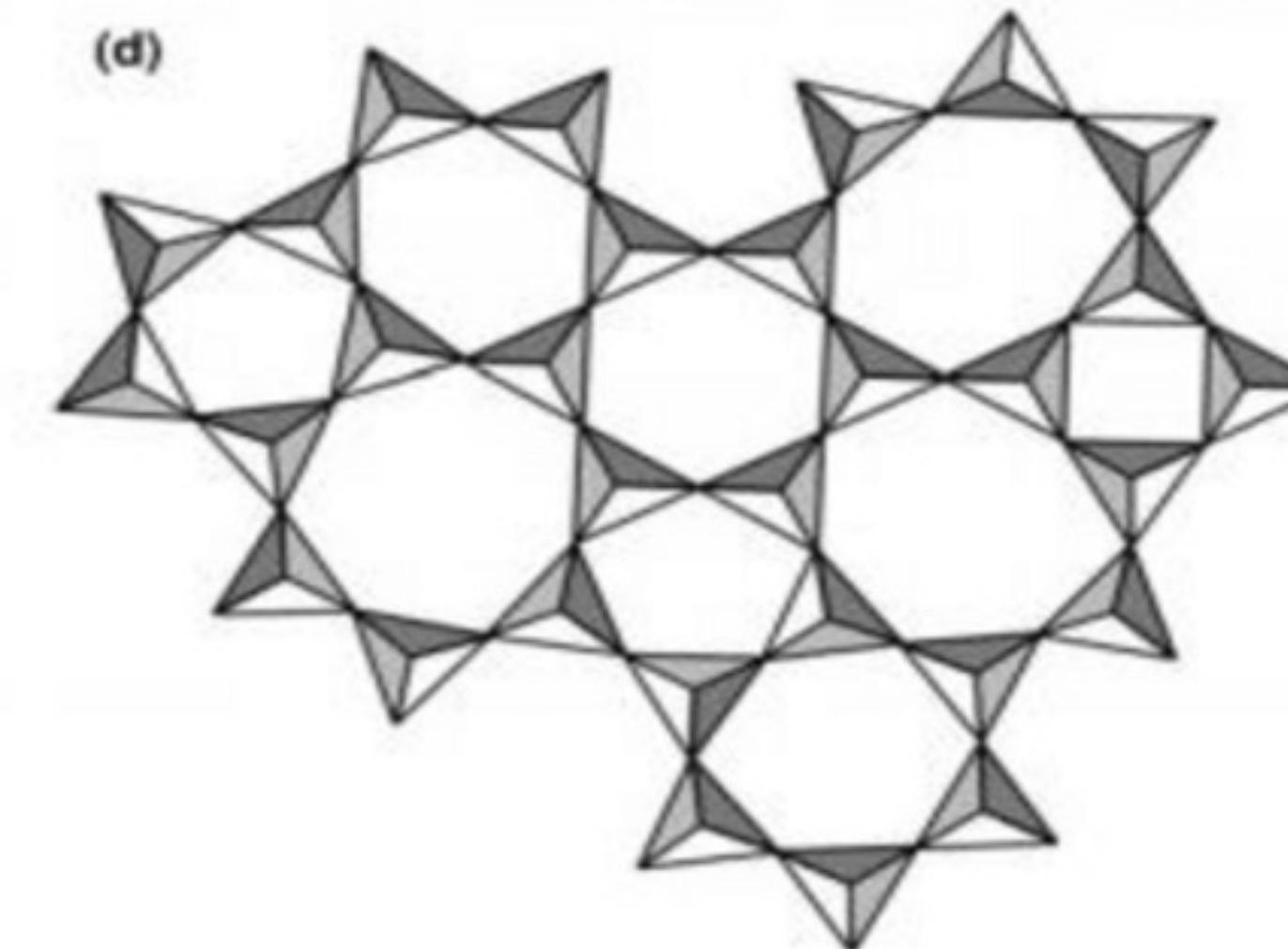
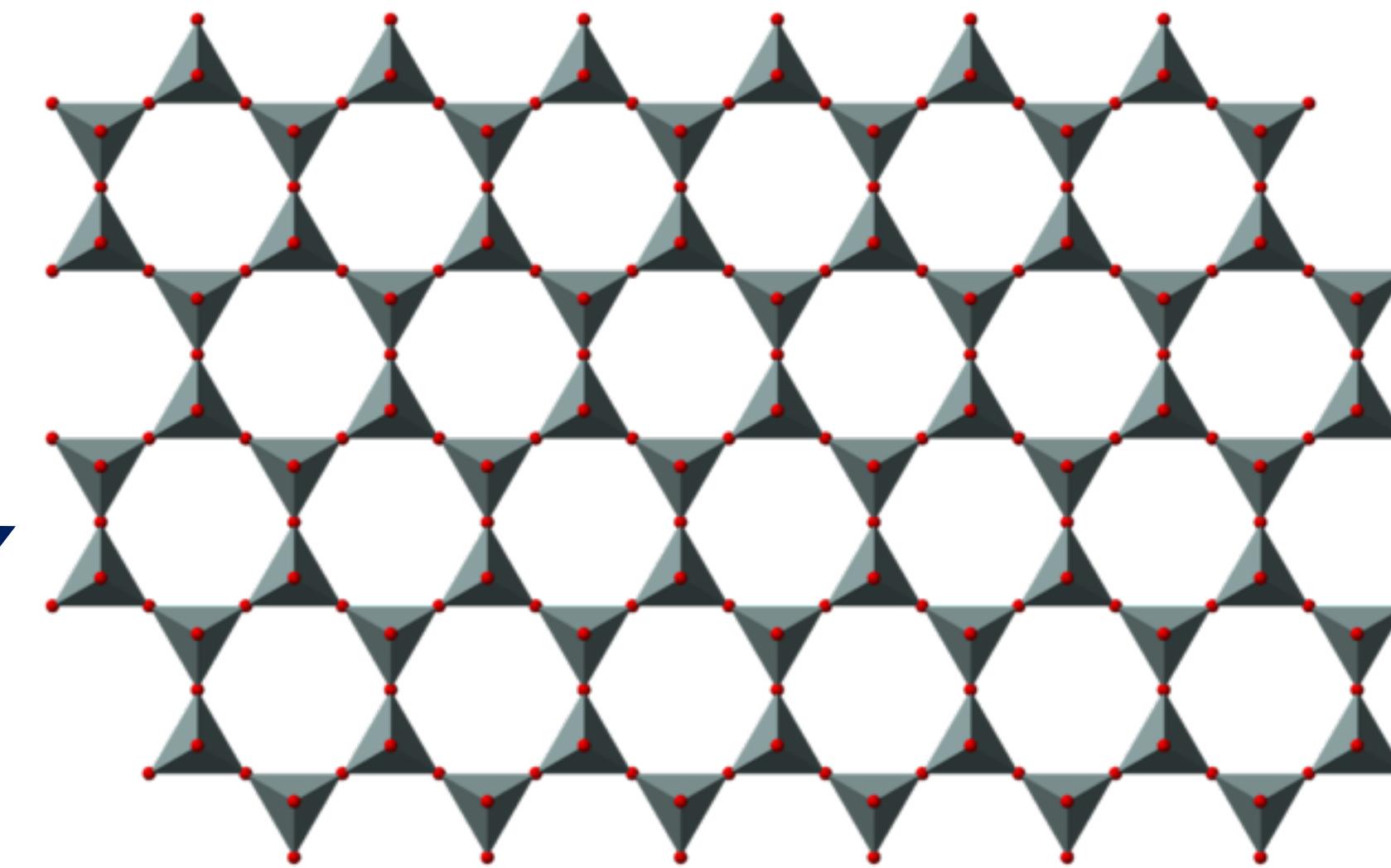
# Three-dimensional network of silicate

*Tetrahedra can rotate*



**Crystalline**  
Slow cooling

**Amorphous**  
Fast cooling



# Lecture 24

## Materials and their structure- Part 2

### Textbooks:

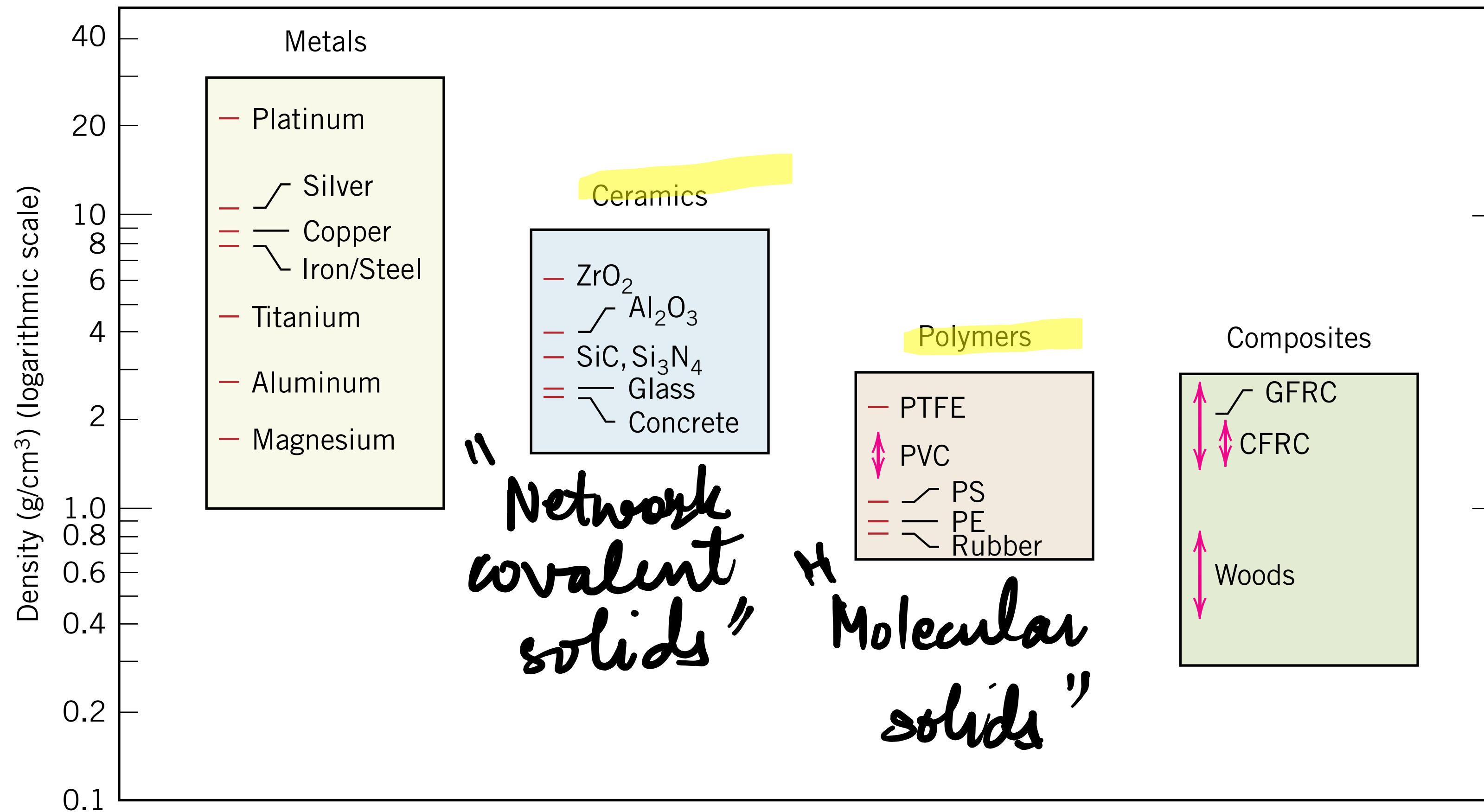
- Introduction to materials science and Engineering: V. Raghavan
- Materials Science and Engineering: Callister and Rethwisch

Prof. Divya Nayar  
Department of Materials Science and Engineering  
[divyanayar@mse.iitd.ac.in](mailto:divyanayar@mse.iitd.ac.in)

# Recap...

1. Classification of materials
2. Different types of solids
3. Non-crystalline solids: amorphous solids (glass)
4. Structure of Silicates

# Classification of materials



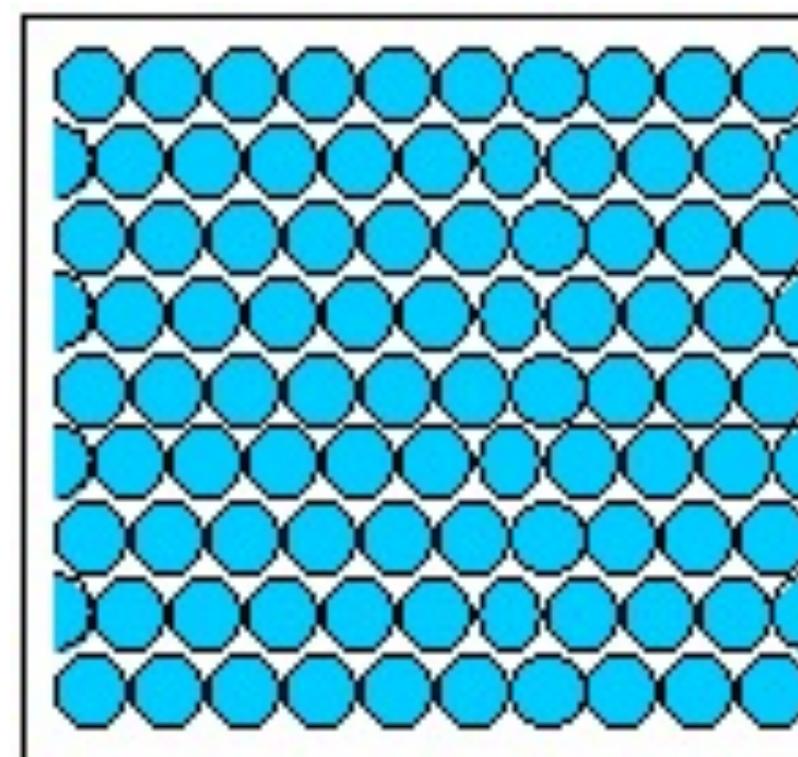
# Crystalline and non-crystalline states

## Crystalline solids

- Long-range order (translational periodicity)
- Defects (vacancy, dislocations etc)
- Atomic arrangement is ordered
- Sharp melting point
- Need slow cooling rates
- Free energy is lowest
- Grain boundaries
- Example: metallic Cu, NaCl

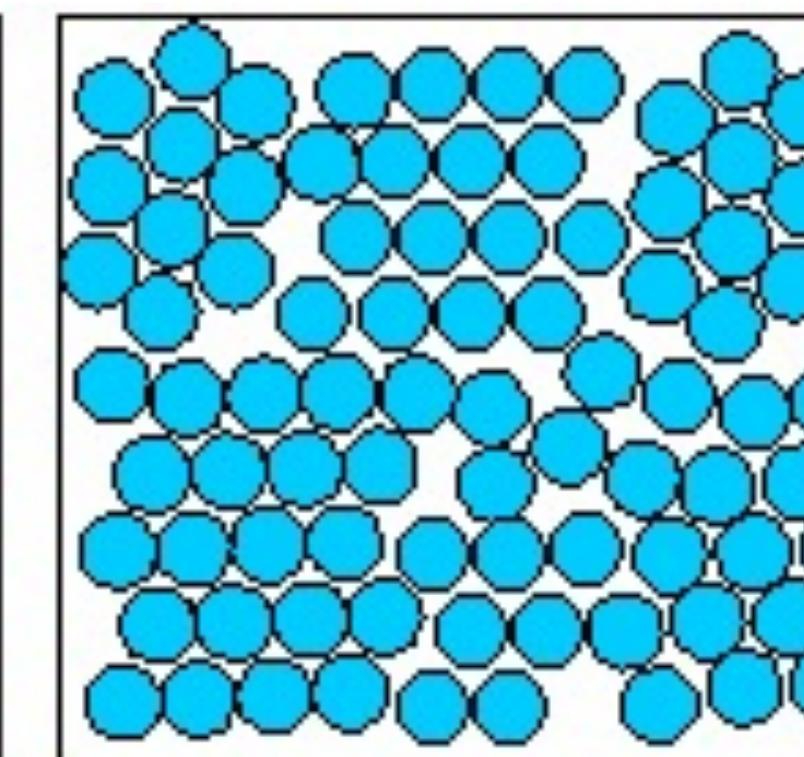
## Amorphous solids

- No long-range translational order i.e. short-range order (not totally random)
- Disordered or random arrangements of atoms
- Gradually softens over a range of temperature.
- Fast cooling rates.
- Free energy is high
- No grain boundaries
- Example: glassy solids (silicates)



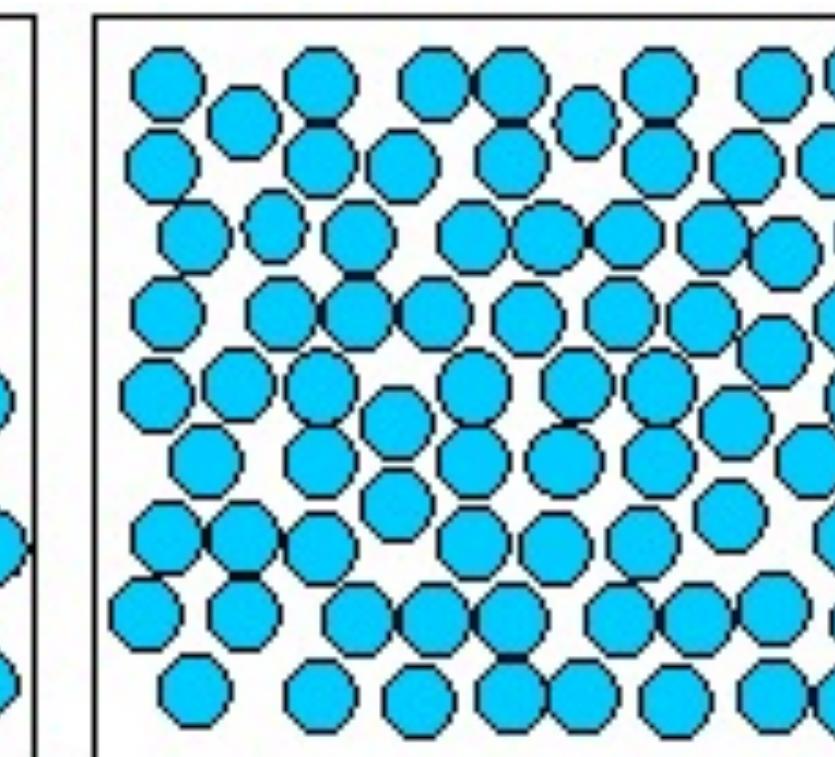
Single crystal

Periodic across the  
whole volume.



Polycrystal

Periodic across  
each grain.



Amorphous solid

Not periodic.

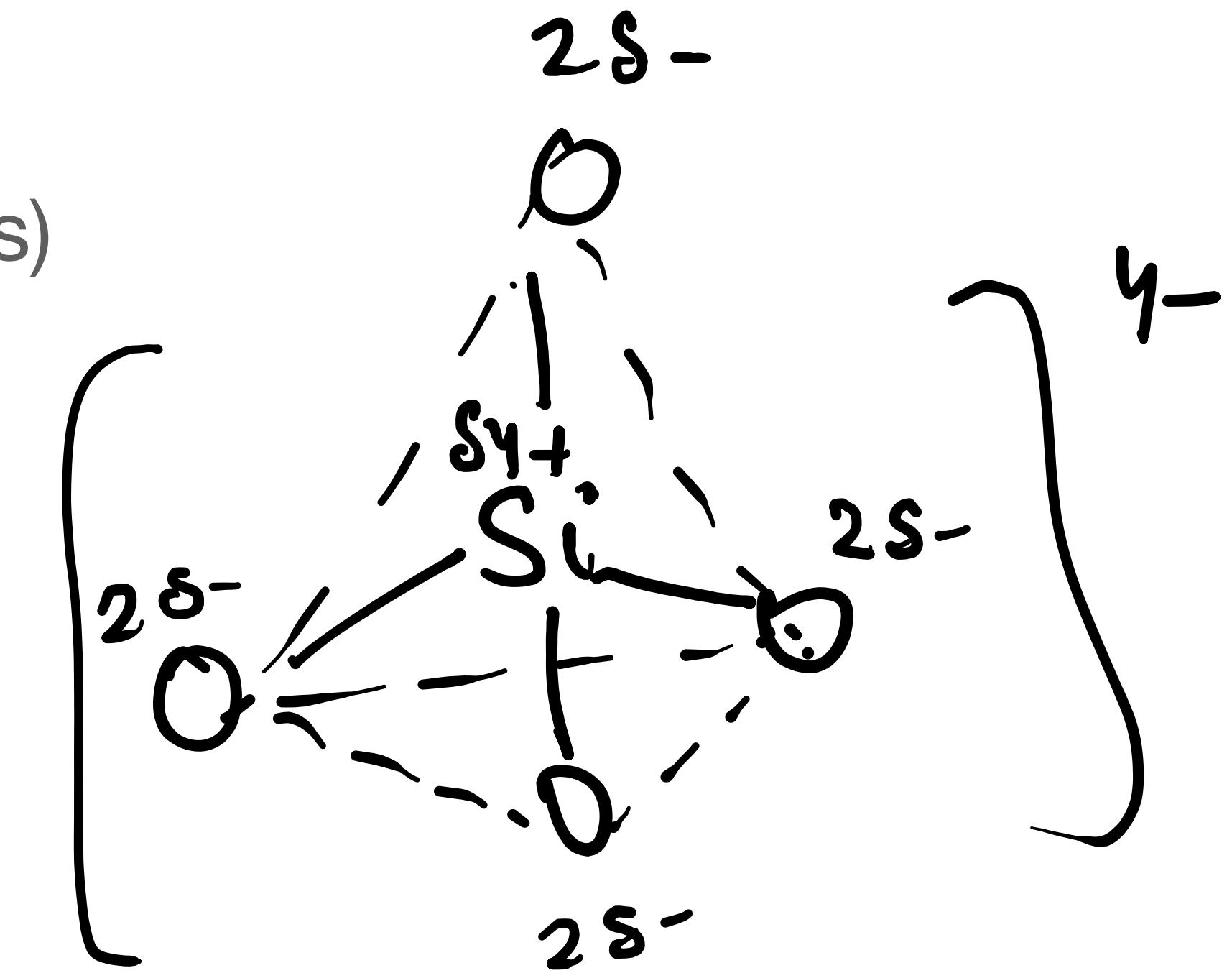
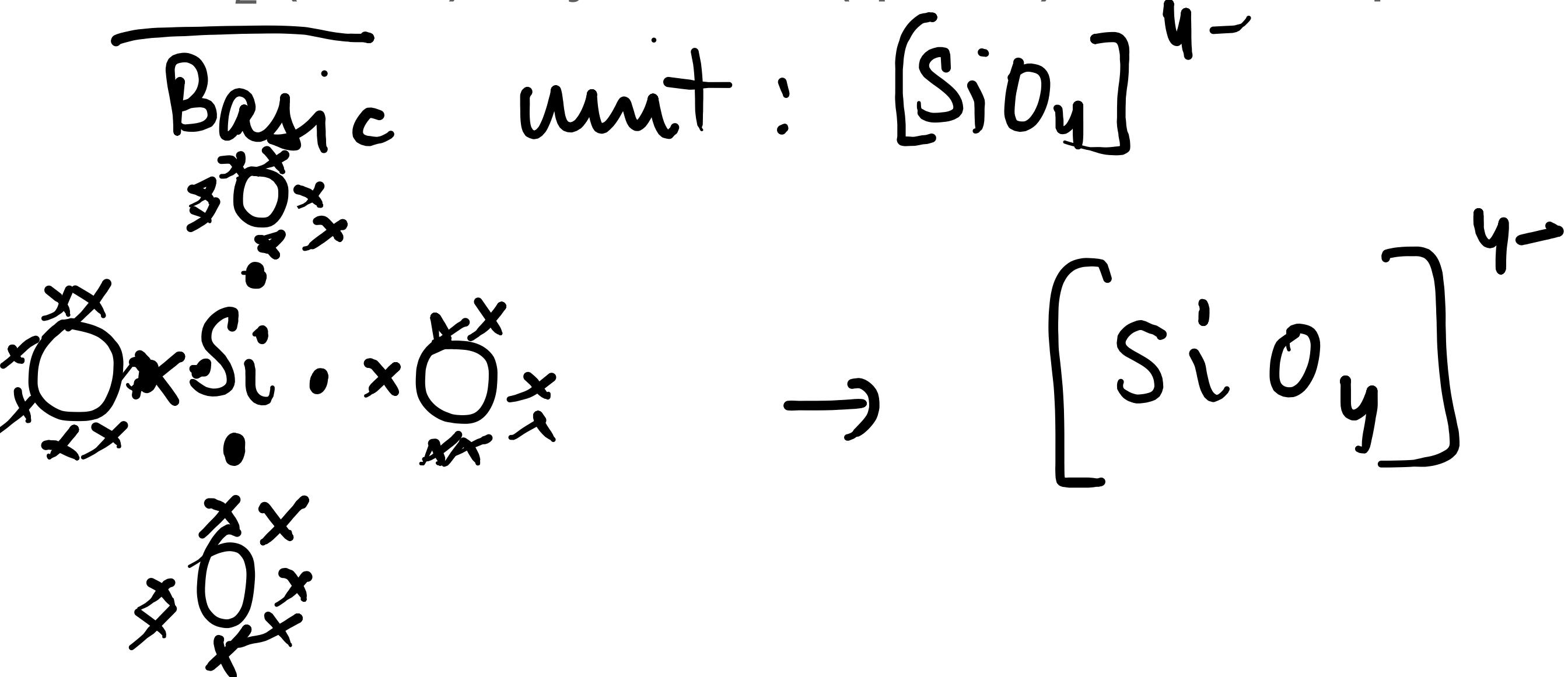
# Amorphous solids (Ceramics: glass)

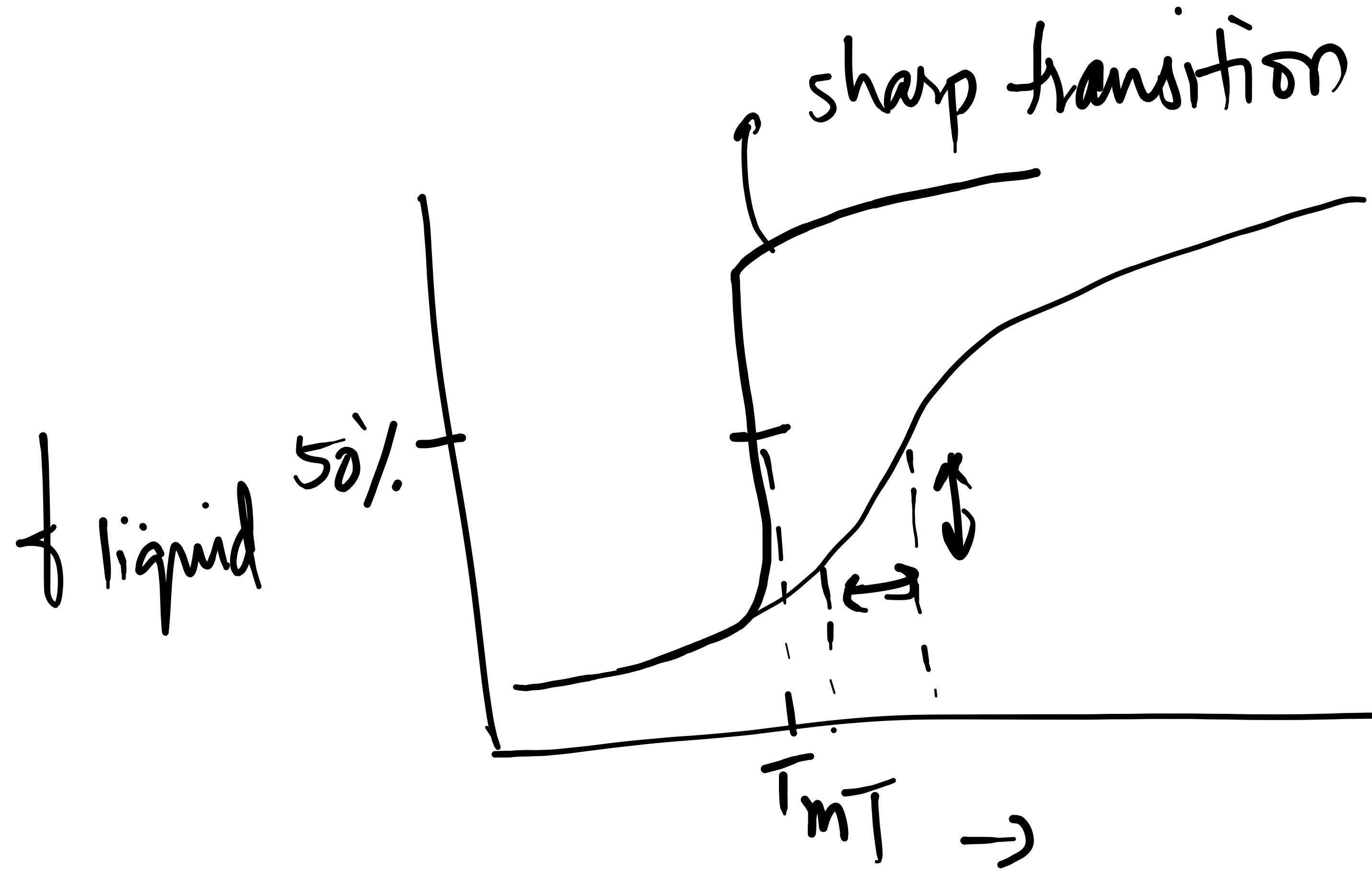
## Silicates: Glassy solids

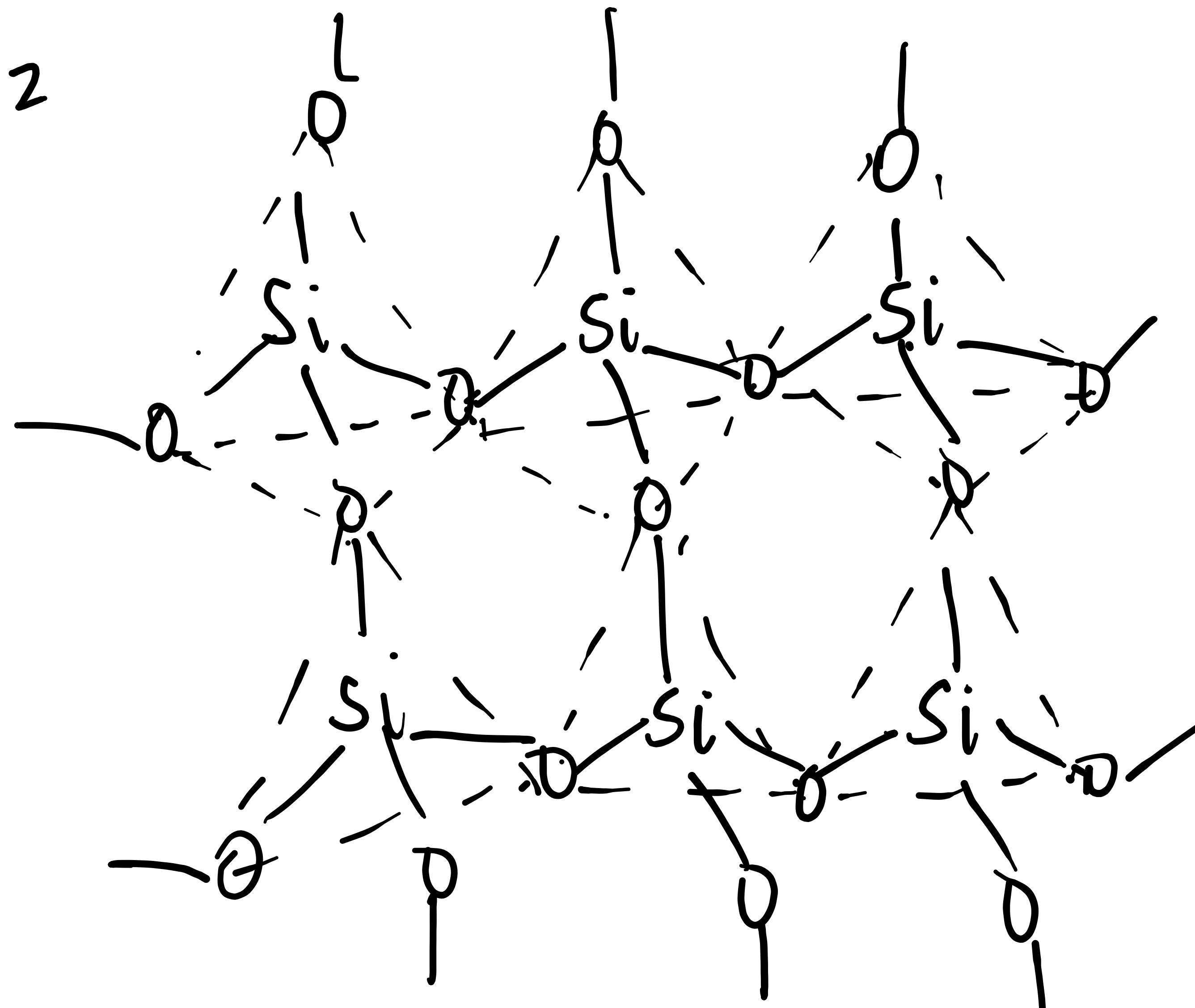
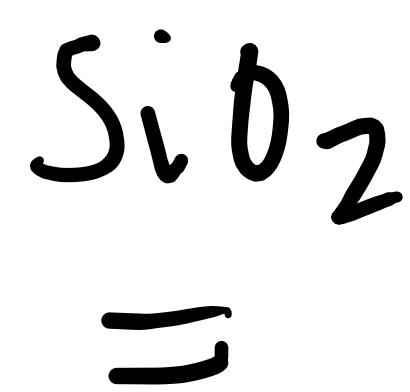
Ceramics: composed of clay minerals (i.e., porcelain), as well as cement, and glass e.g. aluminum oxide (or alumina,  $\text{Al}_2\text{O}_3$ ), silicon dioxide (or *silica*,  $\text{SiO}_2$ ), silicon carbide ( $\text{SiC}$ ), silicon nitride ( $\text{Si}_3\text{N}_4$ )

- stiff and strong
- Brittle (less ductile)
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- Low heat and electrical conductivities

$\text{SiO}_2$  (silica): crystalline (quartz) and amorphous (glass)







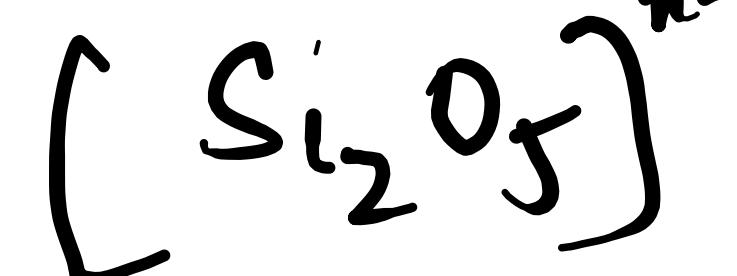
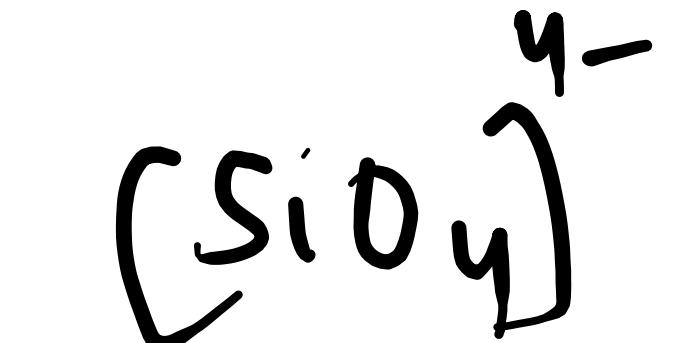
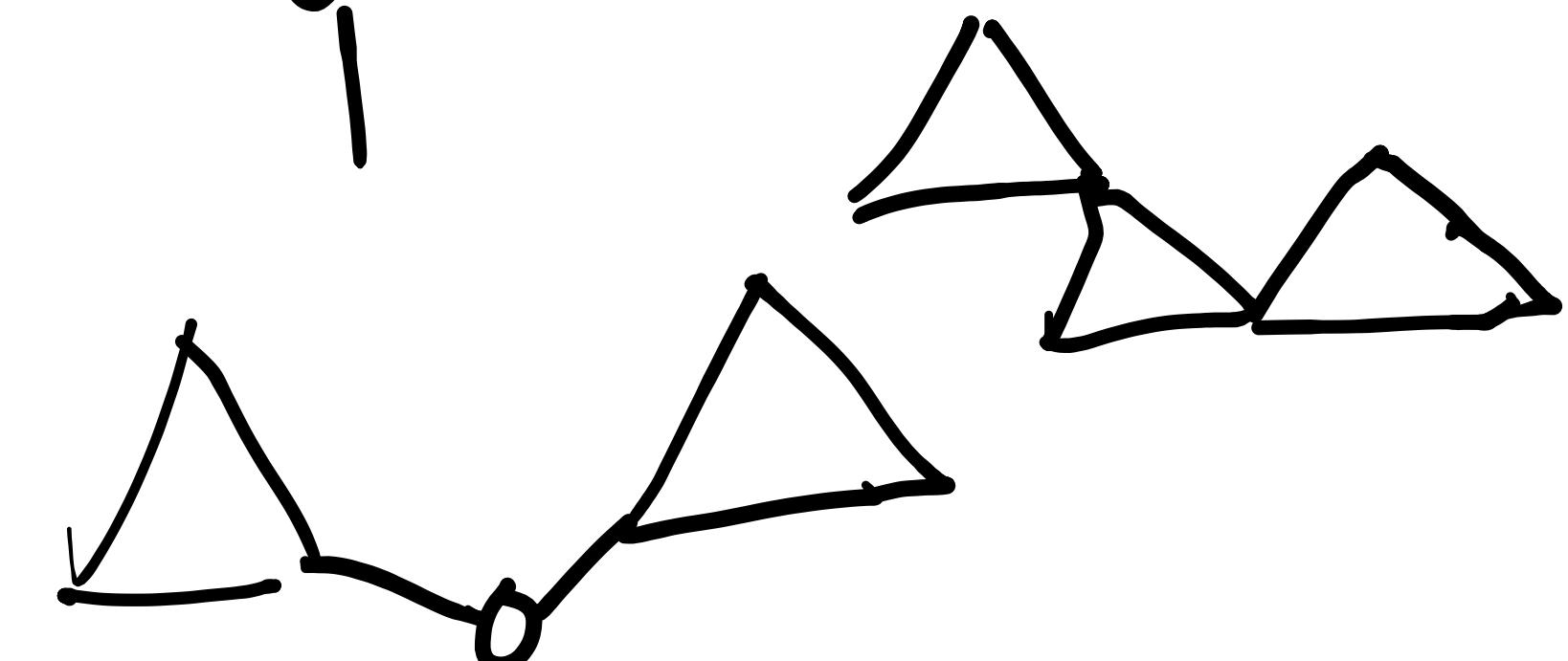
Per tetrahedron :



$$\frac{1}{2} \times 4 \text{ O} = 2 \text{ O atoms}$$

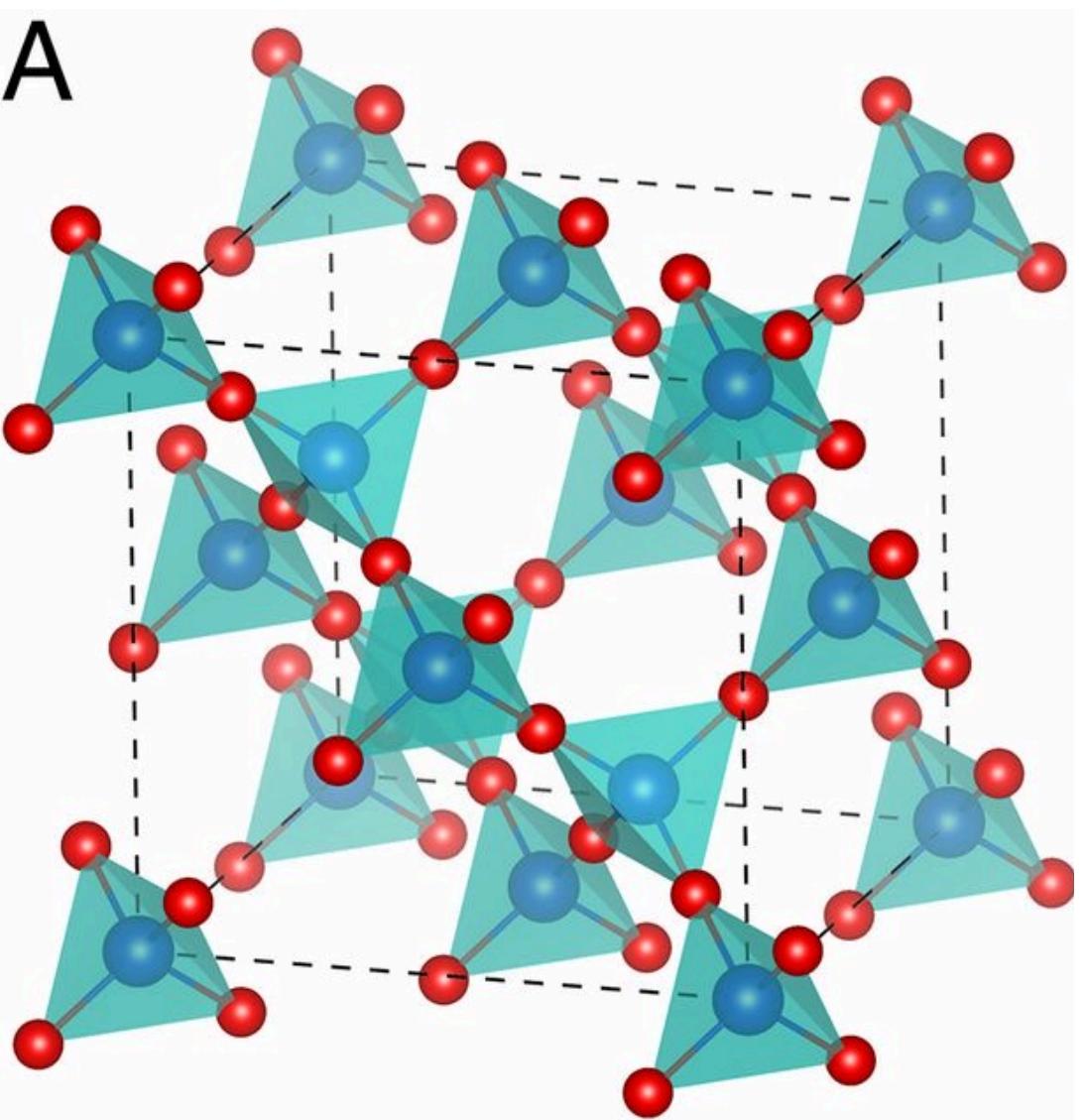
- Composition is maintained

- Charge neutrality.



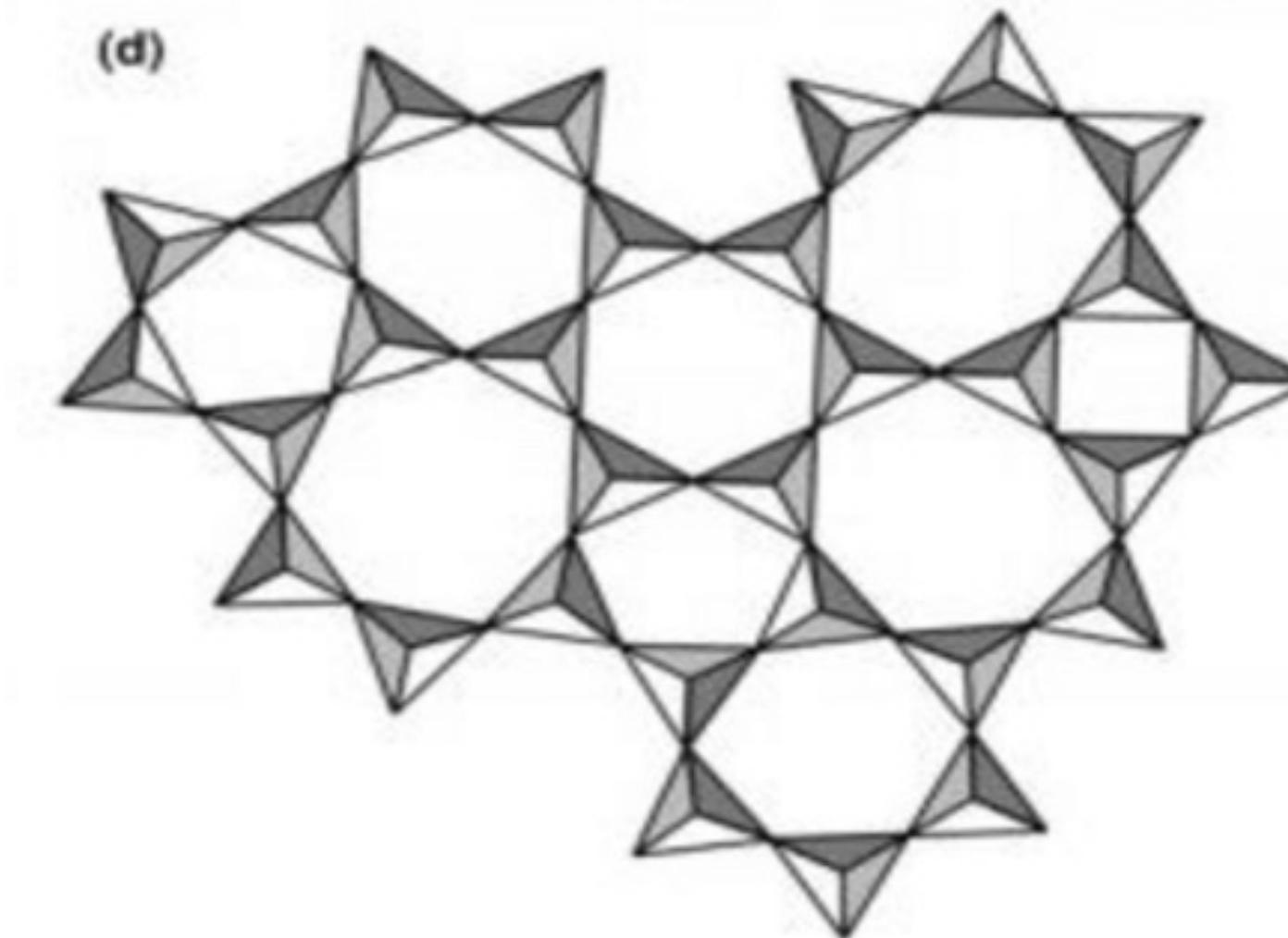
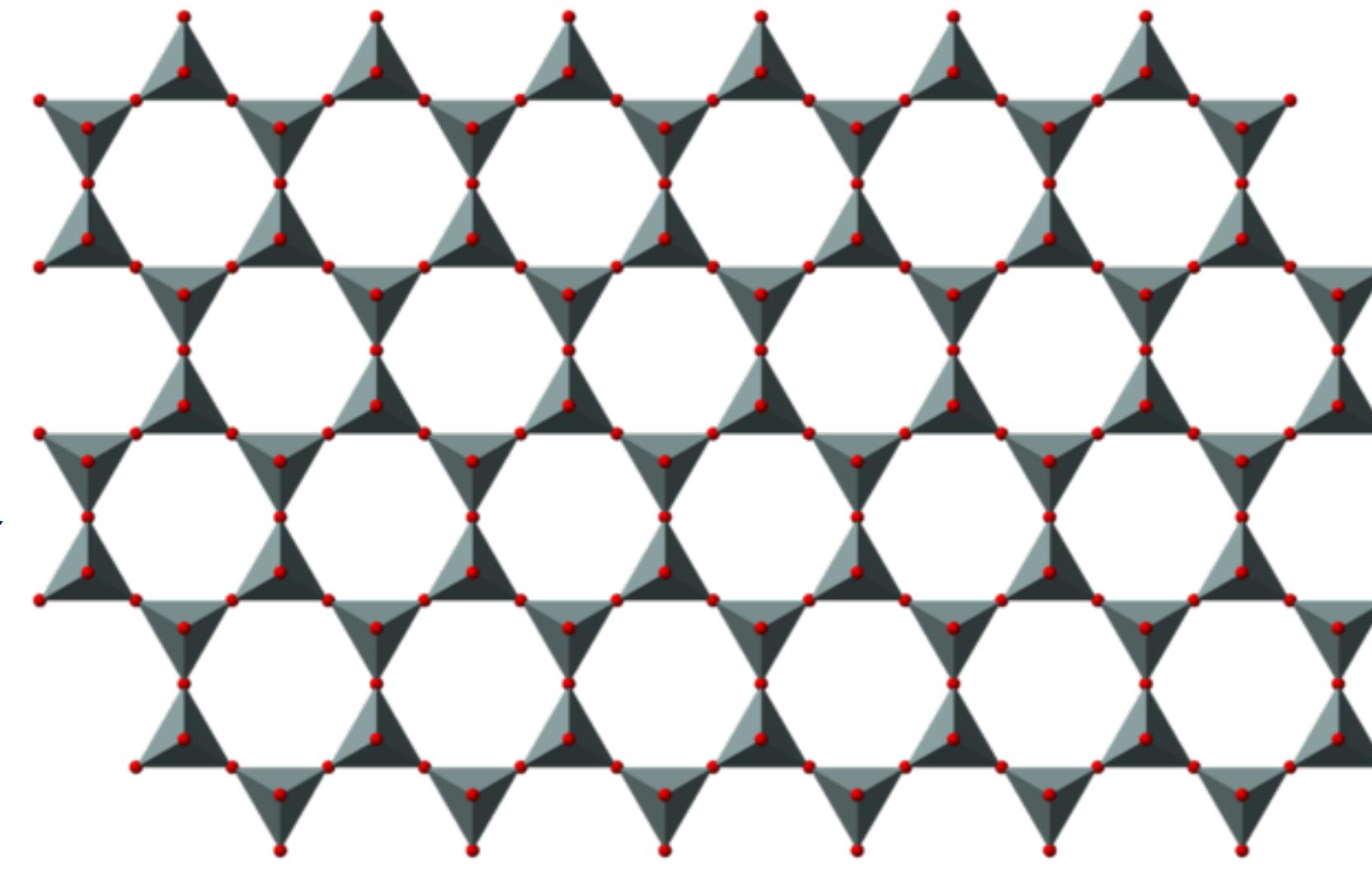
# Three-dimensional network of silicate

*Tetrahedra can rotate*



Crystalline  
Slow cooling

Amorphous  
Fast cooling



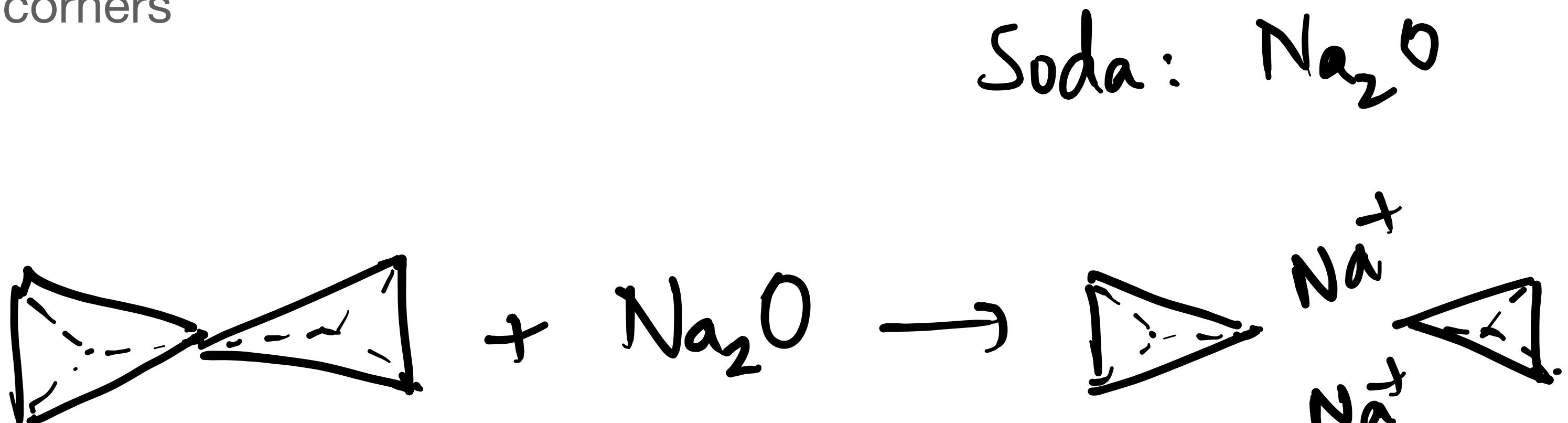
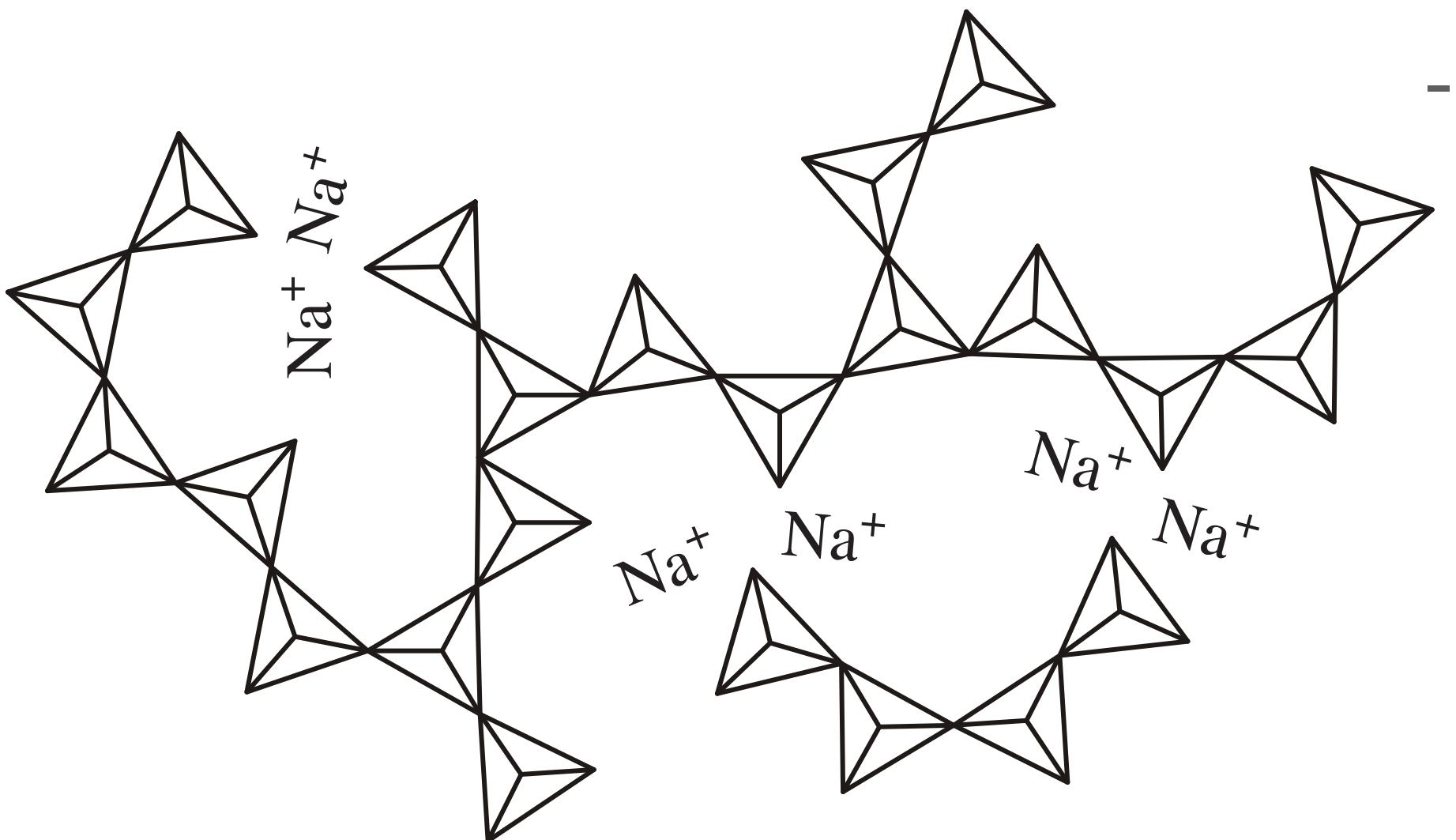
Glass without any additives  
is called FUSED GLASS

# Another non-crystalline silicate: soda lime glass

Sodium oxide and calcium oxide are added

lime :  $\text{CaO}$

- The alkali cations break up the network of the silicate tetrahedra
- For each  $\text{Na}_2\text{O}$  introduced, one Si–O bridge is disrupted and the extra oxygen atom from  $\text{Na}_2\text{O}$  splits up one common corner into separate corners

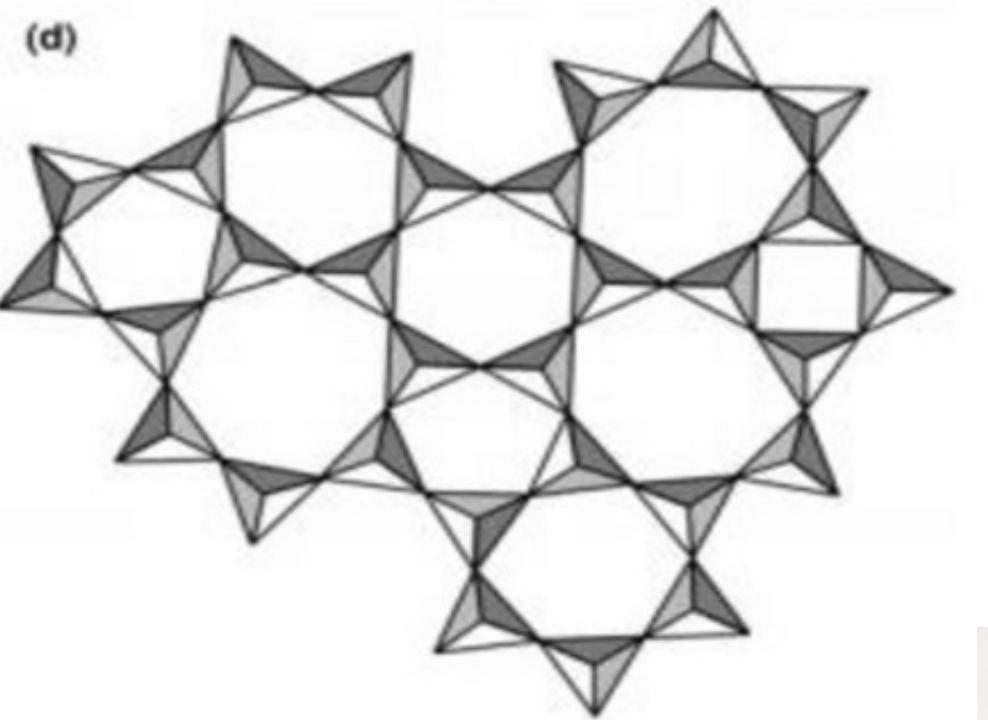


Soda lime glass is used in daily applications.

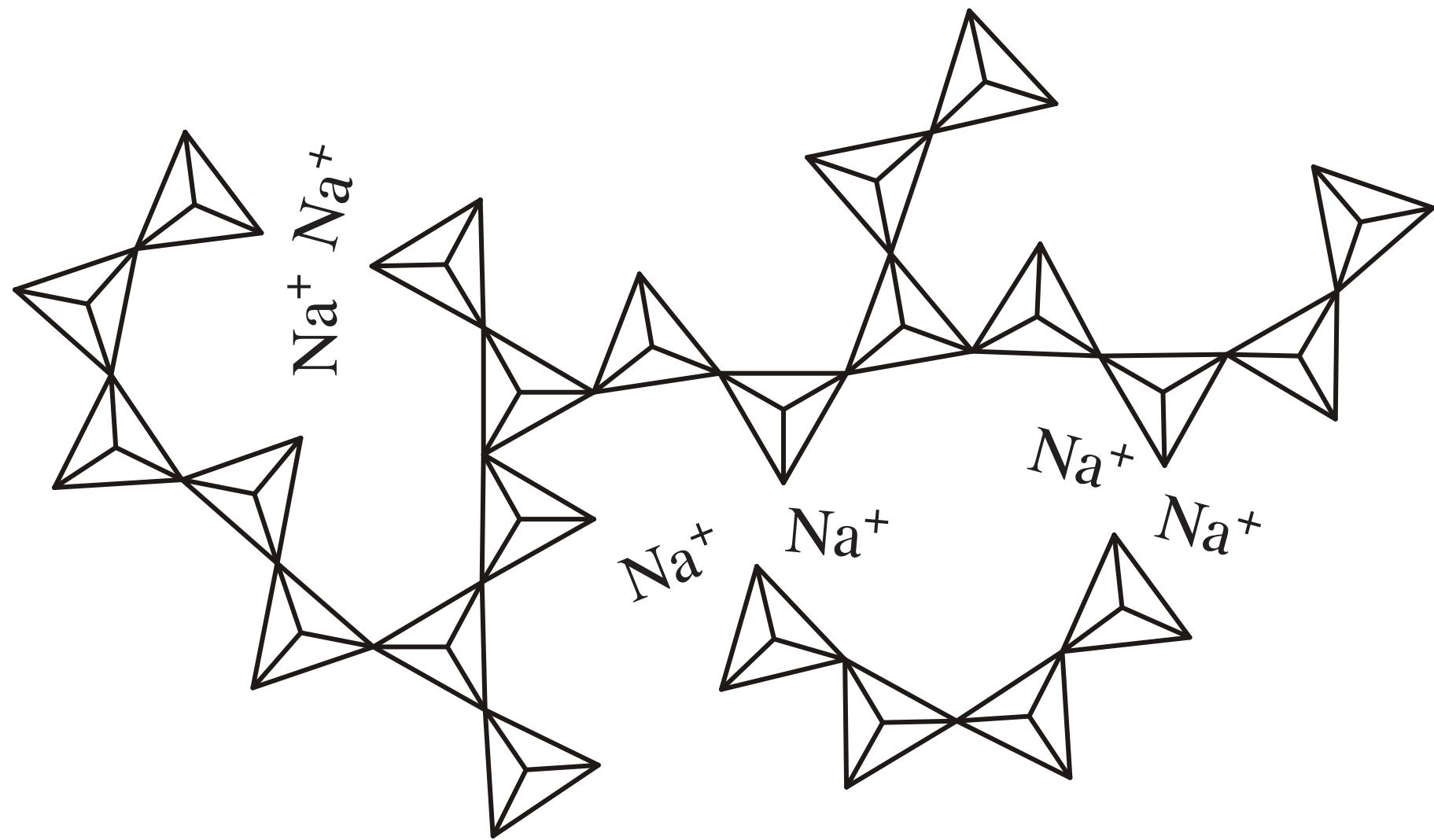


Highly viscous

$10^4$  to  $10^6$  Ns/m<sup>2</sup>



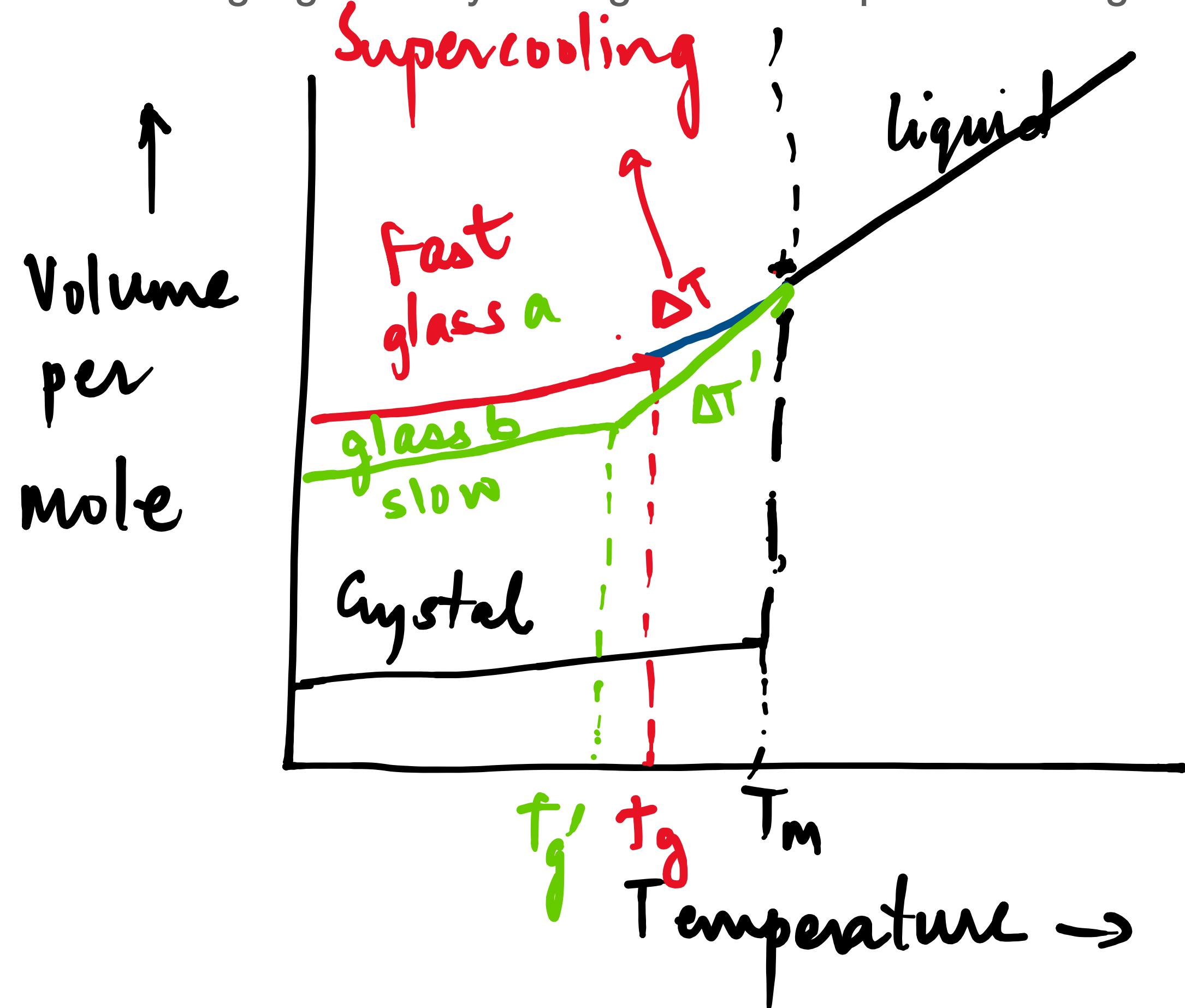
Cut the spaghetti  
into smaller  
pieces!



Less viscous and other properties change

# How is glass formed?

Glasses are disordered materials that lack the periodicity of crystals but behave mechanically like solids. The most common way of making a glass is by cooling a viscous liquid fast enough to avoid crystallization called Supercooling.



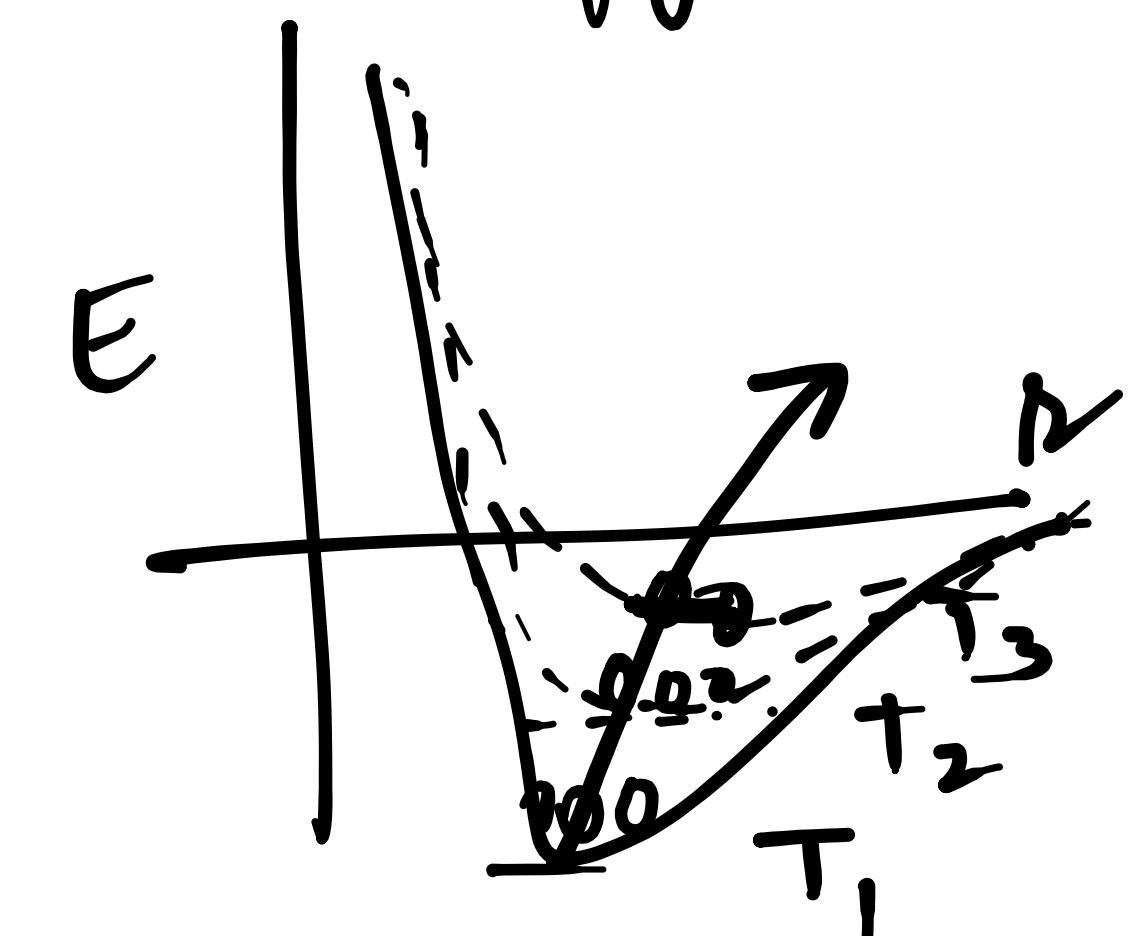
Melting : first order phase transition

Slope =  $\left( \frac{\partial \ln V}{\partial T} \right)_P = \alpha$

"Thermal expansion coefficient"

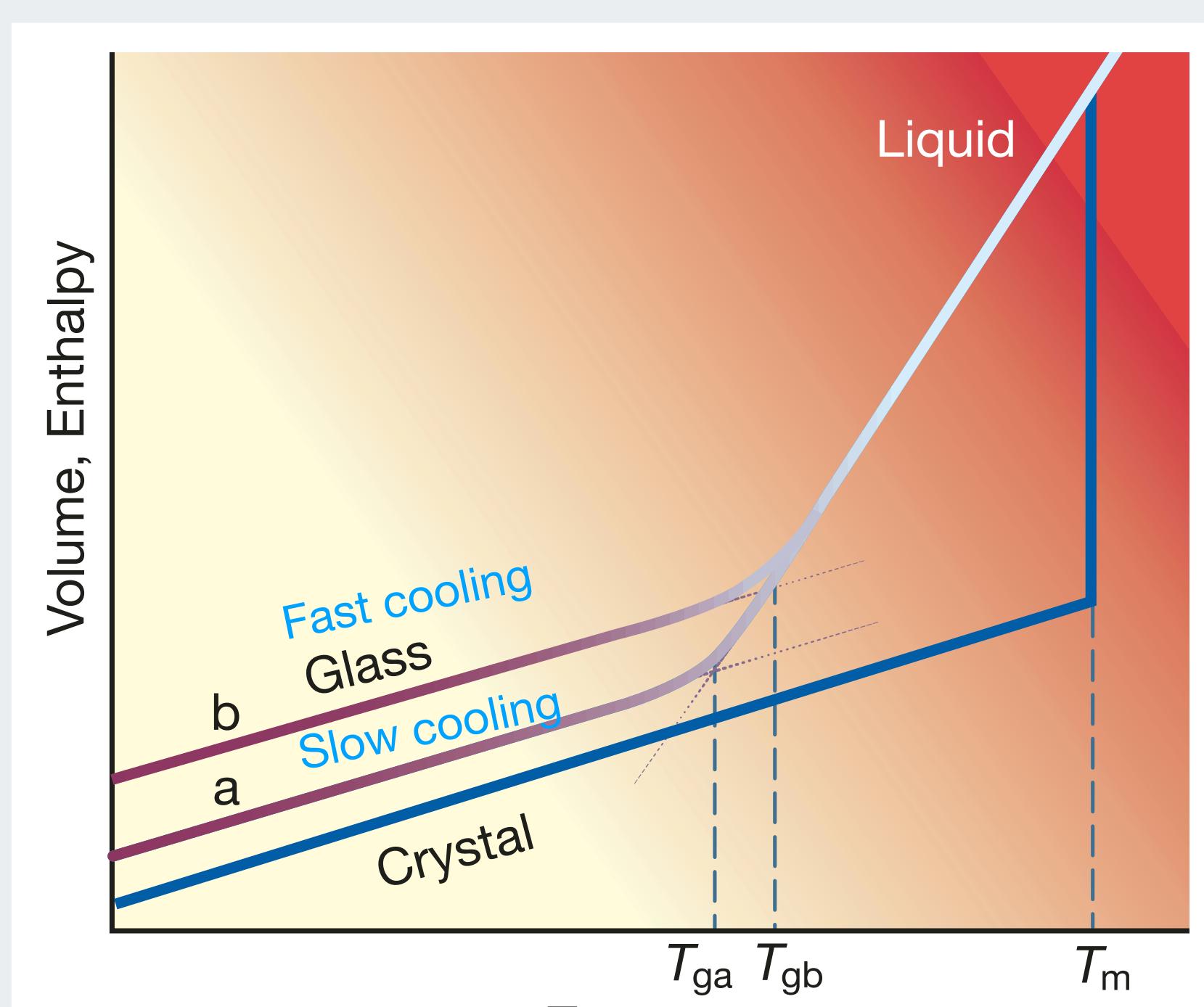
Glass transition

$T_g$  : Glass transition temps.



# The glass transition

**Figure 1** Temperature dependence of a liquid's volume  $v$  or enthalpy  $h$  at constant pressure.  $T_m$  is the melting temperature. A slow cooling rate produces a glass transition at  $T_{ga}$ ; a faster cooling rate leads to a glass transition at  $T_{gb}$ . The thermal expansion coefficient  $\alpha_p = (\partial \ln v / \partial T)_p$  and the isobaric heat capacity  $c_p = (\partial h / \partial T)_p$  change abruptly but continuously at  $T_g$ .



Upon cooling below the freezing point  $T_m$ , molecular motion slows down. If the liquid is cooled sufficiently fast, crystallization can be avoided. Eventually molecules will rearrange so slowly that they cannot adequately sample configurations in the available time allowed by the cooling rate. The liquid's structure therefore appears 'frozen' on the laboratory timescale (for example, minutes). This falling out of equilibrium occurs across a narrow transformation range where the characteristic molecular relaxation time becomes of the order of 100 seconds, and the rate of change of volume or enthalpy with respect to temperature decreases abruptly (but continuously) to a value comparable to that of a crystalline solid. The resulting material is a glass.

The glass transition point,  $T_g$ , (temperature at which a supercooled liquid becomes a glass) is for glasses what the melting point,  $T_m$ , is for crystalline solids.

# Musical chairs= glass formation

People: silicates, chairs: lattice points

1. Speed around chairs (MOBILITY): high mobility, finding lattice sites is easier → crystal. If high viscosity, slow to find lattice sites (getting stuck) → glass
2. Arrangement of chairs (LATTICE COMPLEXITY): higher complexity → glass
3. How fast the music stops (COOLING RATE): sudden stop or fast cooling → glass



MakeAGIF.com

# Rate of supercooling for nucleation

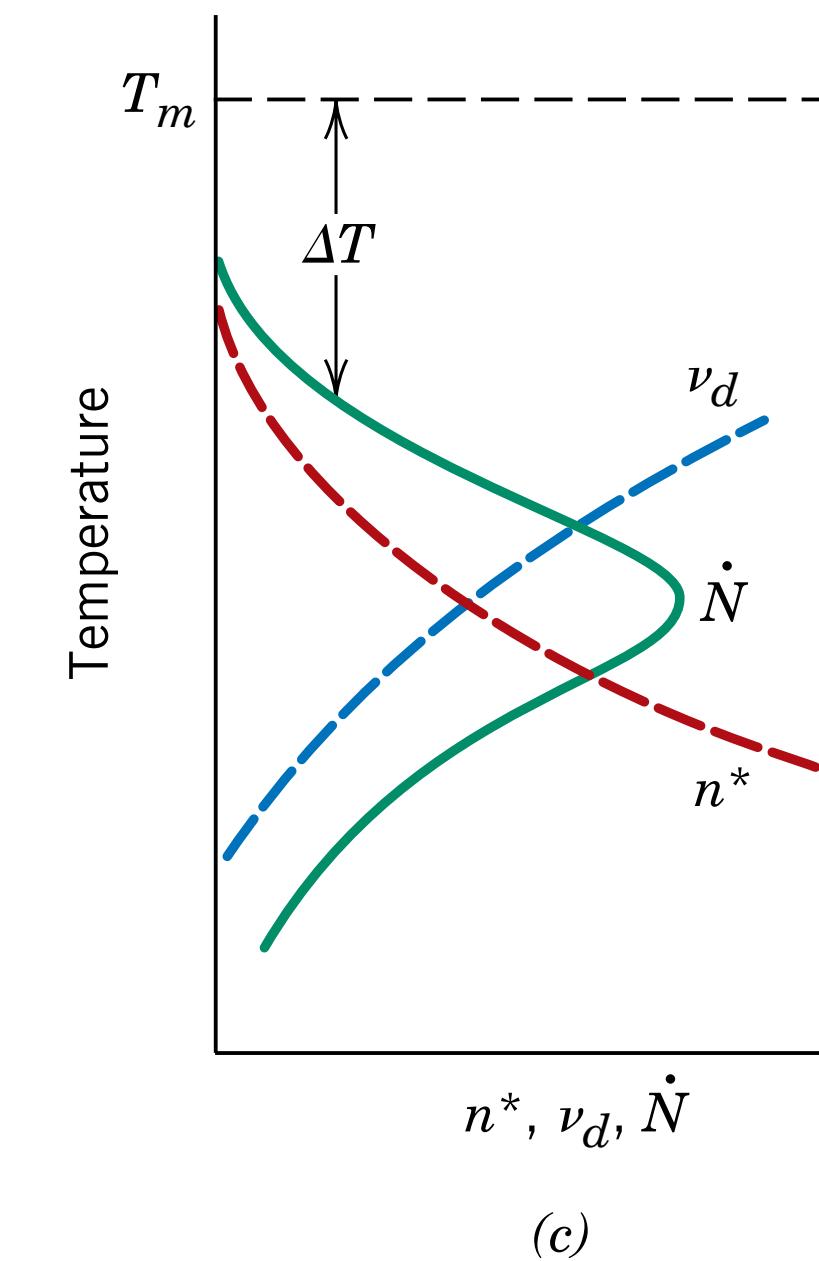
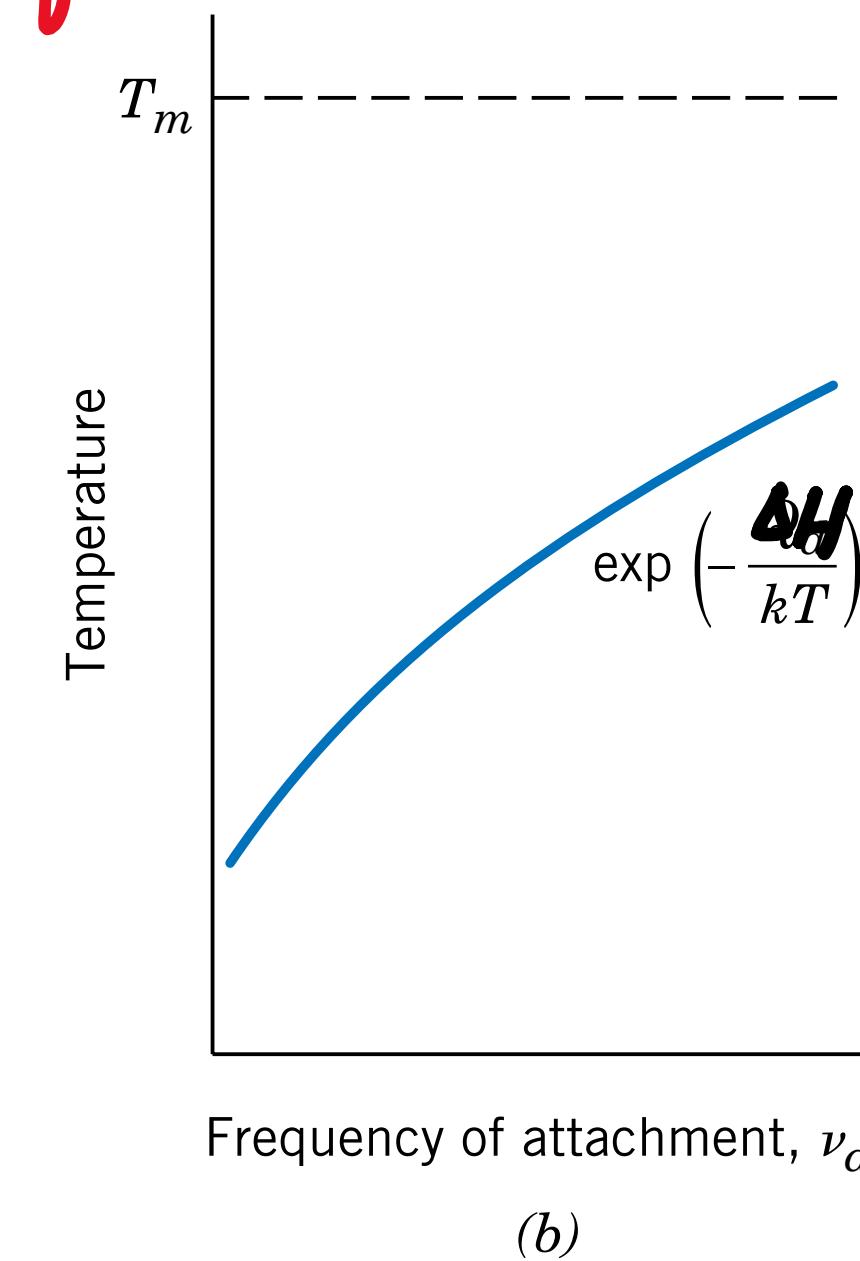
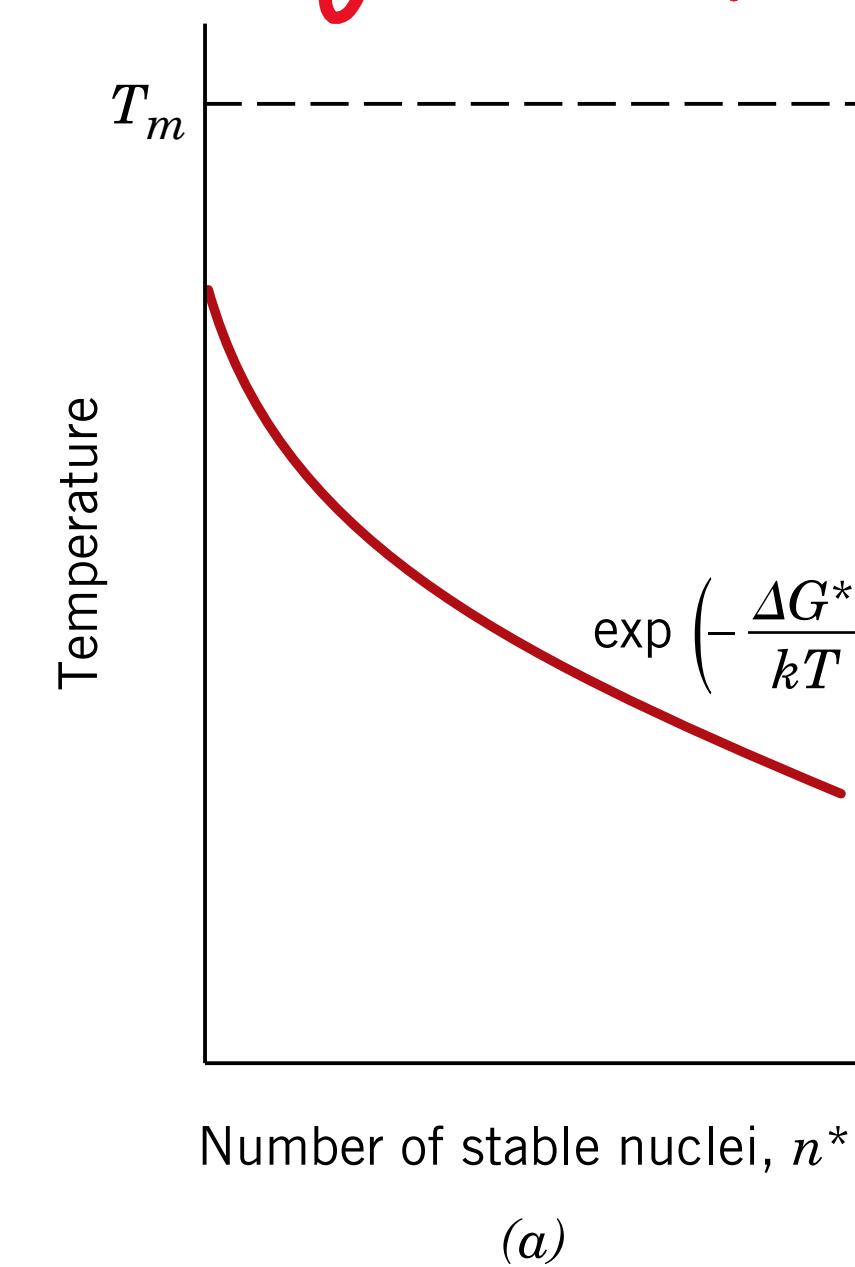
$$\text{Rate of Nucleation, } I = \frac{dN}{dt} \Rightarrow I = N_t \exp\left(-\frac{\Delta G^*}{k_B T}\right) s^{-1} \sim \exp\left(-\frac{\Delta H_d}{k_B T}\right)$$

$N_t$  = no. of particles per unit vol.

$\nu$  = lattice vibration frequency

$\Delta H_d$  = activation barrier to jump into nucleus

$\Delta G^*$  = free energy to form critical nucleus



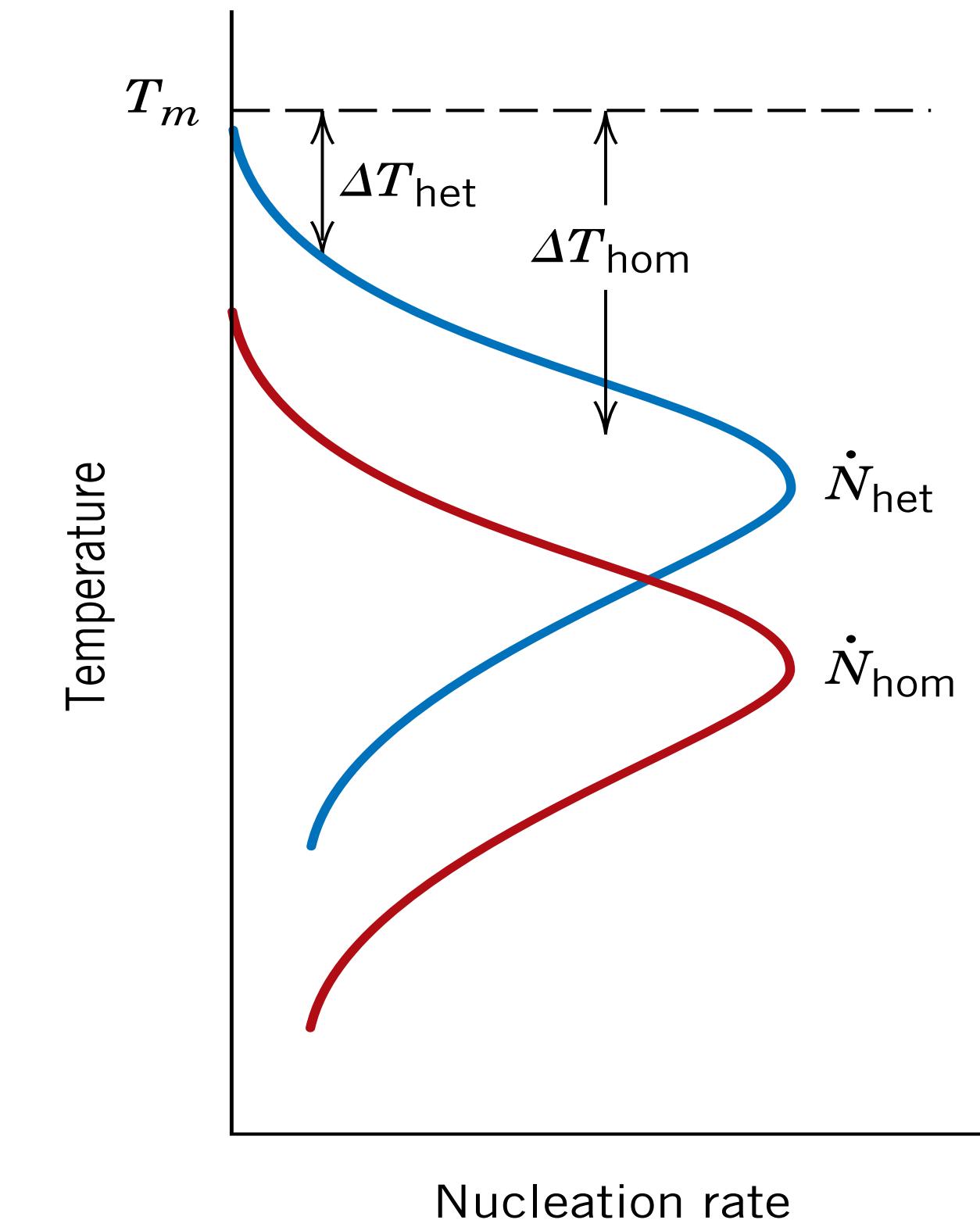
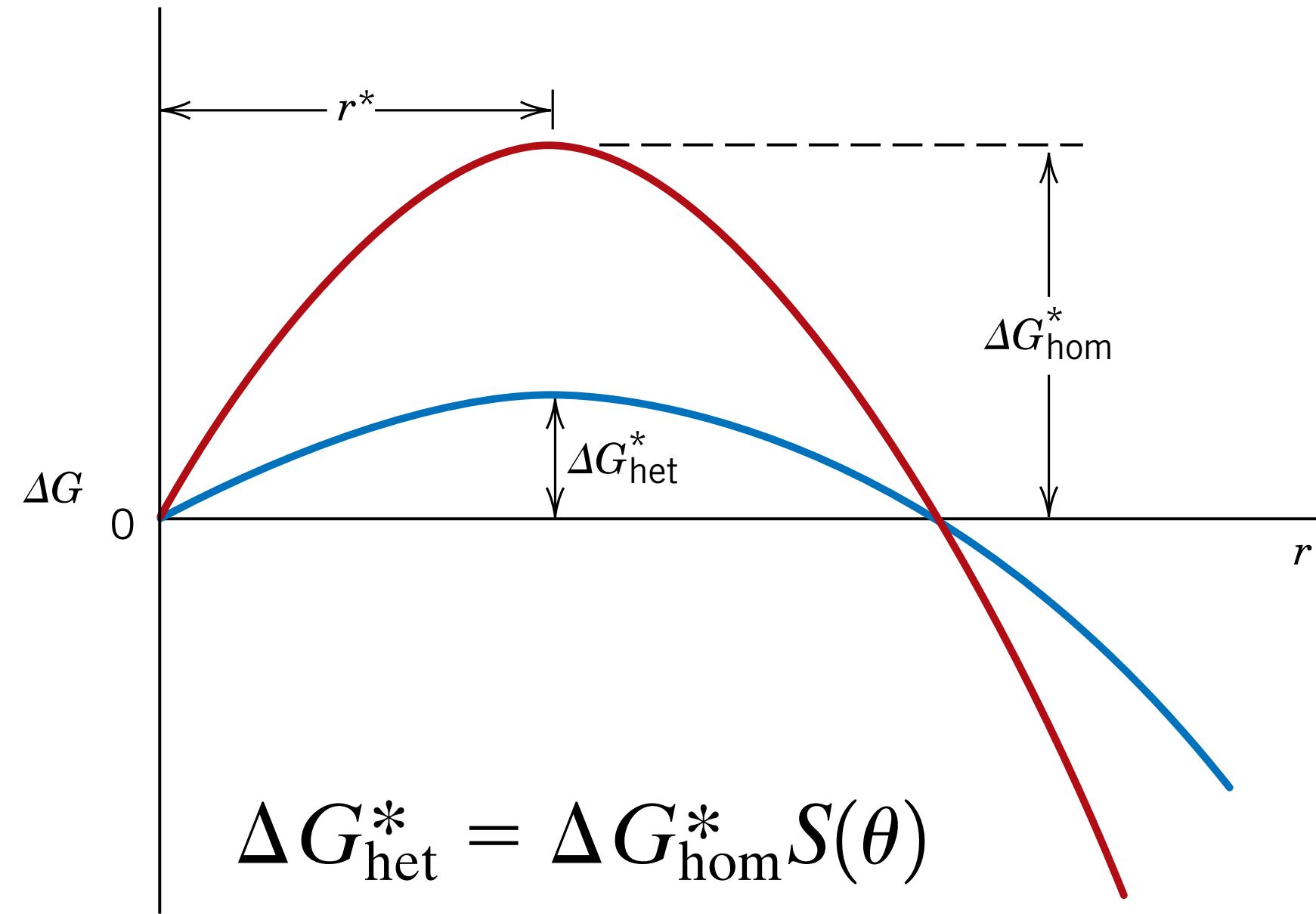
No. of critical sized particles

$\downarrow$   
 $n^*$

frequency with which they become supercritical

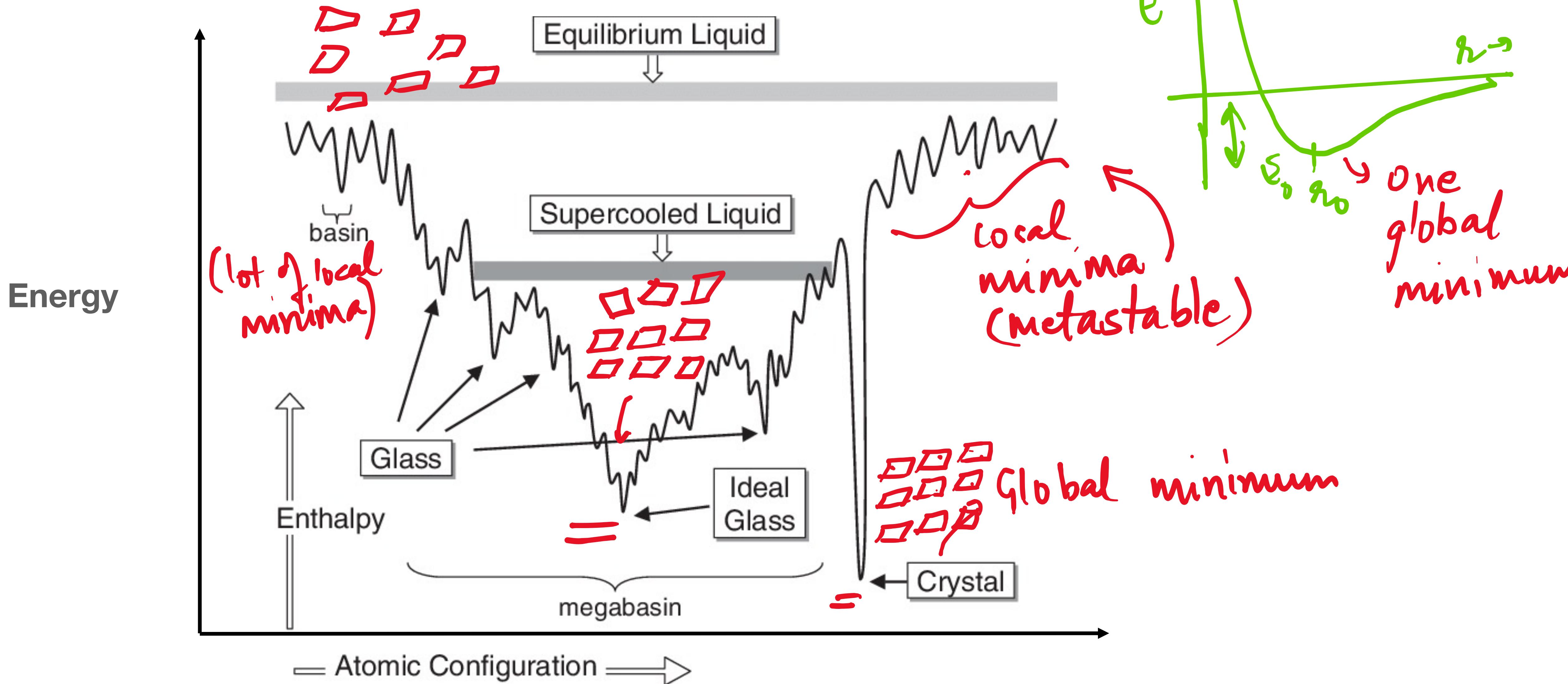
$\downarrow$   
 $\nu_d$

# Smaller rate of supercooling for heterogeneous nucleation



Heterogeneous nucleation occurs more readily due to lower free energy to form critical nucleus

# Energy landscape of glasses

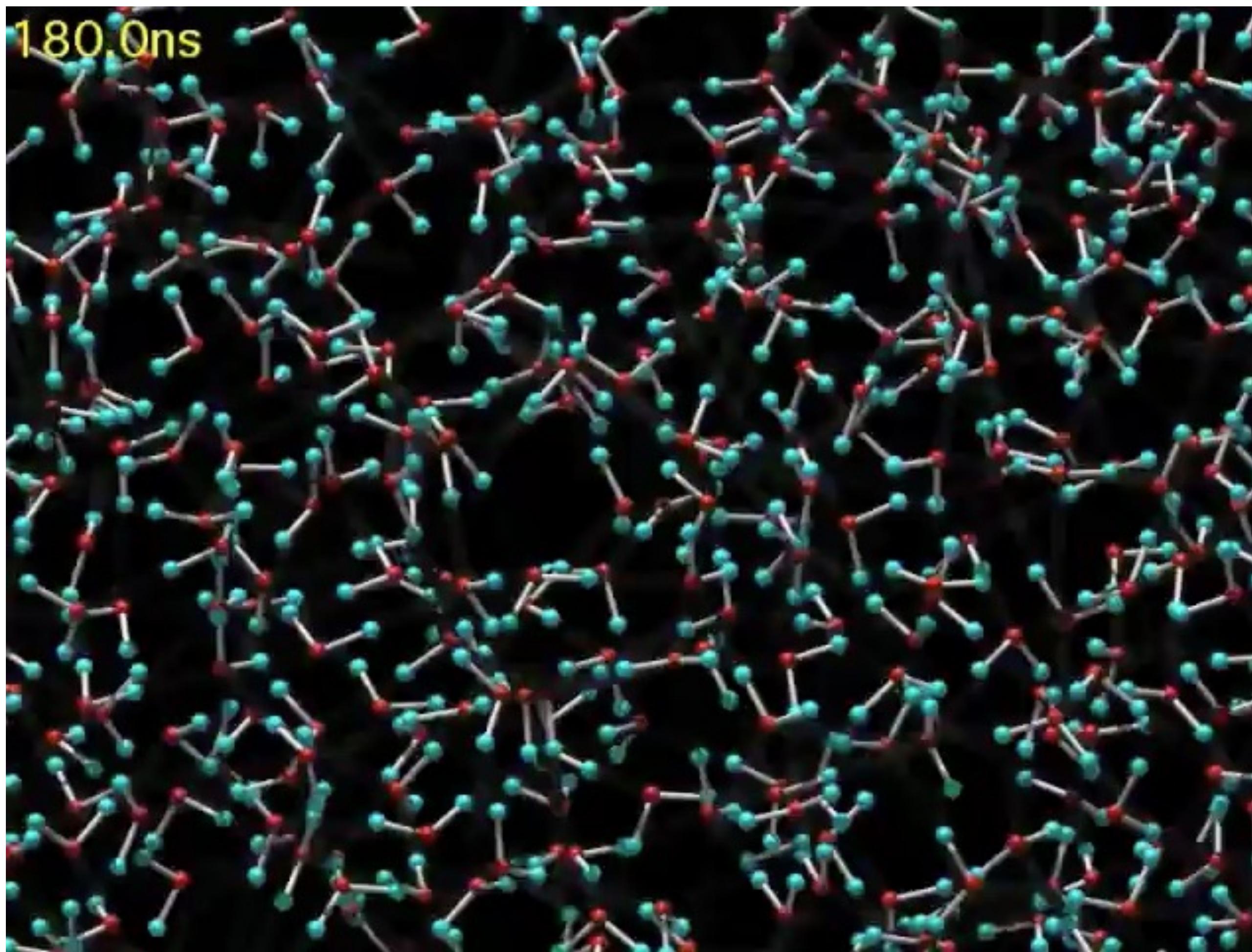


# A video on supercooled water

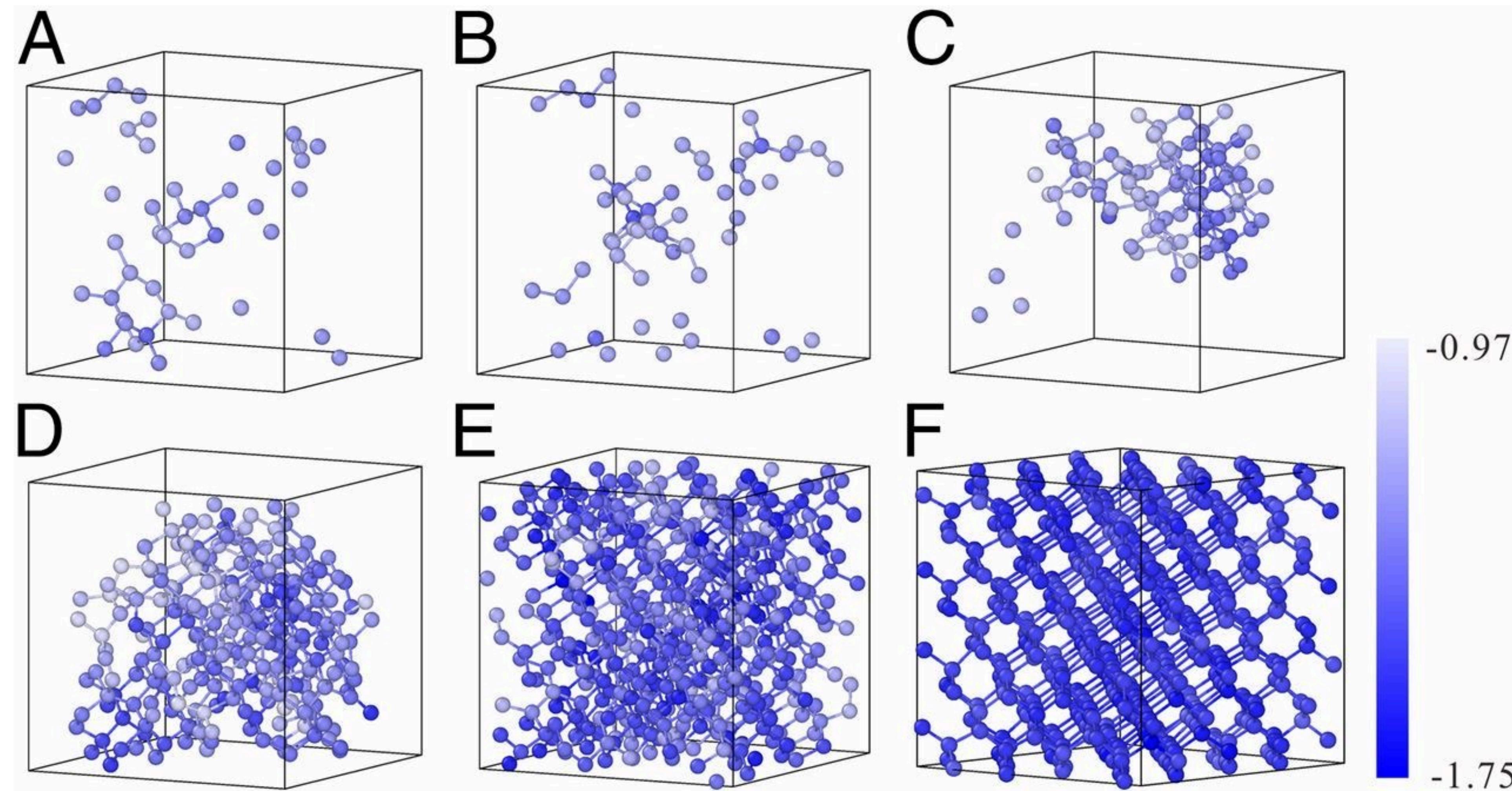
You can try this experiment at home...



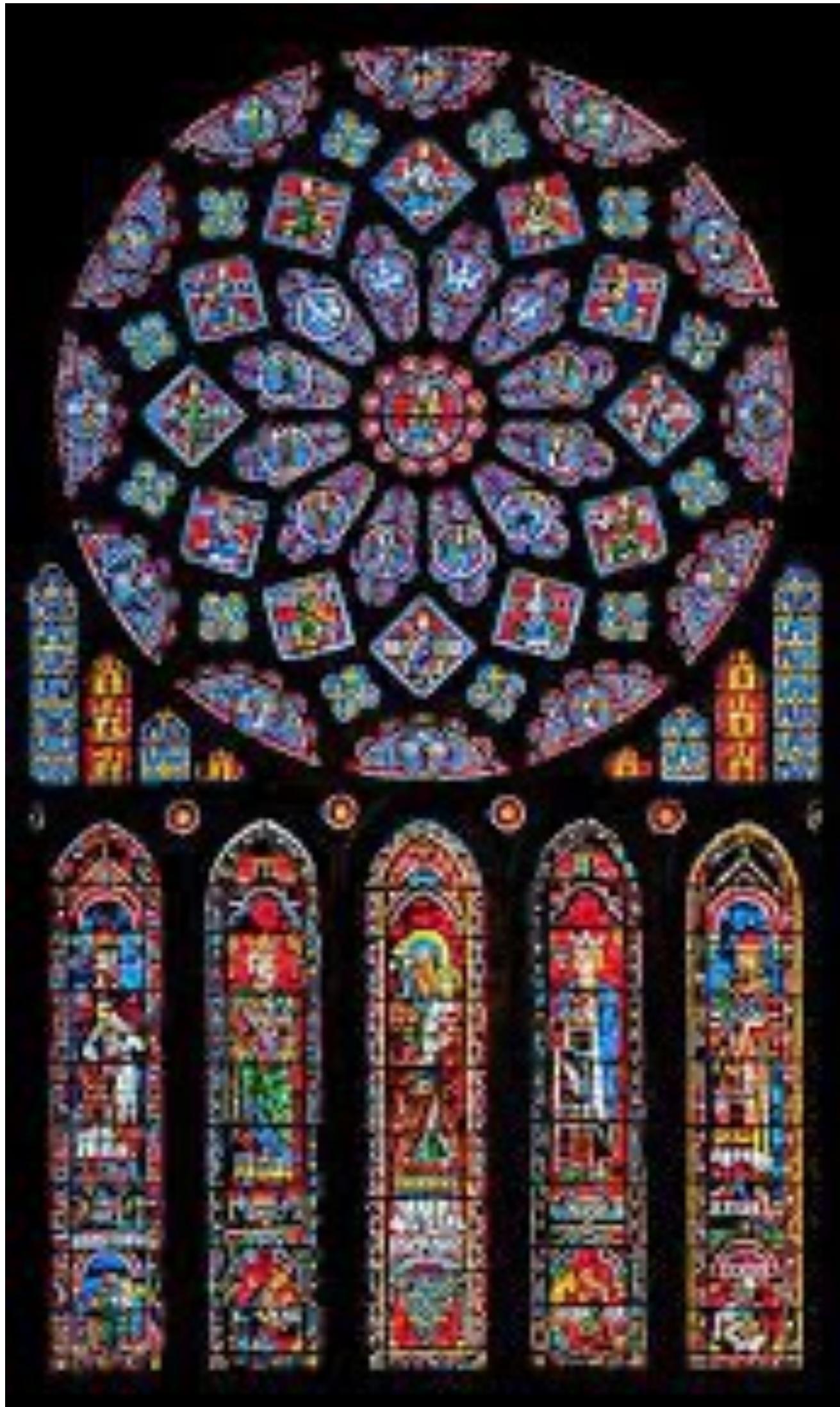
# Molecular dynamics simulation of water crystallizing into ice



# Molecular dynamics simulations of crystallization of silicate



# Are medieval windows melting?



*Glass does not flow*



# Lecture 25

## Materials and their structure- Polymers

### Textbooks:

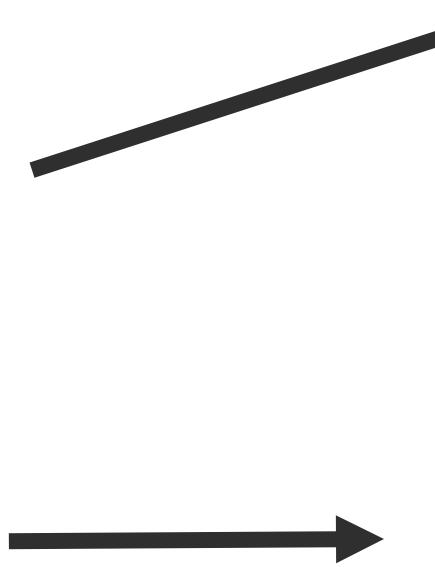
- Introduction to materials science and Engineering: V. Raghavan
- Materials Science and Engineering: Callister and Rethwisch

Prof. Divya Nayar  
Department of Materials Science and Engineering  
[divyanayar@mse.iitd.ac.in](mailto:divyanayar@mse.iitd.ac.in)

# Recap...

1. Non-crystalline solids: amorphous solids (glass)
2. Structure of Silicates
3. Supercooling: glass formation
4. Energy landscape of glasses

# Metals are usually considered more important than wood.. Is that a correct convention?



More robust in ice than  
steel ships

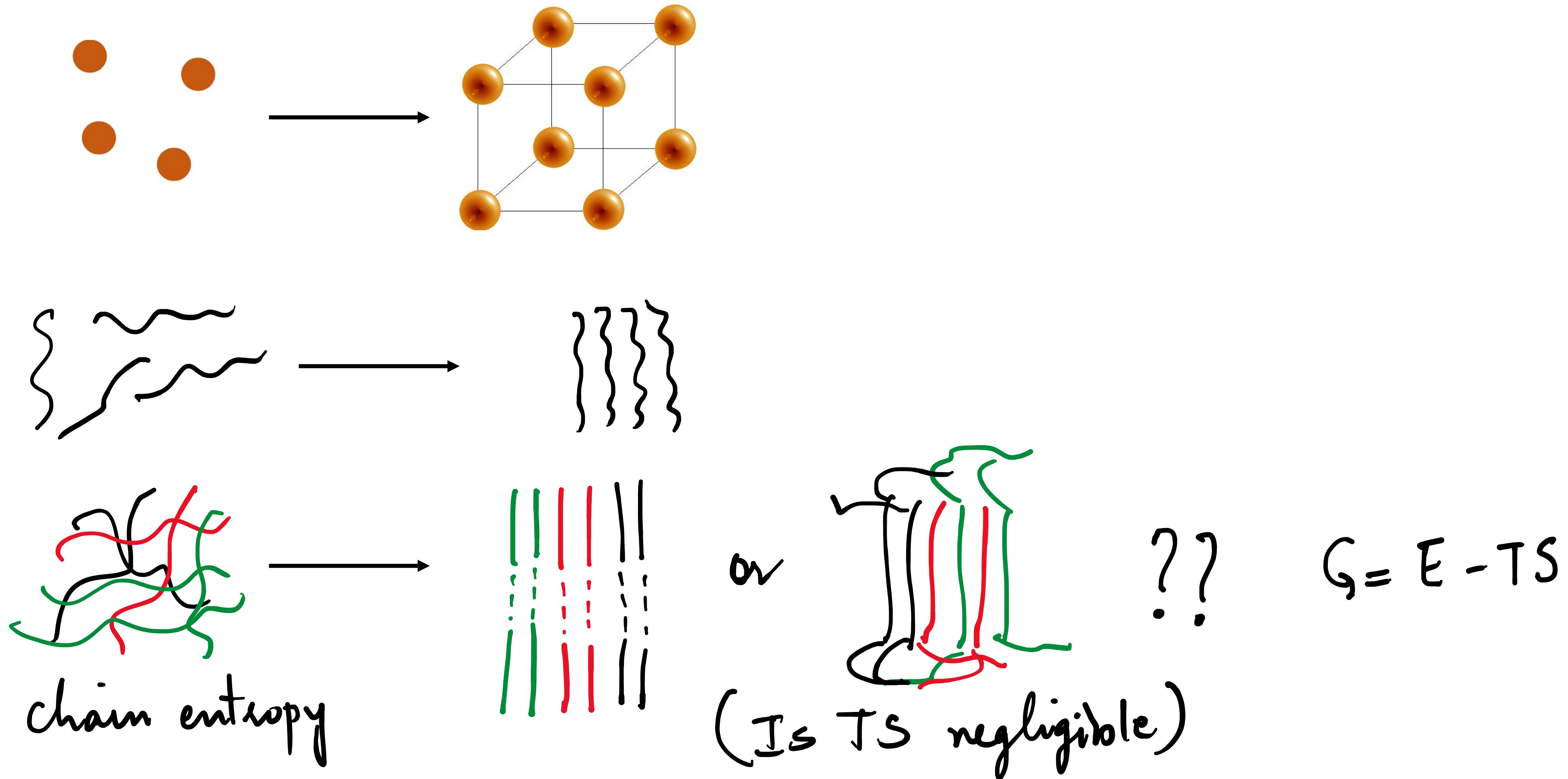
Composed of cellulose: polymer of glucose= SUGAR!

- Strong
- Not brittle



Crystalline sugar is brittle!

# What distinguishes polymers from small molecules and oligomers?

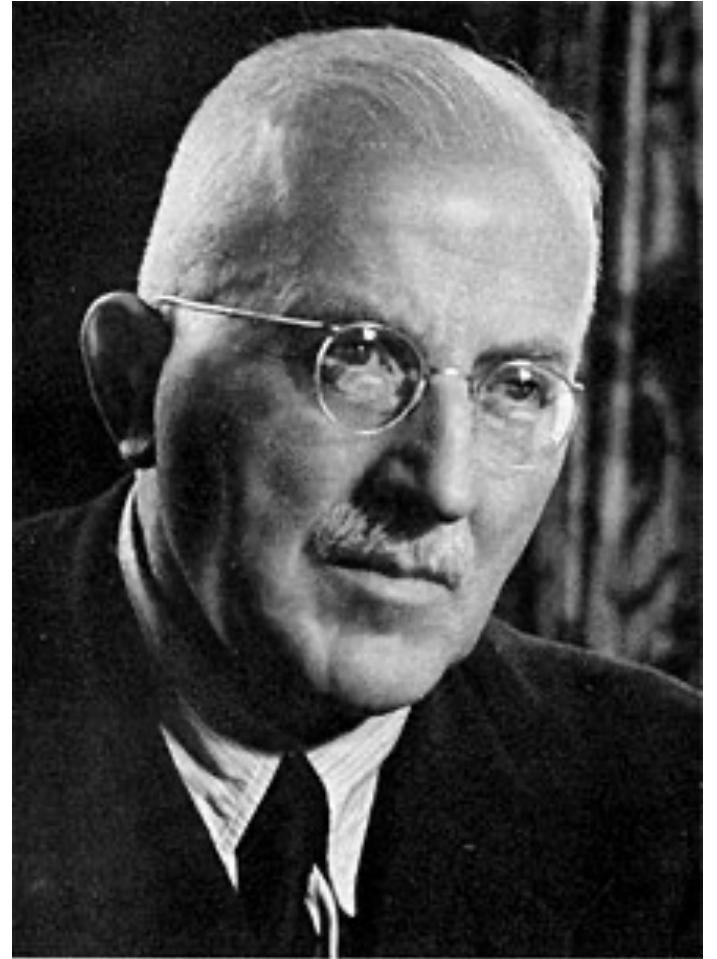


# Poly+mer

- Substances composed of molecules of relatively high mass with repeating units. Long chain molecules containing thousand to million atoms
- **BIG** molecules
- How BIG?
- No. of repeating units: 10+ to  $10^6$
- Molecular weight: molecular mass  $\times (6.023 \times 10^{23})$
- Polymers are mixtures: average values are used

# Hermann Staudinger

## Macromolecular Hypothesis



A polymer model

1920:

- Elementary units of polymers called *monomers*
- Colloidal properties of polymers: sizes of macromolecules

1953 Nobel Prize in Chemistry

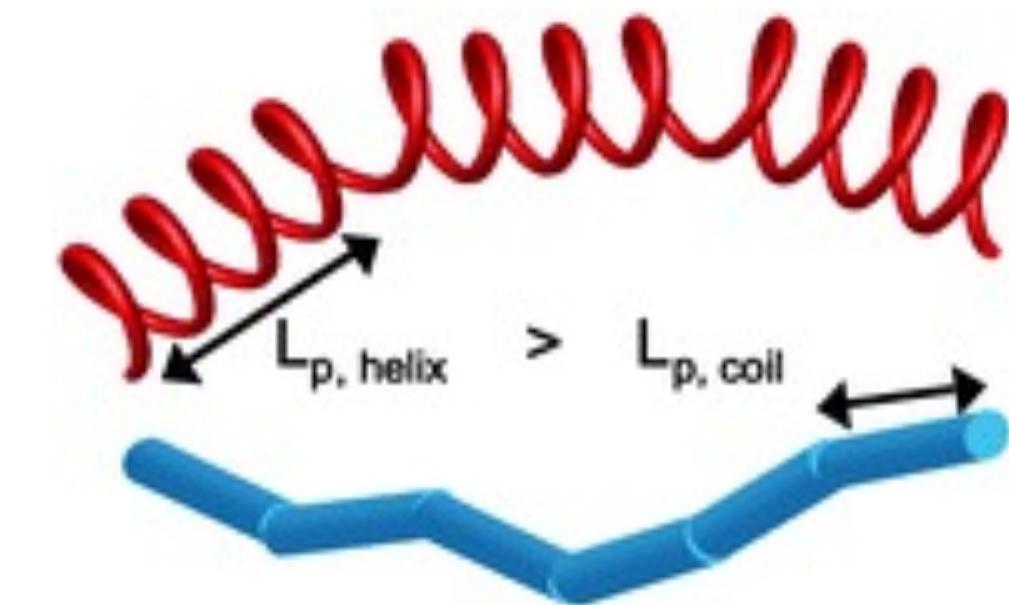
# Hans Kuhn

## Macromolecular sizes



- Decoiling of a random coiled chain molecule in a flowing viscous solvent.

- 1943: Polymer molecules were described as chains of statistical chain elements.



# Paul Flory

## Polymers in solution

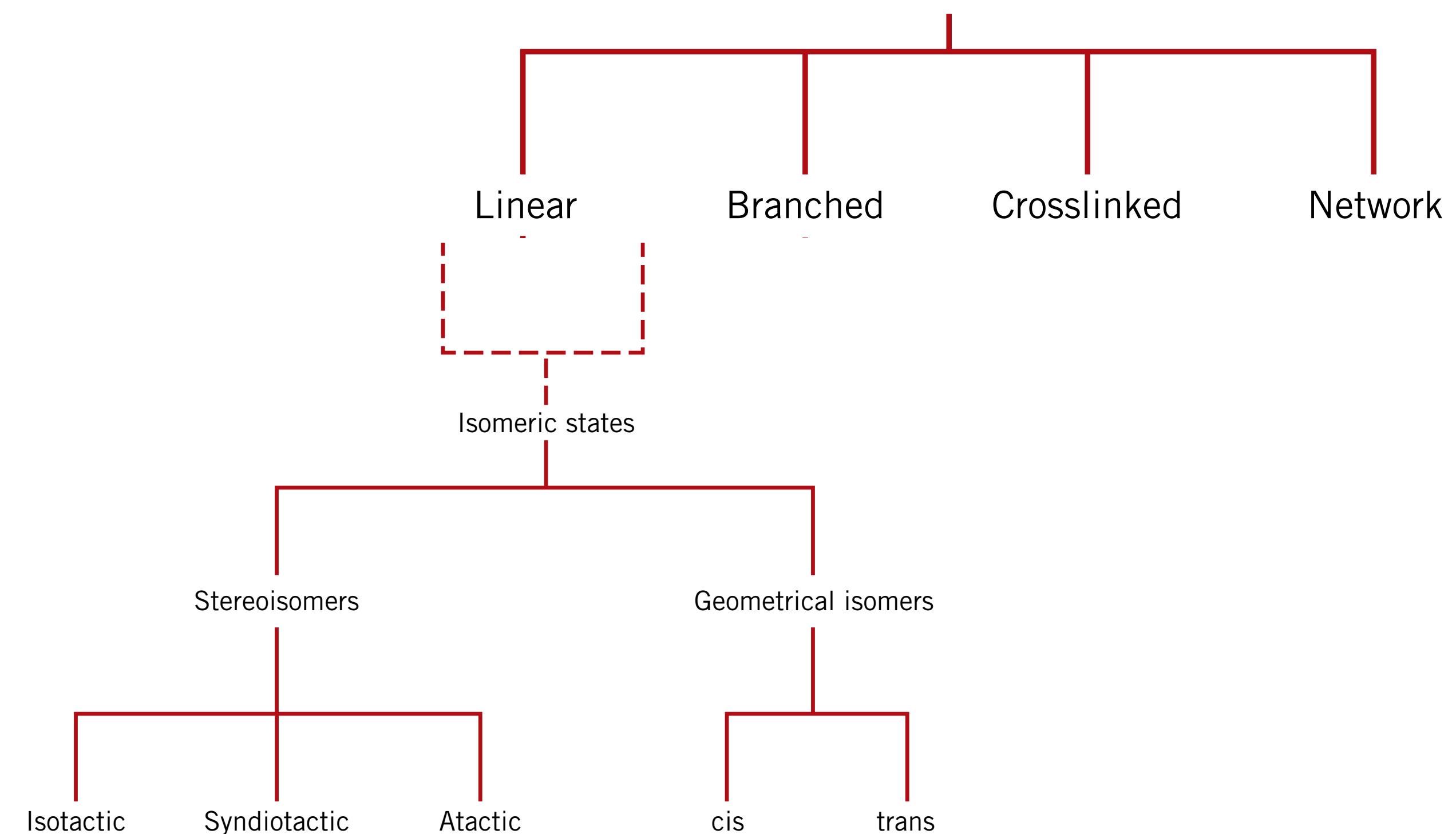


- Swelling of a single chain in a good solvent
- Thermodynamics of polymer solutions along with Huggins
- Distribution of molar mass, hydrodynamics

**M.L. Huggins:** conceived the idea of Hydrogen bonding

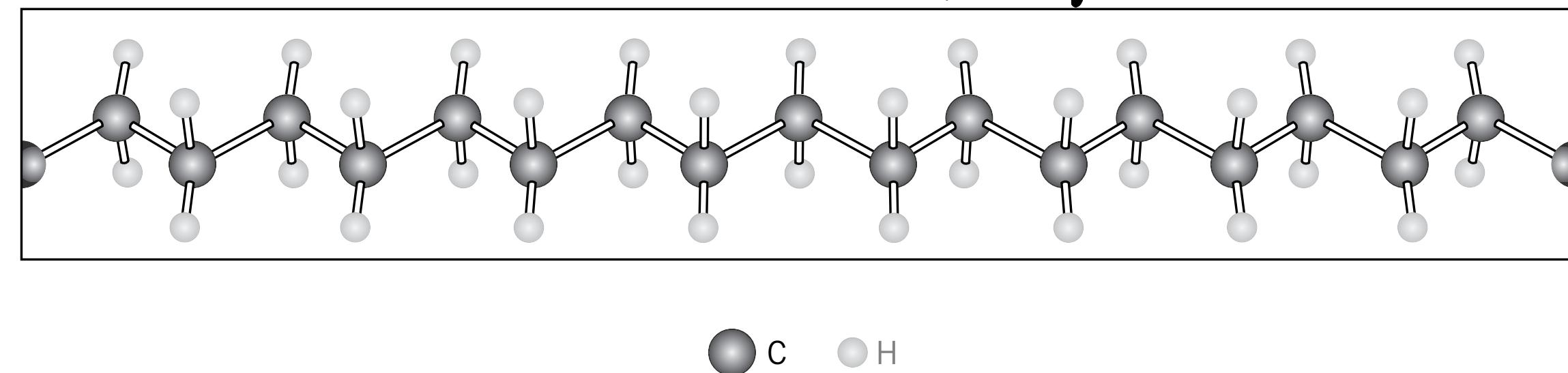
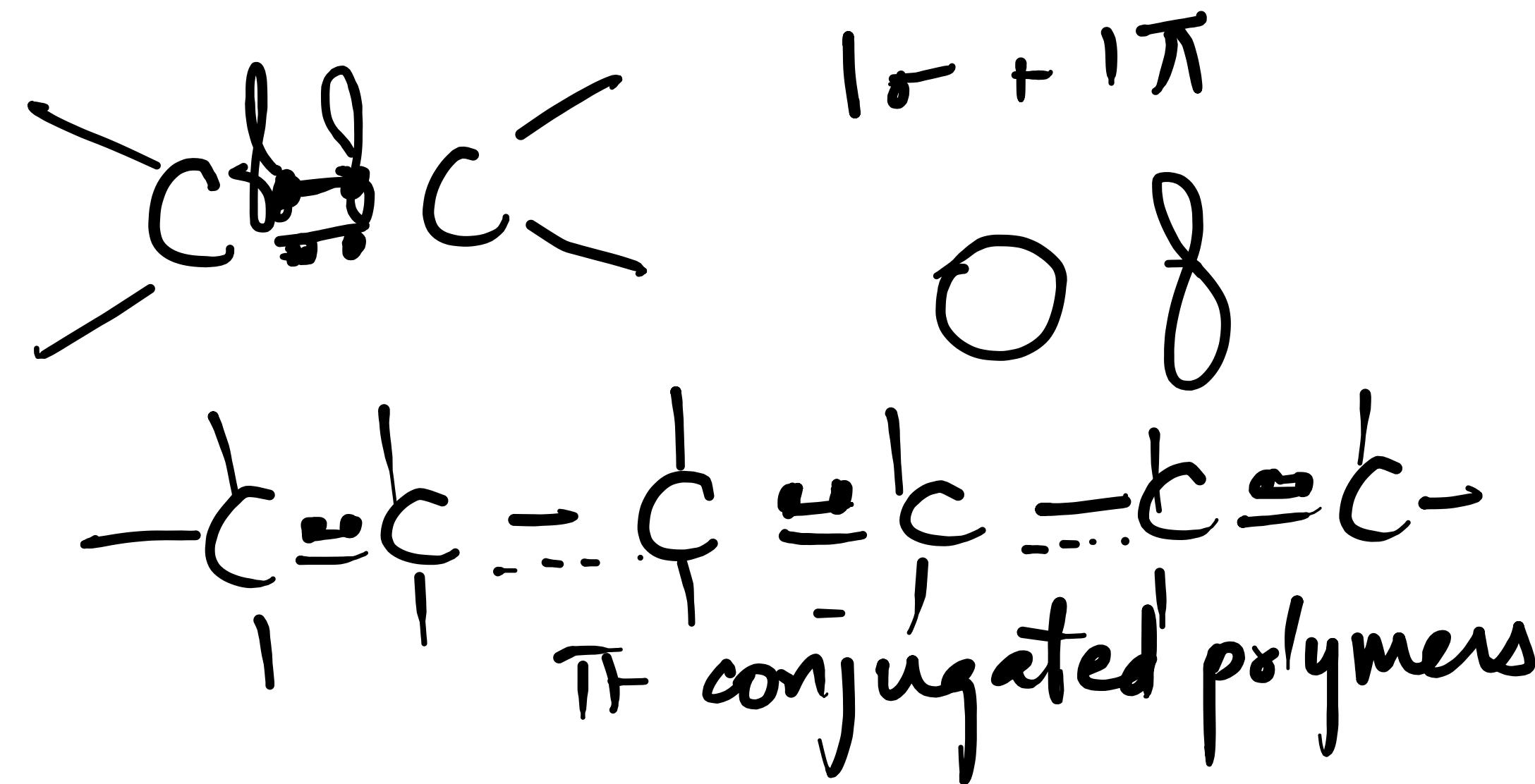
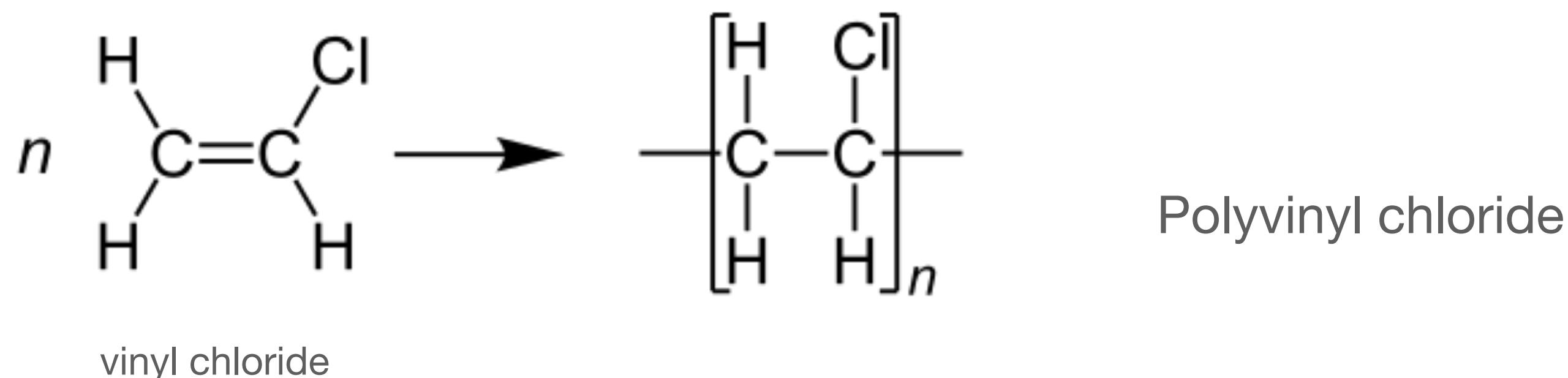
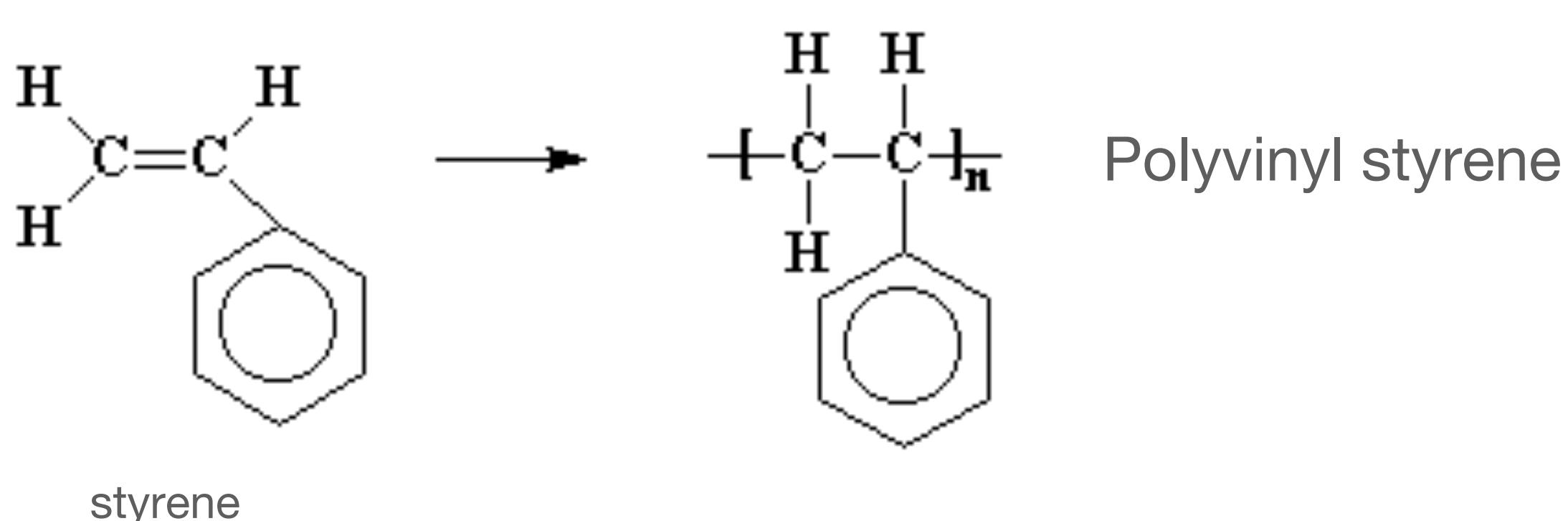
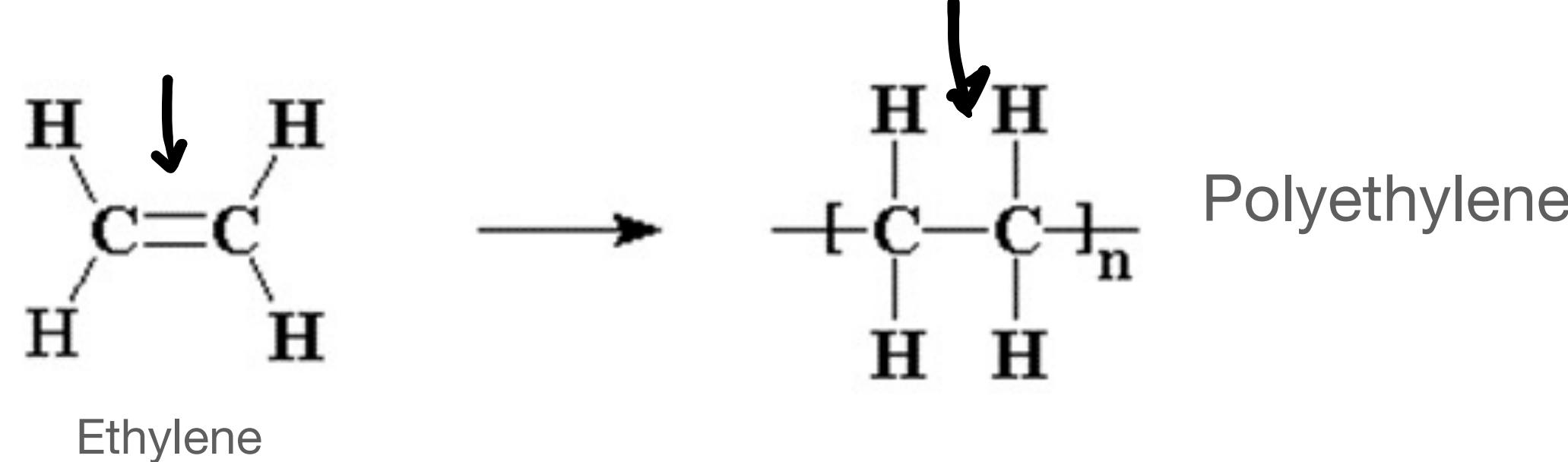
# Four main properties

1. Chemistry: monomer
2. Size: molecular Weight and degree of polymerization
3. Shape: chain twisting, entanglement
4. **Structure:** Density and crystallinity



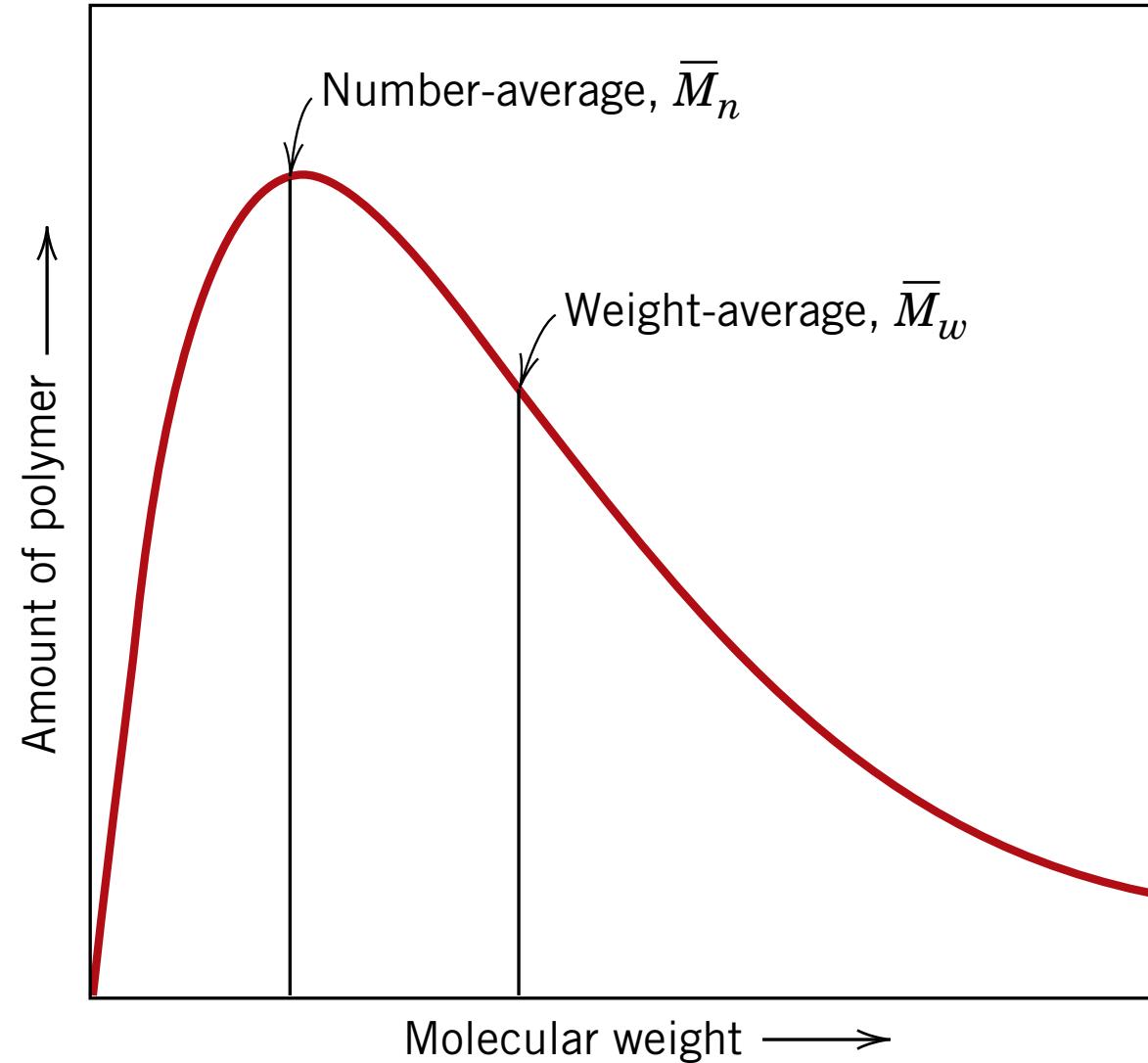
# Chemistry of polymers

## Monomers of vinyl polymers



# Molecular weight of polymers

## Macromolecules



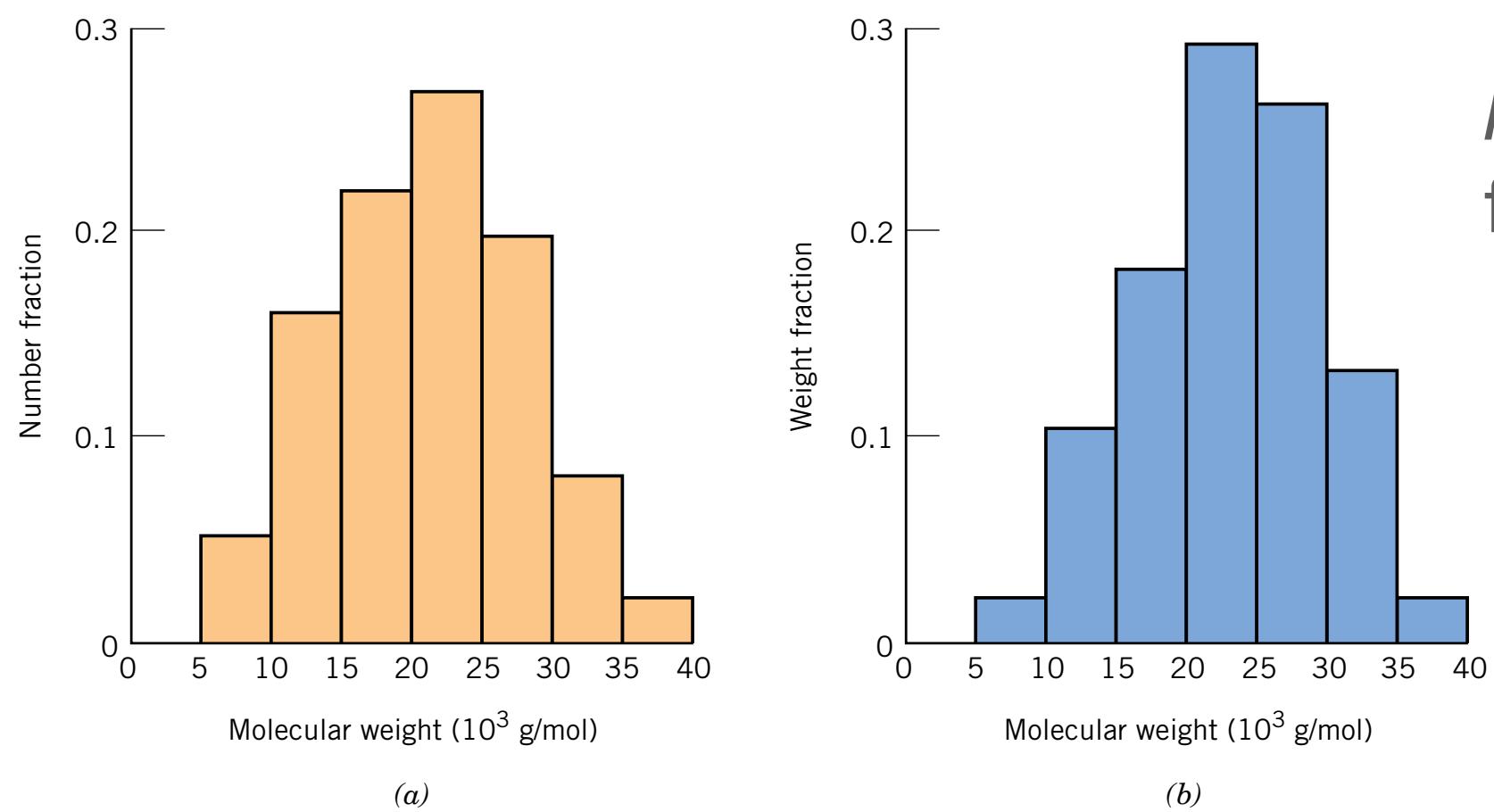
The **number-average molecular weight  $\bar{M}_n$**  is obtained by dividing the chains into a series of size ranges and then determining the number fraction of chains within each size range

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

where  $M_i$  represents the mean (middle) molecular weight of size range  $i$ , and  $x_i$  is the fraction of the total number of chains within the corresponding size range.

A **weight-average molecular weight  $\bar{M}_w$**  is based on the weight fraction of molecules within the various size ranges

$$\bar{M}_w = \sum w_i M_i$$

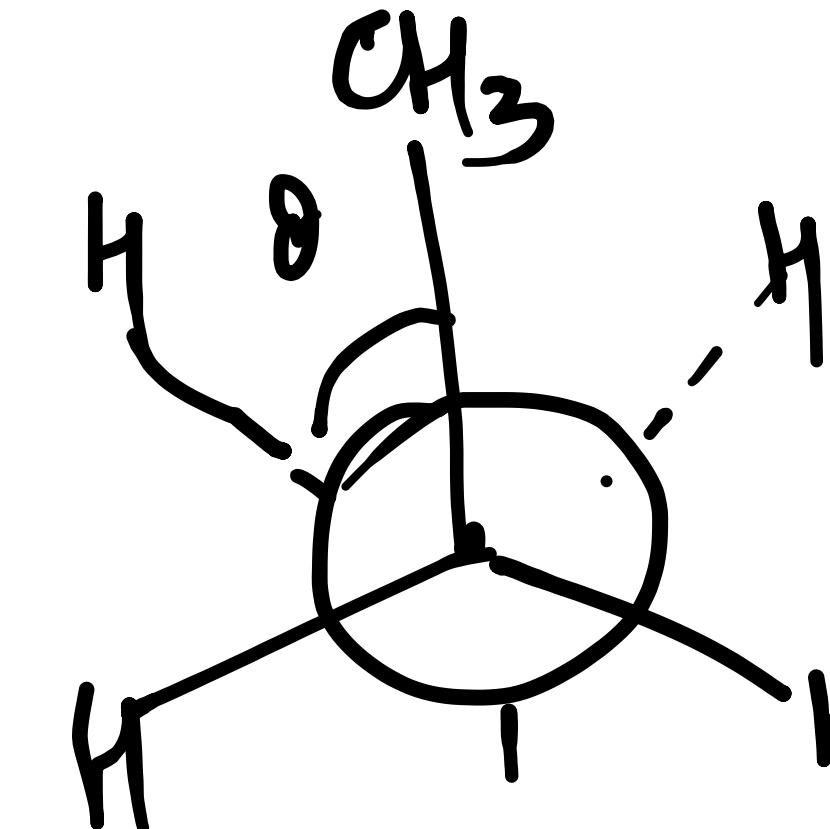
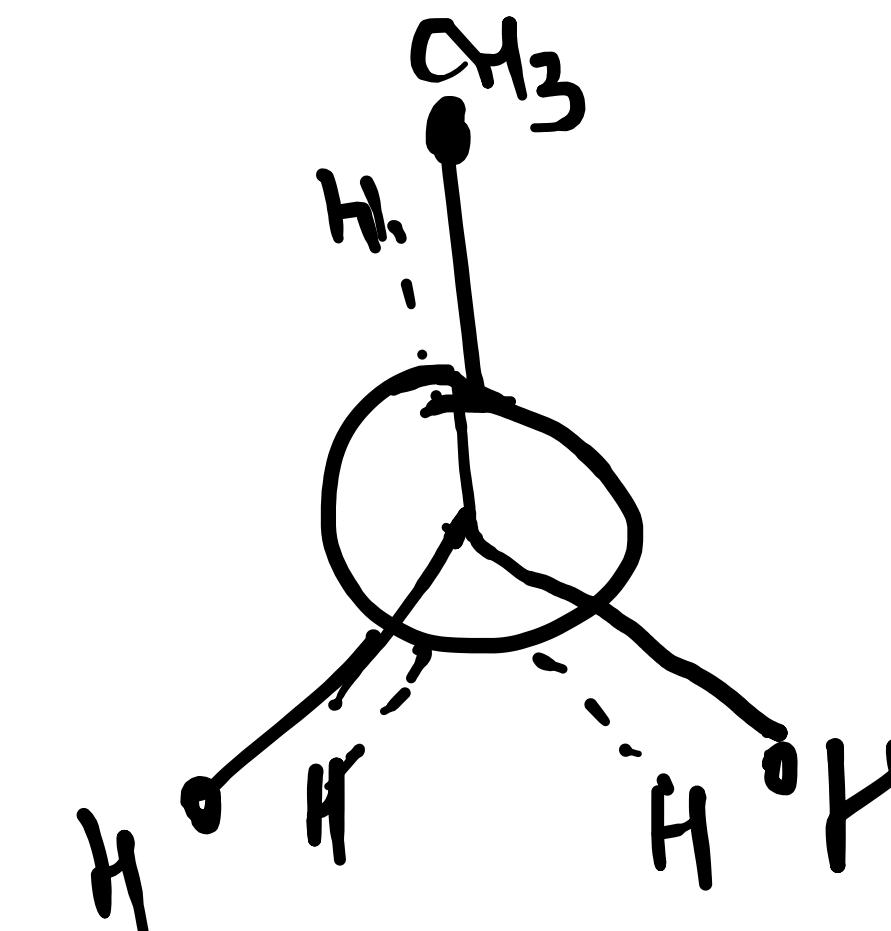
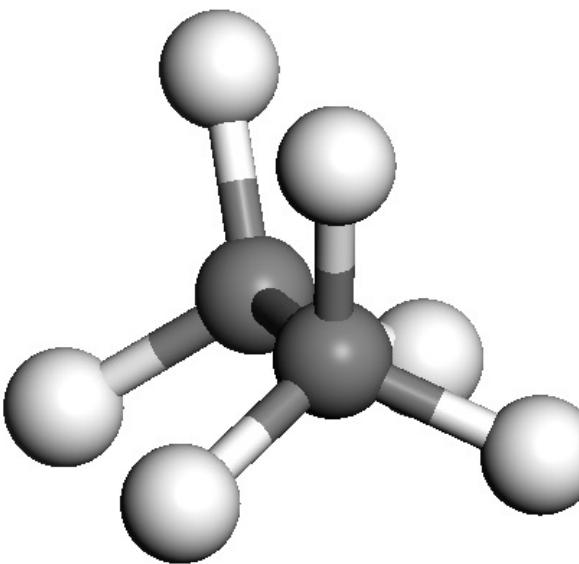
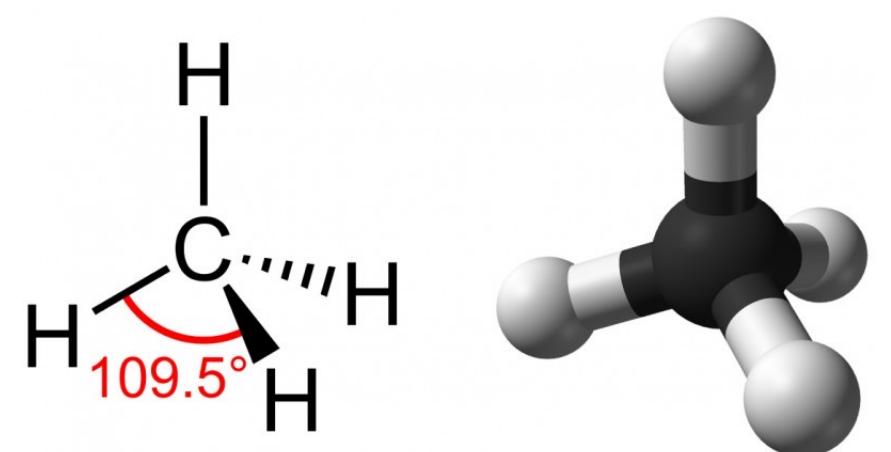


$M_i$  is the mean molecular weight within a size range, whereas  $w_i$  denotes the weight fraction of molecules within the same size interval.

An alternate way of expressing average chain size of a polymer is as the **degree of polymerization,  $DP$** , which represents the average number of repeat units of chain. The relationship between DP and number-average molecular weight is

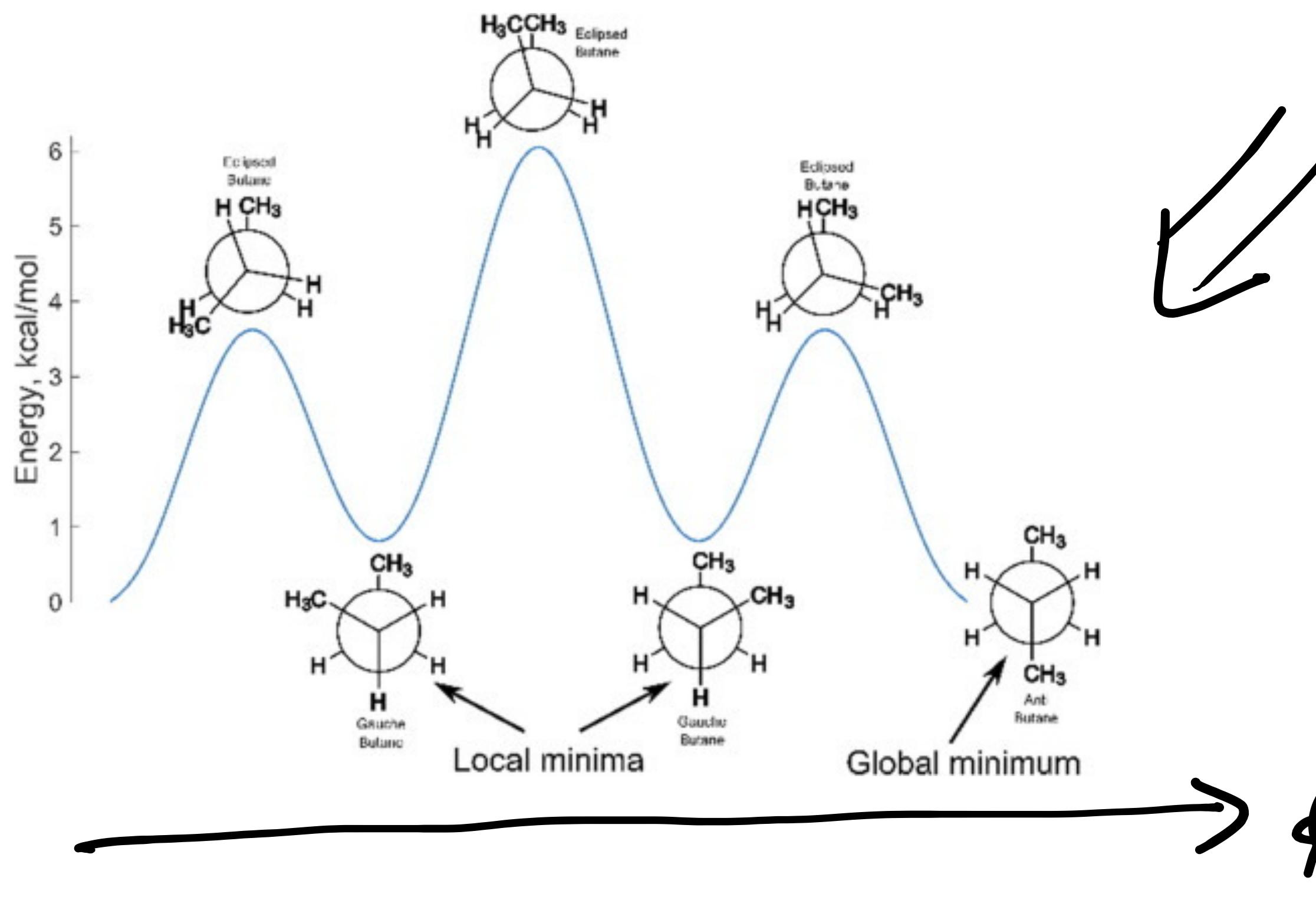
$$DP = \frac{\bar{M}_n}{m}$$

# Molecular shape of polymers or chain conformations



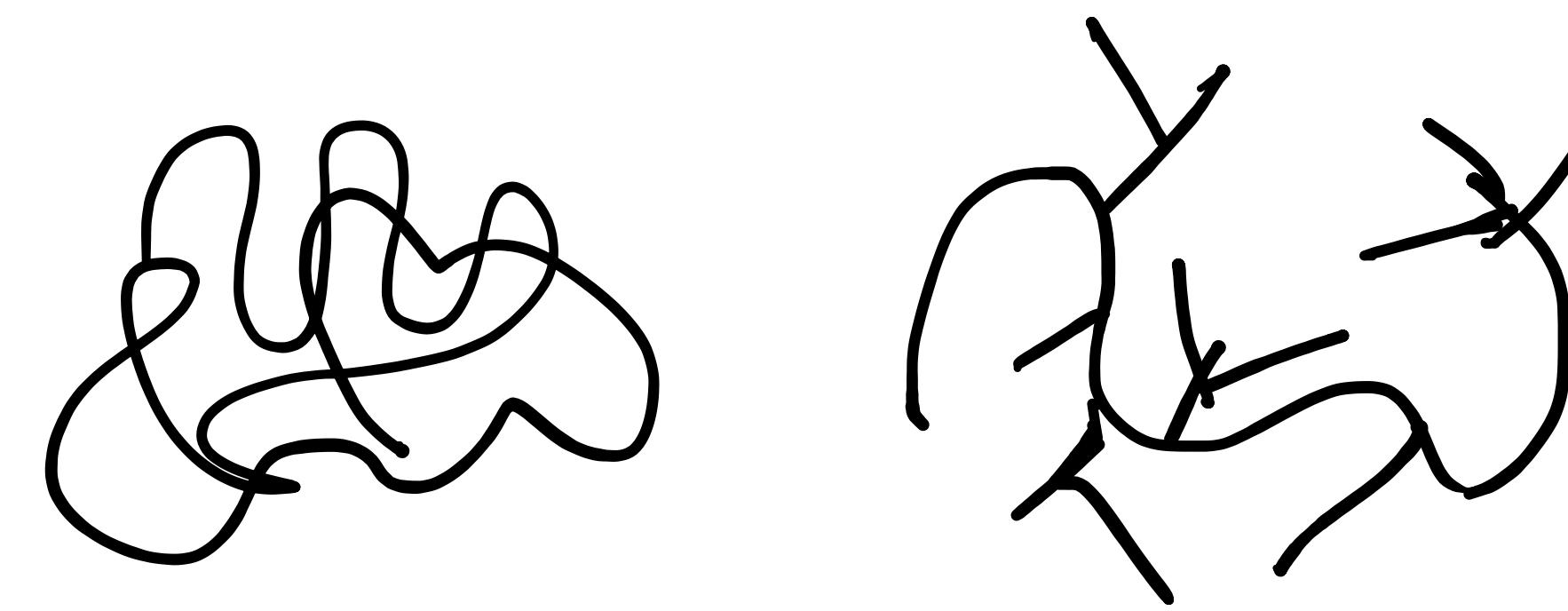
eclipsed  
cis  
gauche

staggered  
trans



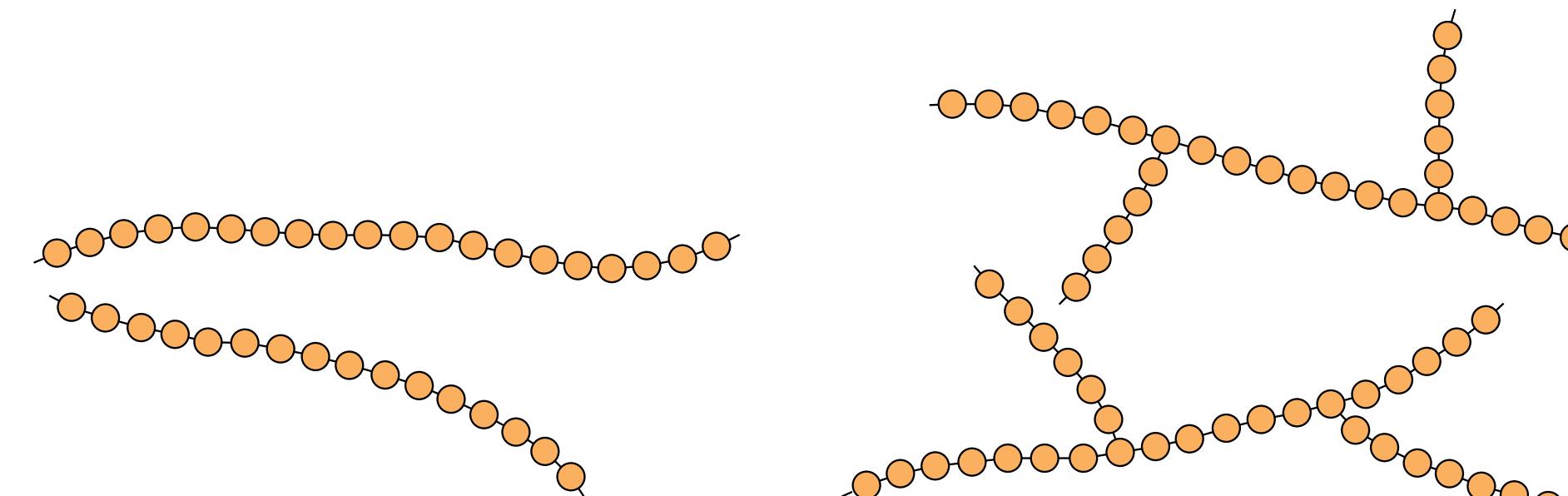
# Structure of Polymers: What decides crystallinity in polymers?

## Branching



linear

branching

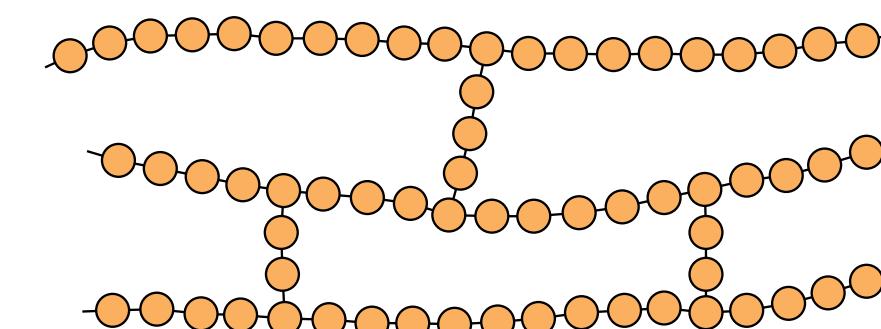


*linear*

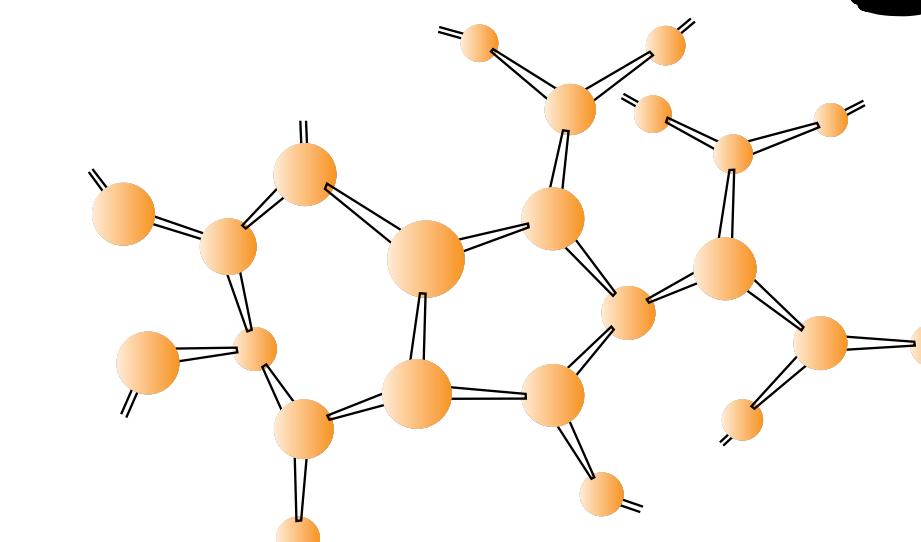
(b)

*Branched*

More branching, crosslinking- lesser is the density of polymer



*Cross linked*



(d)

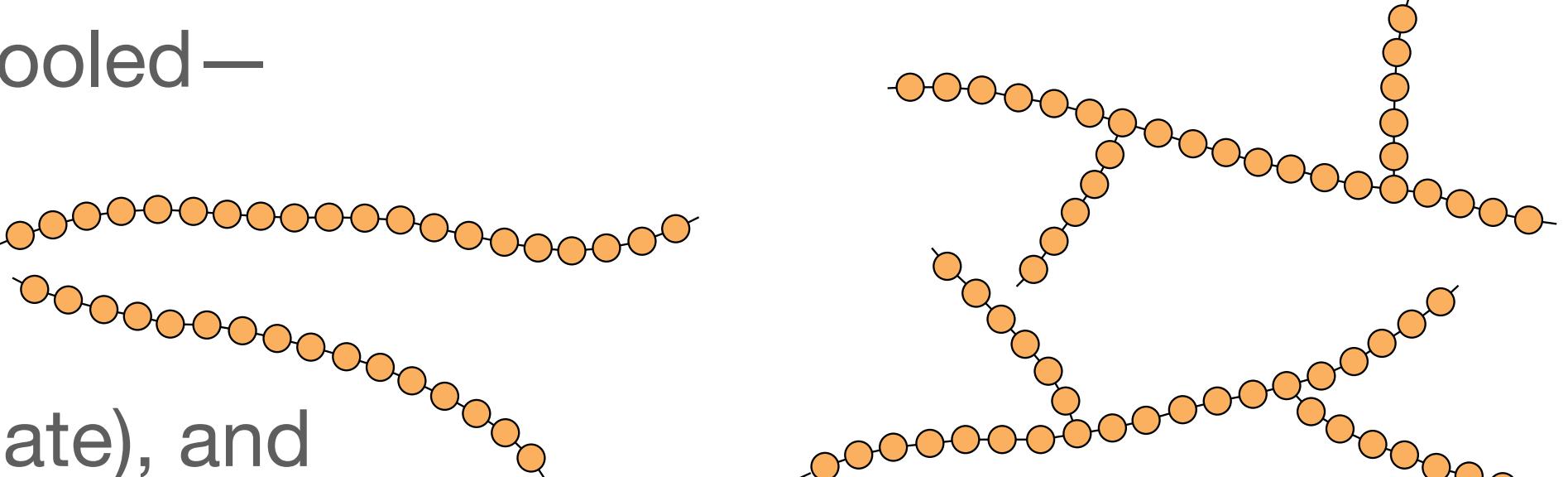
*Network molecular*

# Thermoplasts and Thermosets

## *Classification based on response to temperature*

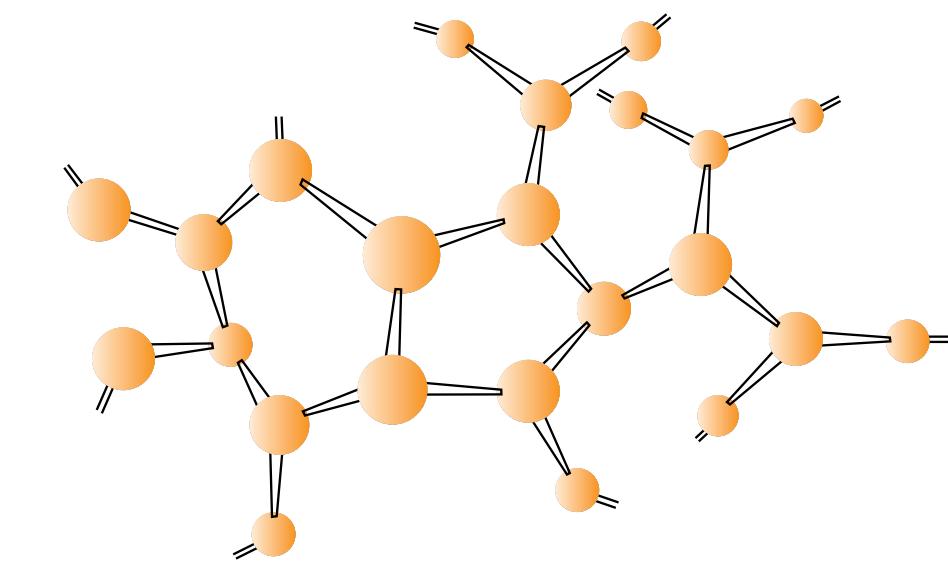
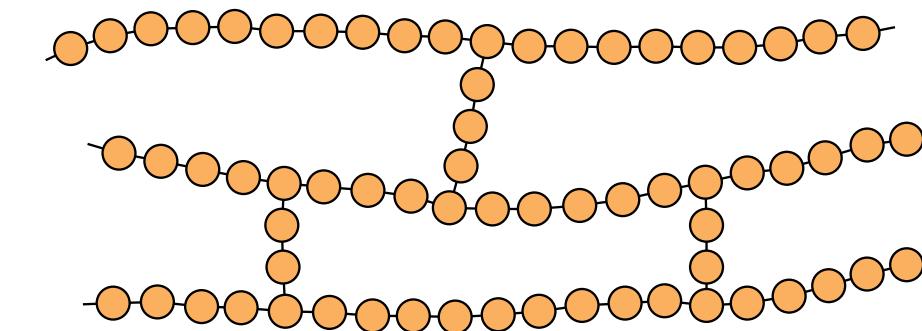
### Thermoplasts:

- soften when heated (and eventually liquefy) and harden when cooled—processes that are totally reversible and may be repeated.
- Secondary forces: van der Waals interactions between chains
- Linear and branched polymers
- Examples: polyethylene, polystyrene, poly(ethylene tere-phthalate), and poly(vinyl chloride)



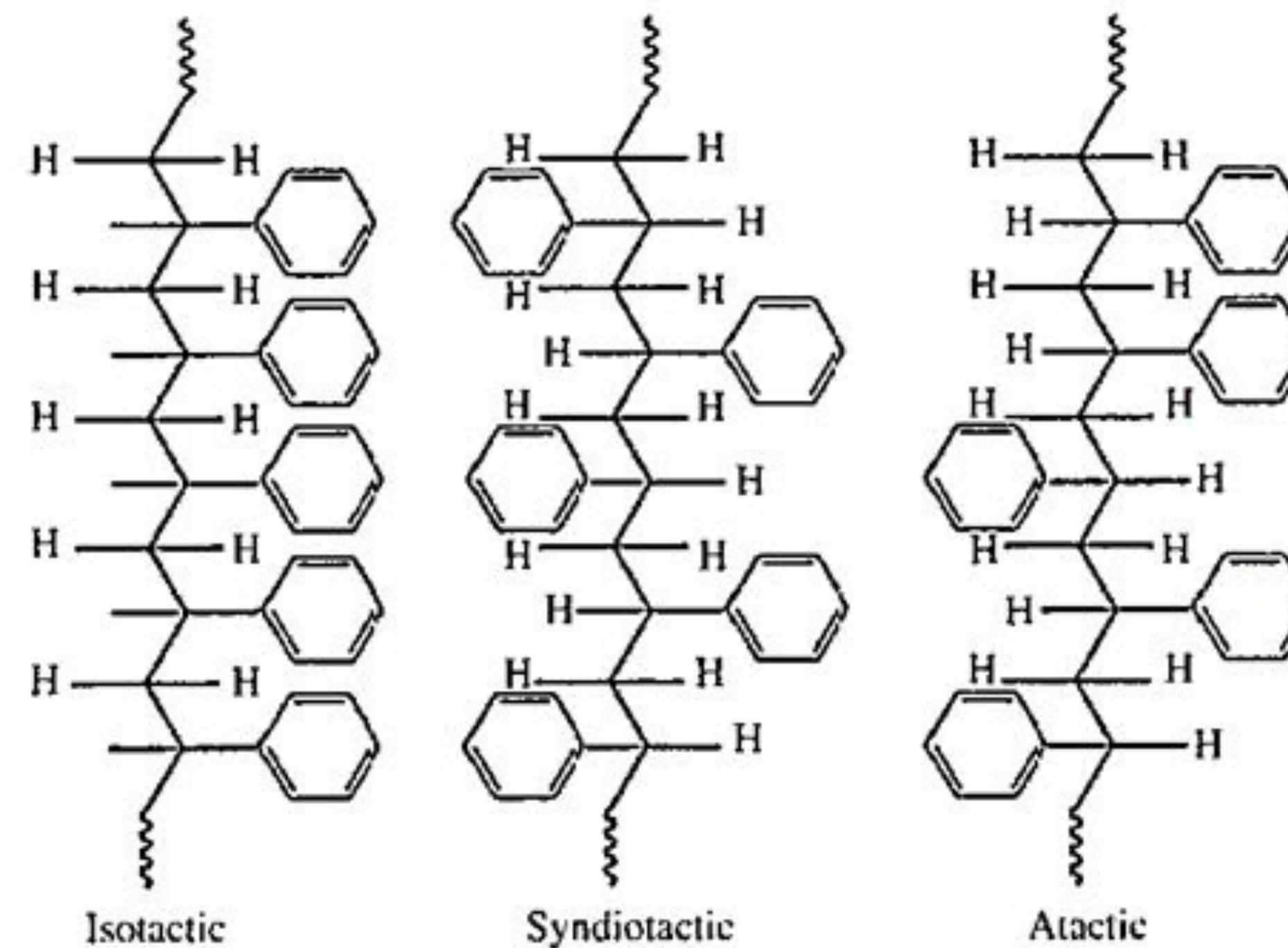
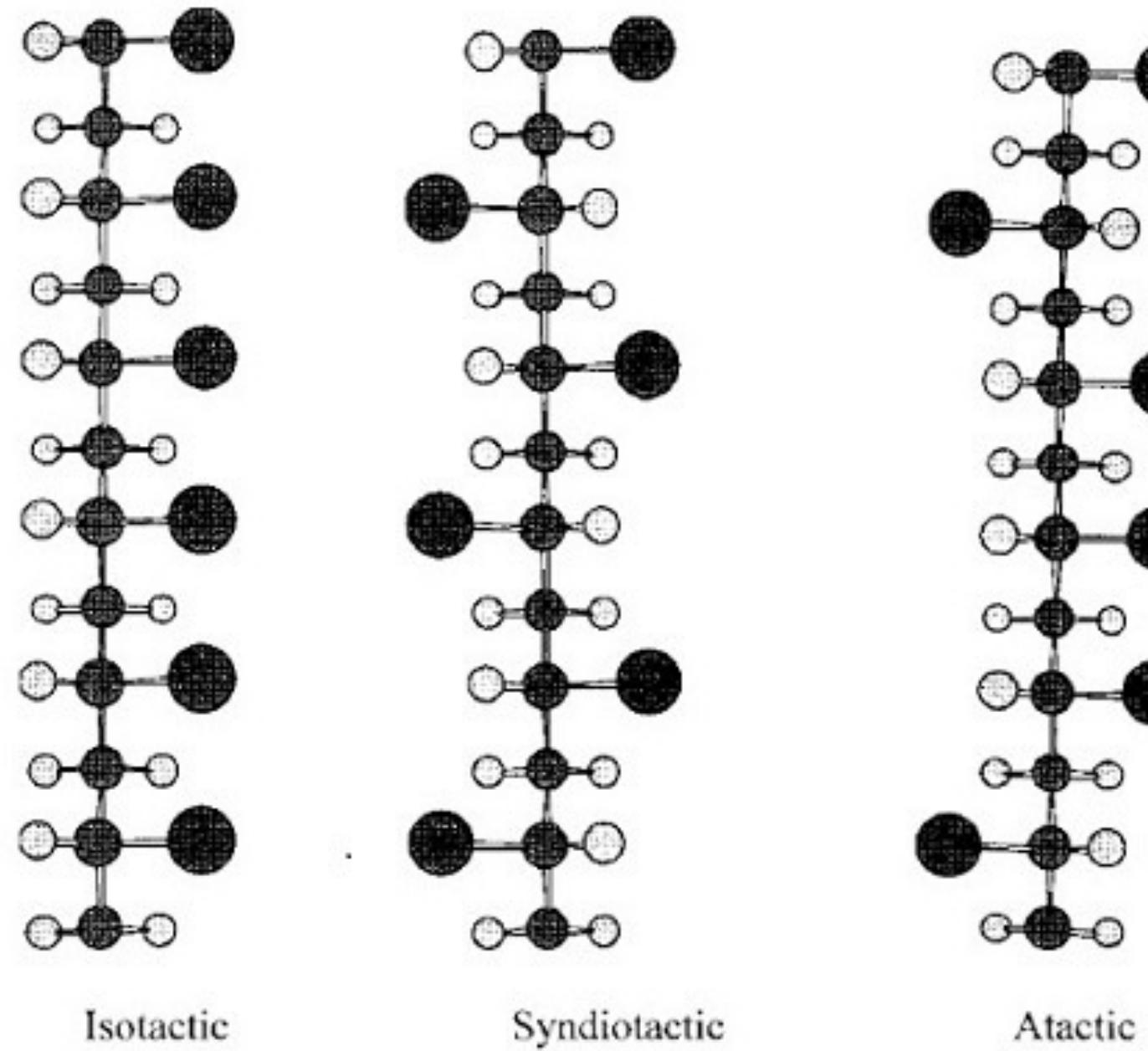
### Thermosets:

- They become permanently hard during their formation, and do not soften upon heating
- Network polymers and covalent cross linked polymers
- Thermoset polymers are generally harder and stronger than thermoplastics and have better dimensional stability.
- Examples: vulcanized rubbers, epoxies, and phenolics and some polyester resins



# Structure of Polymers: What decides crystallinity in polymers?

*Tacticity (Stereochemistry: arrangement or order)*



Isotactic and Syndiotactic  
can pack easily and density  
will be higher

# Lecture 26

## **Materials and their structure- Polymers-Part2 Mechanical Behaviour of Materials**

### **Textbooks:**

- Introduction to materials science and Engineering: V. Raghavan
- Materials Science and Engineering: Callister and Rethwisch

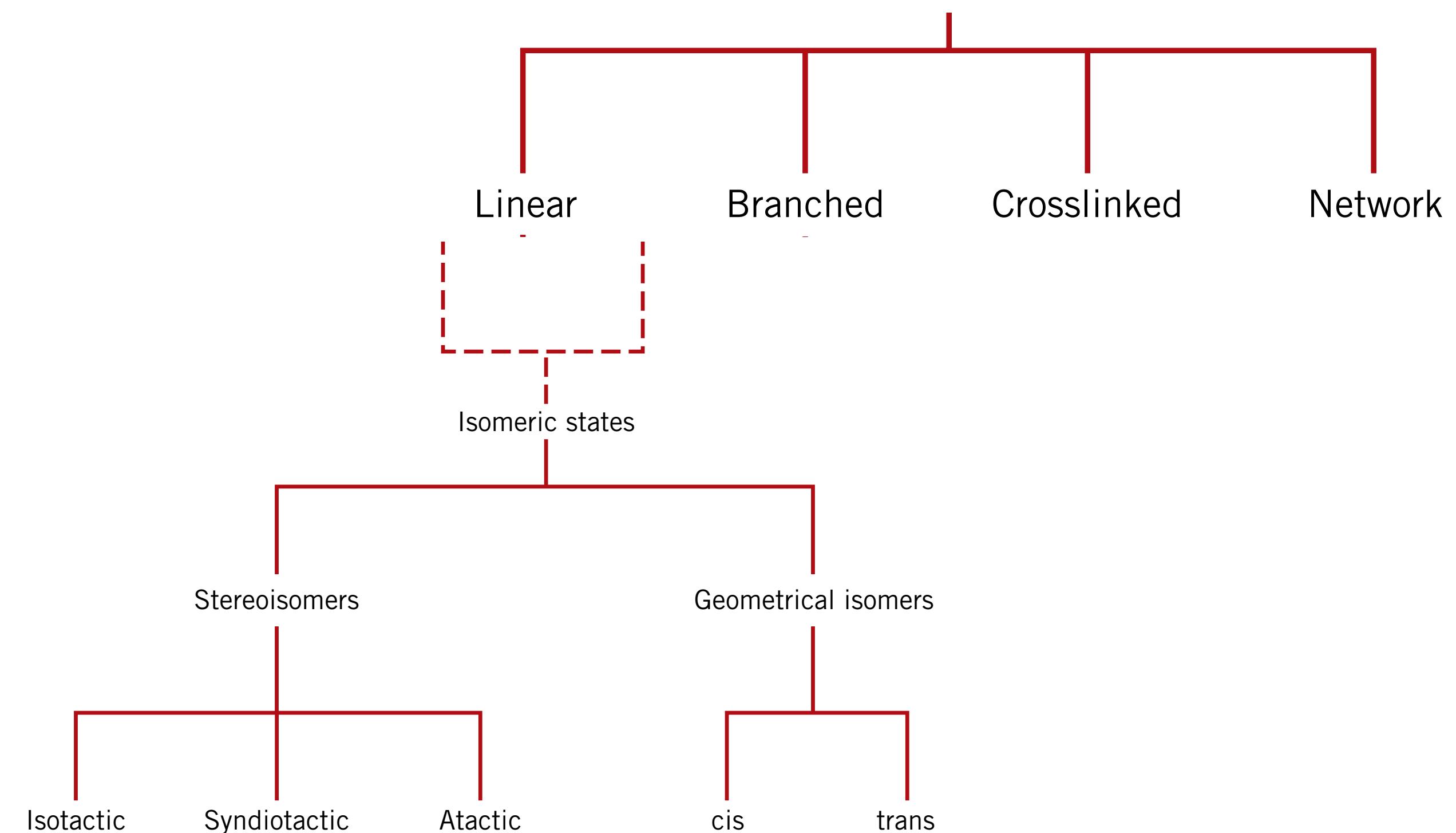
**Prof. Divya Nayar**  
**Department of Materials Science and Engineering**  
**[divyanayar@mse.iitd.ac.in](mailto:divyanayar@mse.iitd.ac.in)**

# Recap...

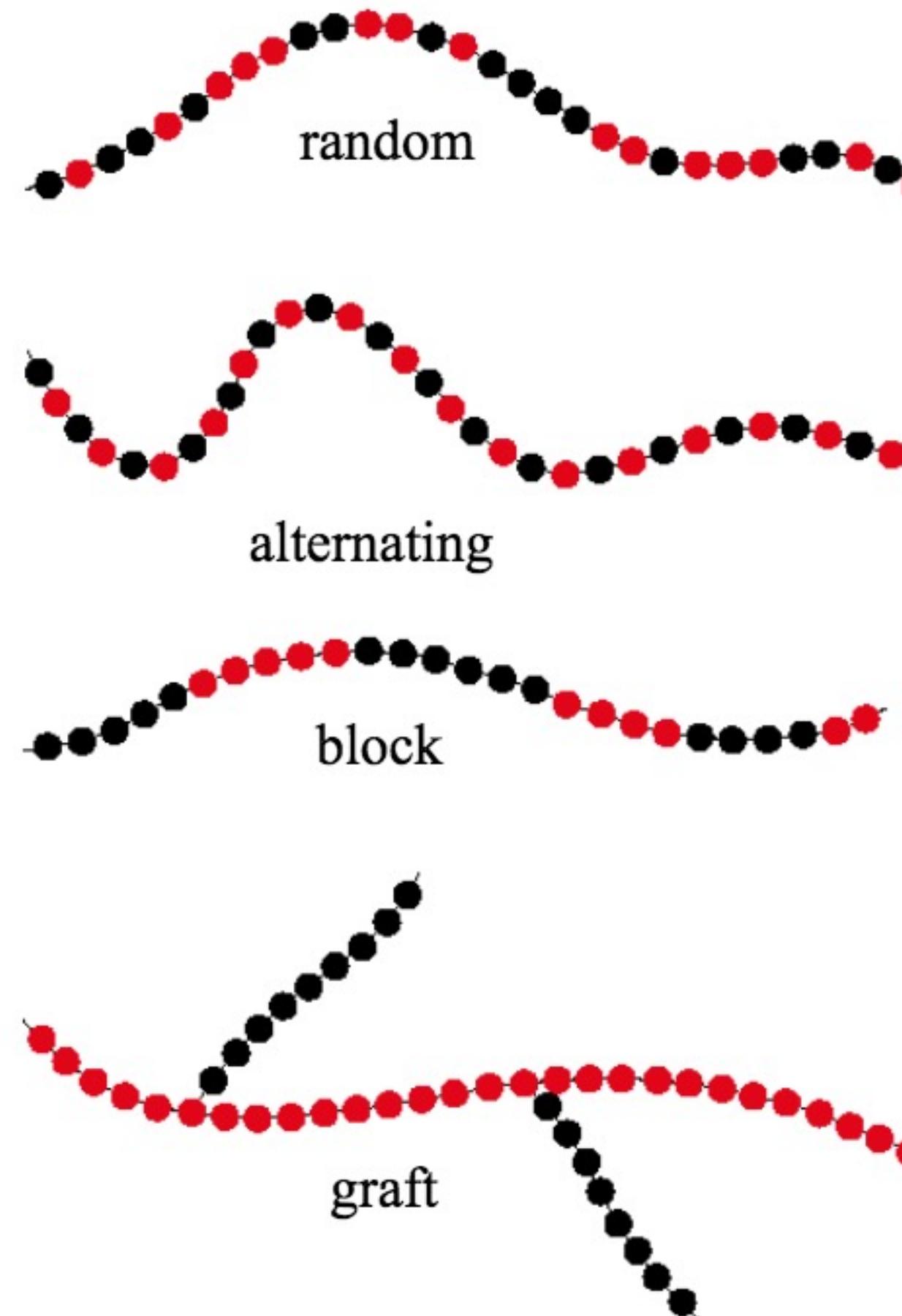
1. Polymers: macromolecules
2. Properties of polymers: chemistry, size, shape, structure
3. Structure of polymers: different categories
4. Linear polymers: tacticity
5. Copolymers
6. Polymer crystallinity

# Four main properties

1. Chemistry: monomer
2. Size: molecular Weight and degree of polymerization
3. Shape: chain twisting, entanglement
4. **Structure:** Density and crystallinity



# Structure of polymers: Copolymers



Degree of polymerization

$$DP = \frac{\bar{M}_n}{\bar{m}}$$

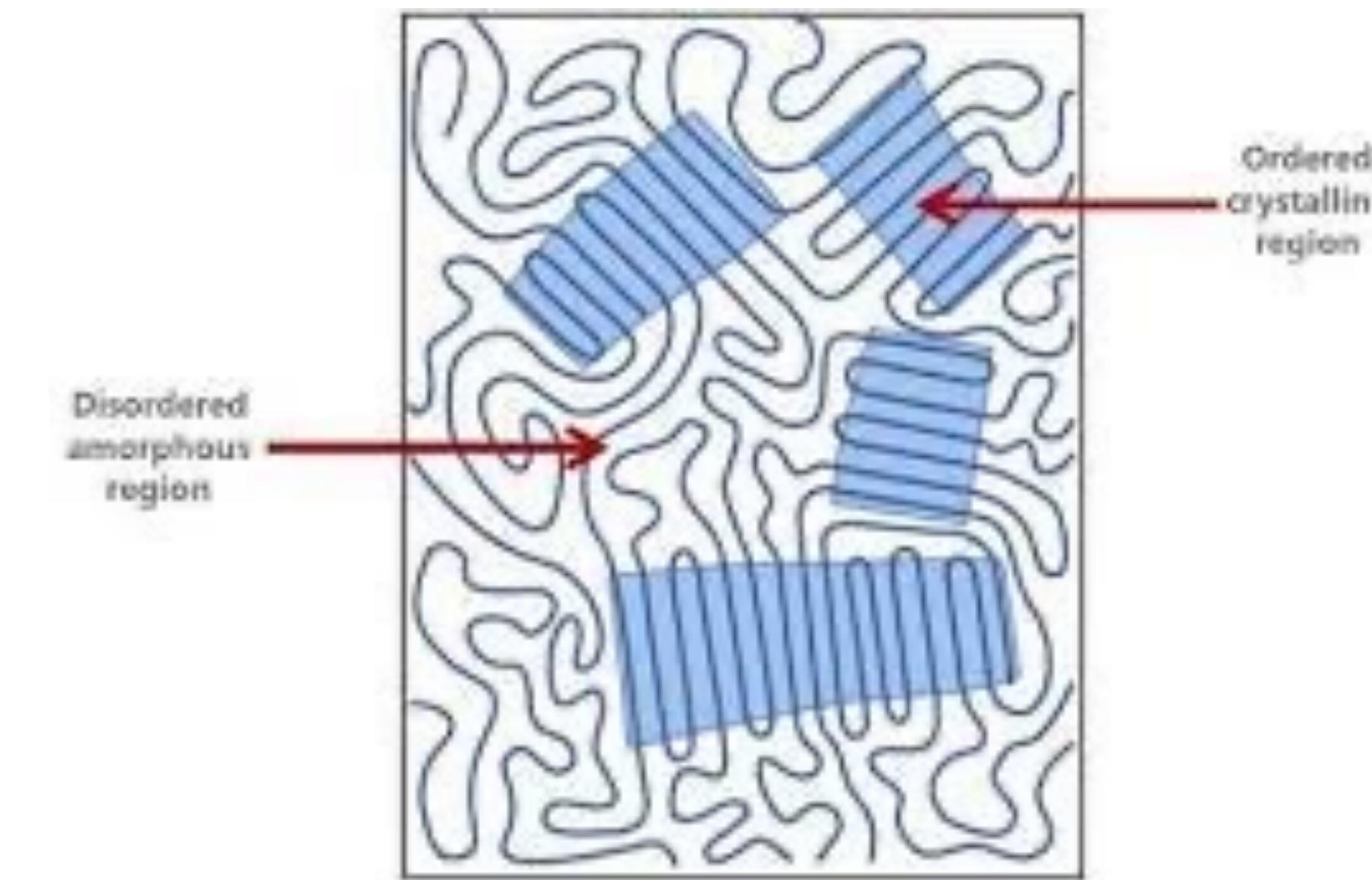
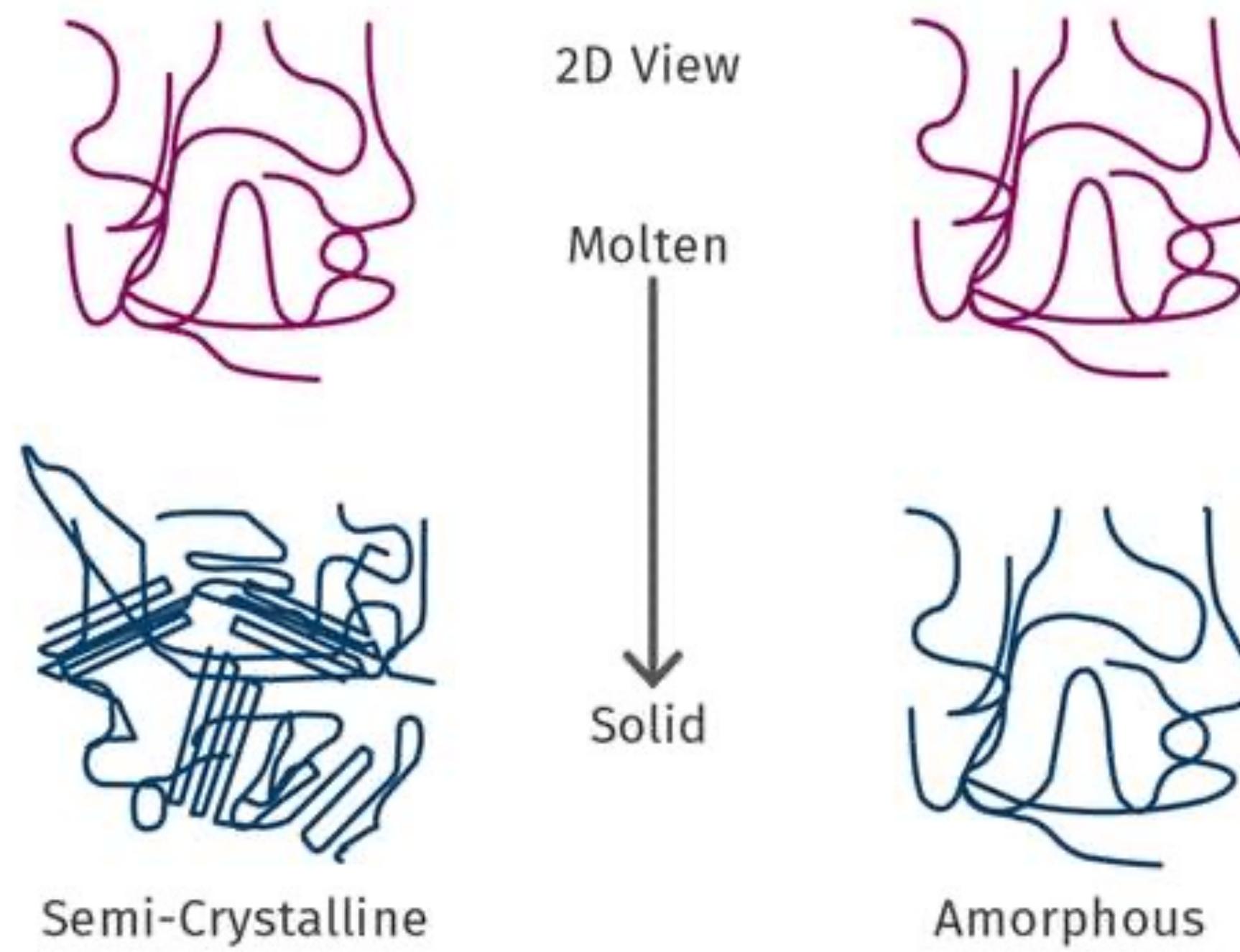
$$\bar{m} = \sum f_j m_j$$

$f_j$  and  $m_j$  are, respectively, the mole fraction and molecular weight of repeat unit  $j$  in the polymer chain.

- Random, block and graft polymers form amorphous structures and alternating forms crystalline structure.
- Examples: Styrene–butadiene rubber (SBR) (random copolymer), Nitrile rubber (NBR) (random copolymer)

# Polymers are semi-crystalline

Structure Difference Between Semi-Crystalline and Amorphous Polymer Chains

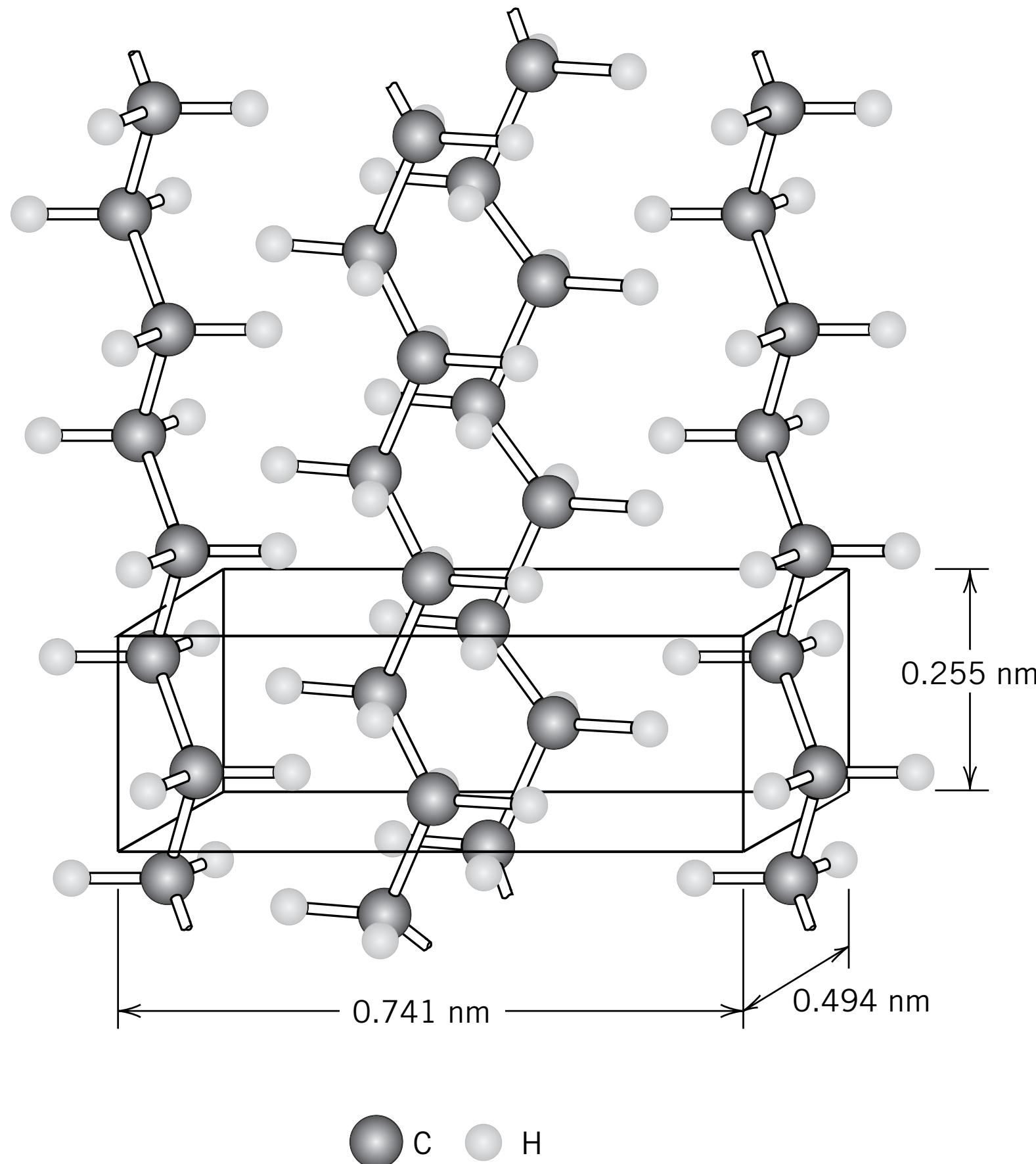


- Crystalline regions dispersed within the remaining amorphous material.
- Long chains fold and form crystalline part
- A given chain may belong to both crystalline and amorphous regions
- A given crystal consists of more than one chains.
- Chain disorder or misalignment (kinking, twisting, coiling) will lead to amorphous region.

# Polymer crystallinity

## Density and degree of crystallinity

-**Polymer crystallinity** is the packing of molecular chains to produce an ordered atomic array

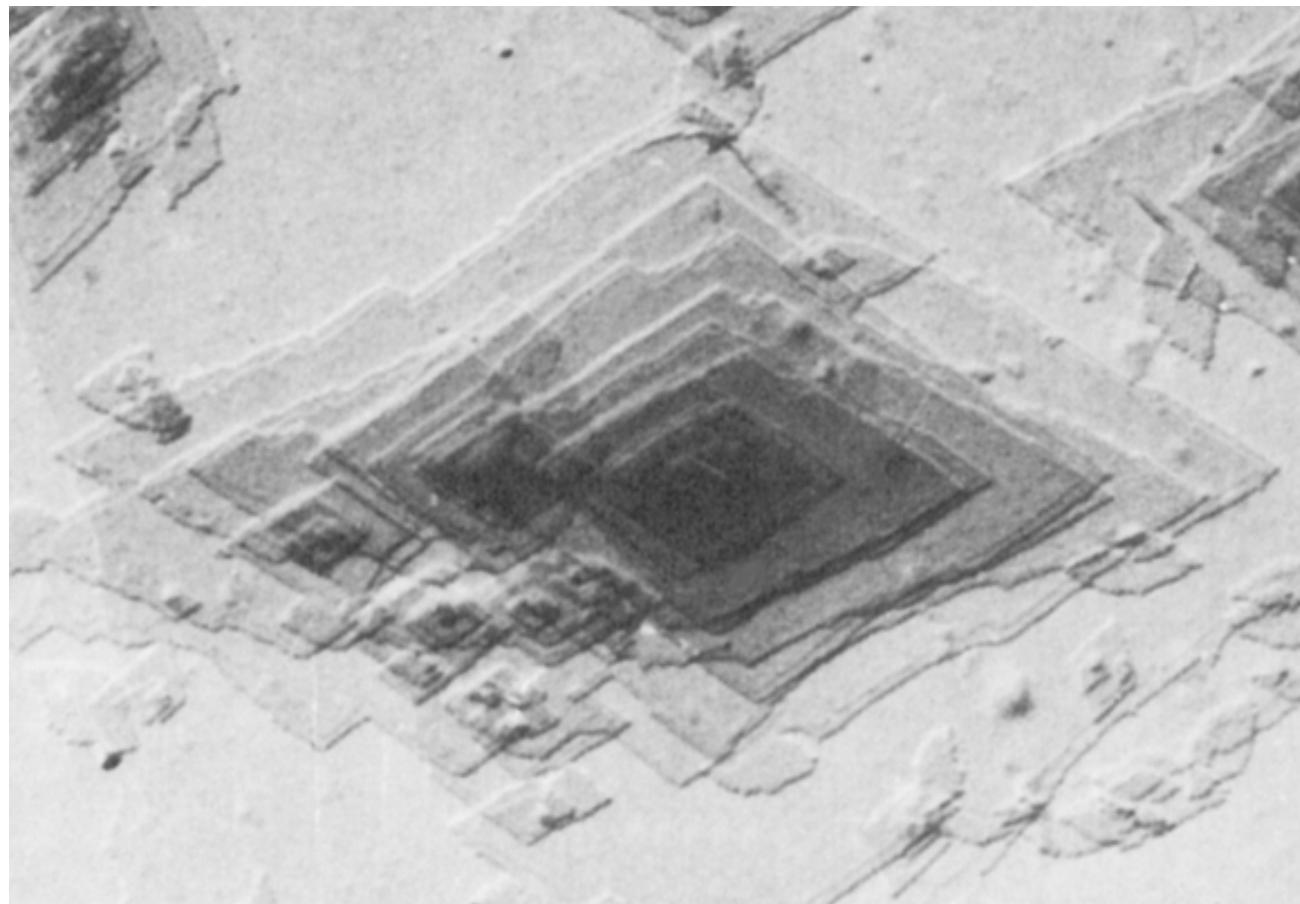


Arrangement of molecular chains in a unit cell for polyethylene

$$\% \text{ crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$

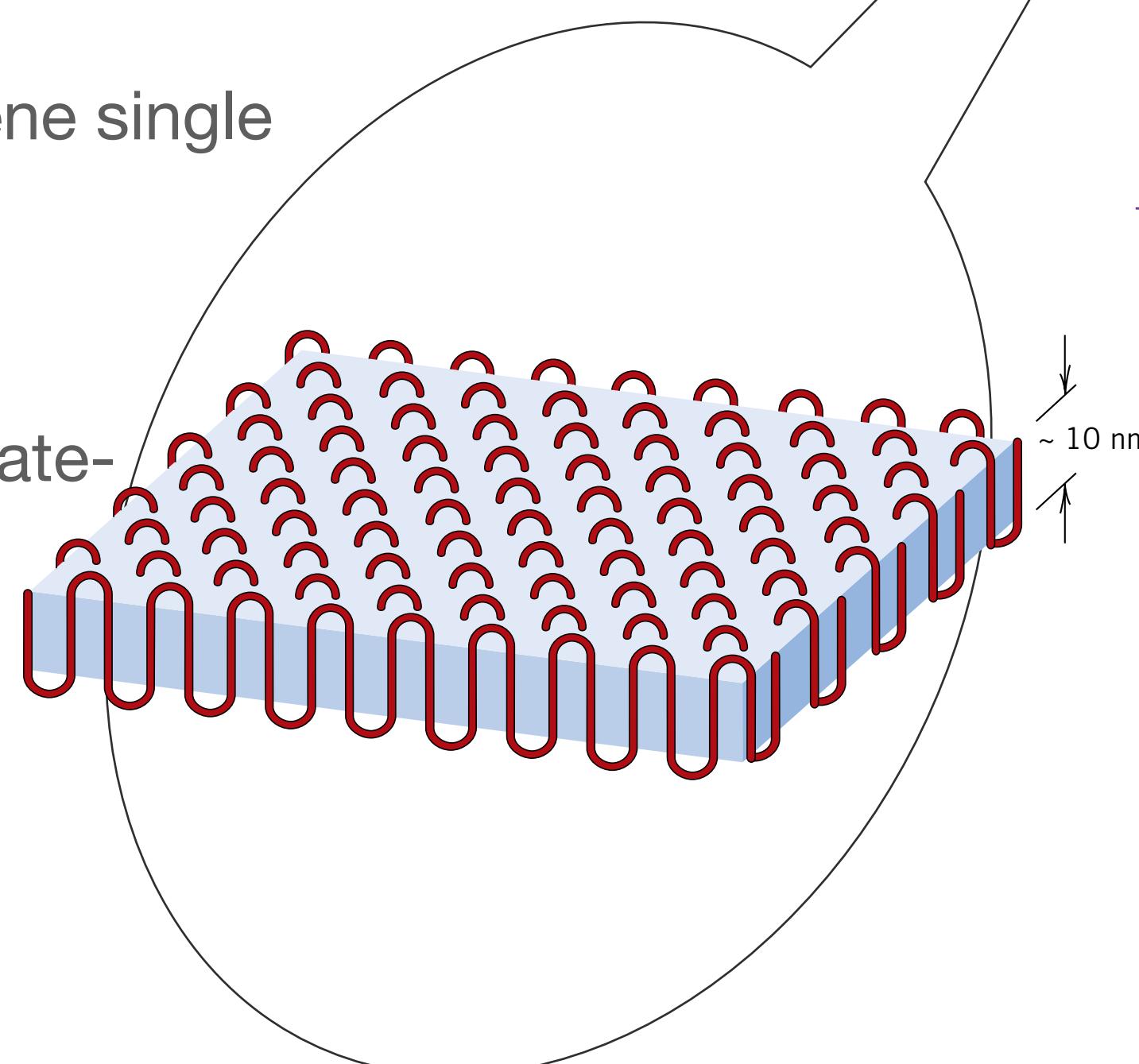
- $\rho_s$  : is the density of a specimen for which the percent crystallinity is to be determined  
 $\rho_a$  : density of the totally amorphous polymer  
 $\rho_c$  : density of the perfectly crystalline polymer.

# Polymer crystals: Lamellae and Spherulites

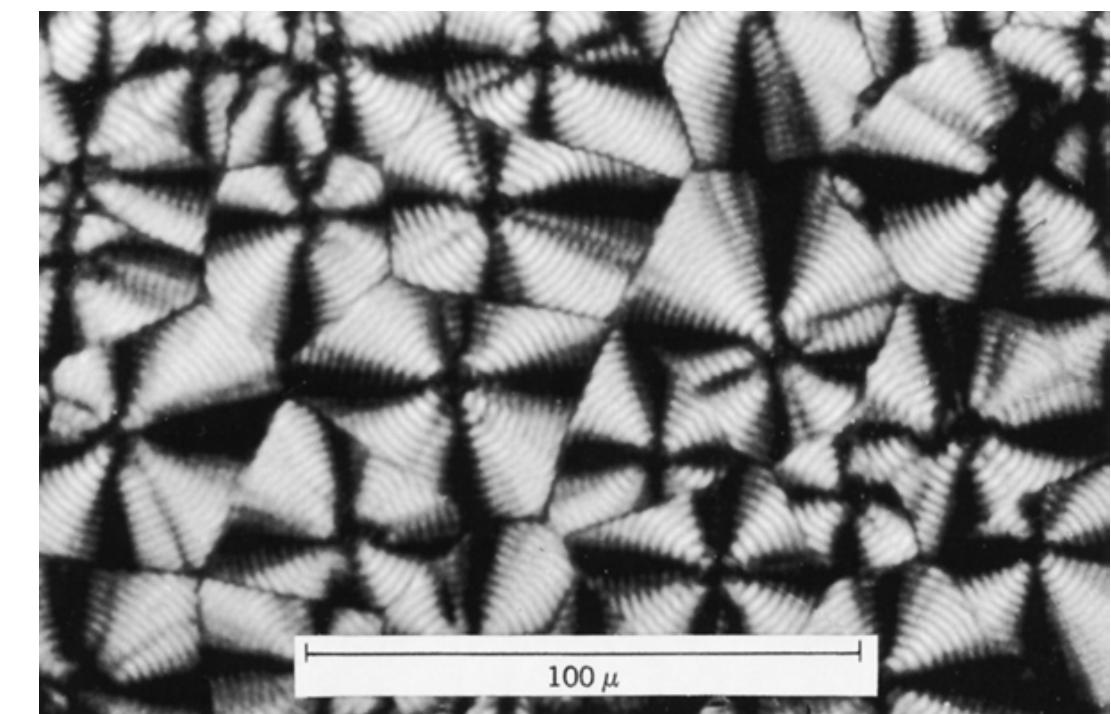
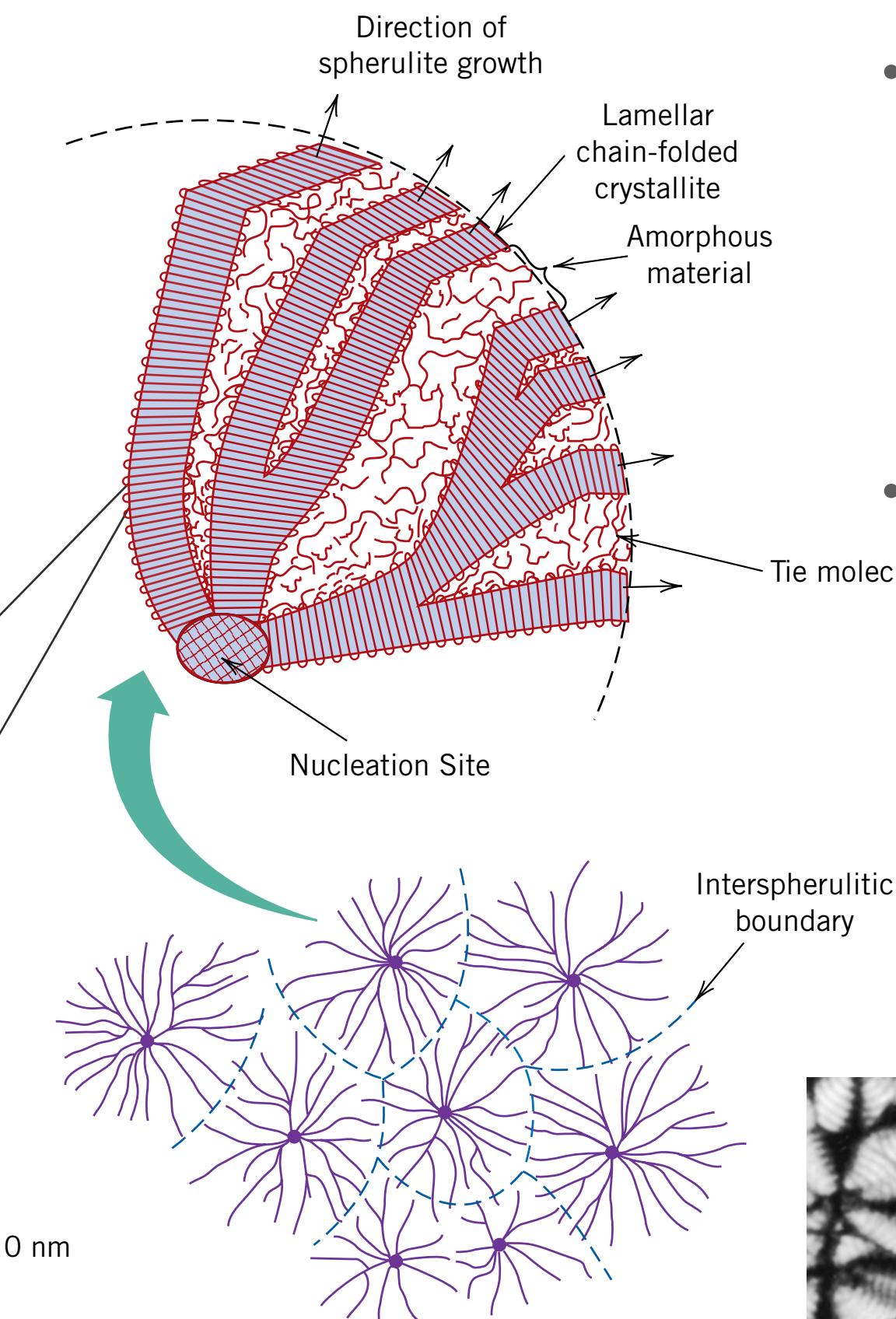


Electron micrograph of a polyethylene single crystal. 20,000X

The chain-folded structure for a plate-shaped polymer crystallite



- These crystals are regularly shaped, thin platelets (or lamellae), approximately 10 to 20 nm thick, and on the order of 10 micrometer long.
- platelets will form a multilayered structure



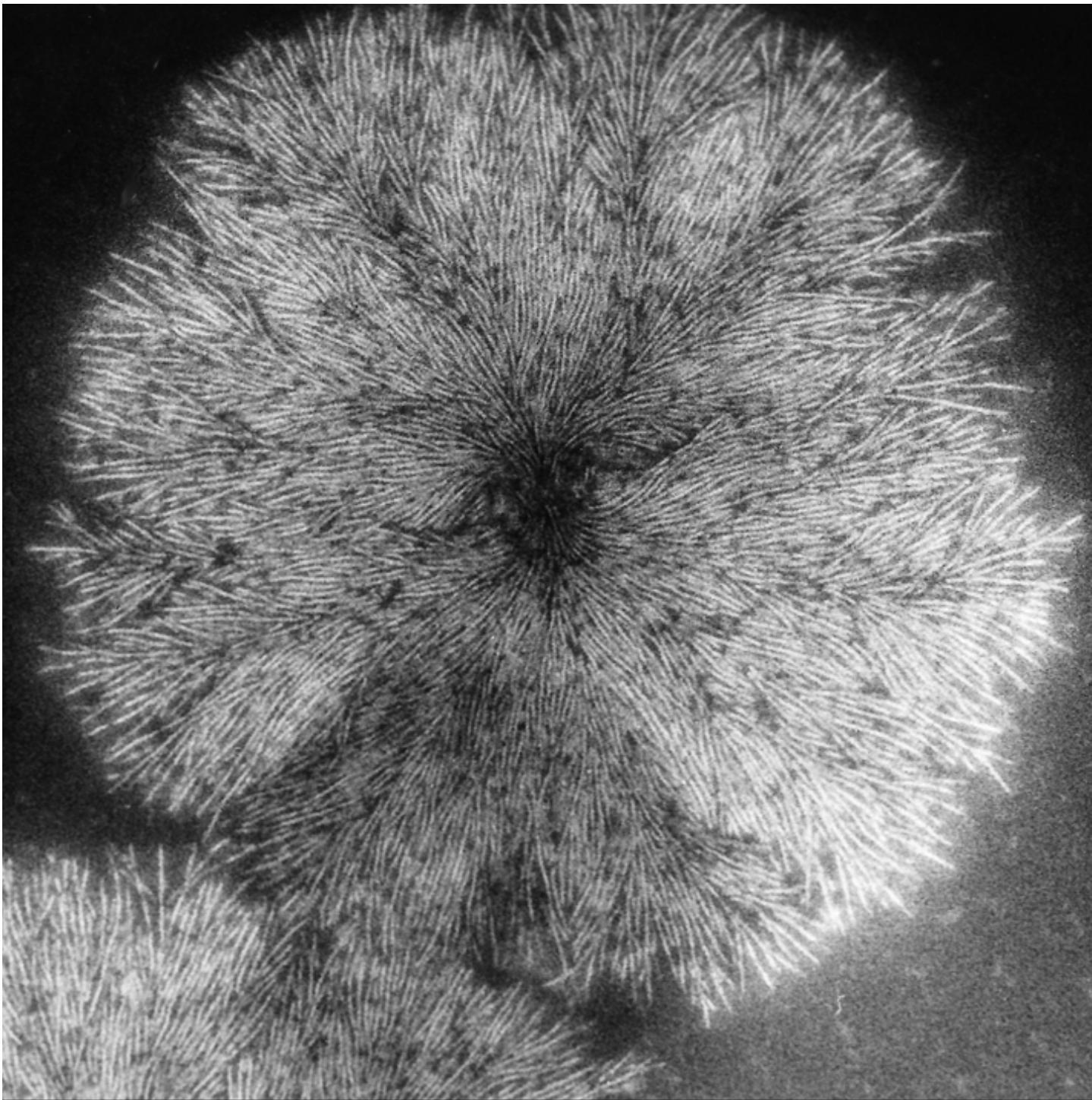
TEM image of spherulite structure of polyethylene

- The spherulite consists of an aggregate of ribbon-like chain-folded crystallites (lamellae) approximately 10 nm thick that radiate outward from a single nucleation site in the center.
- individual chain-folded lamellar crystals that are separated by

# What are the factors affecting crystallinity in polymers?

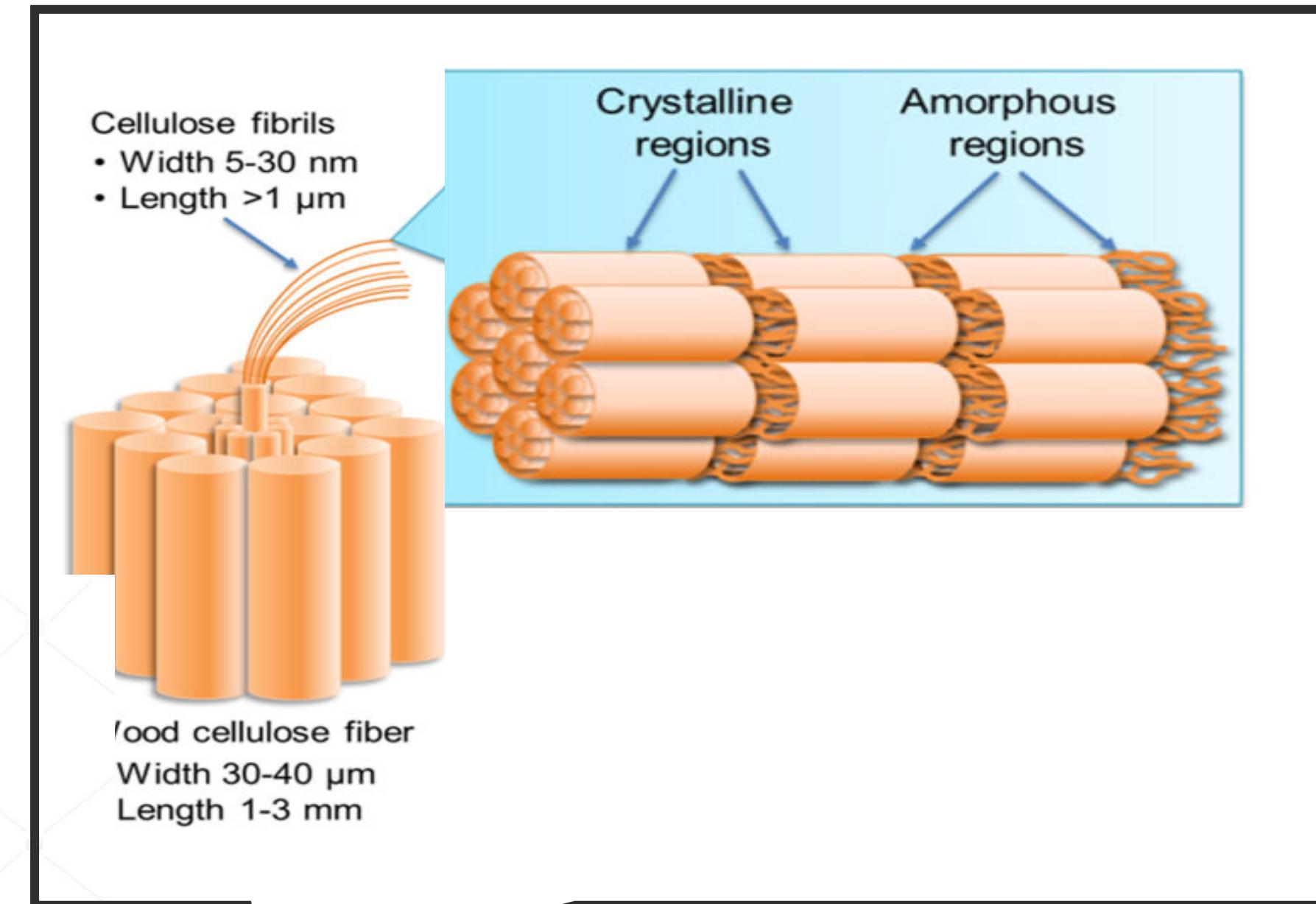
- Length of chain: longer chain → amorphous
- Branching of chains: branched chains, cross-linked → amorphous
- Copolymers: alternating copolymer → crystalline, rest form amorphous
- Tacticity or Stereoisomerism: isotactic and syndiotactic → crystalline, atactic → amorphous
- Plasticizers: low molecular weight additives added to separate the chains and prevent crystallization e.g. glycerol, polyethylene glycol

# Spherulite in natural rubber



Transmission electron micrograph showing the spherulite structure in a natural rubber specimen. Chain-folded lamellar crystallites approximately 10 nm thick extend in radial directions from the center; they appear as white lines in the micrograph. 30,000X.

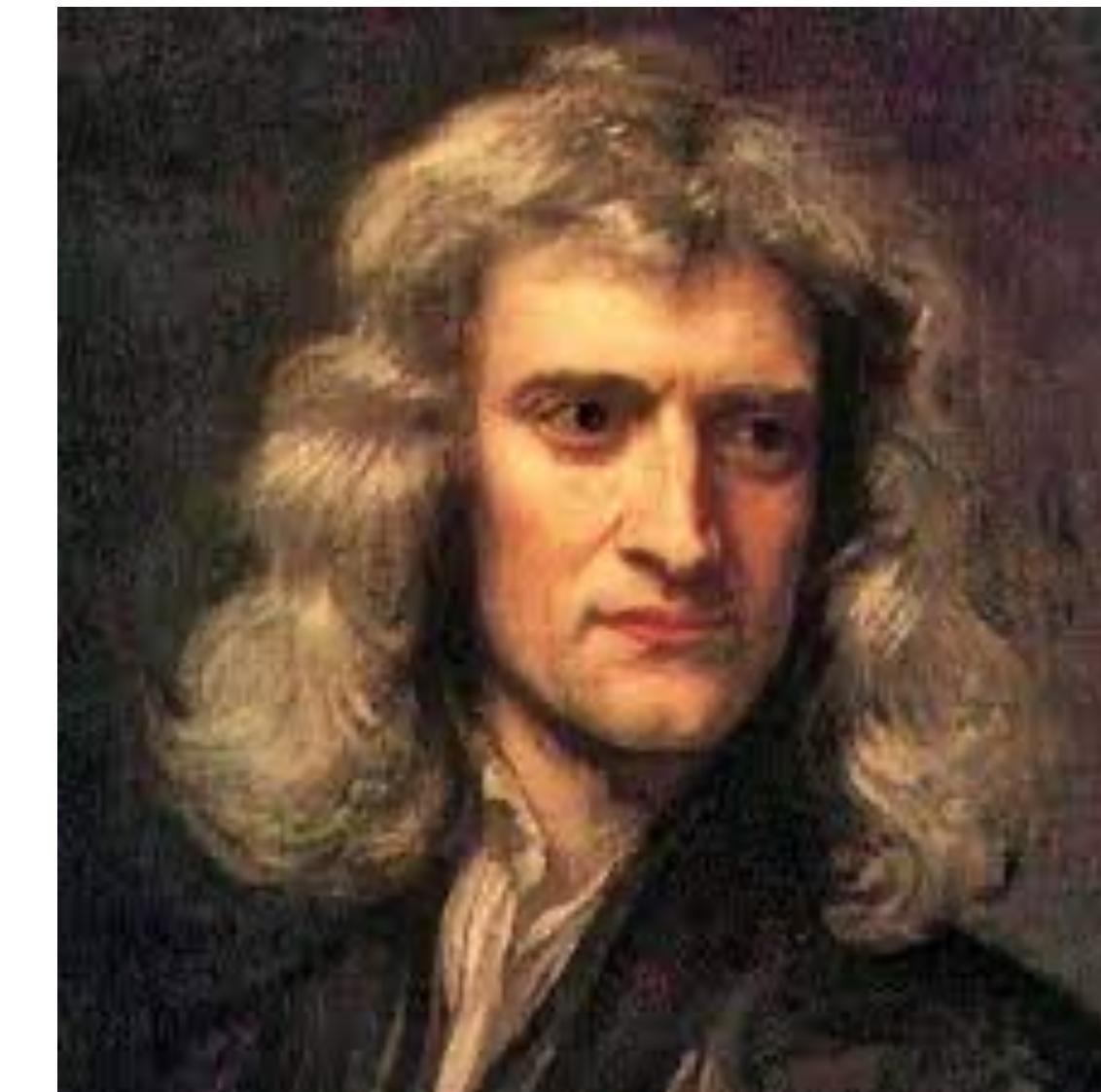
# Semi-crystalline cellulose fibres in wood



# Mechanical behaviour of materials



Robert Hooke

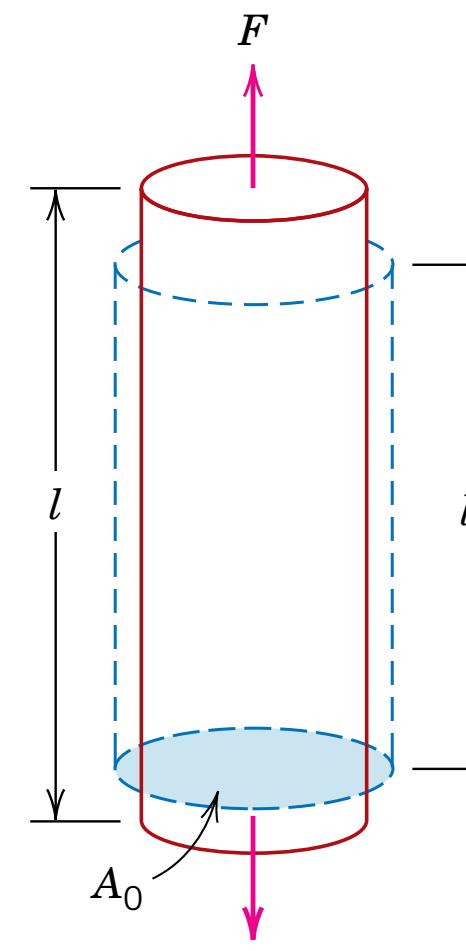


Isaac Newton

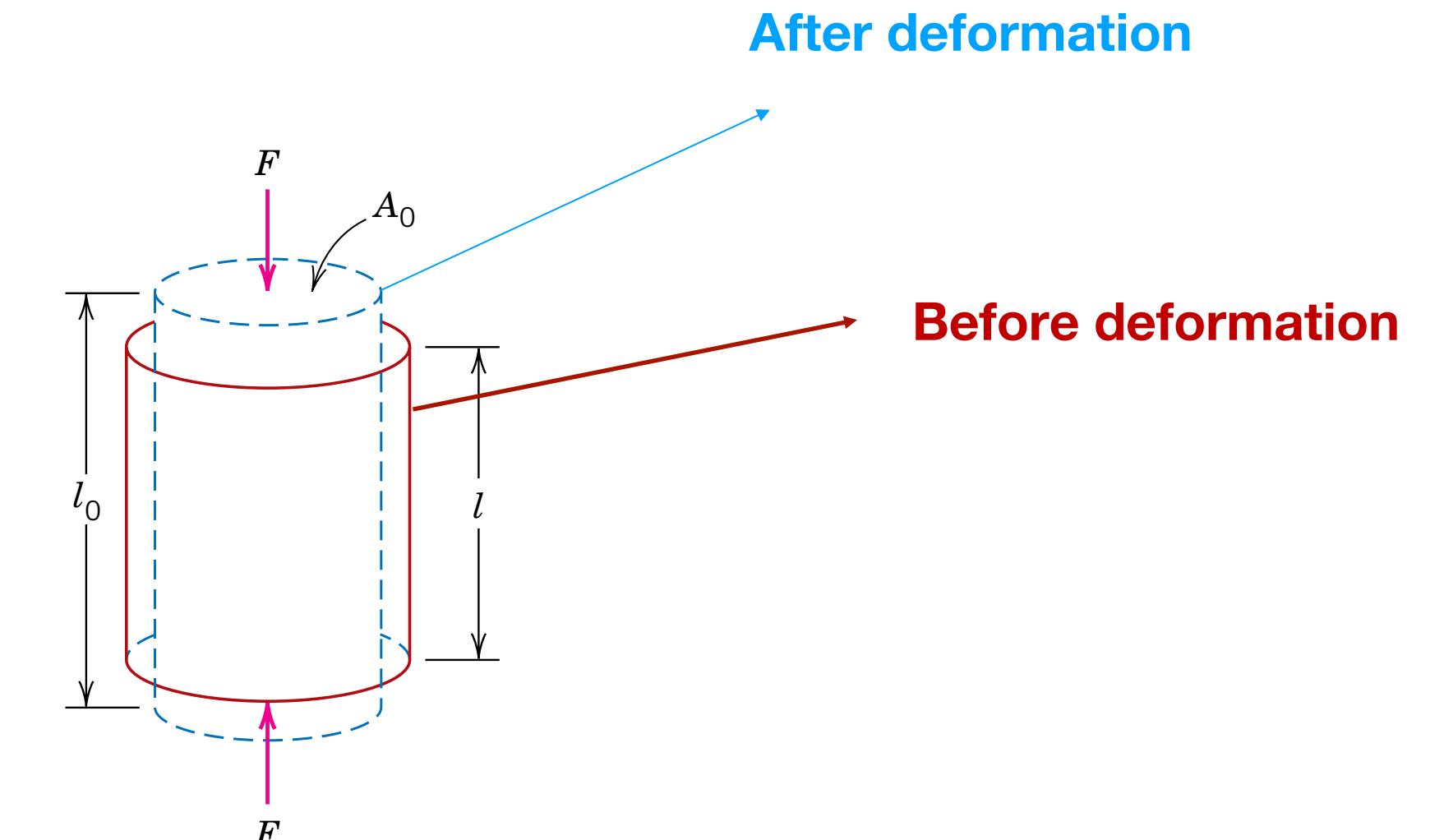
# Mechanical Behaviour of Materials

## Force (or Load) on material

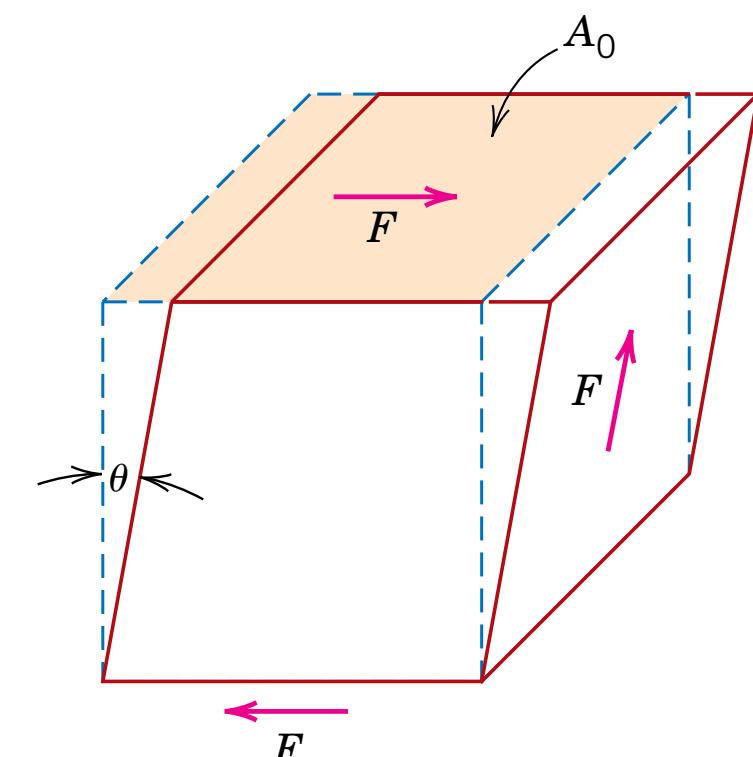
- Tension
- Compression
- Shear
- Torsion



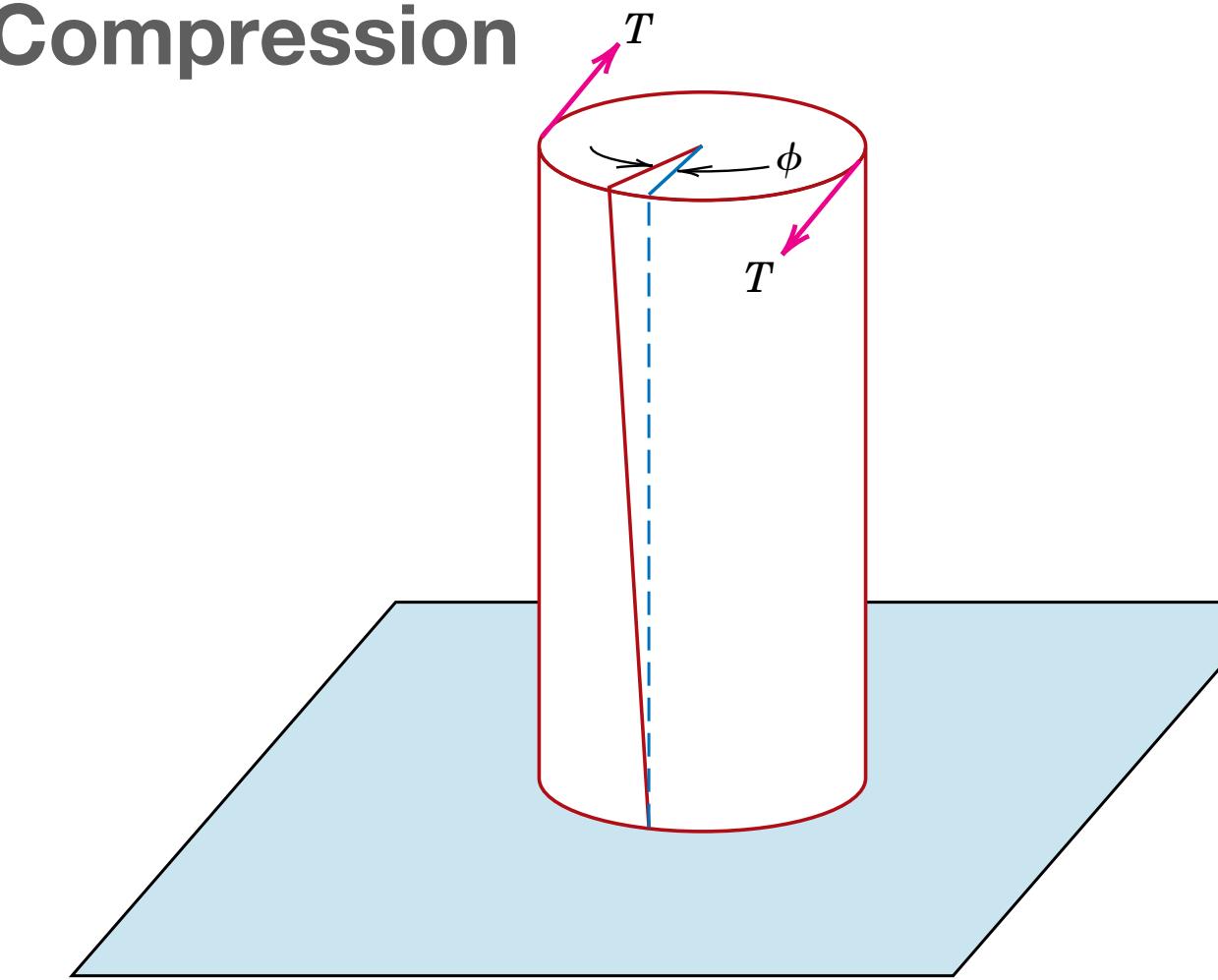
(a)  
Elongation



(b)  
Compression



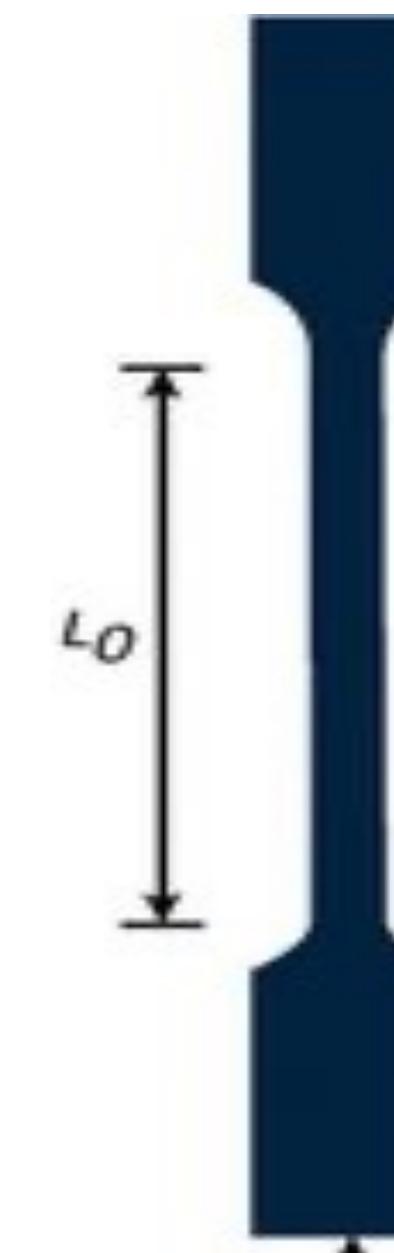
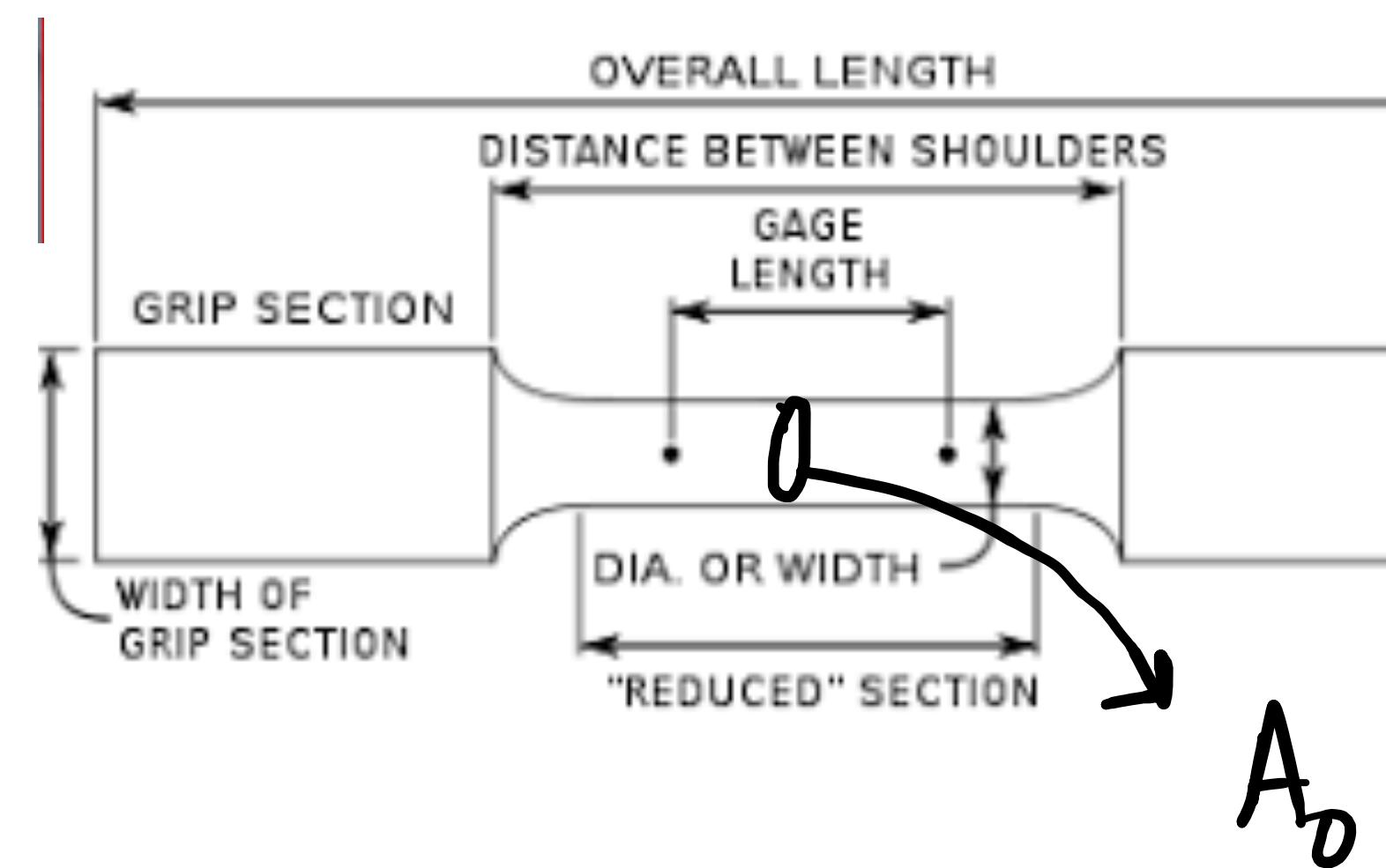
(c)  
Shear



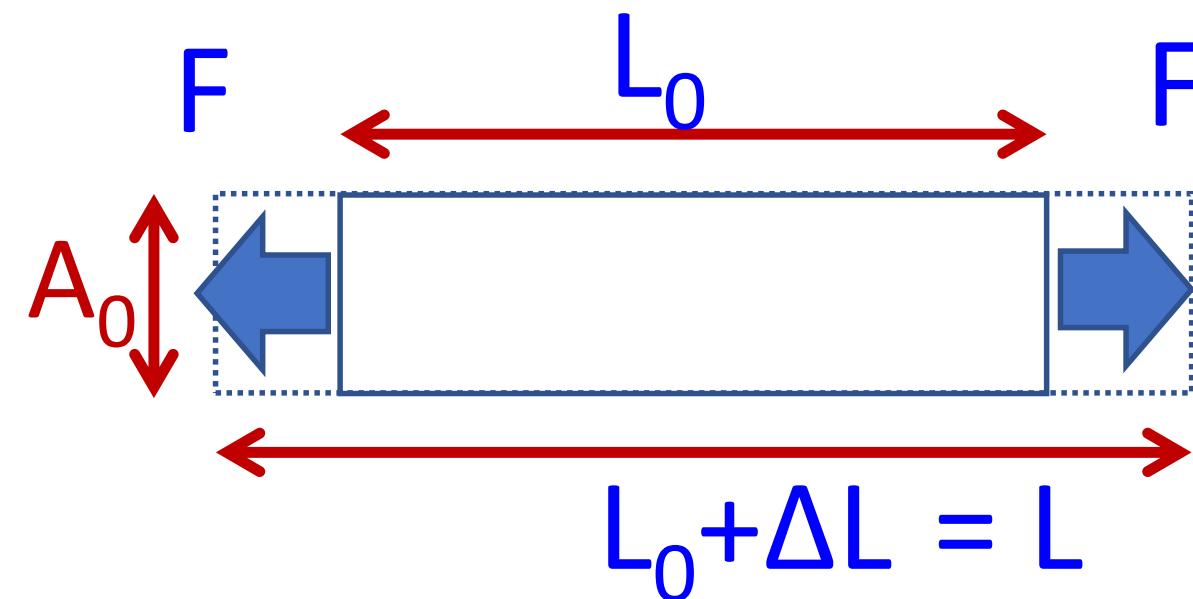
(d)  
Torsion

# Uniaxial Tensile Test

- If a load is static or changes relatively slowly with time and is applied uniformly over a cross section or surface of a member, the mechanical behavior may be ascertained by a simple stress-strain test; these are most commonly conducted for metals at room temperature.
- A specimen is deformed, usually to fracture, with a gradually increasing tensile load that is applied uniaxially along the long axis of a specimen.
- This “dogbone” specimen configuration was chosen so that, during testing, deformation is confined to the narrow center region (which has a uniform cross section along its length), and, also, to reduce the likelihood of fracture at the ends of the specimen.
- The specimen is mounted by its ends into the holding grips of the testing apparatus.



# Engineering Stress and Strain



Engineering Stress = Instantaneous Force  
Initial cross-section area

Engineering Strain = Elongation  
Initial Length

$$\sigma = \frac{F}{A_0} \left( \text{units } \frac{\text{N}}{\text{m}^2} = \text{Pa} \right)$$

$$\epsilon = \frac{\Delta L}{L_0} = \frac{L - L_0}{L_0}$$

$$\Rightarrow \epsilon = \frac{L - L_0}{L_0}$$

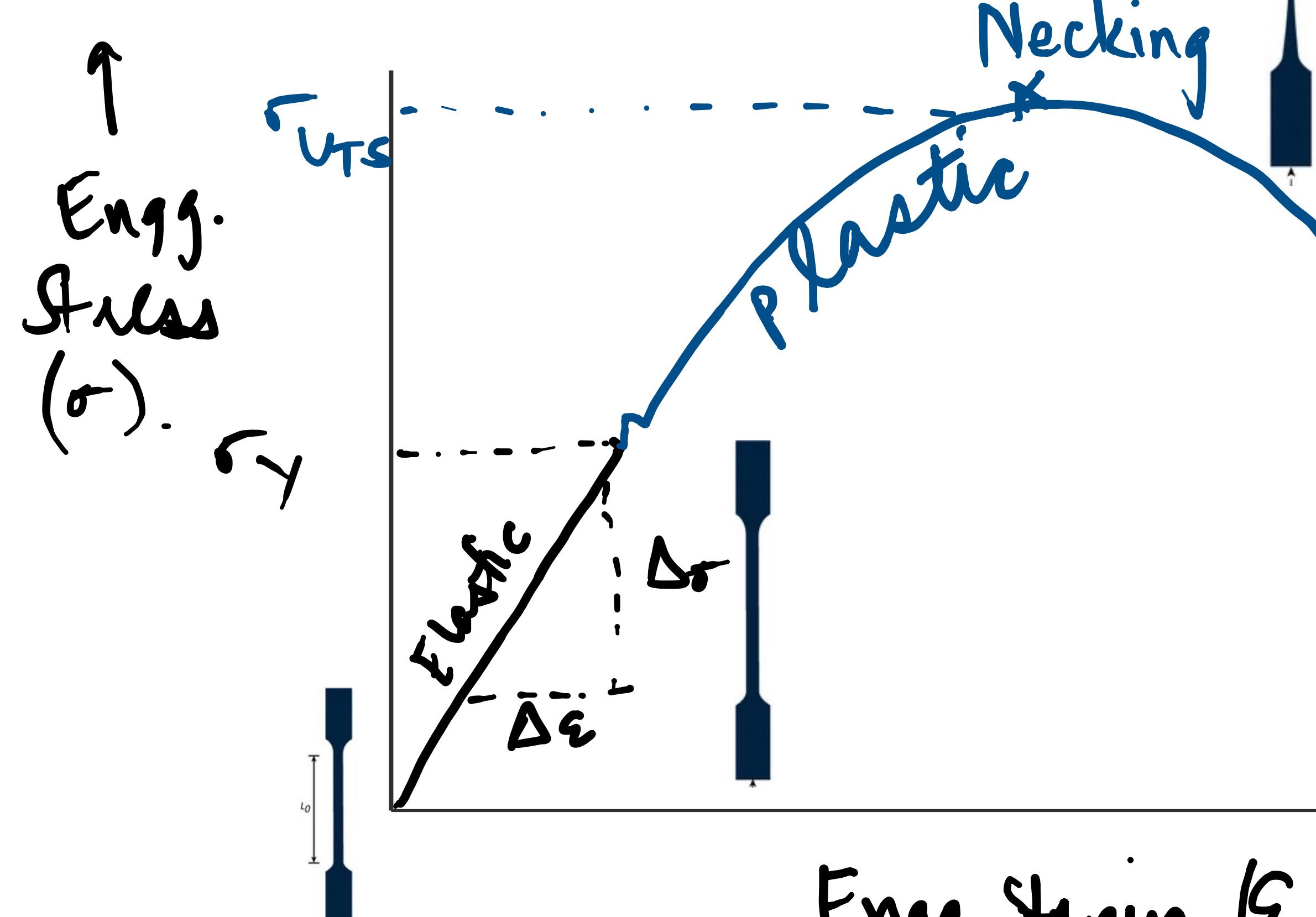
(dimensionless quantity)

Why divide by area?  
Suppose you want to find the stress of a weight of 200 pounds on a steel material of area of 3 inches by 4 inches. And compare the performance of the same steel in a part of a bridge with area 20 feet by 5 feet when it is crossed by a vehicle weighing 100 tons (or 224000 pounds).

The stress in both the cases is 16.67 pounds/sq.inch

# Stress-strain curve

Load-Elongation curve



Energy per unit vol reqd to cause fracture

$$\text{Eng. Strain } (\varepsilon = \Delta L / L_0)$$

$$\begin{aligned} \text{Units of area} &= \text{Nm}^{-2} = \frac{\text{Nm}}{\text{m}^2} \\ &= \text{J m}^{-3} \end{aligned}$$

- $\sigma_y$  = Yield stress (plastic deformation begins)
- $\sigma_{UTS}$  = Ultimate tensile stress (where Necking happens: decrease in  $A_0$ )
- $\epsilon_f$  = fracture strain
- Elastic modulus or Young's modulus

$$Y = \frac{\Delta \sigma}{\Delta \varepsilon} \quad (\text{stiffness})$$

• Area under curve = work done to fracture

• Tensile strength

= Max load

$$A_0$$

# Mechanical Properties derived from Tensile test

- **Strength:** Yield stress or ultimate tensile strength  $(\sigma_{UTS})$   
 $(\sigma_y)$   
*(Ability to resist plastic deformation)*
- **Stiffness:** Young's modulus: Ability to resist elastic deformation
- **Toughness:** Area under the curve: Energy absorbed per unit volume upto fracture.
- **Ductility:** Elongation strain at fracture point: Ability to undergo plastic deformation

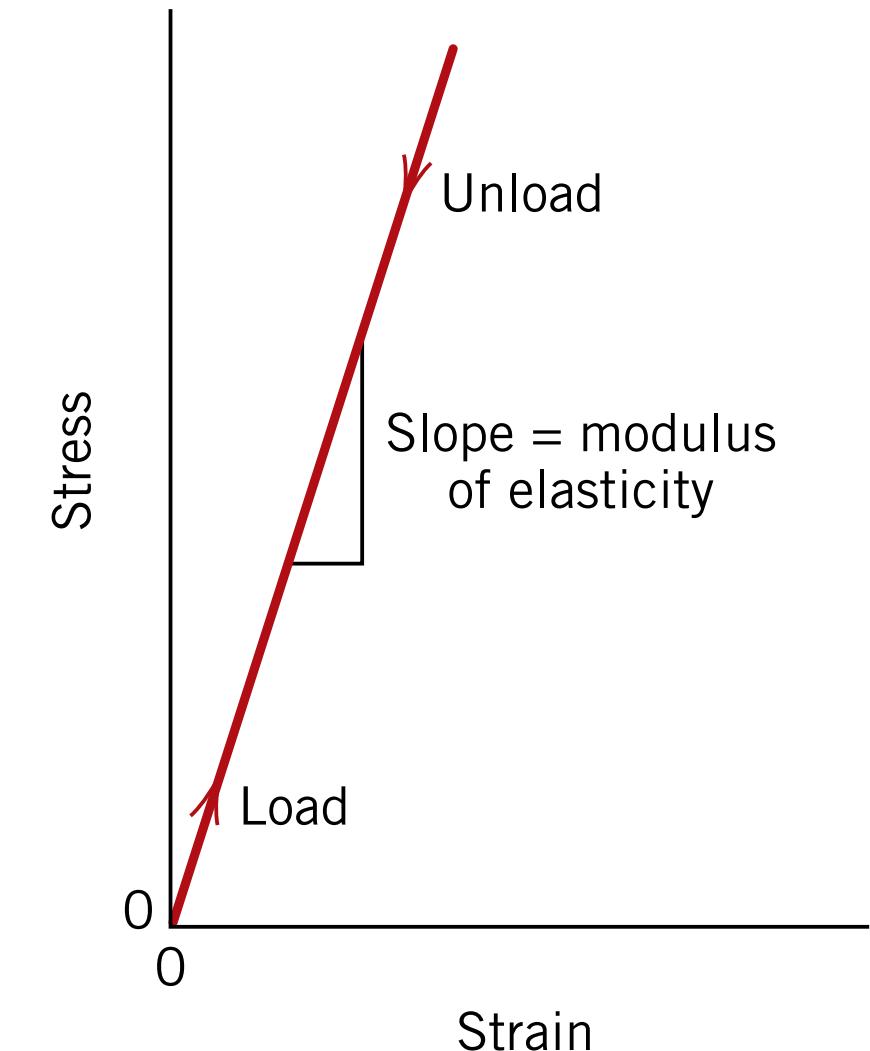
# Elastic deformation

*Deformation in which stress and strain are linearly proportional*

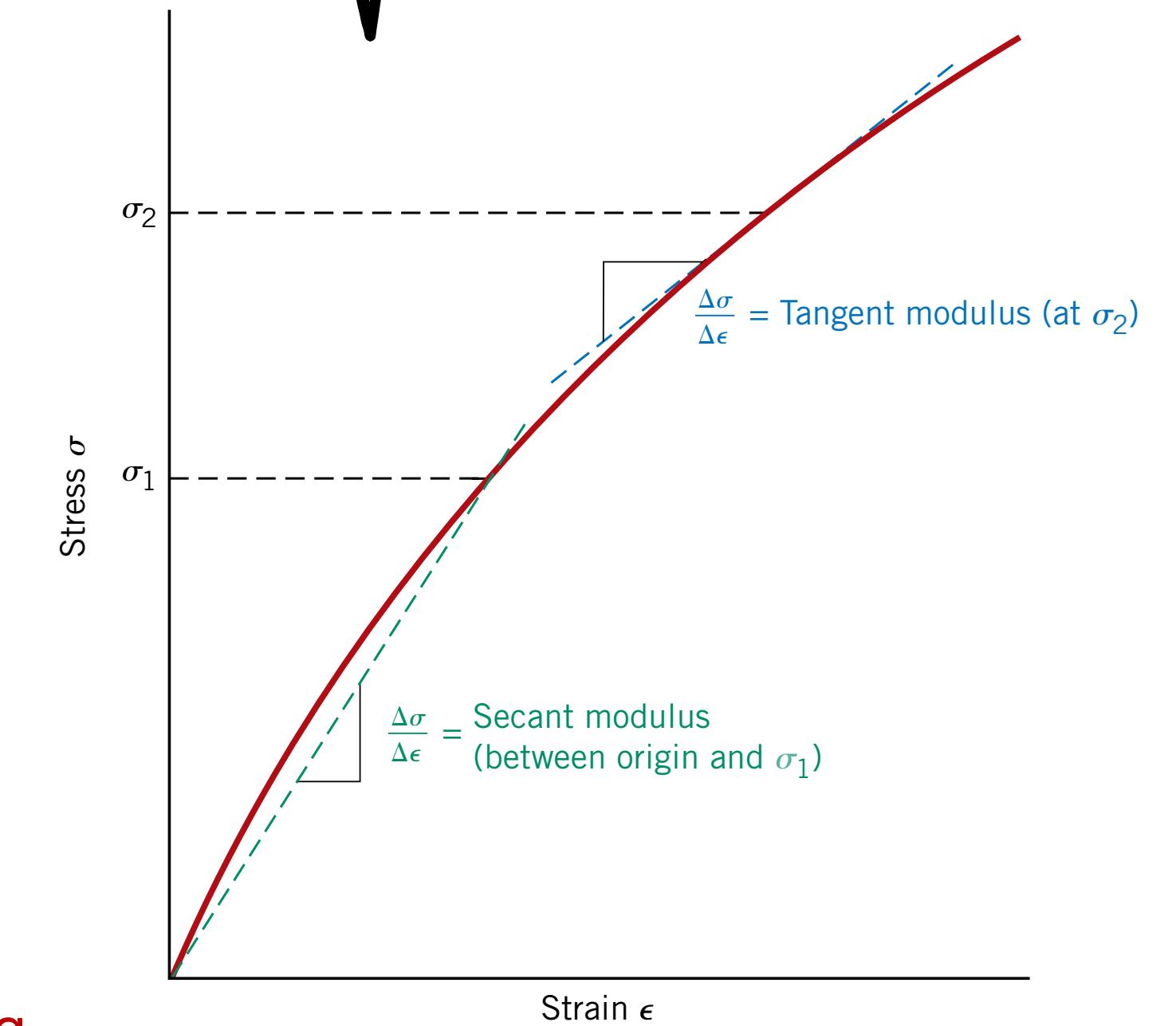
- Hooke's law:

$$(F = k \cdot \Delta x) \Rightarrow \sigma = Y \epsilon, \text{ where } Y = \text{Young's modulus or modulus of elasticity}$$

- For most typical metals the magnitude of this modulus ranges between 45 GPa ( $6.5 \times 10^6$  psi), for magnesium, and 407 GPa ( $59 \times 10^6$  psi), for tungsten.
- The greater the modulus, the stiffer the material, or the smaller the elastic strain that results from the application of a given stress.
- Elastic deformation is *non-permanent*: when the applied load is released, the piece returns to its original shape
- Young's modulus is a characteristic of each substance due to its chemical nature.

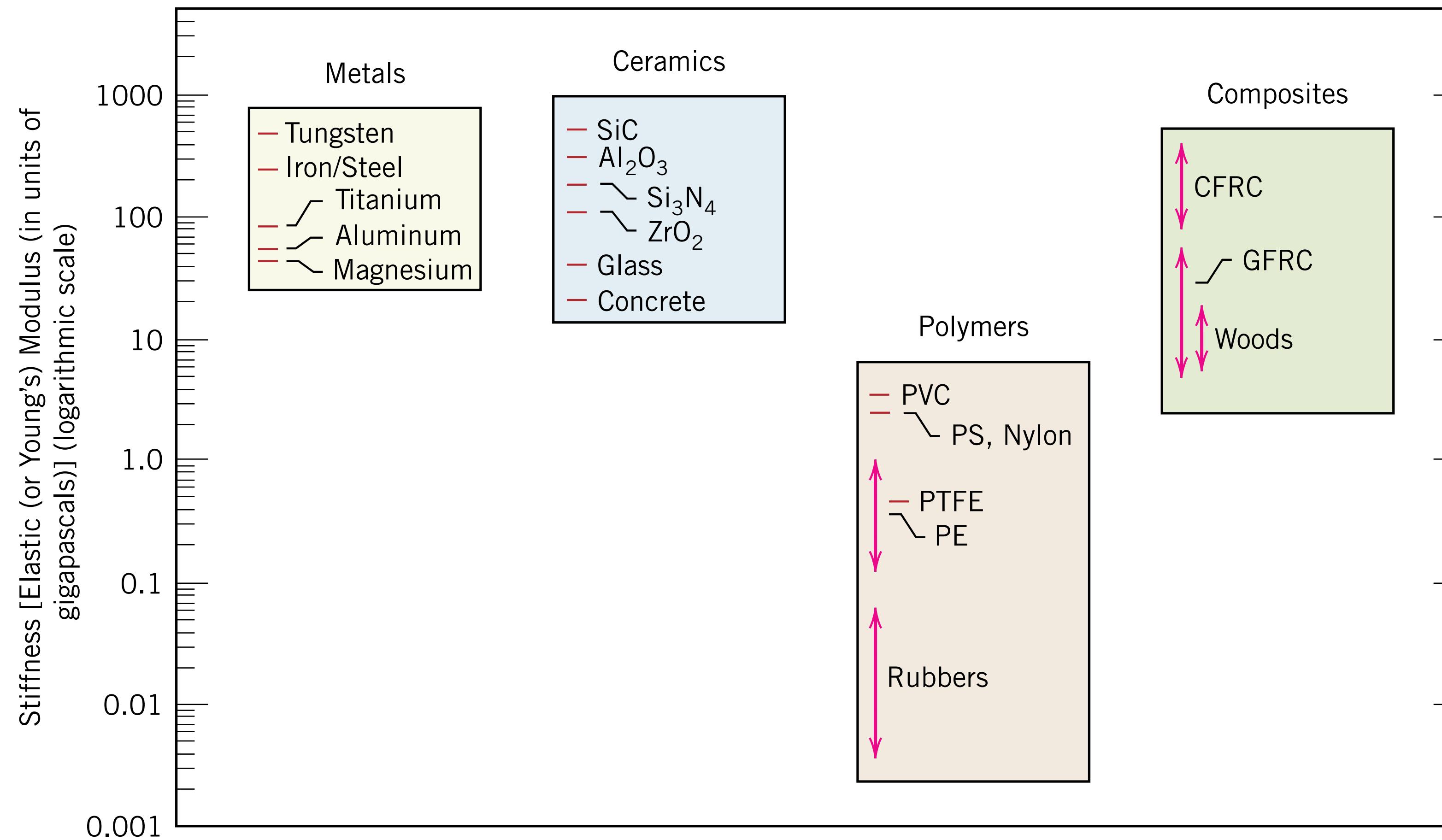


stress-strain diagram showing linear elastic deformation for loading and unloading cycles



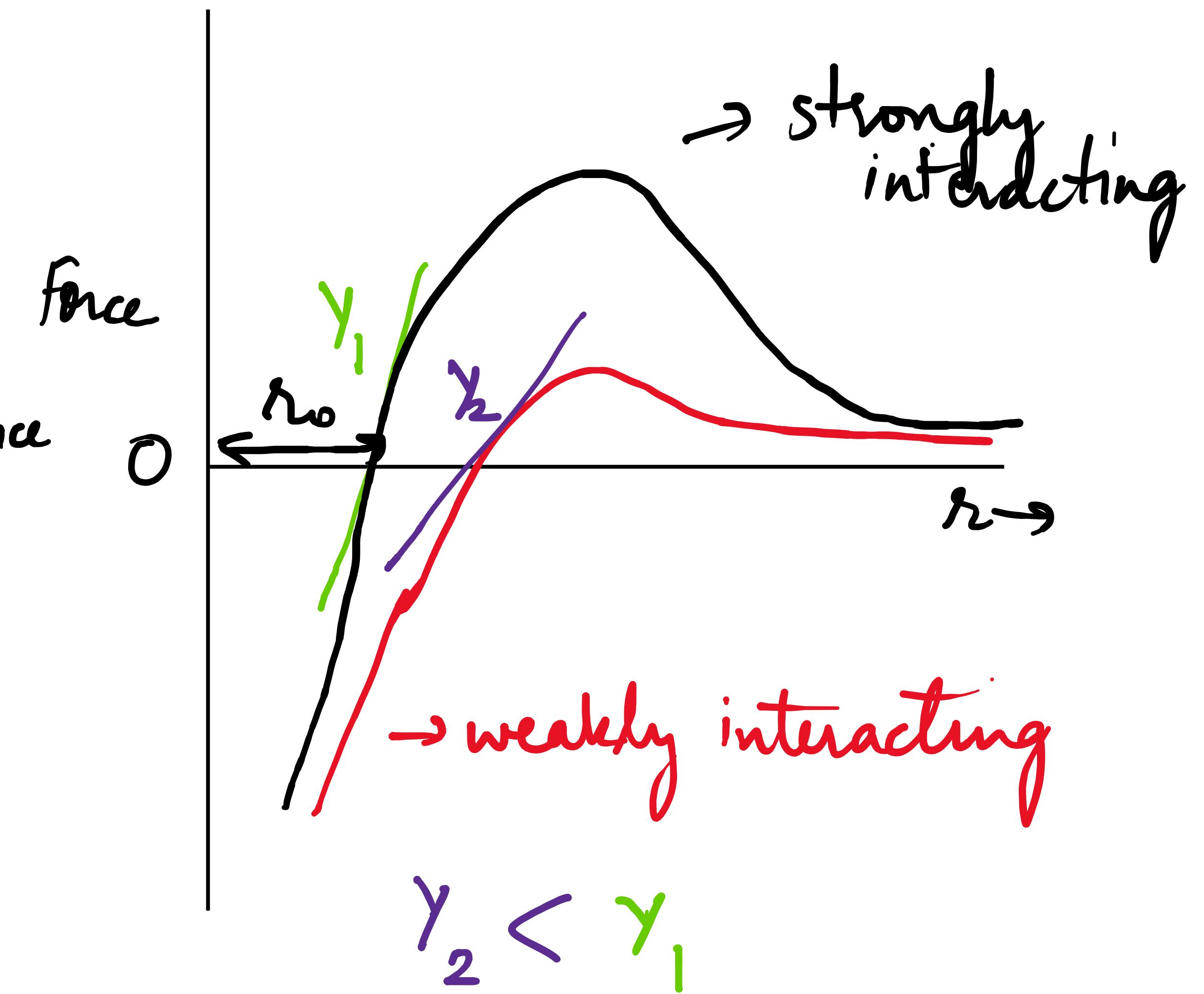
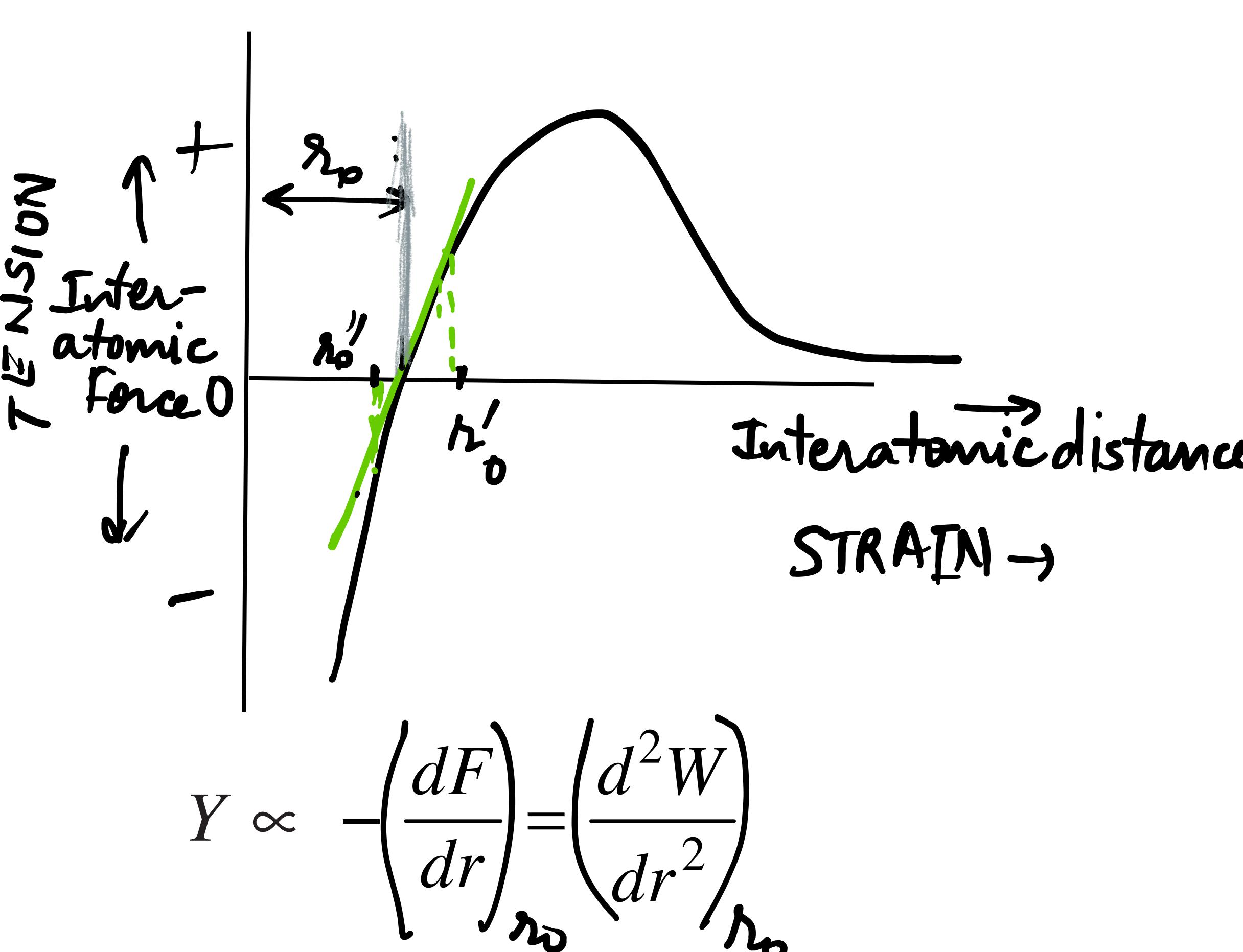
tangent or secant modulus for gray cast iron, concrete, and many polymers

# Classification of materials based on elastic modulus



# Atomic model of Elastic deformation

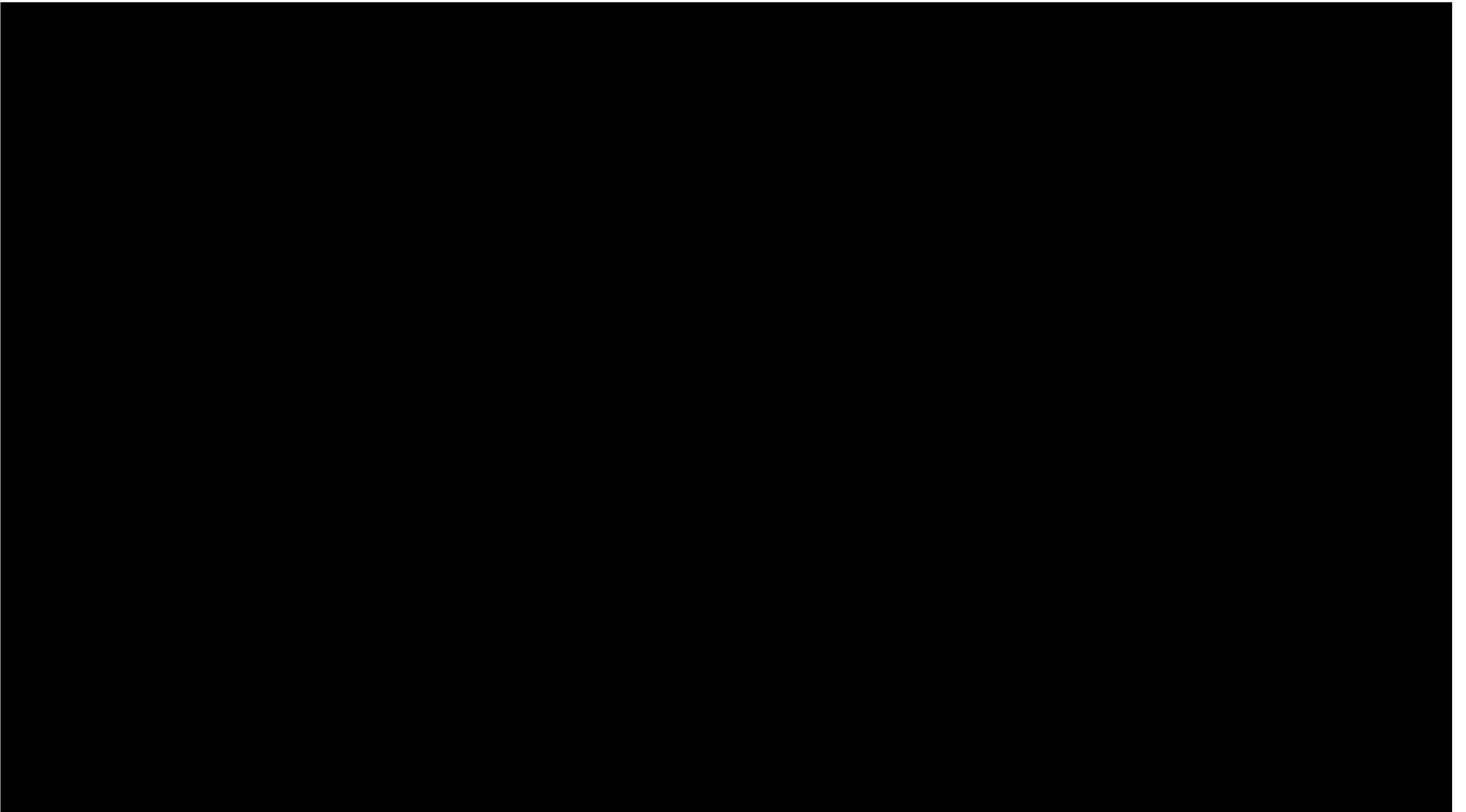
- Elastic strain is manifested as small changes in the interatomic spacing and the stretching of interatomic bonds.
- Magnitude of the modulus of elasticity is a measure of the resistance to separation of adjacent atoms, that is, the interatomic bonding forces.



# Hold on to it!

We will study ***why we don't fall through the floor*** in the next class using concepts studied today and as given by both the geniuses: Hooke and Newton!

Here's a preview...



# **Quiz-3 on 15th March 2022 (Online mode)**

- Syllabus: topics covered after Minor till 11<sup>th</sup> March (including lecture 26)

# Lecture 27

## Mechanical Behaviour of Materials

### Textbooks:

- Introduction to materials science and Engineering: V. Raghavan
- Materials Science and Engineering: Callister and Rethwisch

Prof. Divya Nayar

Department of Materials Science and Engineering

[divyanayar@mse.iitd.ac.in](mailto:divyanayar@mse.iitd.ac.in)

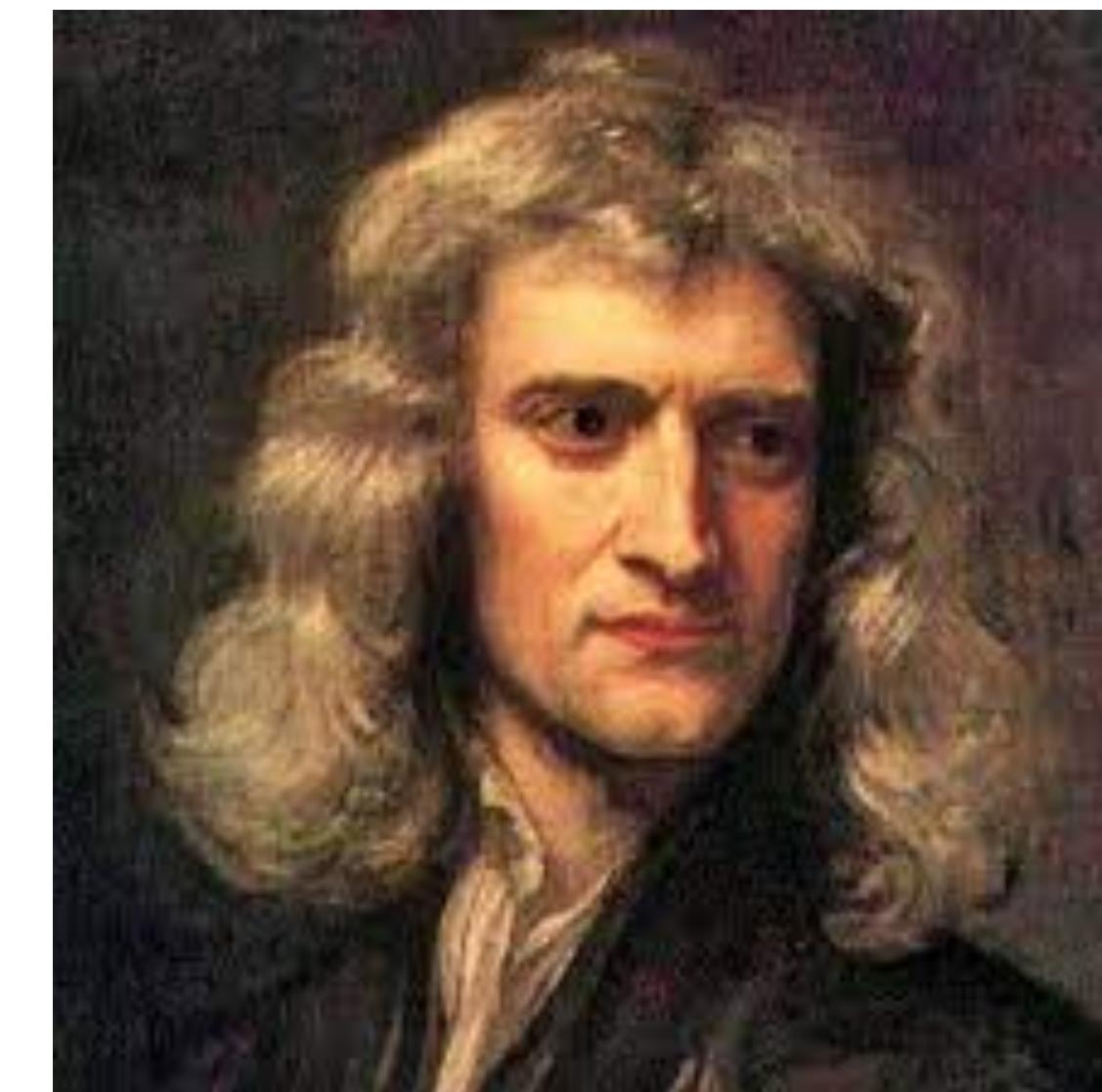
# Recap...

1. Polymers semi-crystallinity: lamellae and spherulites
2. Engineering Stress and Strain
3. Tensile test
4. Different mechanical properties from tensile test

# Mechanical behaviour of materials



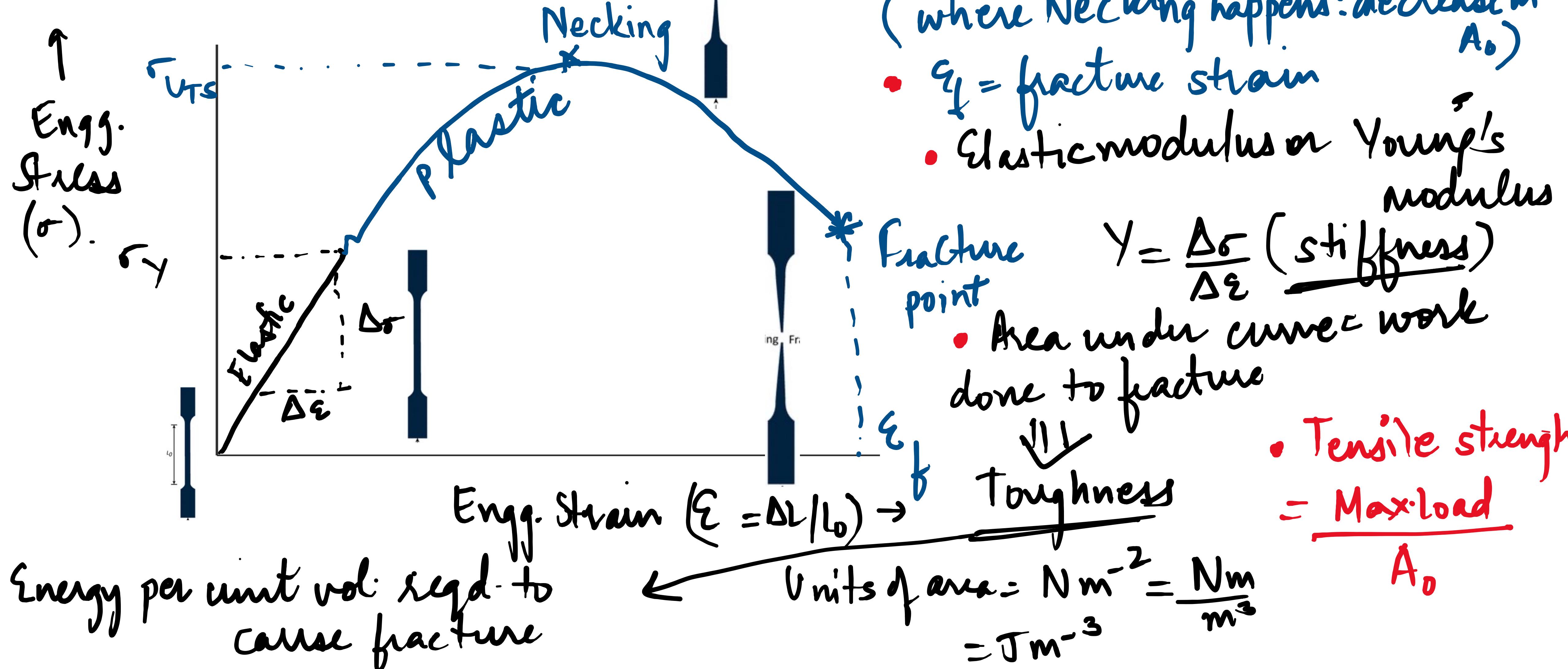
Robert Hooke



Isaac Newton

# Stress-strain curve

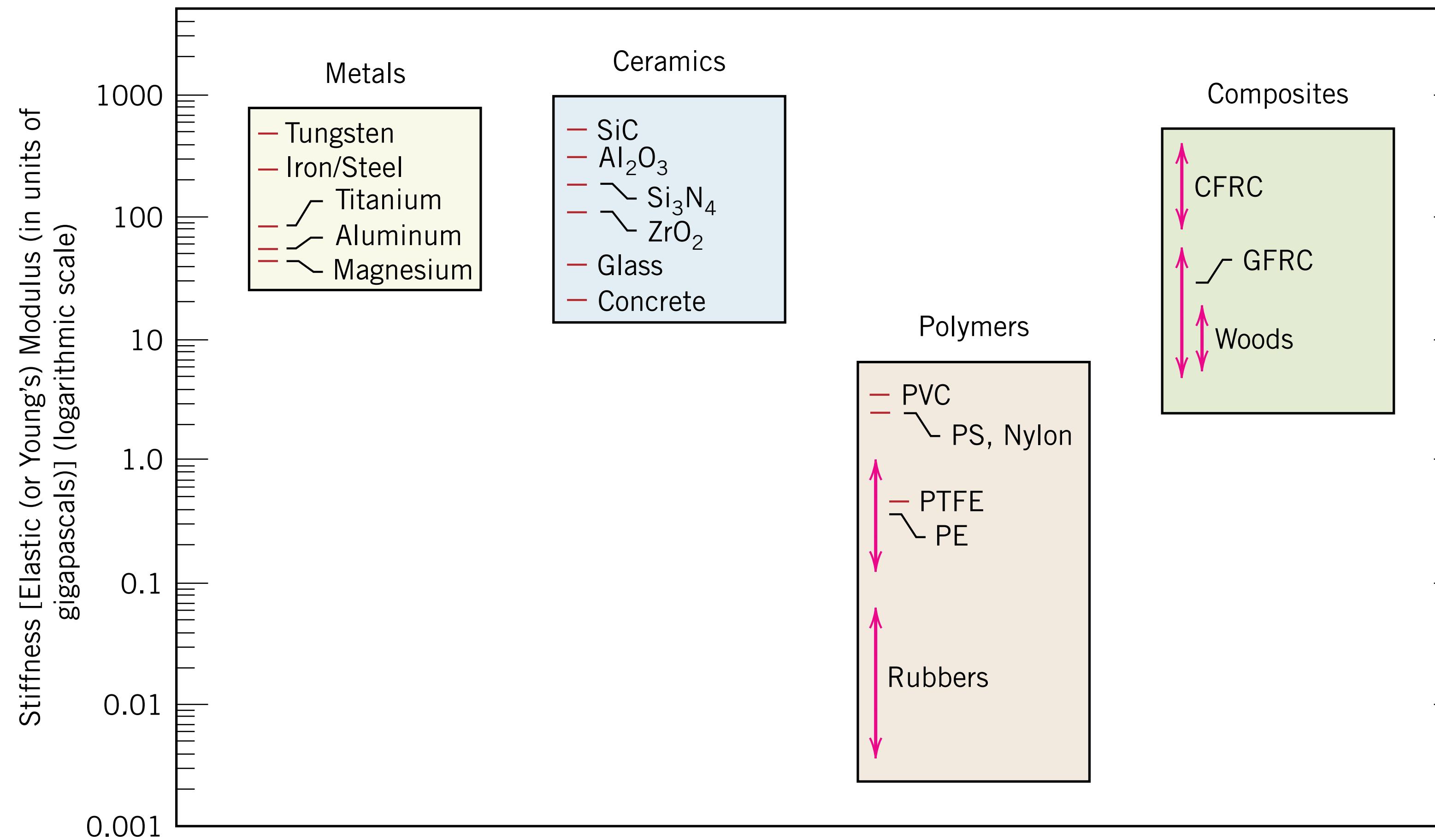
Load-Elongation curve



# Mechanical Properties derived from Tensile test

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 $(\sigma_y)$   
*(Ability to resist plastic deformation)*
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# Classification of materials based on elastic modulus



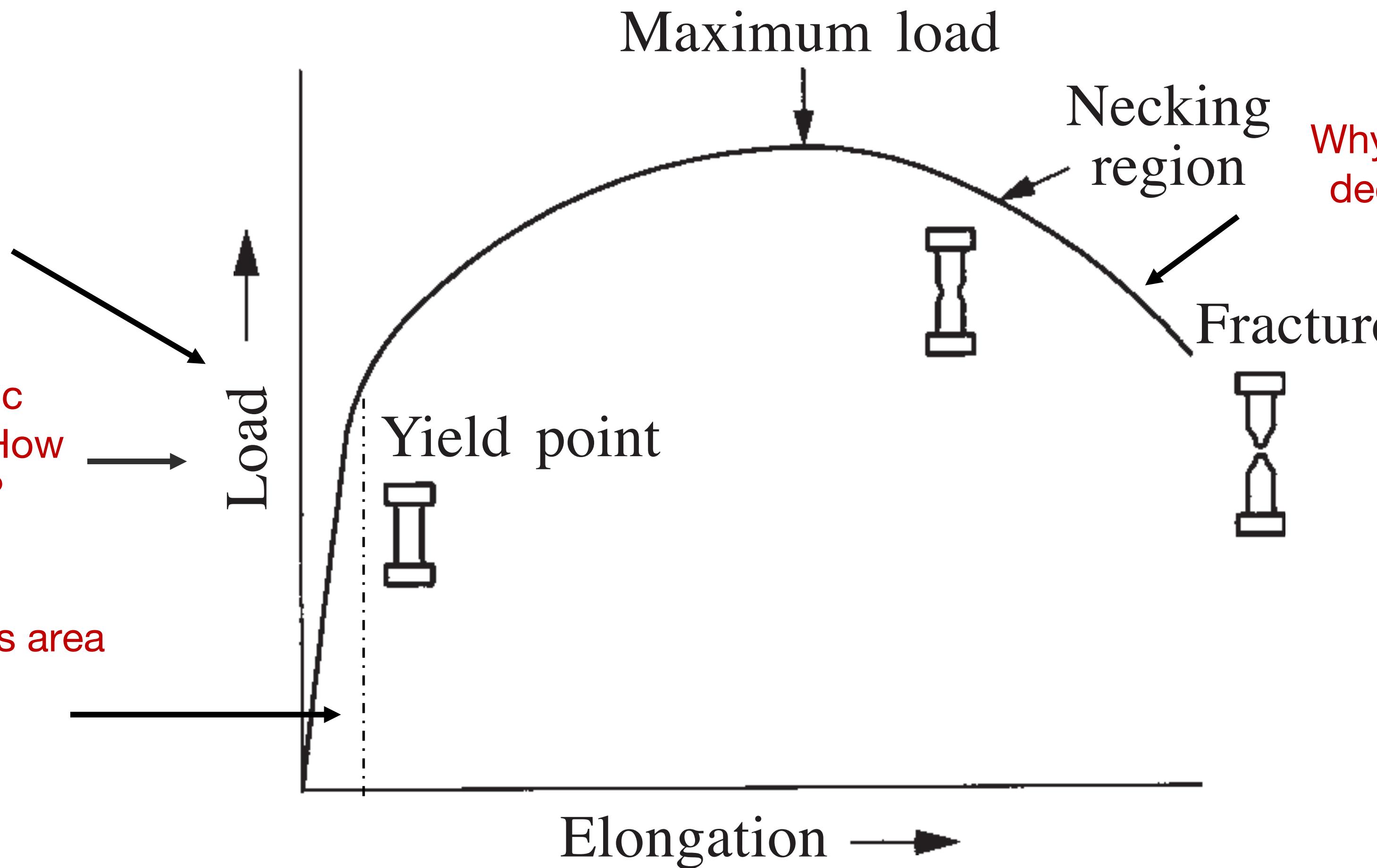
# Some obvious questions from stress-strain curve?

What if the elastic regime is non-linear? How to find Young's modulus?

What if elastic-to-plastic deformation is smooth? How to find the yield point?

What property does this area provide?

Why the Engineering stress decreases after necking?



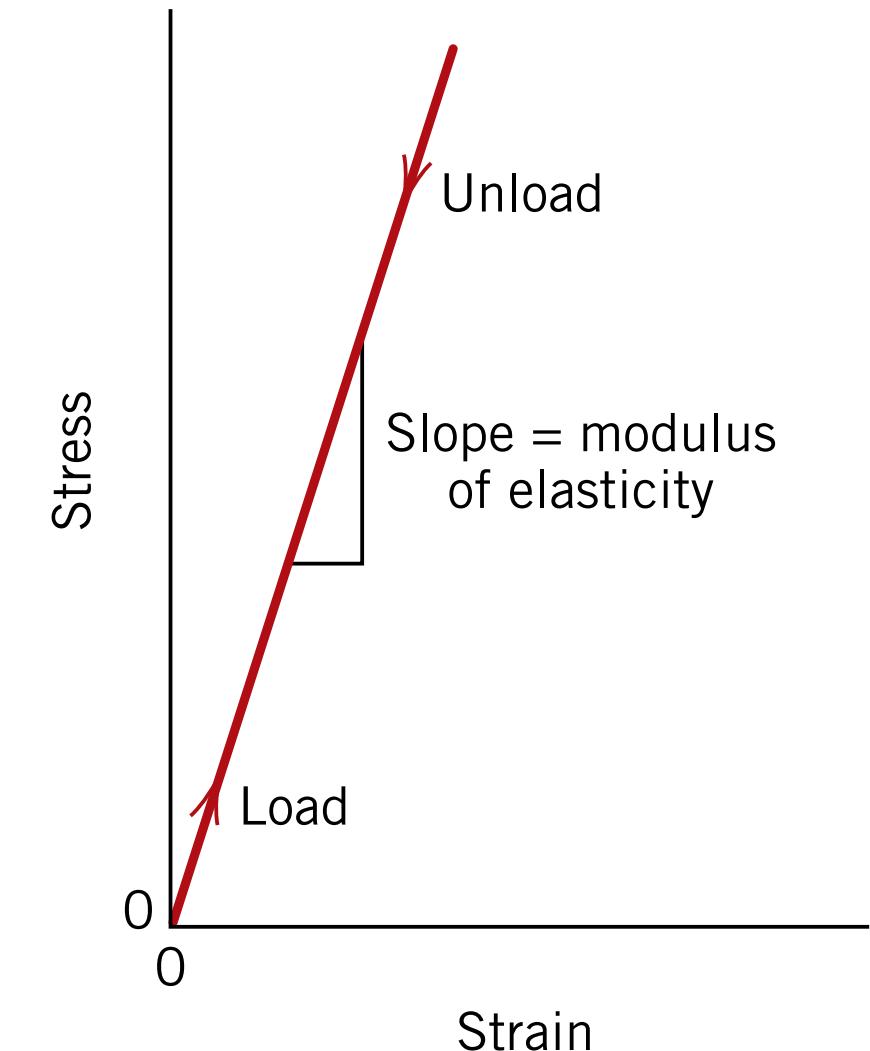
# Elastic deformation

*Deformation in which stress and strain are linearly proportional*

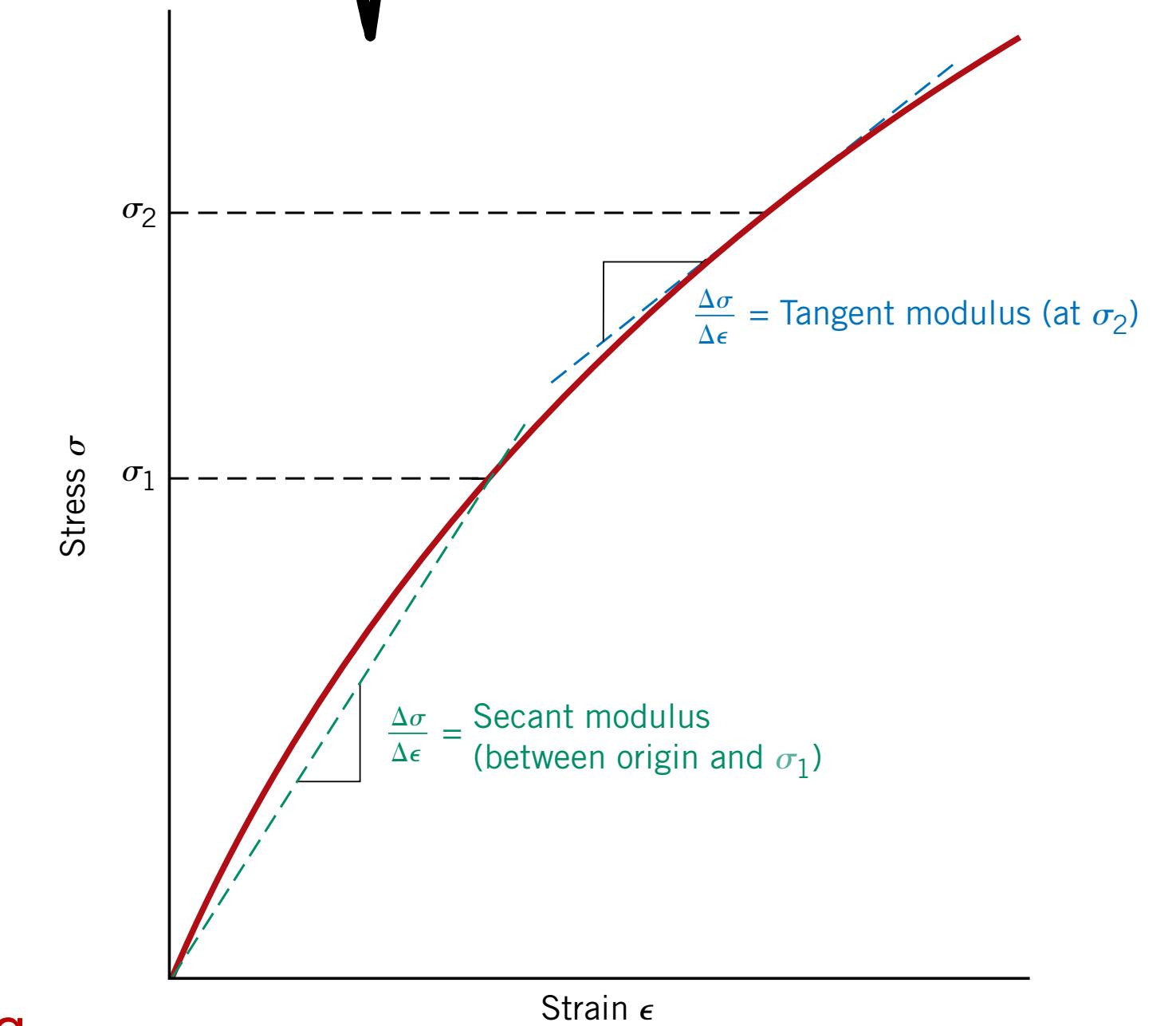
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- The greater the modulus, the stiffer the material, or the smaller the elastic strain that results from the application of a given stress.
- Elastic deformation is *non-permanent*: when the applied load is released, the piece returns to its original shape
- Young's modulus is a characteristic of each substance due to its chemical nature.



stress-strain diagram showing linear elastic deformation for loading and unloading cycles



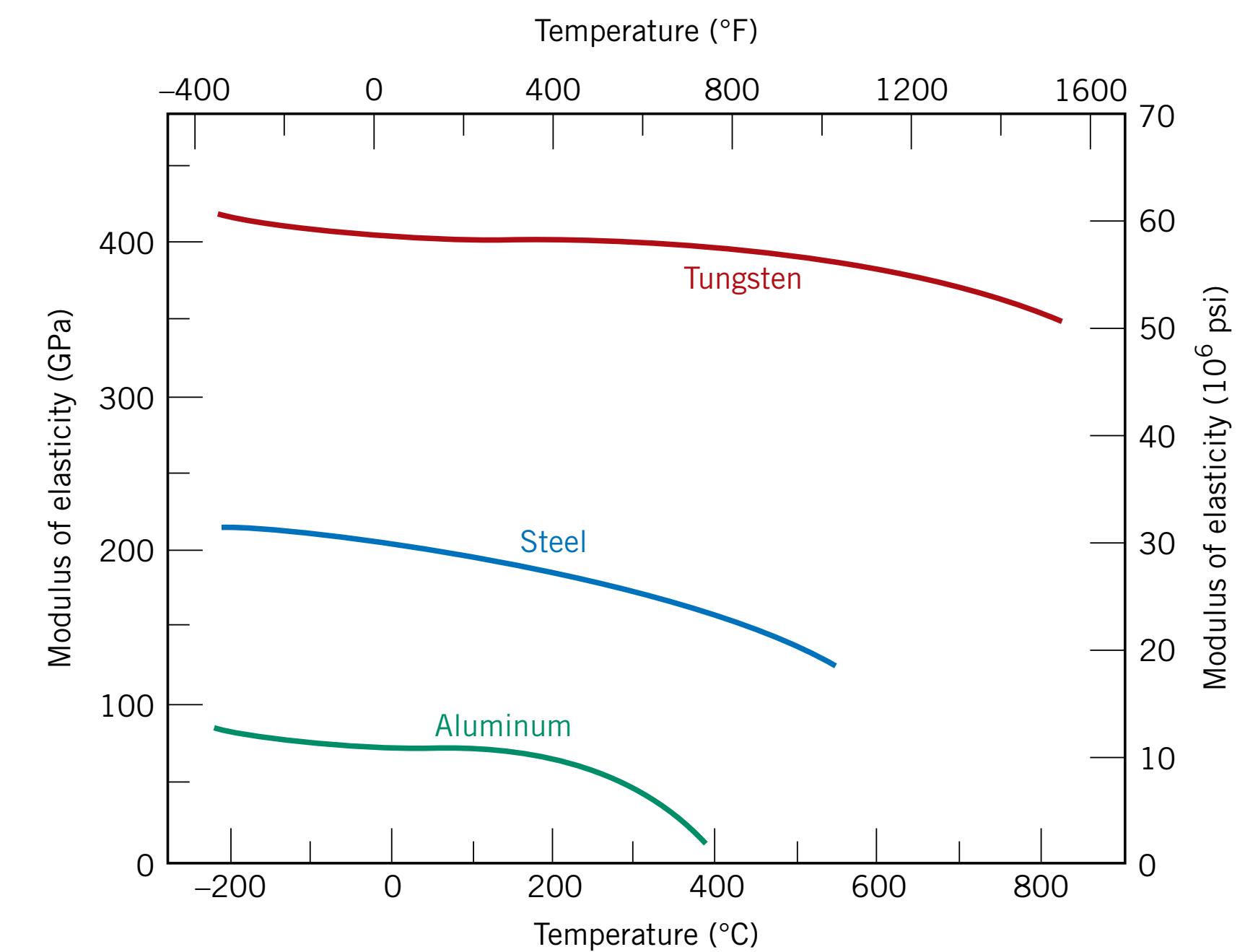
tangent or secant modulus for gray cast iron, concrete, and many polymers

# Tensile properties: Young's modulus

Element	Li	Be	B	C (dia)
Atomic number $Z$	3	4	5	6
Young's modulus $Y$ , GN m $^{-2}$	11.5	289	440	1140

Elements beyond carbon do not form solids with a three-dimensional network of covalent bonds. These would have moduli according to the strength of the secondary bonds in the solid, which are primarily stretched by an external stress

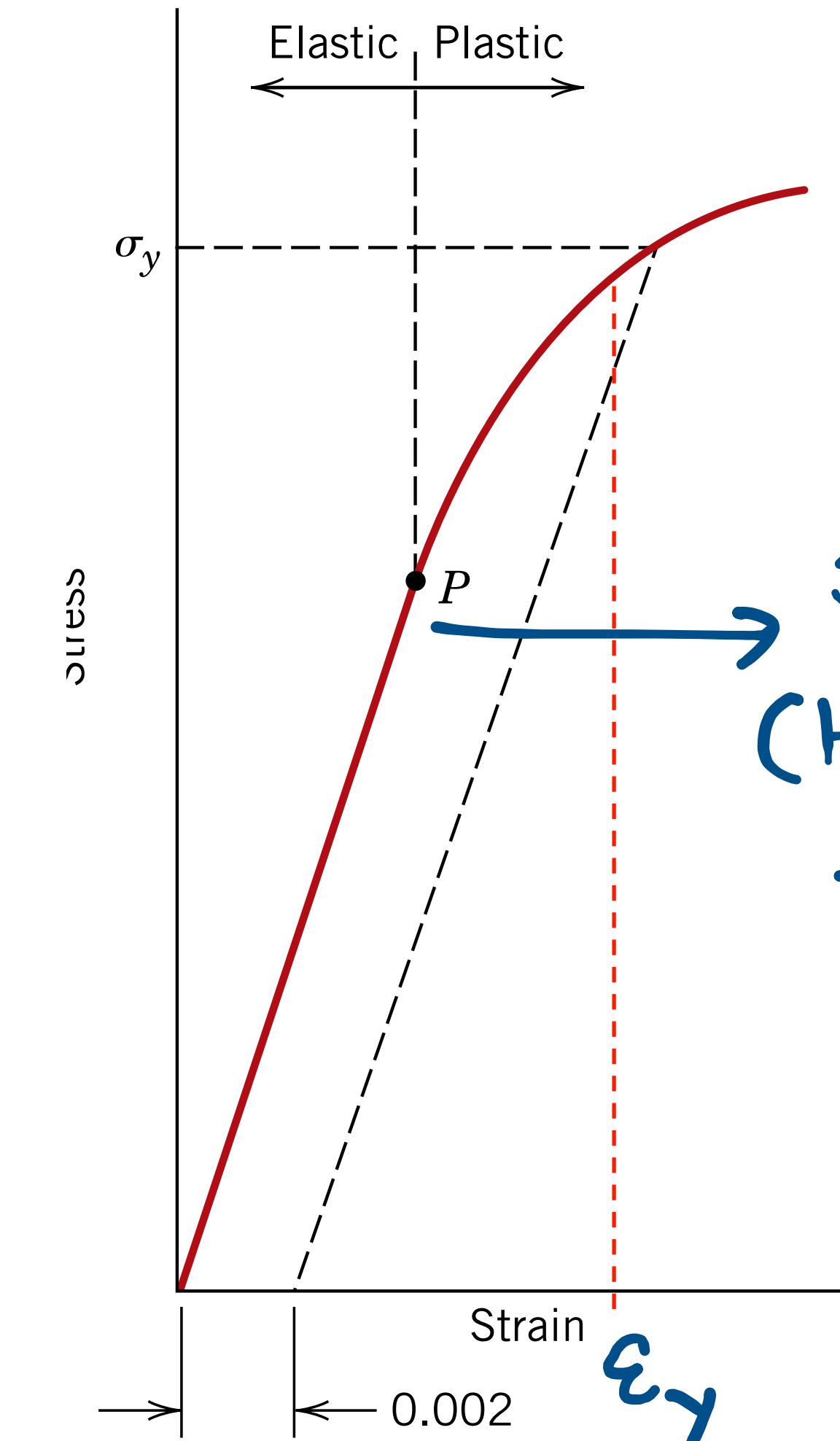
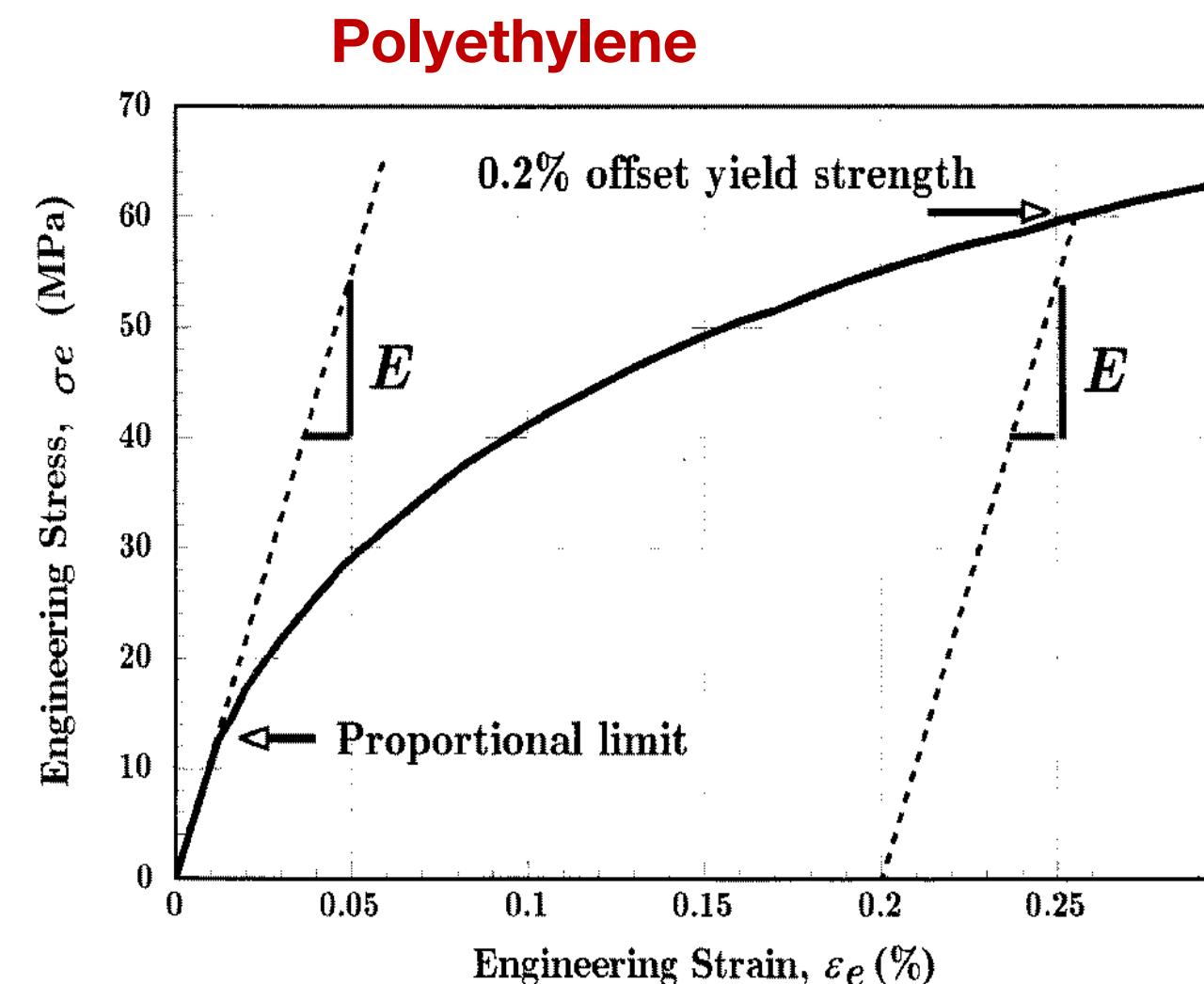
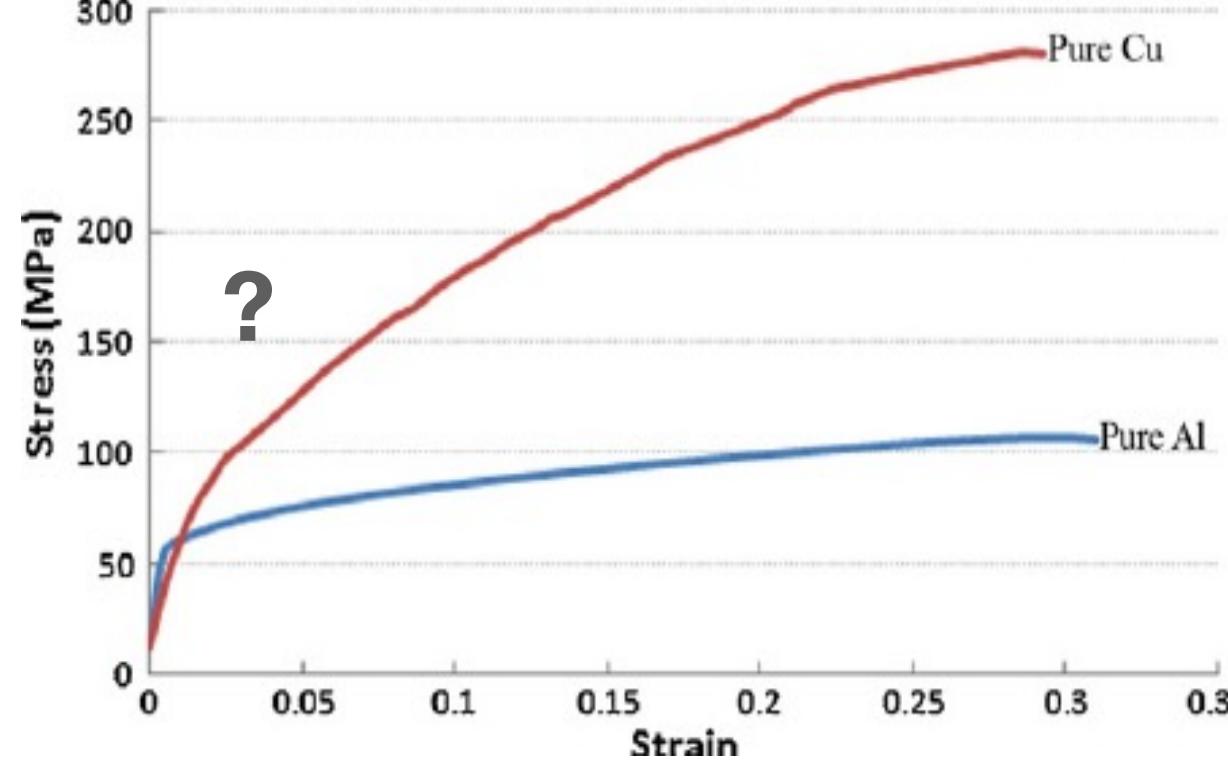
Element	C (dia)	Si	Ge	Sn	Pb	Graphite
Atomic number $Z$	6	14	32	50	82	6
Young's modulus $Y$ , GN m $^{-2}$	1140	103	99	52	16	8



**Elastic anisotropy:** the elastic properties become a function of the crystal direction. This anisotropy is particularly evident in materials which have two kinds of bonds. For example, the Young's modulus of graphite in the  $a$  direction parallel to the sheets is 950 GN m $^{-2}$ , which is much larger than that averaged over all directions, which is only 8 GN m $^{-2}$ .

# Tensile Properties: Yield stress

Offset yield stress: How to determine yield stress for gradual elastic-plastic deformation?



Proportional limit  
(Hooke's law is valid till this point)

0.2% proof strain

- **Proportional Limit:** initial departure from linearity of the stress-strain curve
- A straight line is constructed parallel to the elastic portion of the stress-strain curve at some specified strain offset, usually 0.002.
- For those materials having a nonlinear elastic region, use of the strain offset method is not possible, and the usual practice is to define the yield strength as the stress required to produce some amount of strain (e.g.,  $\varepsilon = 0.005$ ).

# Lecture 28

**Mechanical properties of Materials- Part 2**  
**True stress and true strain**



Robert Hooke



Isaac Newton

**Prof. Divya Nayar**  
**Department of Materials Science and Engineering**  
**[divyanayar@mse.iitd.ac.in](mailto:divyanayar@mse.iitd.ac.in)**

# **Quiz-4 : 2<sup>nd</sup> April 2022 (Saturday)**

## ***Offline mode: “Fun Quiz”***

- Syllabus: whole syllabus (including Prof. Sangeeta Santra's part)
- Duration: 2 hrs (**Suggested timings: 10 am-12 pm or 3 pm-5 pm**)
- Group activity: homogeneously distributed groups will be formed to participate in the quiz
- Marks: same weightage as earlier quizzes conducted
- Content (or questions) will be fun-based activities covering the topics taught in the lectures.
- Venue and final timing details will be shared soon.

# Recap...

1. Engineering Stress and Strain
2. Tensile test
3. Defined mechanical properties from tensile test
4. Offset yield stress

# Why do we need to study Tensile test?

***Why do we need to understand the strength of materials?***



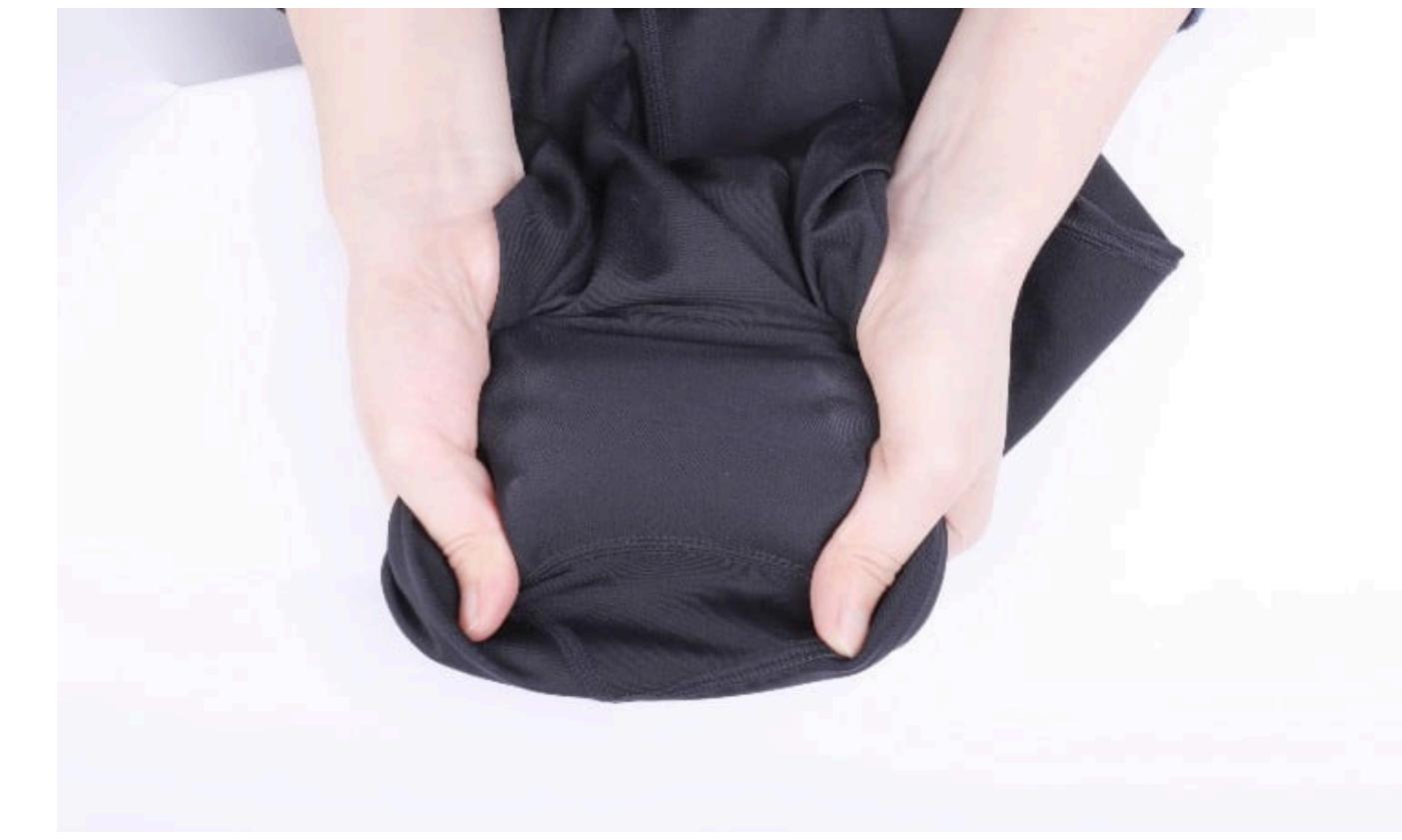
**Biscuit**

Stiff but weak



**Steel**

Stiff and strong



**Nylon**

Flexible and strong



**Bones**

Stiff, strong BUT brittle !!

**FRACTURE!!**

- STIFF
- STRONG
- FLEXIBLE
- WEAK
- BRITTLE

# Why do we need to study Tensile test?

***Why do we need to understand the failure of materials?***



We want some materials to bend



We want some materials to break

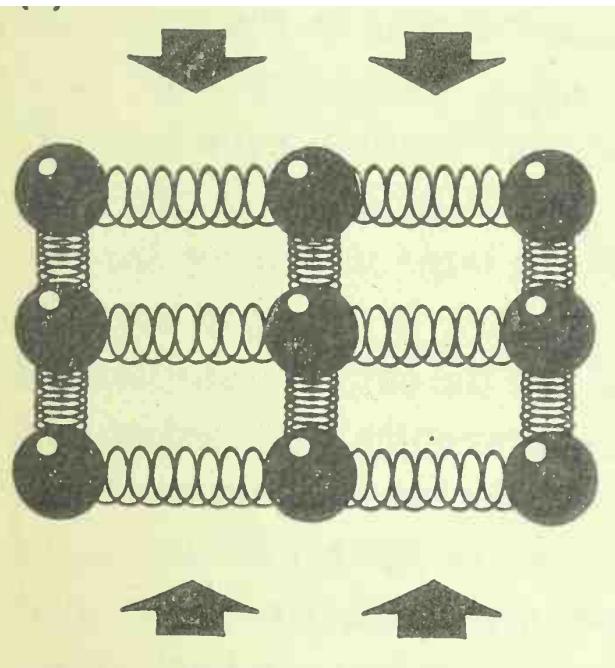
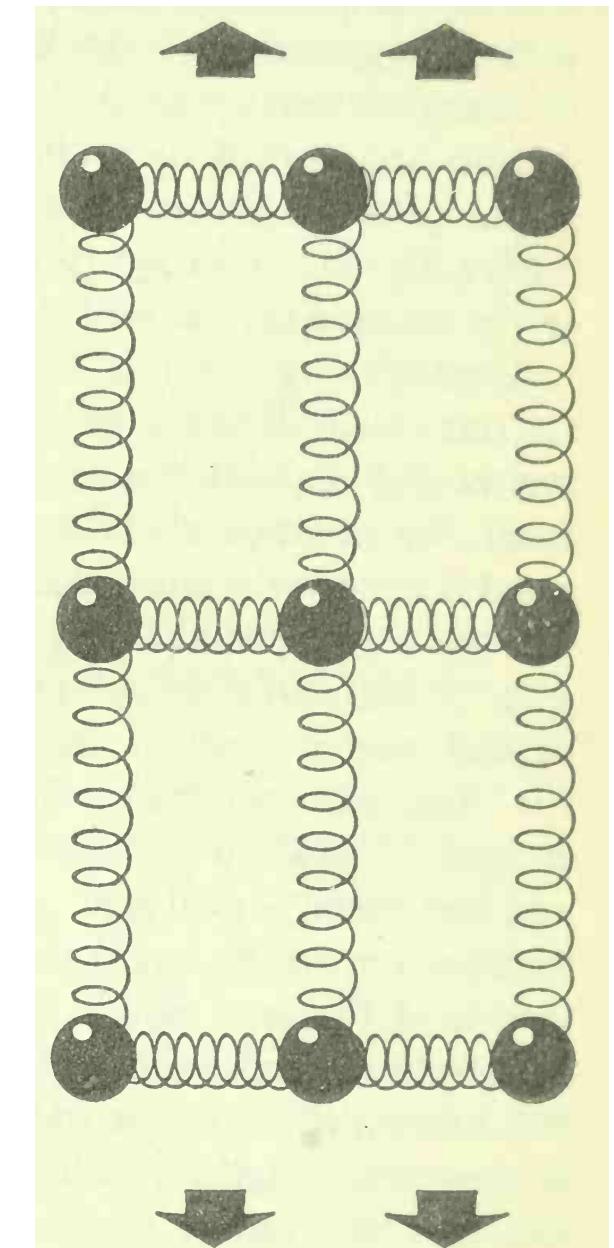
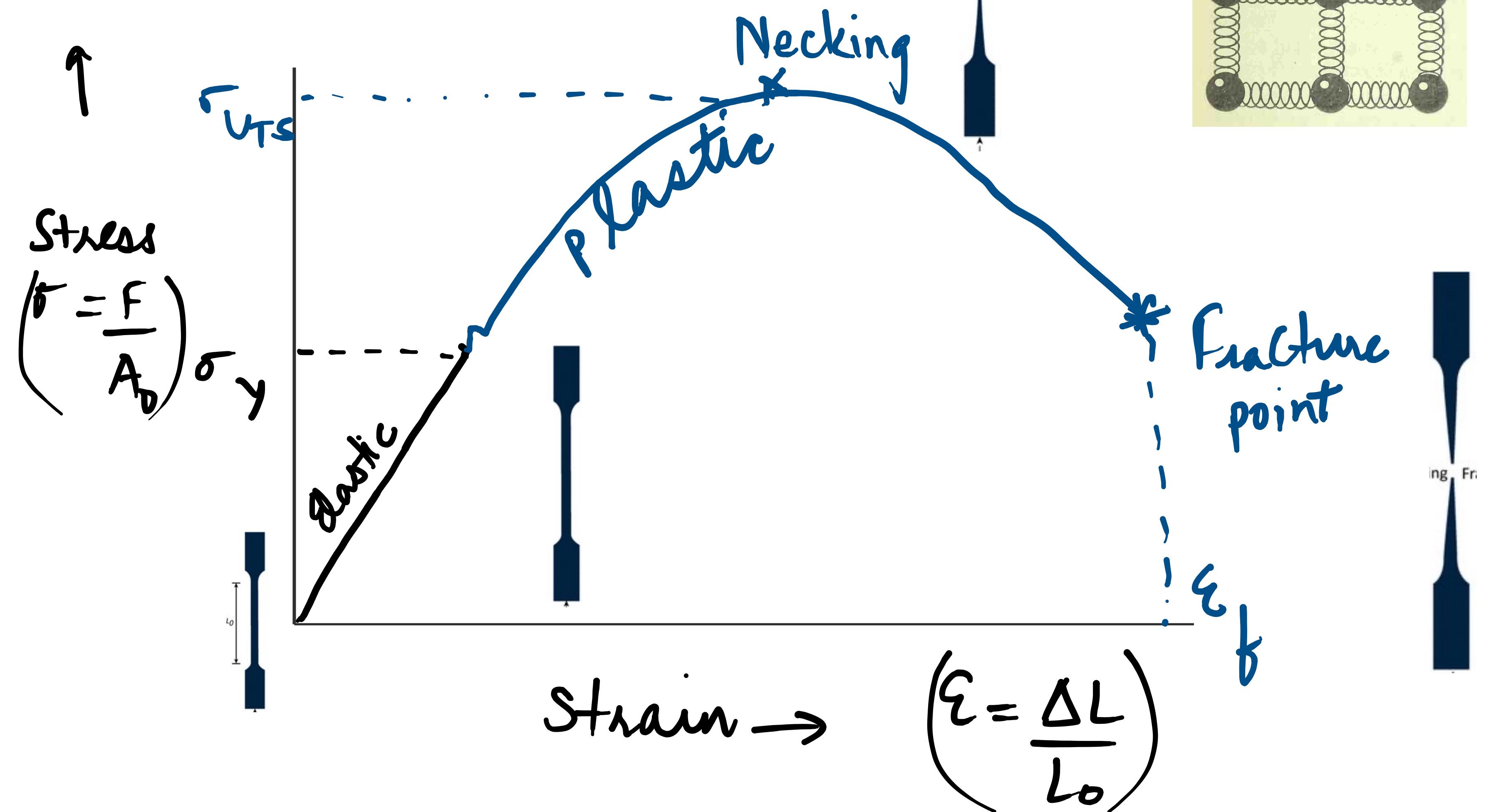


We want some materials NOT to fail !!

*Designing materials with tailored properties!*

# Stress-strain curve

## Load-Elongation curve



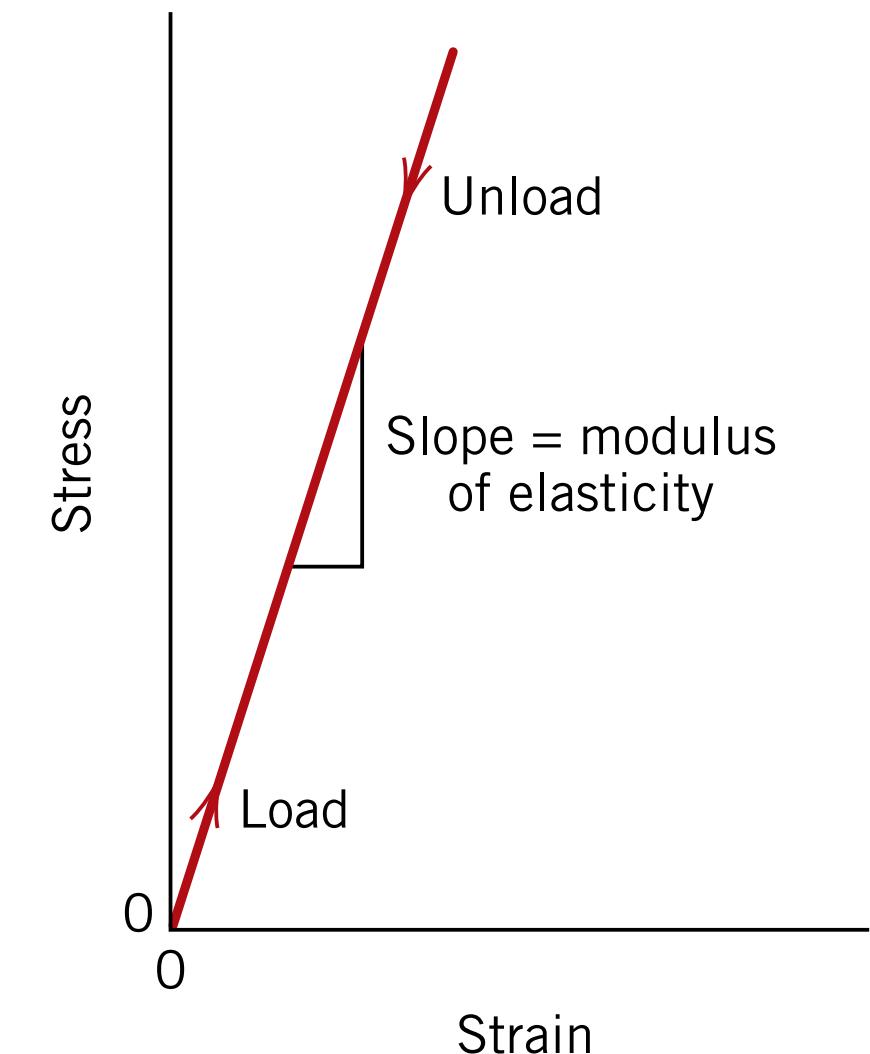
# Elastic deformation

*Deformation in which stress and strain are linearly proportional*

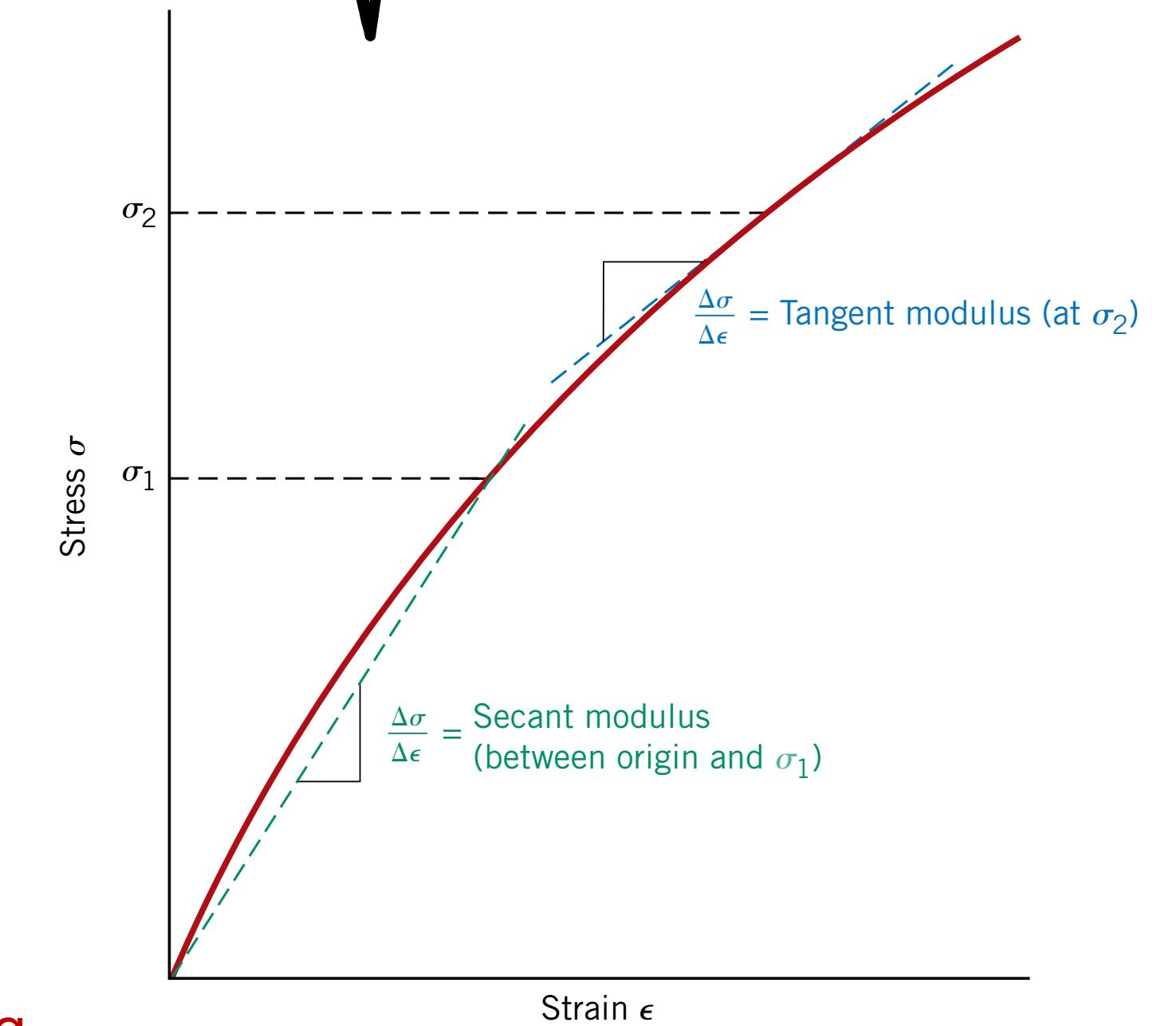
- Hooke's law:

$$(F = k \cdot \Delta x) \Rightarrow \sigma = Y \epsilon, \text{ where } Y = \text{Young's modulus or modulus of elasticity}$$

- For most typical metals the magnitude of this modulus ranges between 45 GPa ( $6.5 \times 10^6$  psi), for magnesium, and 407 GPa ( $59 \times 10^6$  psi), for tungsten.
- The greater the modulus, the stiffer the material, or the smaller the elastic strain that results from the application of a given stress.
- Elastic deformation is *non-permanent*: when the applied load is released, the piece returns to its original shape
- Young's modulus is a characteristic of each substance due to its chemical nature.



stress-strain diagram showing linear elastic deformation for loading and unloading cycles



tangent or secant modulus for gray cast iron, concrete, and many polymers

# Some obvious questions from stress-strain curve?

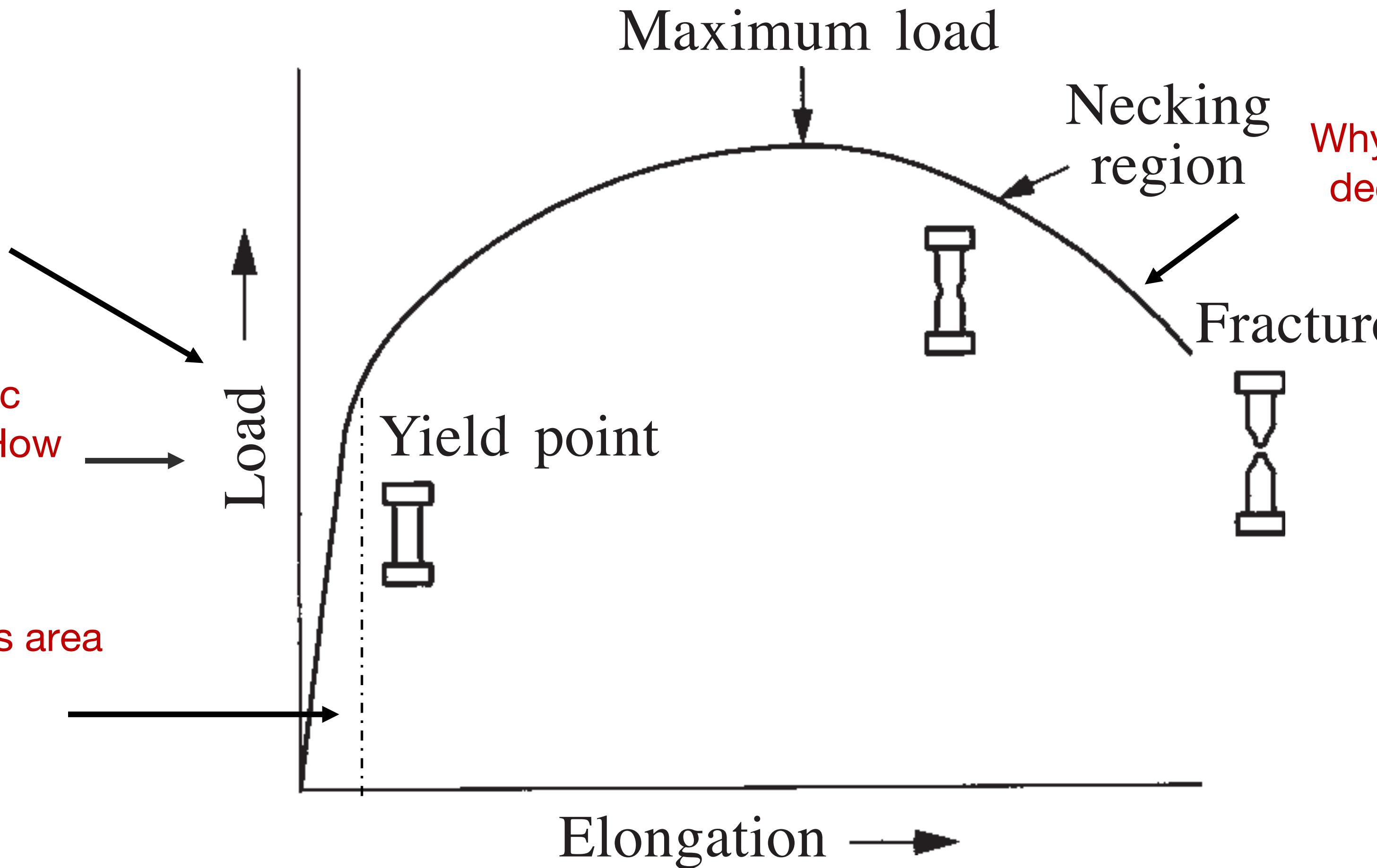


What if the elastic regime is non-linear? How to find Young's modulus?



What if elastic-to-plastic deformation is smooth? How to find the yield point?

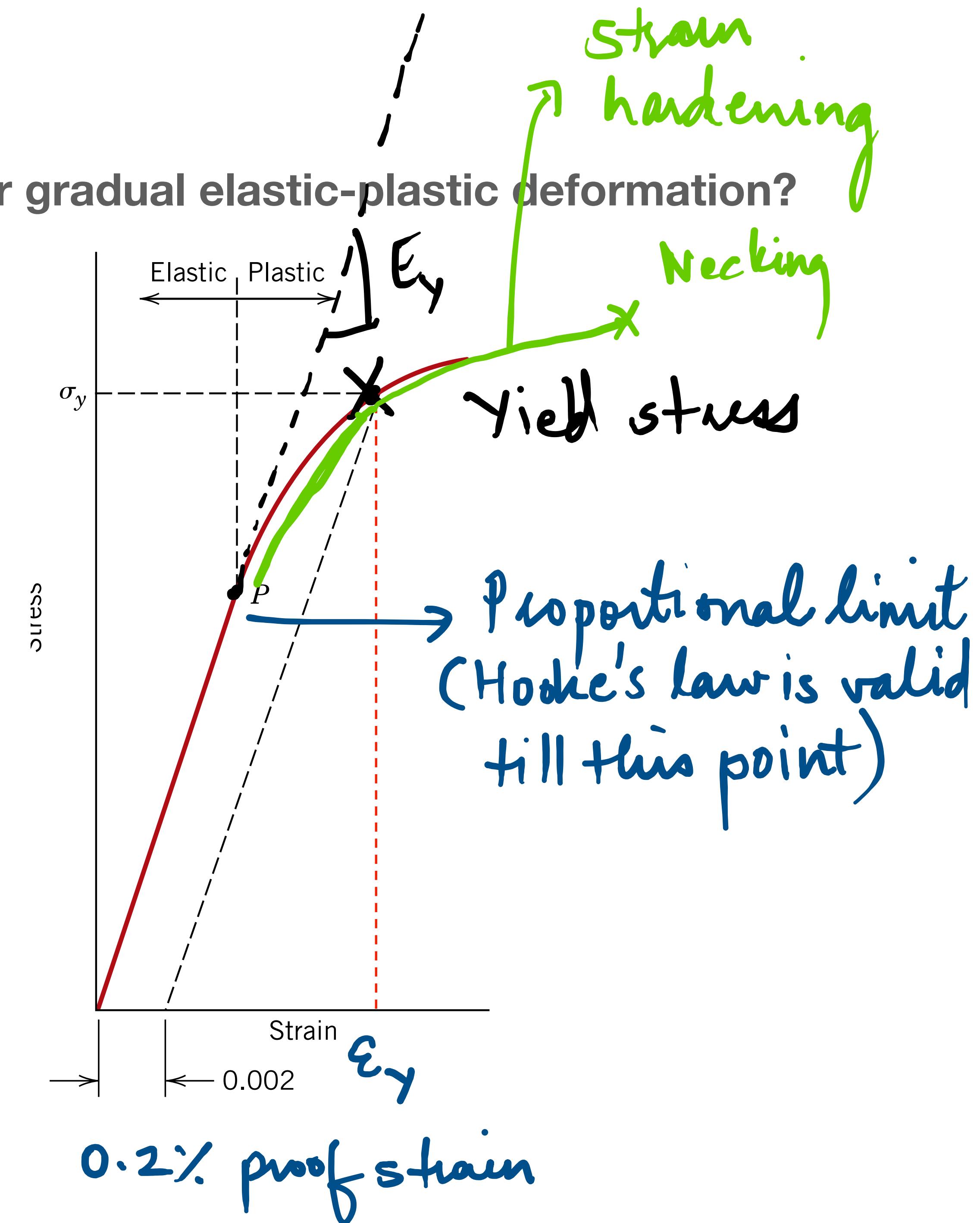
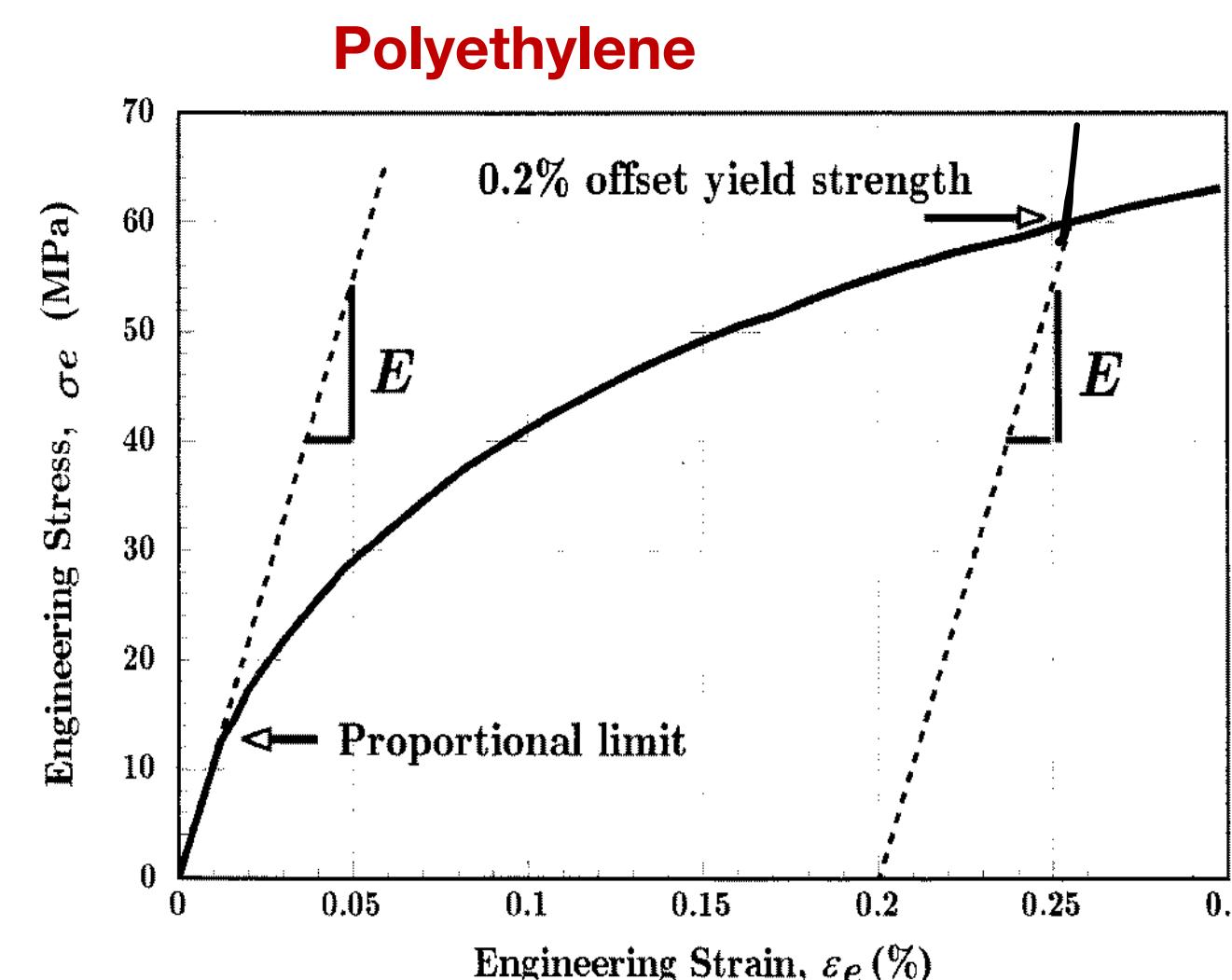
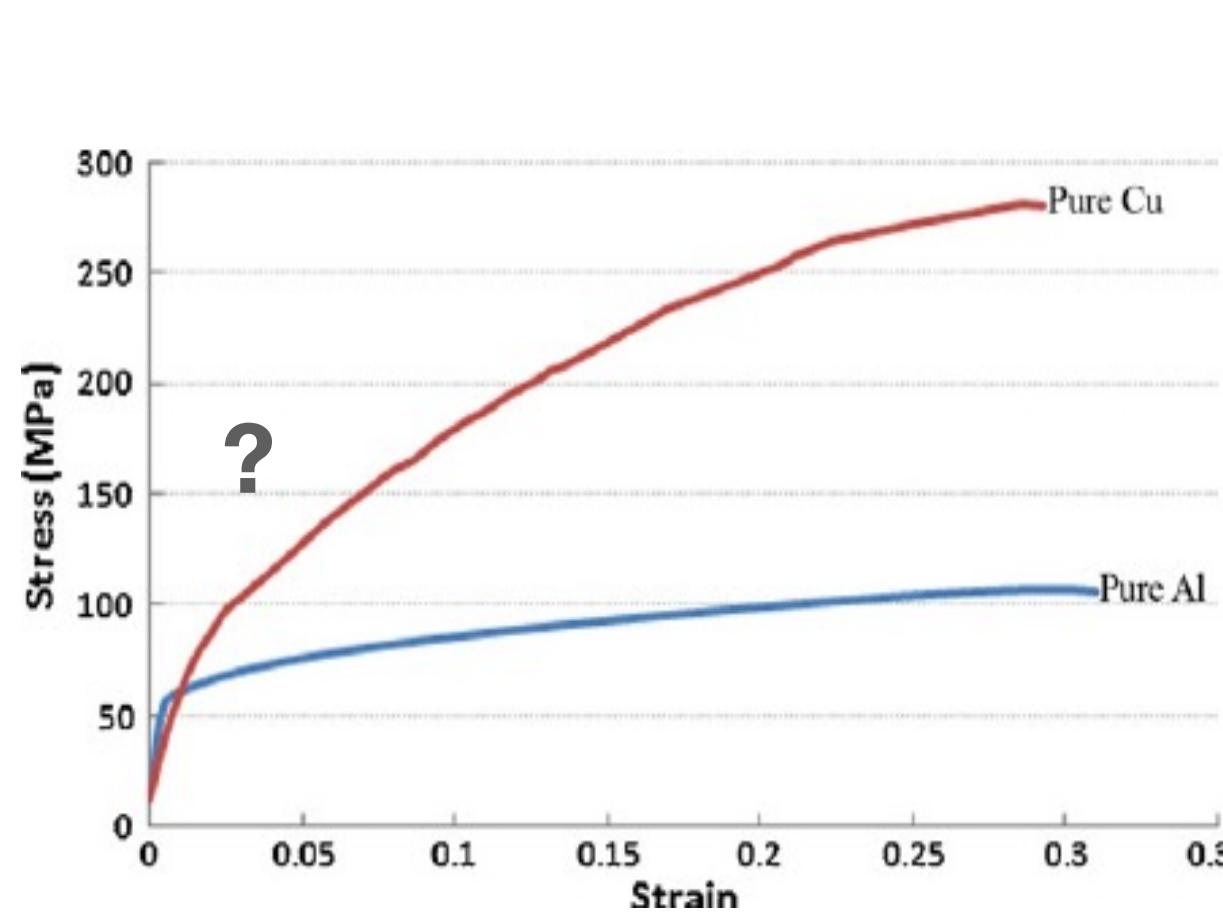
What property does this area provide?



Why the Engineering stress decreases after necking?

# Tensile Properties: Yield stress

Offset yield stress: How to determine yield stress for gradual elastic-plastic deformation?

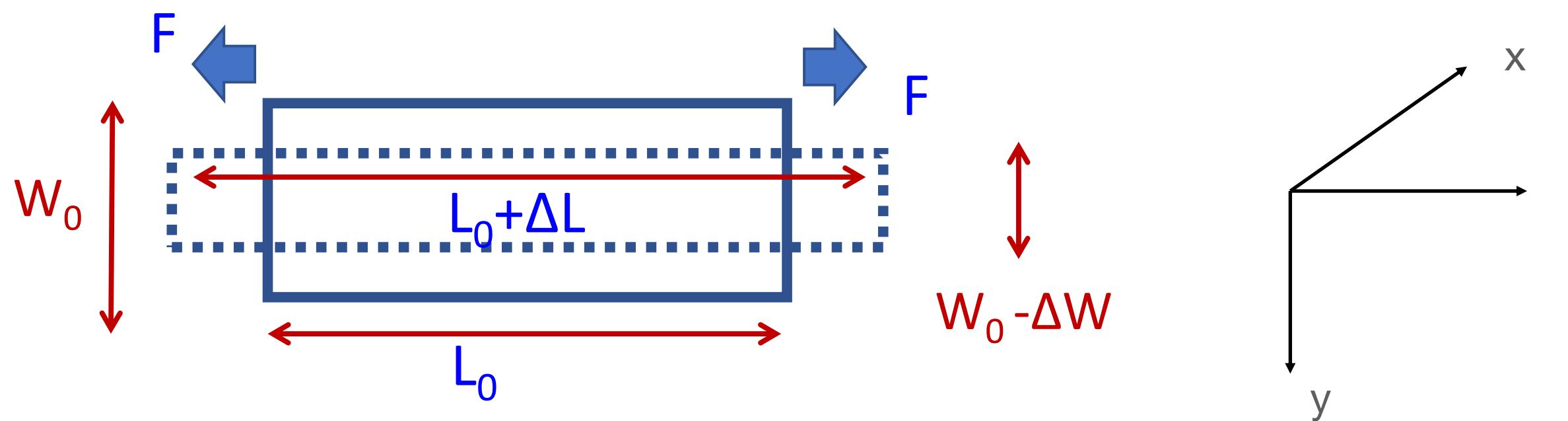


- **Proportional Limit:** initial departure from linearity of the stress-strain curve
- A straight line is constructed parallel to the elastic portion of the stress-strain curve at some specified strain offset, usually 0.002.
- Slope of this constructed straight line gives the Young's modulus

# Elastic properties of materials

## Poisson's ratio: What happens to the cross-section area on elongation?

Poisson's ratio measures the deformation in the material in a direction perpendicular to the direction of the applied force



$$\varepsilon_{longitudinal} = \frac{\Delta L}{L_0}$$

$$\varepsilon_{lateral} = \frac{-\Delta W}{W_0}$$

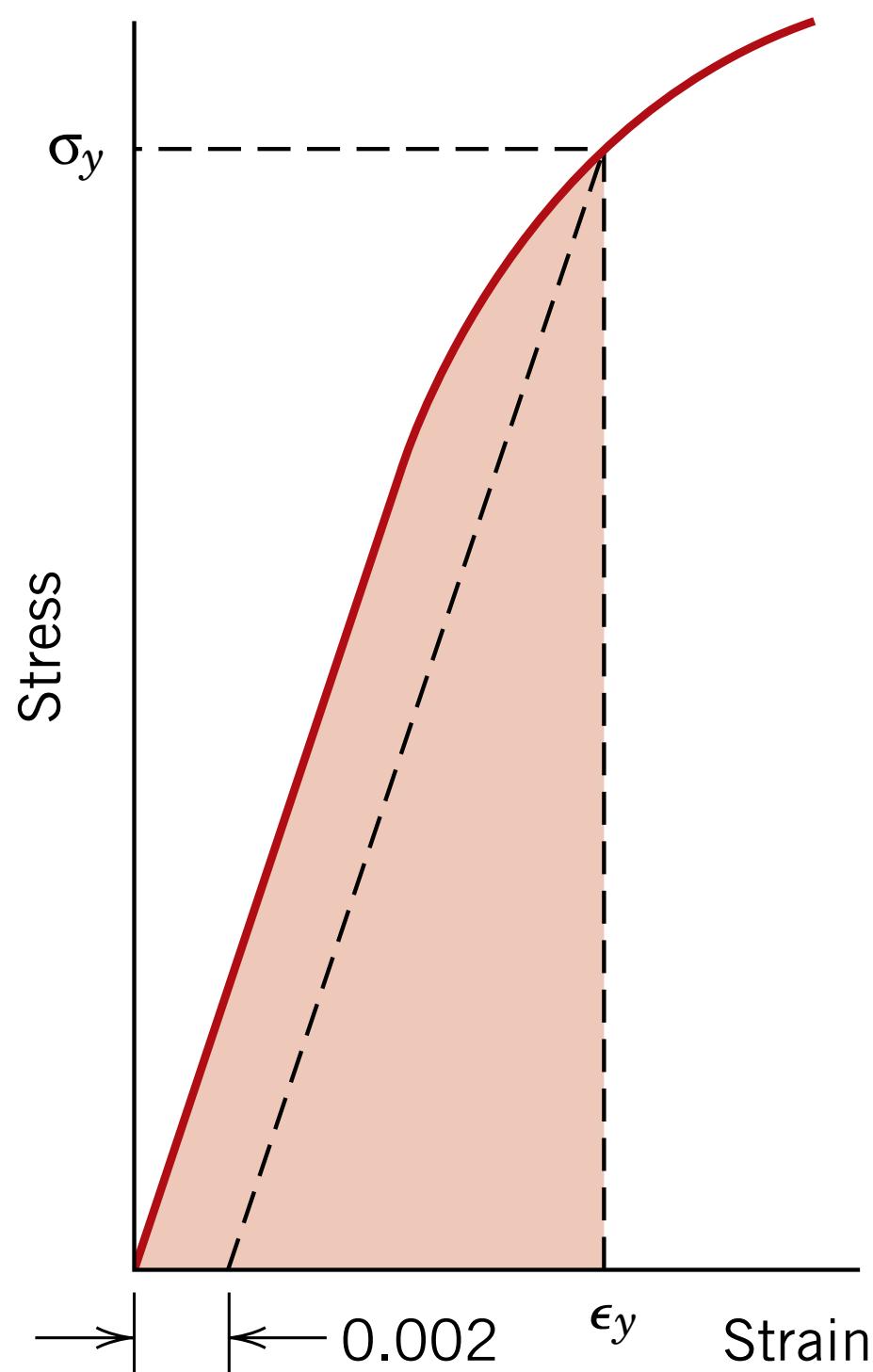
$$\nu = - \left[ \frac{\frac{-\Delta W}{W_0}}{\frac{\Delta L}{L_0}} \right] = - \left[ \frac{\varepsilon_{lateral}}{\varepsilon_{longitudinal}} \right]$$

$$\nu = - \frac{\epsilon_x}{\epsilon_z} = - \frac{\epsilon_y}{\epsilon_z}$$

- If the applied stress is uniaxial (only in the  $z$  direction), and the material is isotropic, then  $\varepsilon_x = \varepsilon_y$  ( $x$  and  $y$  are lateral and  $z$  is longitudinal direction).
- It is the ratio of lateral strain to longitudinal strain
- The negative sign is so that the ratio is always positive
- $\varepsilon_x$  or  $\varepsilon_y$  and  $\varepsilon_z$  will always be of opposite sign.
- A high Poisson's ratio denotes that **the material exhibits large elastic deformation, even when exposed to small amounts of strain.**
- Metals: ~0.33, ceramics: ~0.25 and polymers: ~0.40

# Resilience

What property does the area under stress-strain give before yielding point?



- **Resilience:** the capacity of a material to absorb energy when it is deformed elastically and then, upon unloading, to have this energy recovered.
- **Modulus of resilience:** strain energy per unit volume required to stress a material from an unloaded state up to the point of yielding
- *Modulus of resilience is the area under the stress-strain curve taken to yielding.*
- Resilience is energy absorbed per unit volume upto elastic limit.

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

Assuming linear elastic region,

$$U_r = \frac{1}{2} \sigma_y \epsilon_y$$

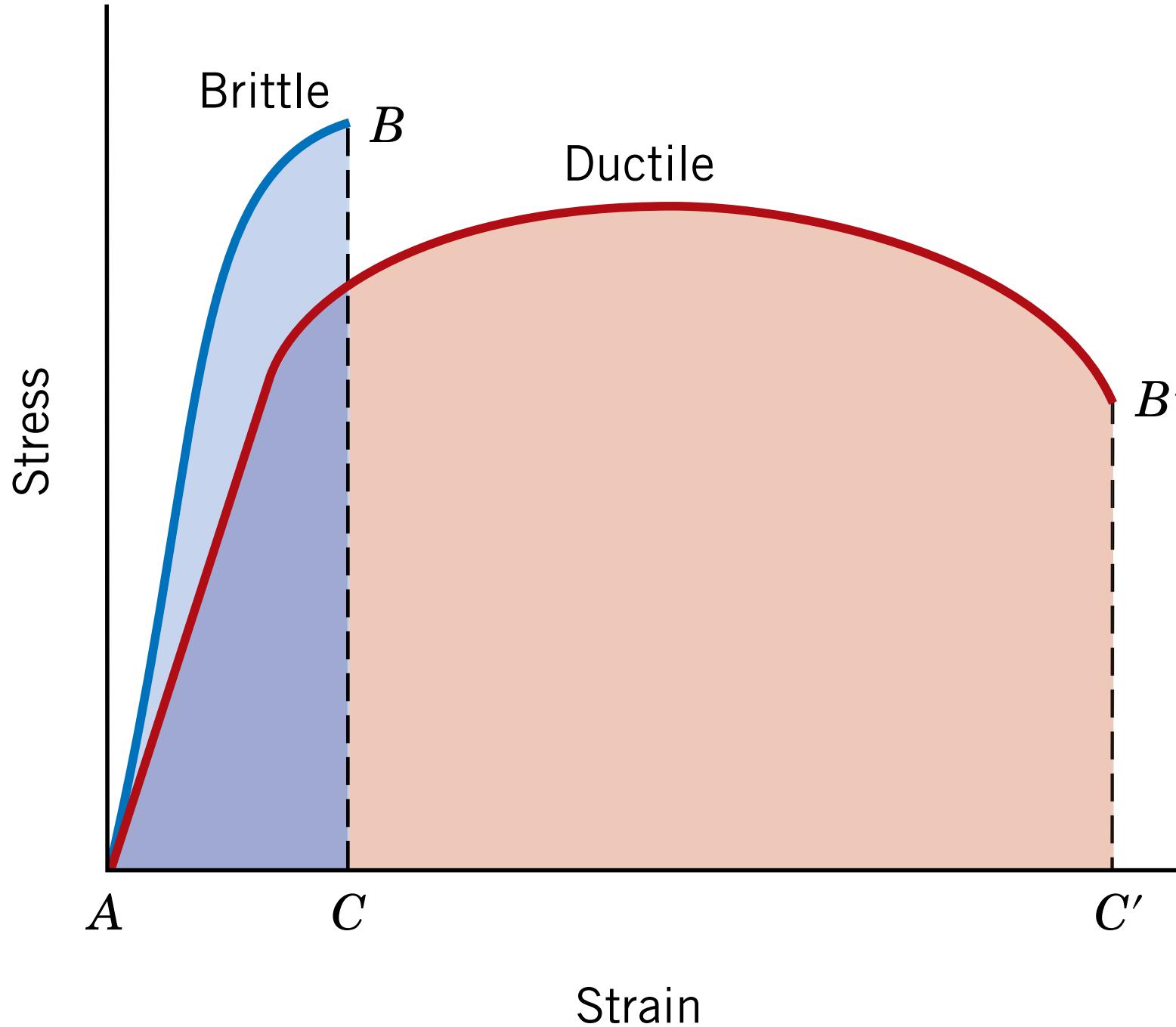
$\sigma_y$  = yield stress  
 $\epsilon_y$  = yield strain

Incorporating Hooke's law :  $\sigma = E \epsilon$  (E: Young's modulus)

$$\Rightarrow U_r = \frac{1}{2} \sigma_y \left( \frac{\sigma_y}{E} \right) = \frac{\sigma_y^2}{2E}$$

∴ Resilient materials have high yield strengths & low elastic modulus.  
(SPRING)

# Ductility and Brittle



- **Ductility:** A measure of the degree of plastic deformation that has been sustained at fracture.
- **Brittle:** A material that experiences very little or no plastic deformation upon fracture. Brittle materials are *approximately* considered to be those having a fracture strain of less than about 5%.
- Ductility may be expressed quantitatively as either *percent elongation* or *percent reduction in area*.

$$\% \text{ EL} = \left( \frac{L_f - L_0}{L_0} \right) \times 100$$

$\% \text{ EL}$  =  $\% \text{ of plastic strain at fracture}$

$L_f$  = fracture length

$L_0$  = original gauge length

$$\% \text{ RA} = \left( \frac{A_0 - A_f}{A_0} \right) \times 100$$

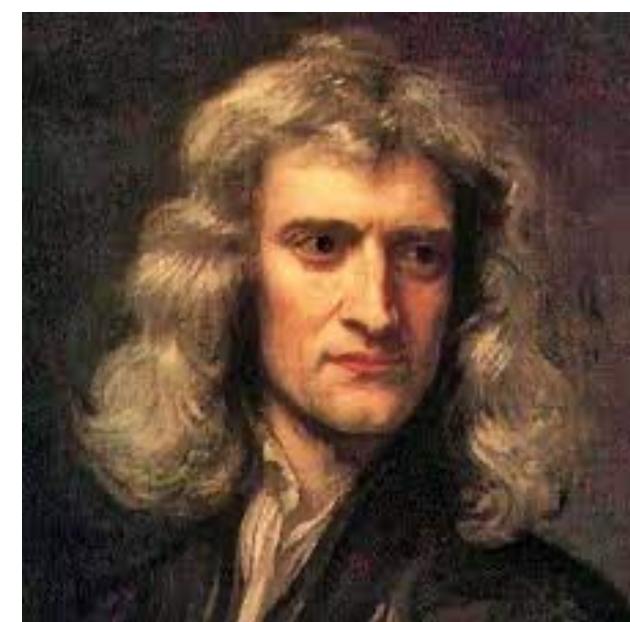
$\% \text{ RA}$  =  $\% \text{ reduction in area}$ ,  $A_0$  = original cross-section area  
 $A_f$  = cross-sectional area at fracture

## Ductility in design:

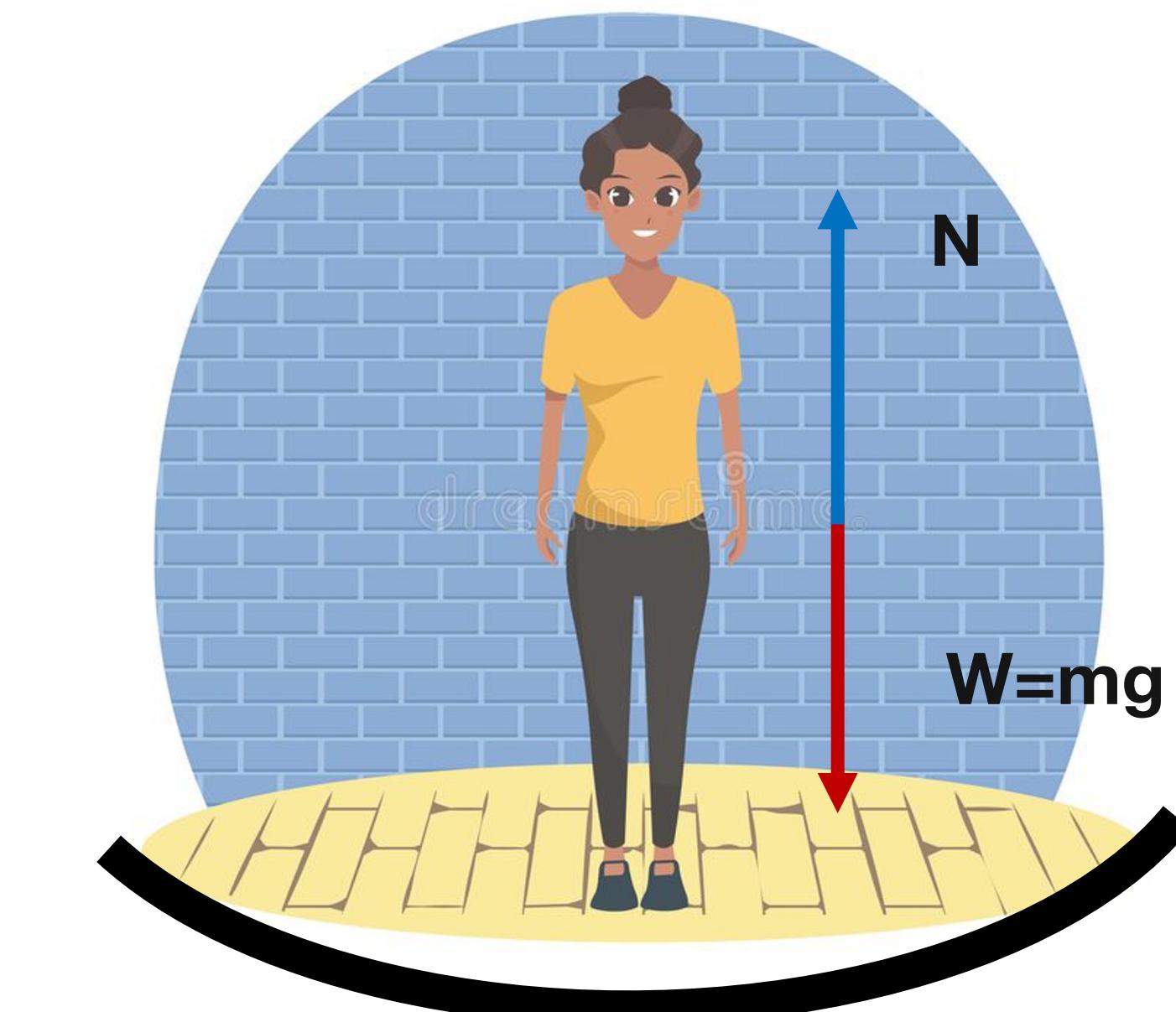
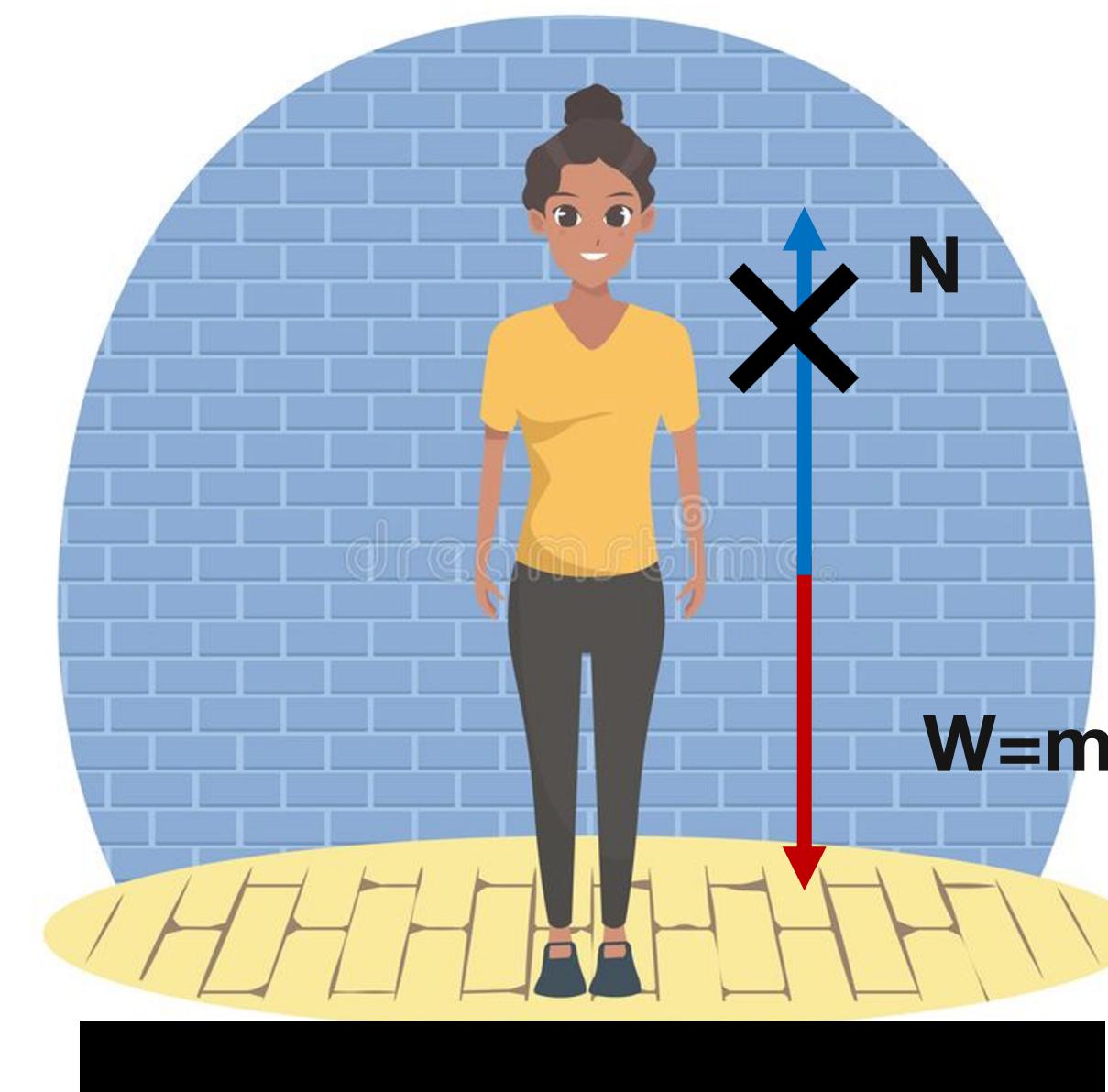
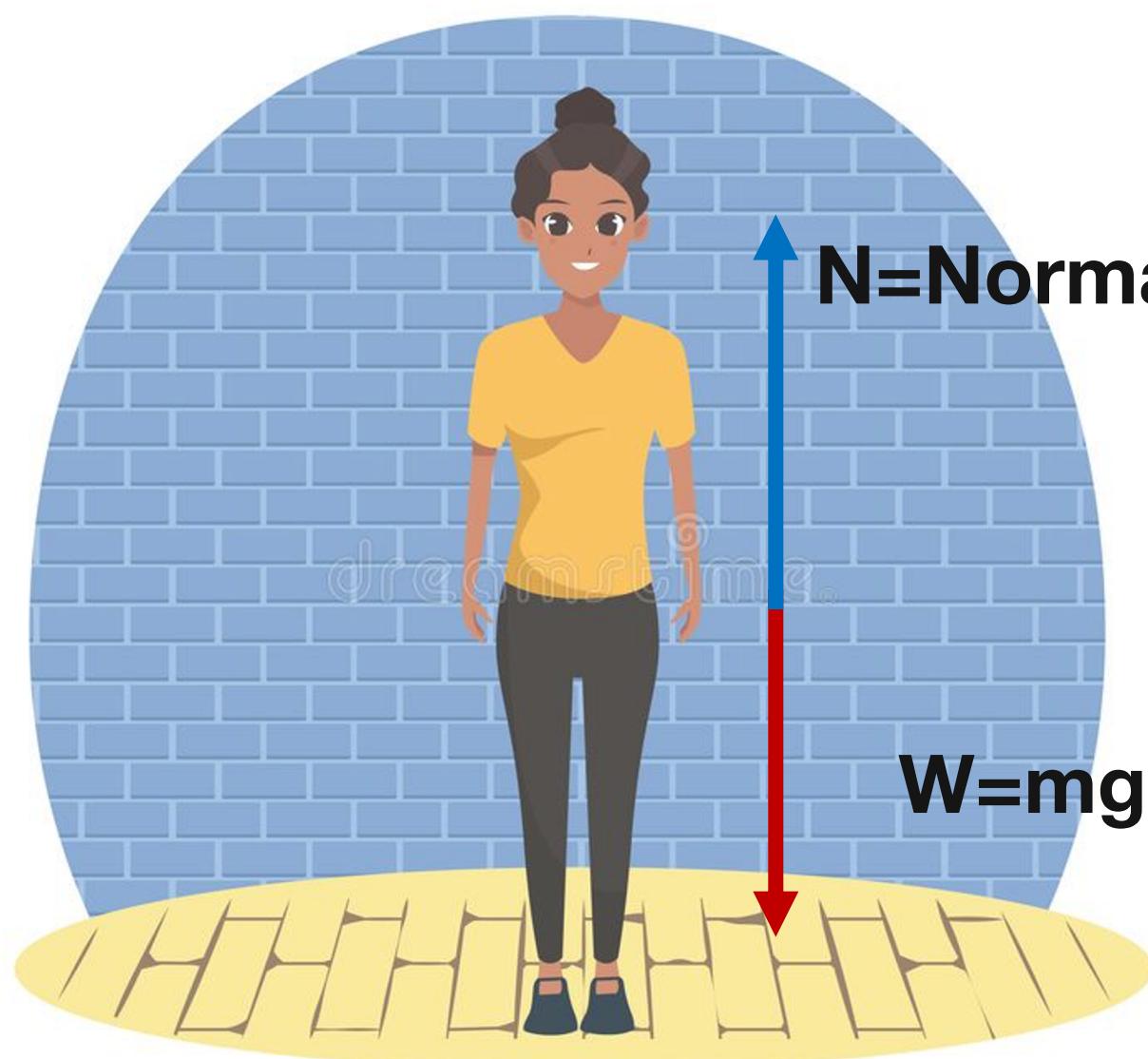
- Degree of allowable deformation
- Degree to which structure deforms plastically before fracture.



So now let us see why we don't fall through the floor?  
*Unless you are sitting on a missile!*



Is floor rigid or deformable?

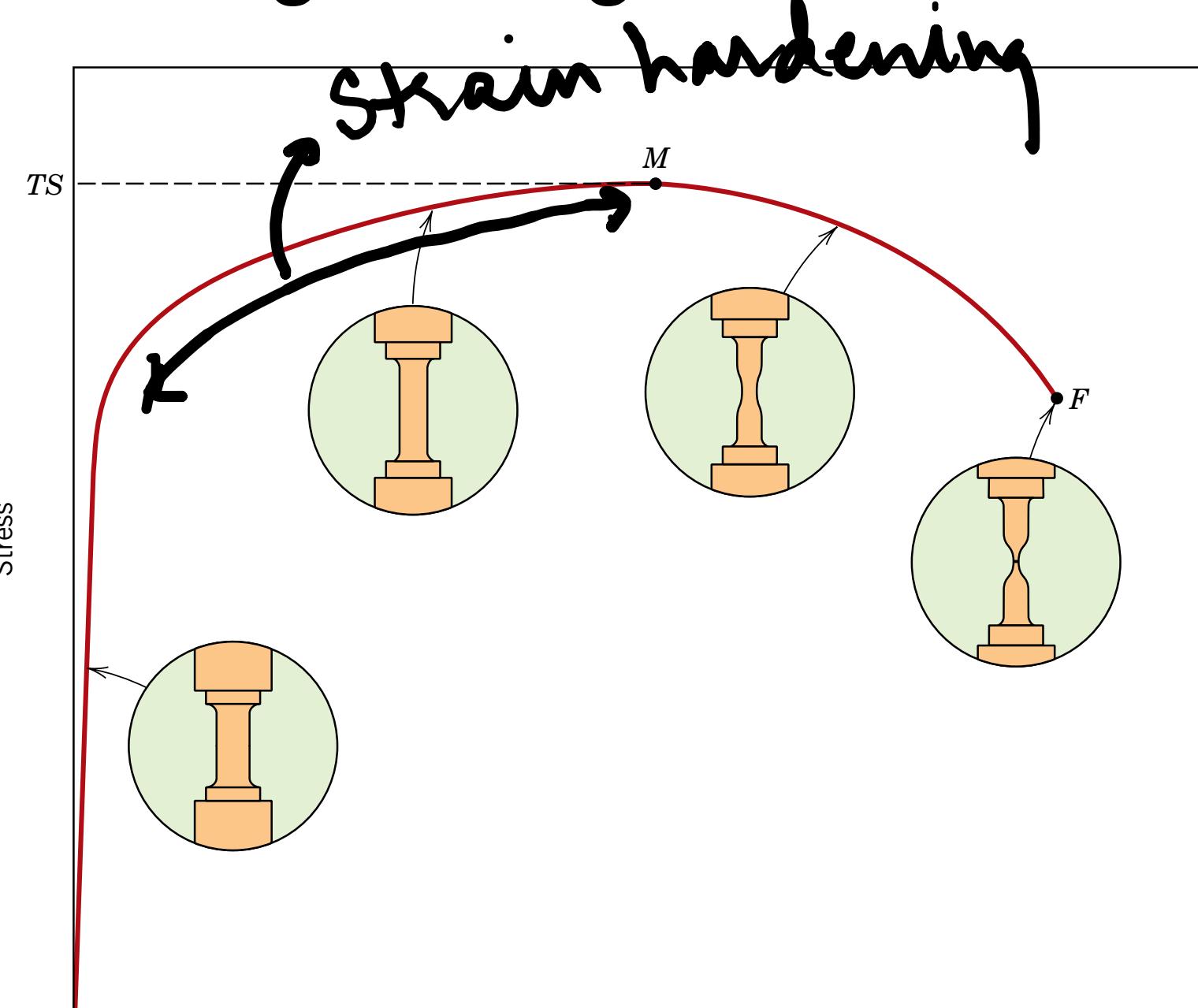


Floor is elastically deformable  
Hooke's law

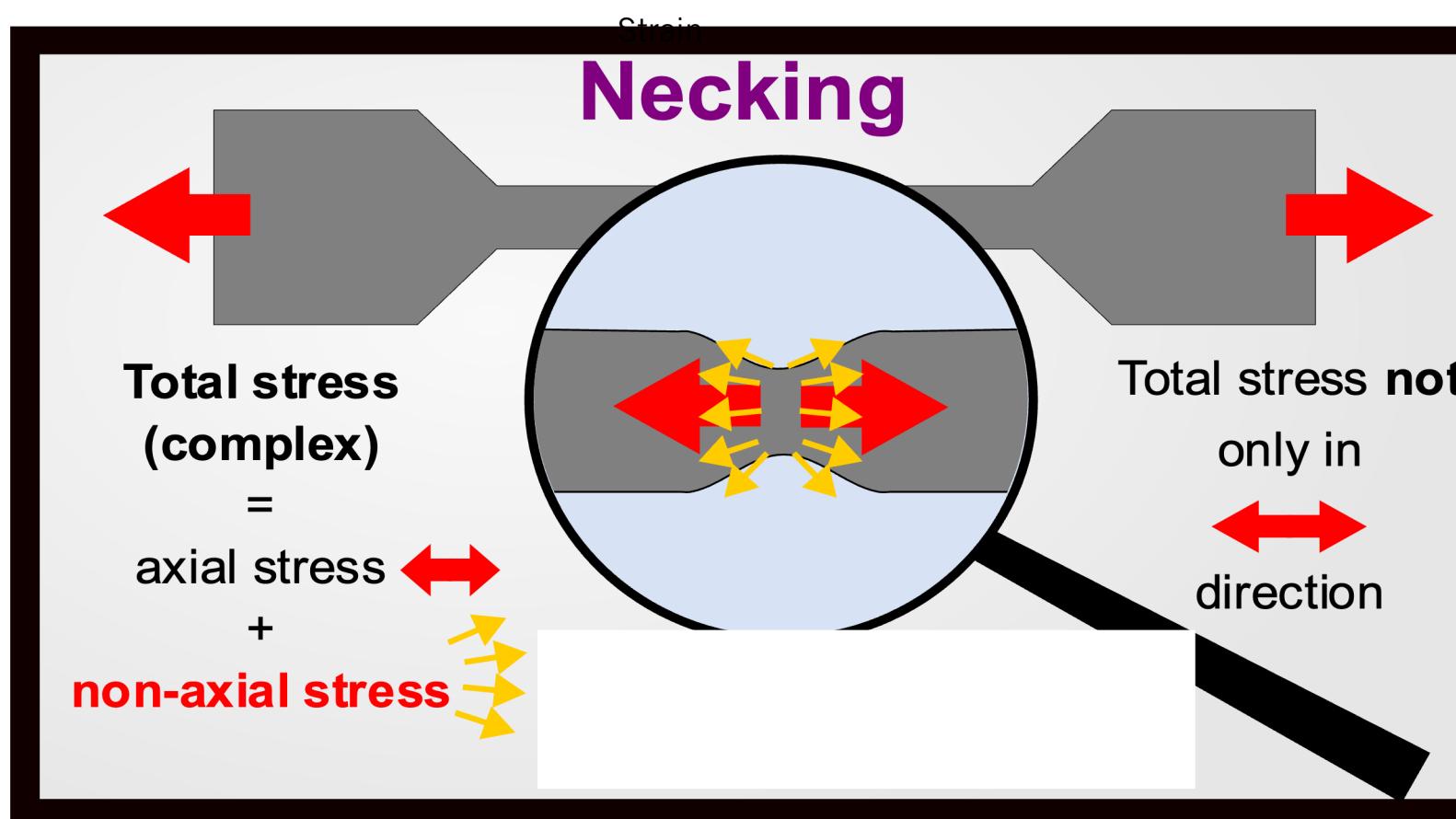
Under the weight of the person, the floor deforms and in order to come back to original state, it creates the normal force

# True stress

**Engineering stress does not consider the instantaneous change in the cross-section area**



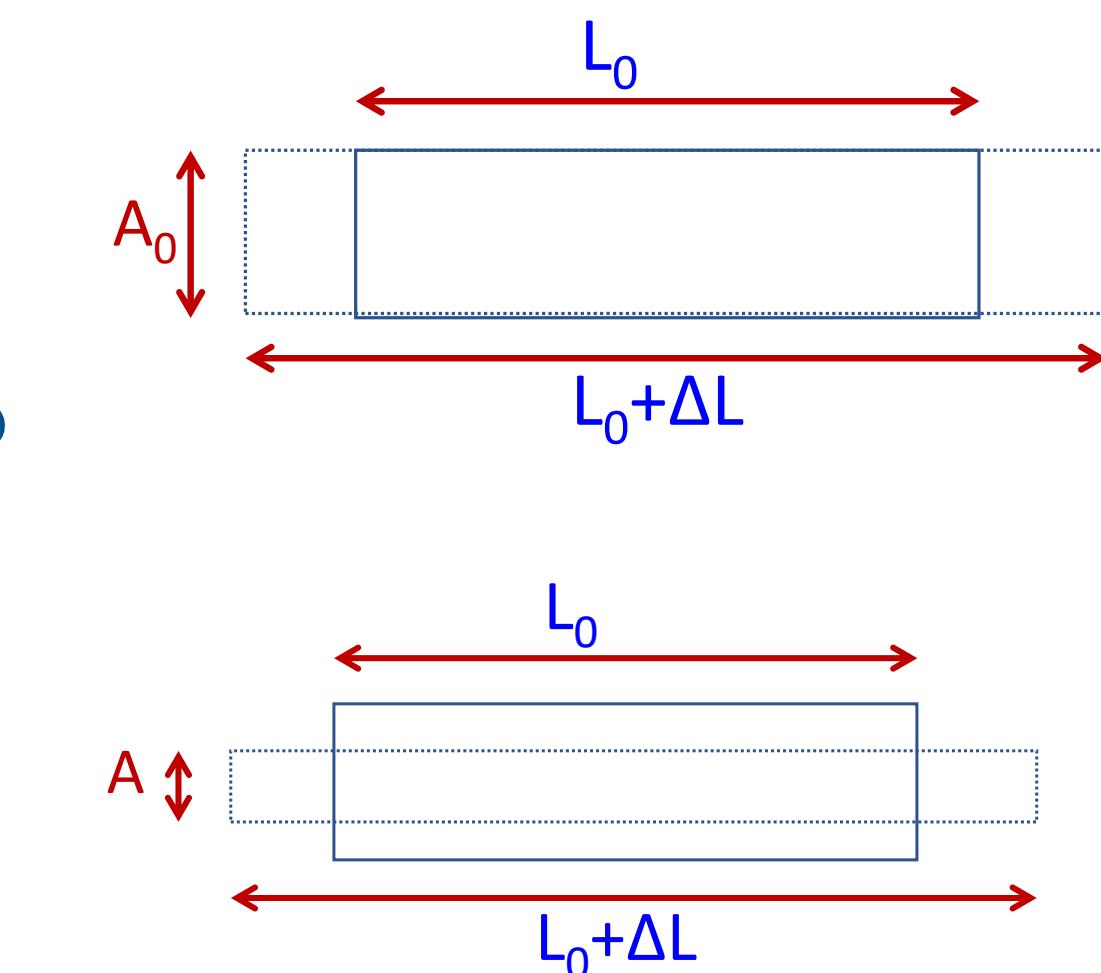
- Once the maximum in the engineering curve has been reached, the localized deformation at this site cannot be compensated by further strain hardening, so the cross-section area is reduced further. This increases the local stress even more, which accelerates the deformation further. This localized and increasing deformation soon leads to a “neck” in the gage length of the specimen.
- Material at necking point experiences stress which is no longer uniaxial. The Engineering stress does not take into account the reduction in cross-sectional area at necking.



$$\text{Engineering stress, } \sigma_E = \frac{F}{A_0}$$

$$\text{True stress, } \sigma_T = \frac{F}{A}$$

Instantaneous area



# Relationship between Engineering stress and True stress

$$\sigma_T = \frac{F}{A}, \quad \sigma_E = \frac{F}{A_0}$$

Assuming volume is constant,

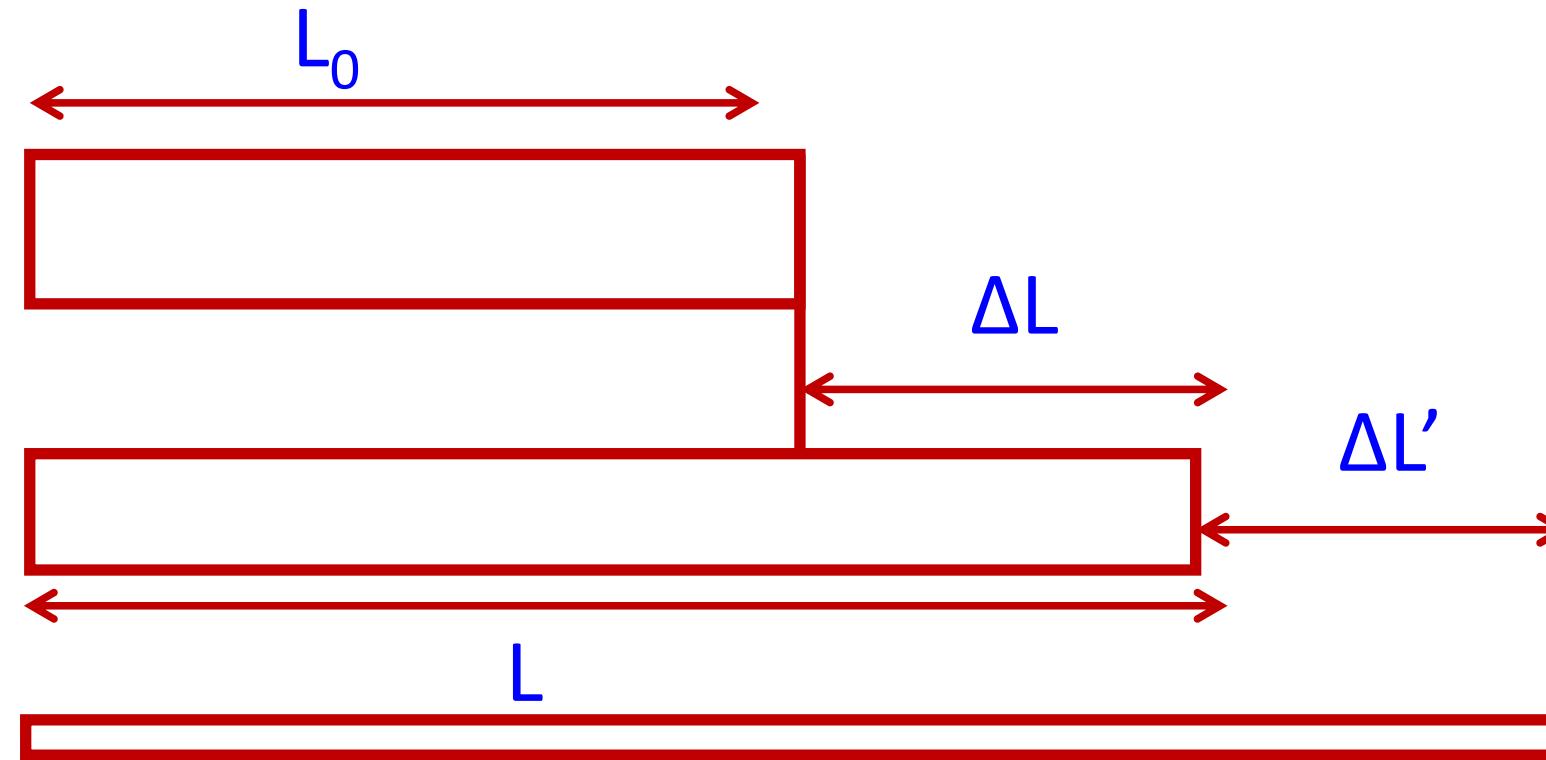
$$A \cdot L = A_0 \cdot L_0 \Rightarrow \frac{A_0}{A} = \frac{L}{L_0}$$
$$\Rightarrow \sigma_T = \frac{F}{A_0} \cdot \left( \frac{A_0}{A} \right) = \frac{F}{A_0} \cdot \left( \frac{L}{L_0} \right) = \frac{F}{A_0} \cdot \frac{(L_0 + \Delta L)}{L_0} = \frac{F}{A_0} \cdot \left( 1 + \frac{\Delta L}{L_0} \right)$$

$$= \frac{F}{A_0} \cdot (1 + \varepsilon_E) = \sigma_E (1 + \varepsilon_E)$$

∴  $\boxed{\sigma_T = \sigma_E (1 + \varepsilon_E)}$

# True strain

Engineering strain does not consider the instantaneous change in the elongation



$$\varepsilon_E = \frac{\Delta L}{L_0},$$

True incremental strain,

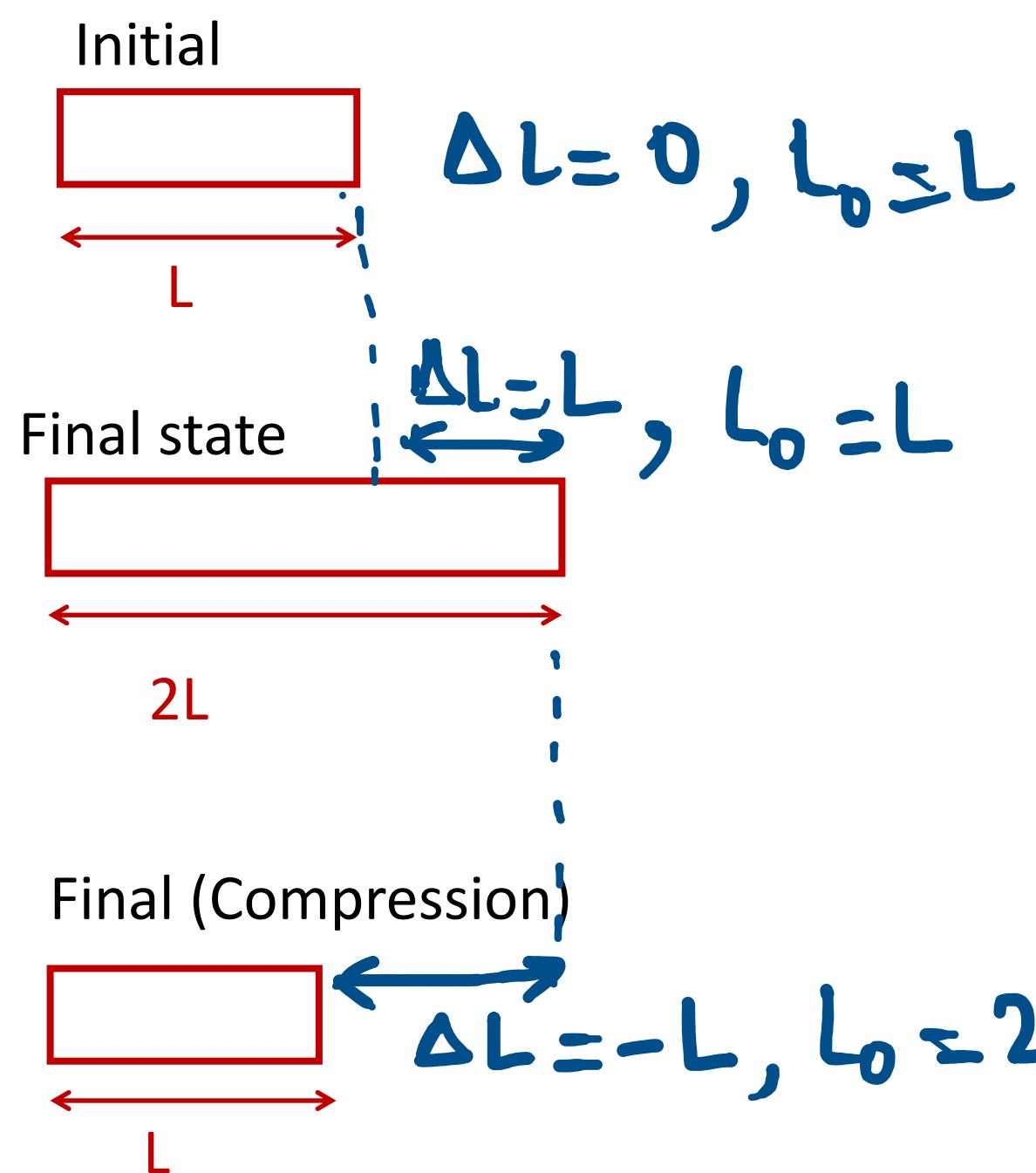
$$d\varepsilon_T = \frac{dL}{L}$$

$$\begin{aligned} \varepsilon_T &= \int_0^{\varepsilon_T} d\varepsilon_T = \int_{L_0}^L \frac{dL}{L} = \ln \frac{L}{L_0} = \ln \left( \frac{L_0 + \Delta L}{L_0} \right) \\ &\quad = \ln(1 + \varepsilon_E) \end{aligned}$$

∴  $\boxed{\varepsilon_T = \ln(1 + \varepsilon_E)}$

# Implications

True strain is the real strain: for practical purposes



Engineering strain

$$\varepsilon_E = \frac{\Delta L}{L_0} = 0$$

$$\varepsilon_E = \frac{\Delta L}{L_0} = \frac{L}{L} = 1$$

$$\varepsilon_E = \frac{\Delta L}{L_0} = \frac{-L}{2L} = -0.5$$

---

$$\text{Net } \varepsilon_E = 0.5$$

---

True strain

$$\varepsilon_T = \ln \frac{L}{L_0} = 0$$

$$\varepsilon_T = \ln \frac{2L}{L} = \ln 2 = 0.69$$

$$\varepsilon_T = \ln \frac{L}{2L} = -\ln 2 = -0.69$$

---

---

$$\text{Net } \varepsilon_T = 0$$

---

# Lecture 29

## Stress-strain curves for Polymers



Ludwig Boltzmann

**Prof. Divya Nayar**  
**Department of Materials Science and Engineering**  
**[divyanayar@mse.iitd.ac.in](mailto:divyanayar@mse.iitd.ac.in)**

# Recap...

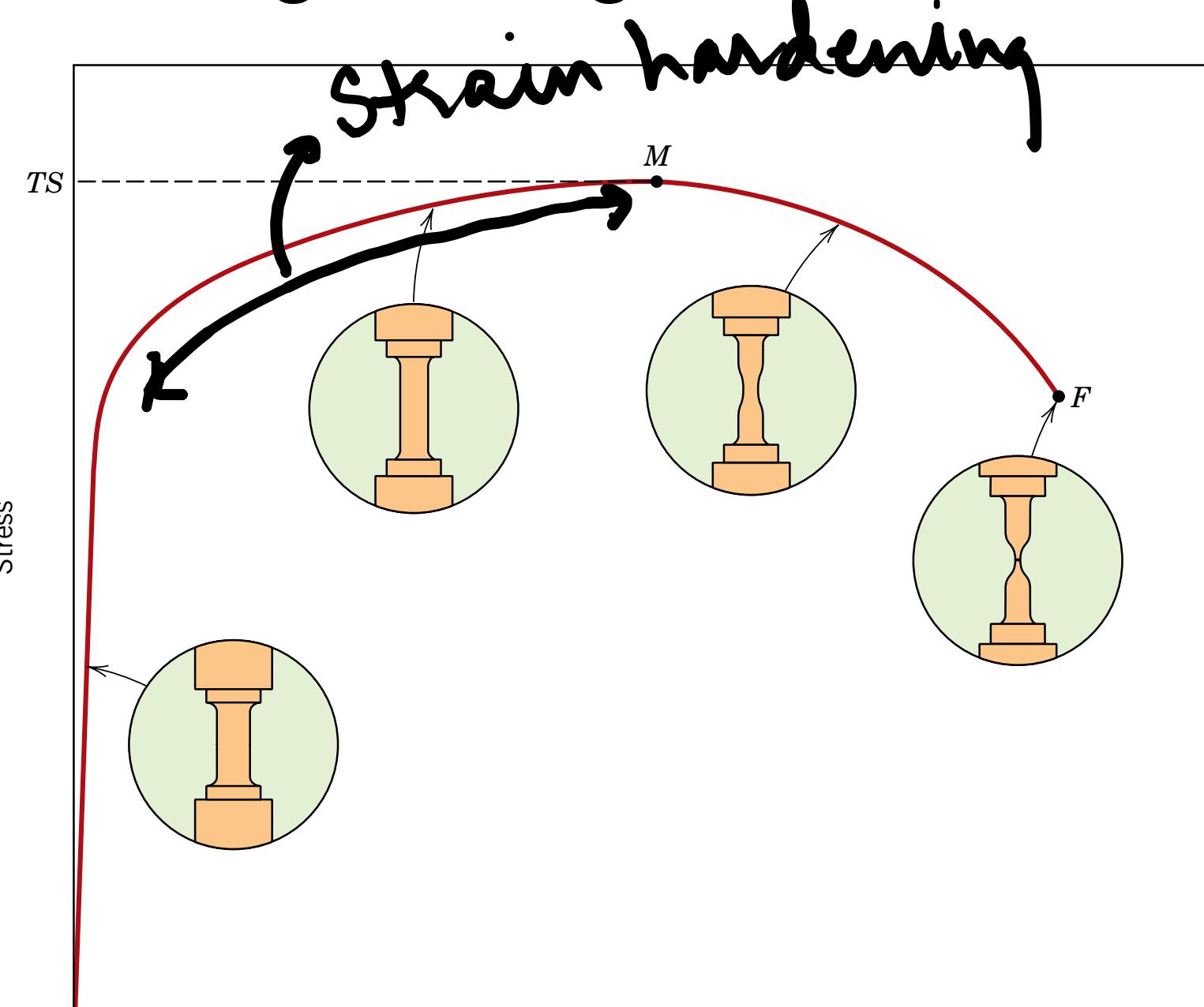
1. Elastic properties of materials
2. True stress-strain
3. Relationship between Engineering stress-strain

# Precap

1. True stress-strain curve
2. Stress-strain curves for Polymers
3. A new definition of entropy explaining elastic deformation

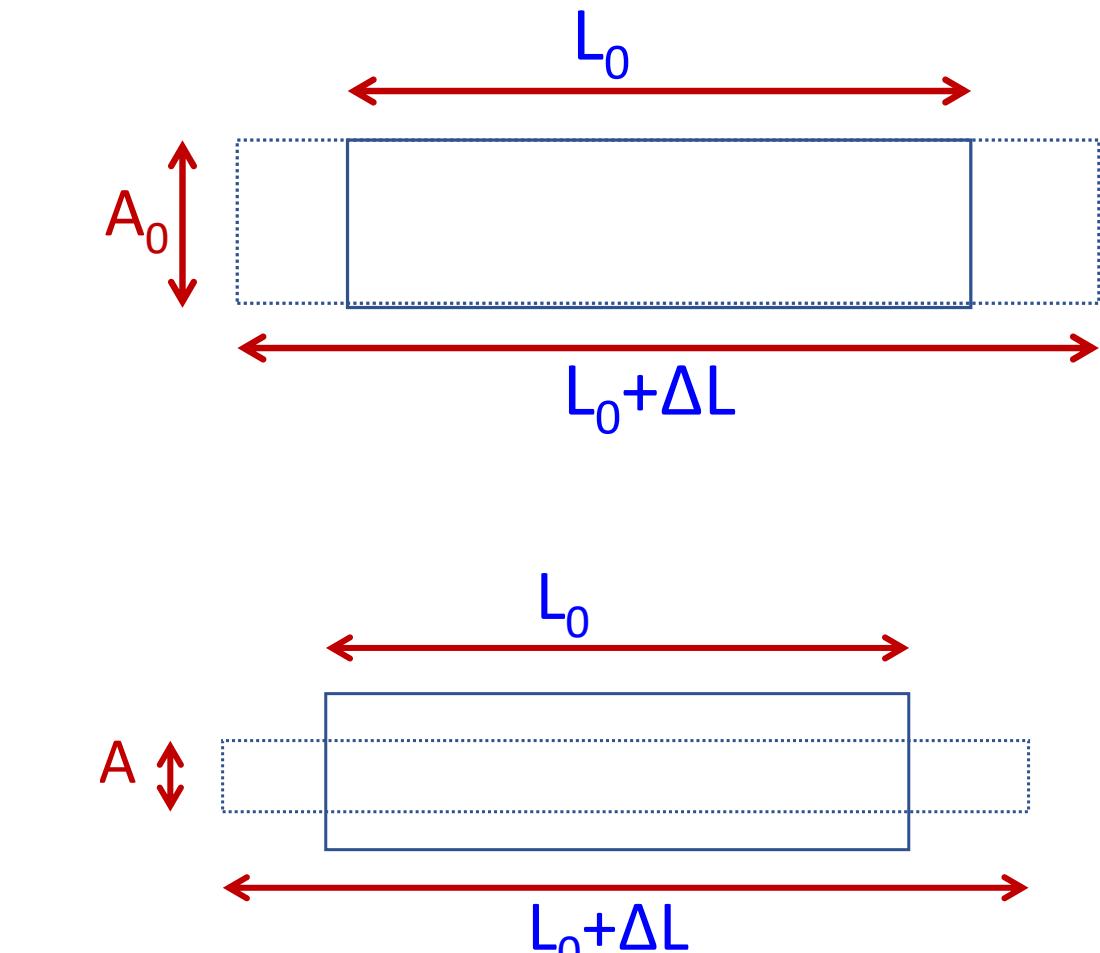
# True stress

Engineering stress does not consider the instantaneous change in the cross-section area

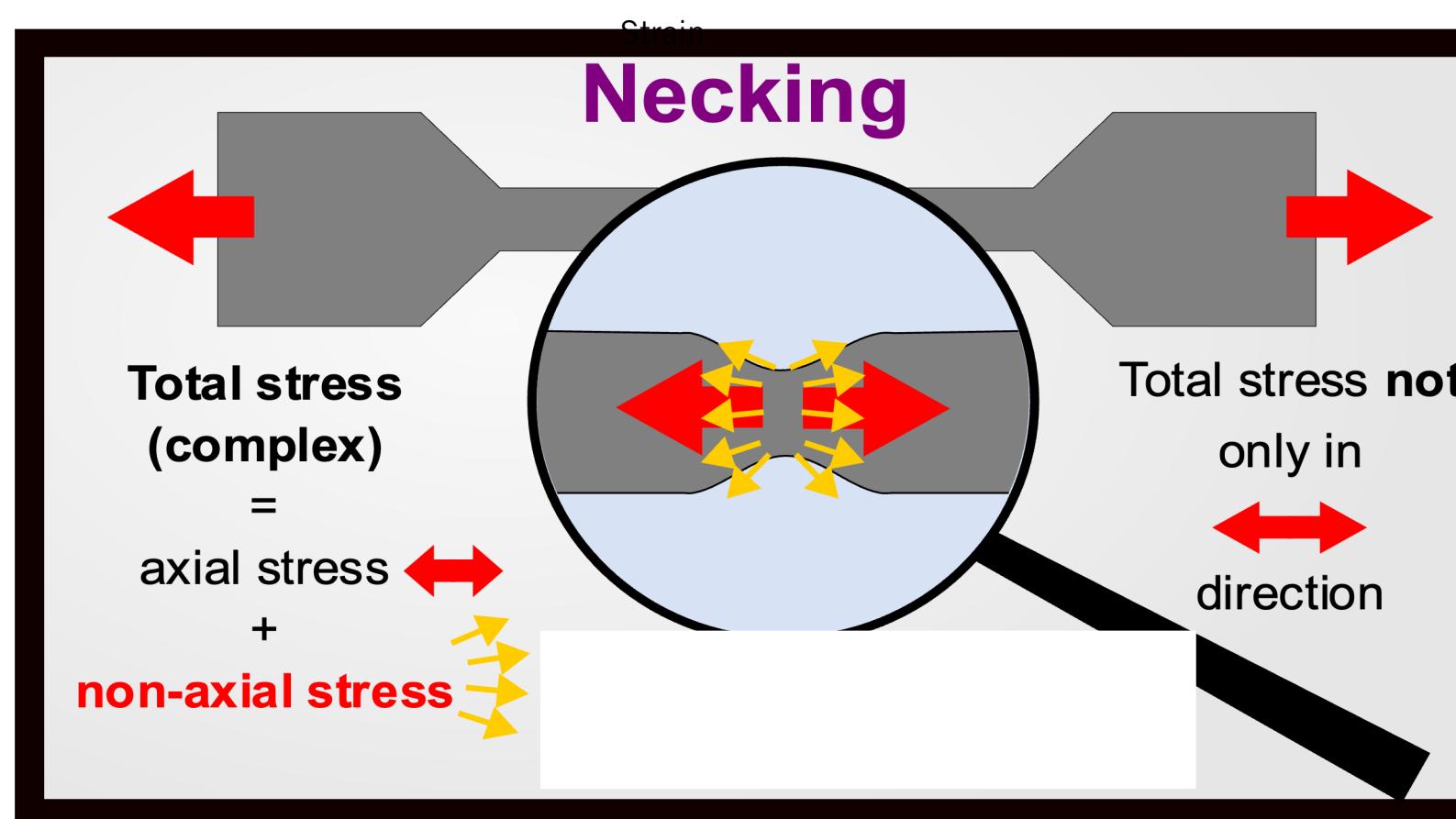


$$\text{Engineering stress, } \sigma_E = \frac{F}{A_0}$$

$$\text{True stress, } \sigma_T = \frac{F}{A}$$



Instantaneous area



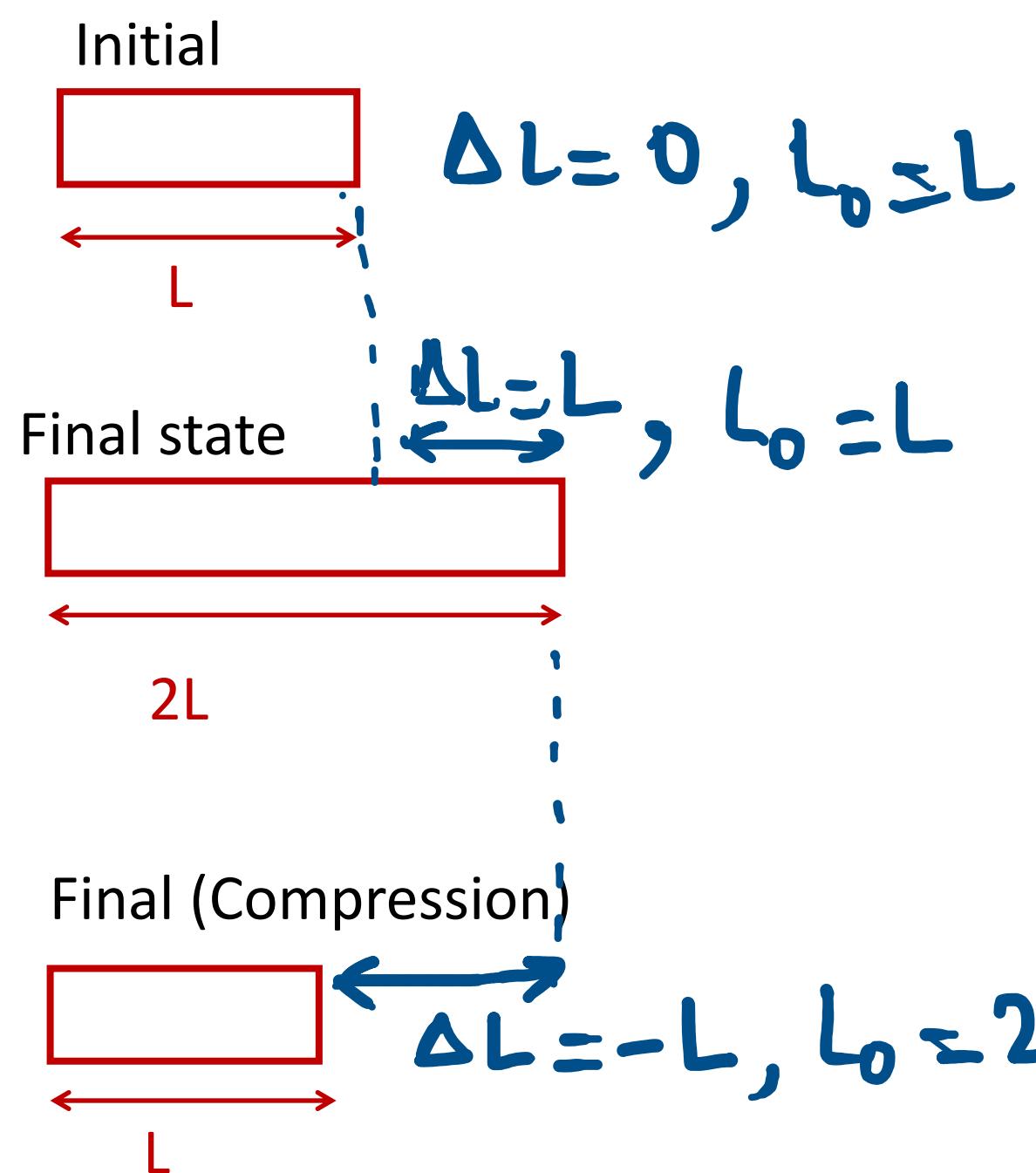
$$\sigma_T = \sigma_E (1 + \epsilon_E)$$

$$\text{True strain, } \epsilon_T = \ln (1 + \epsilon_E) = \ln \frac{L}{L_0}$$

$$\text{Engineering strain, } \epsilon_E = \frac{\Delta L}{L_0}$$

# Implications

True strain is the real strain: for practical purposes



Engineering strain

$$\varepsilon_E = \frac{\Delta L}{L_0} = 0$$

$$\varepsilon_E = \frac{\Delta L}{L_0} = \frac{L}{L} = 1$$

$$\varepsilon_E = \frac{\Delta L}{L_0} = \frac{-L}{2L} = -0.5$$

---

$$\text{Net } \varepsilon_E = 0.5$$

---

True strain

$$\varepsilon_T = \ln \frac{L}{L_0} = 0$$

$$\varepsilon_T = \ln \frac{2L}{L} = \ln 2 = 0.69$$

$$\varepsilon_T = \ln \frac{L}{2L} = -\ln 2 = -0.69$$

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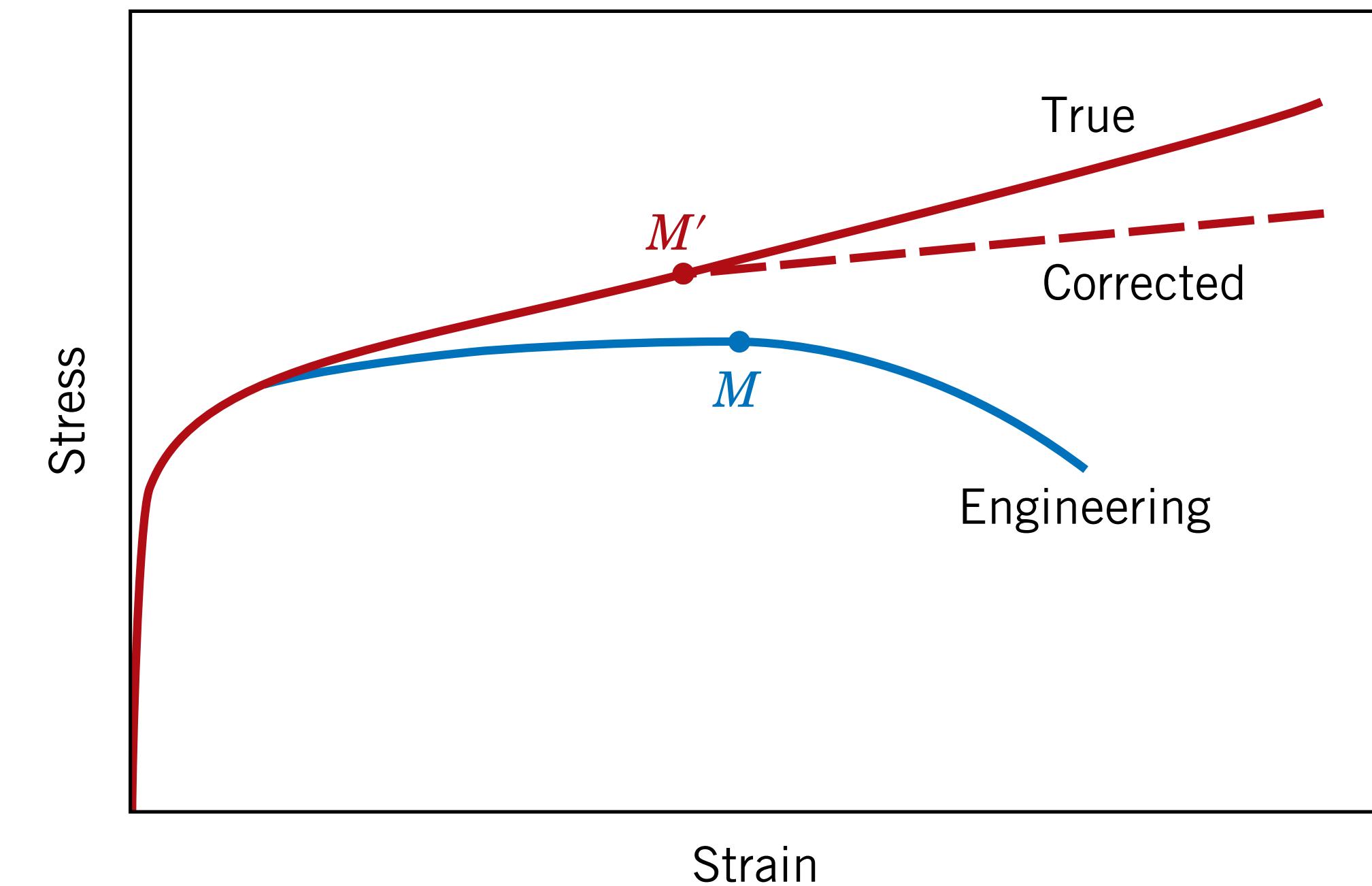
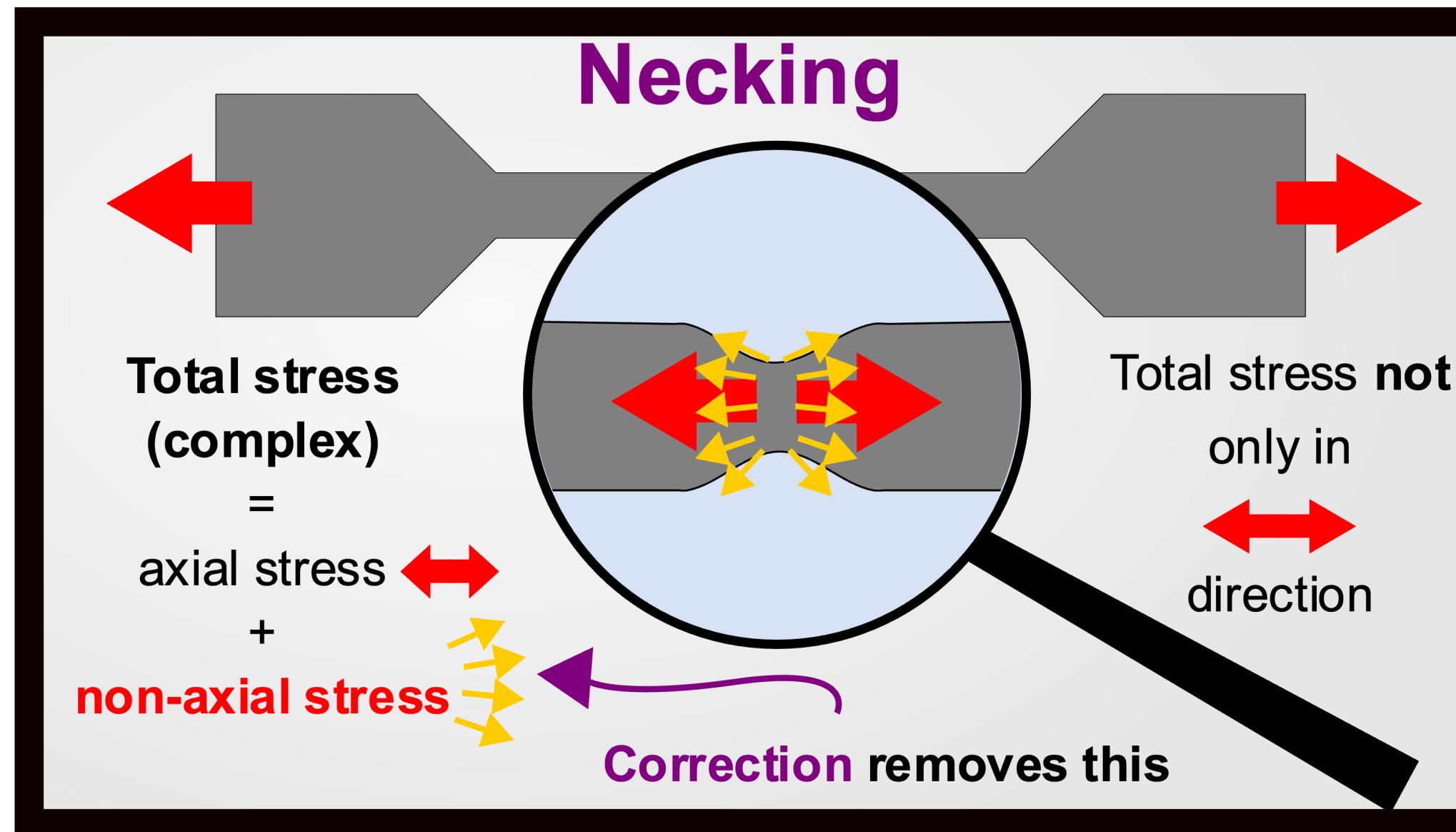
$$\text{Net } \varepsilon_T = 0$$

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# True vs Engineering stress-strain

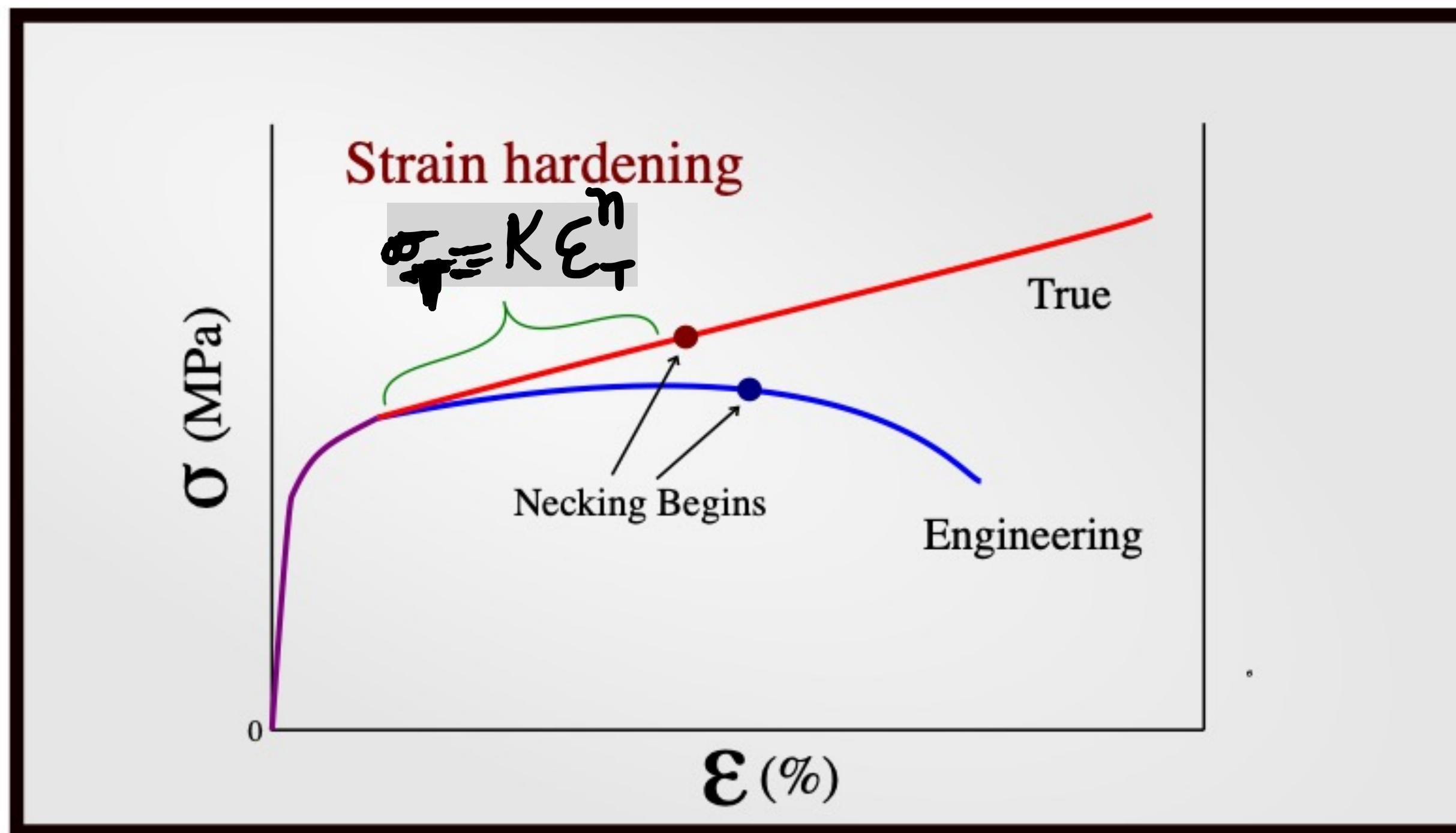
## Necking region: existence of other stress components in addition to the axial stress

The “correct” stress (axial) within the neck is slightly lower than the stress computed from the applied load and neck cross- sectional area.



# Strain hardening

Region of the true stress–strain curve from the onset of plastic deformation to the point at which necking begins



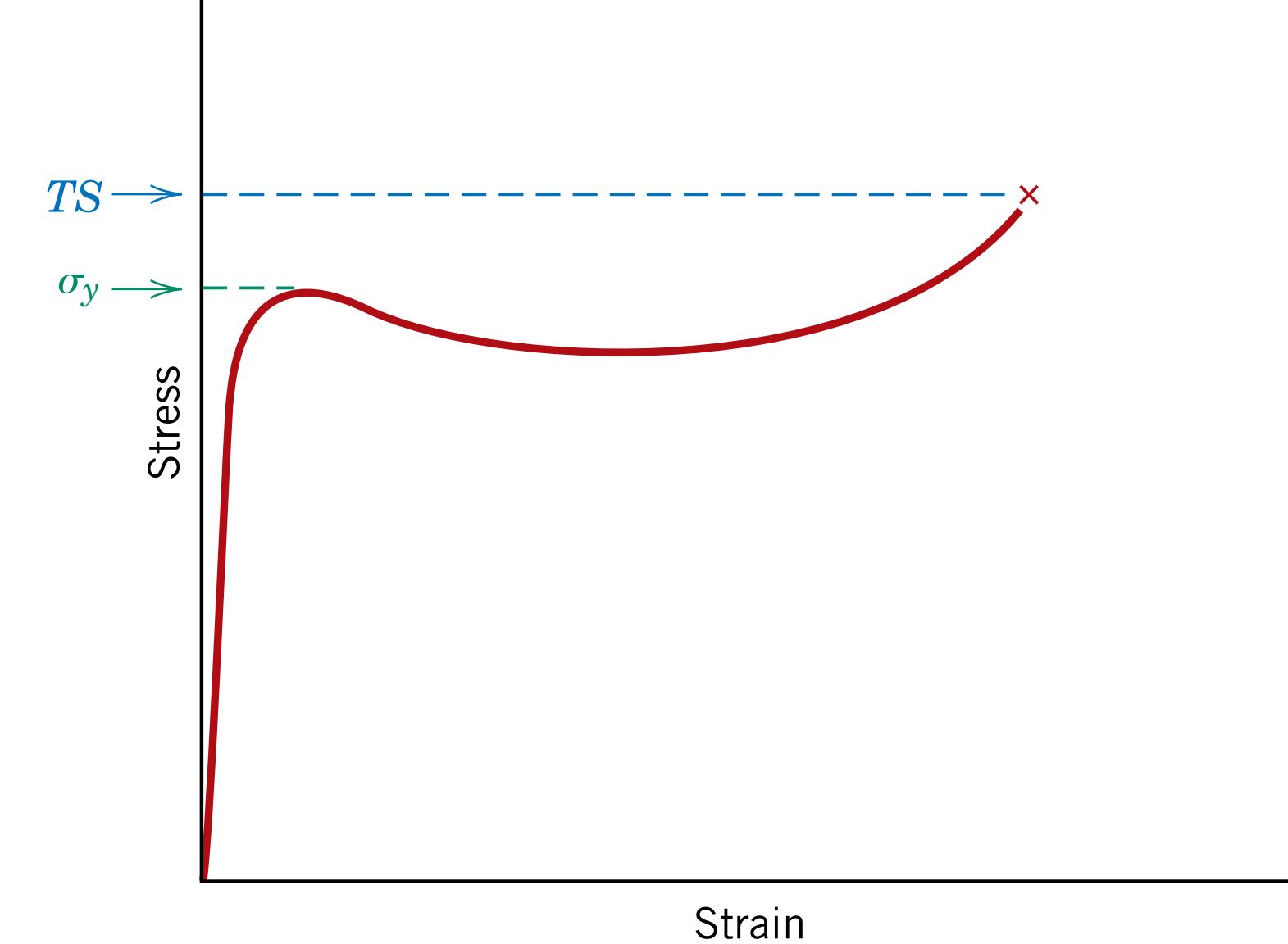
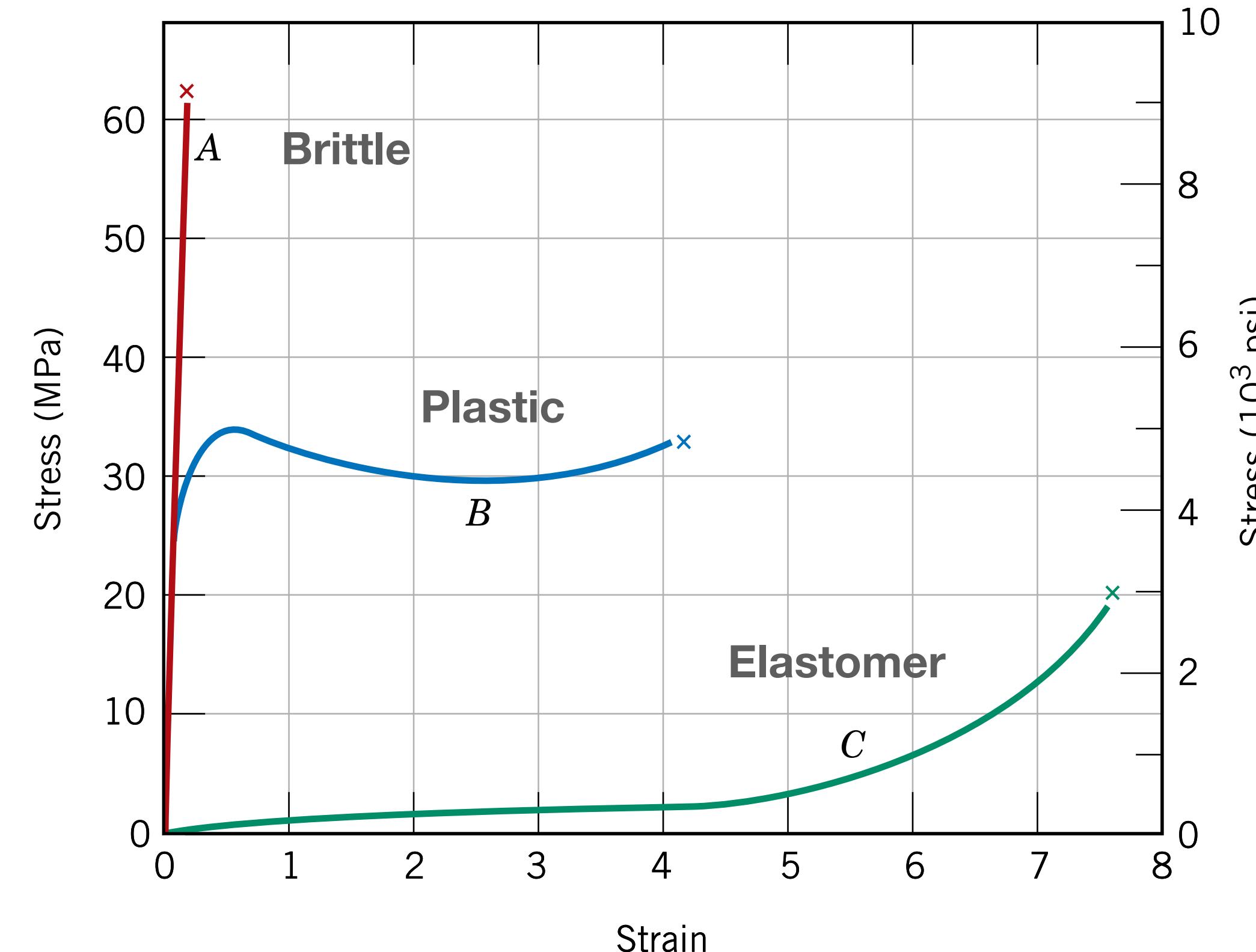
$$(n < 1)$$

$n$  = strain hardening exponent (we will do this when we learn more about plastic deformation)  
 $K$  = strength coefficient

# Stress-strain curve for Polymers

## Three categories

- Fibres (A)
- Plastics (B)
- Elastomers (C)



# Stress-strain curve for Polymers

## Three categories



Plastics



Elastomers



Fibres

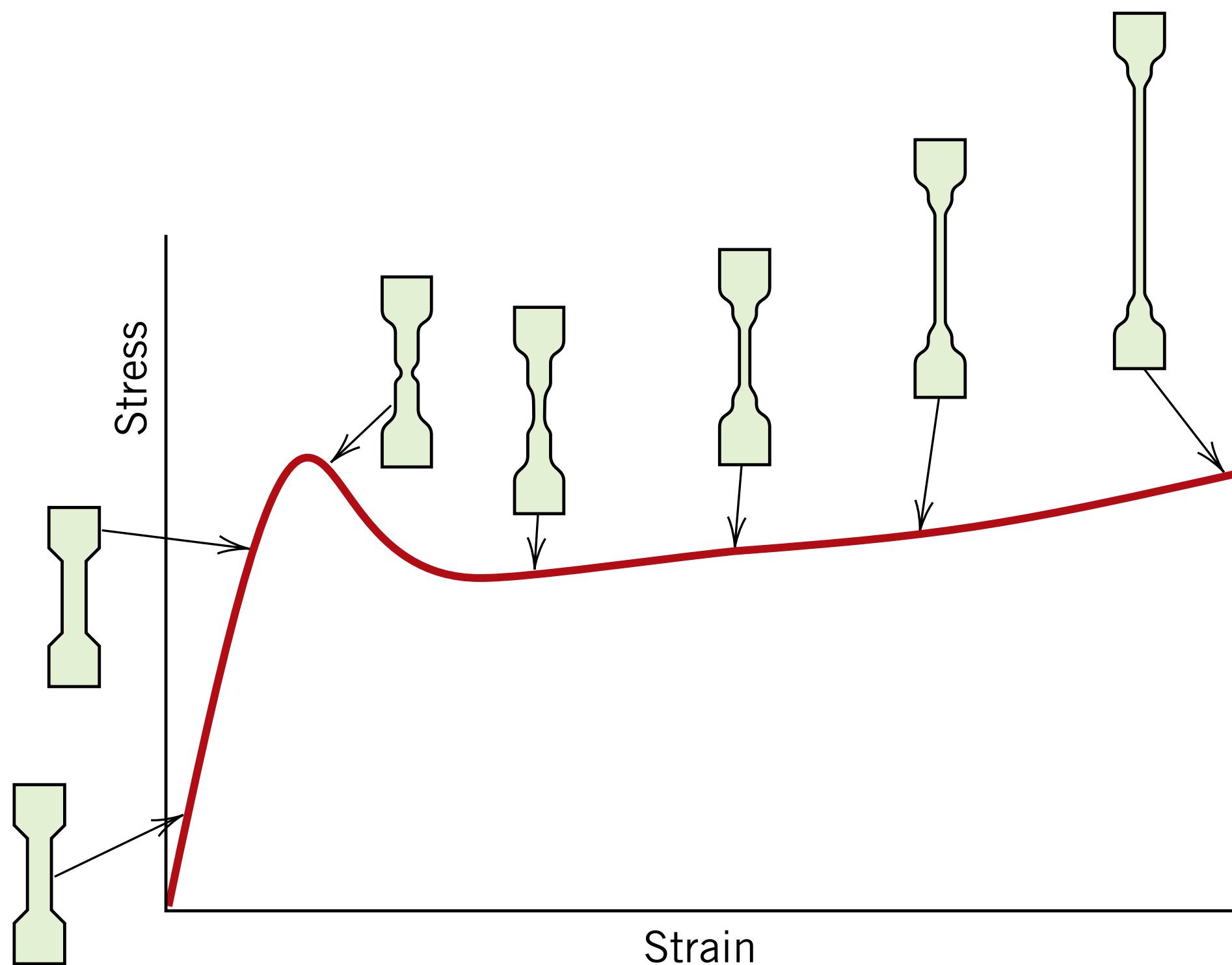
**Plastics:** are materials that have some structural rigidity (stiffness) under load. Examples: Polyethylene, polypropylene, poly(vinyl chloride), polystyrene, and the fluorocarbons, epoxies, phenolics, and polyesters.

- Can be rigid (stiff) and brittle
- Can be flexible (elastic and plastic deformation)
- May have any degree of crystallinity
- All molecular structures and configurations (linear, branched, isotactic, etc.) are possible.
- Thermoplastic or thermosetting

# Viscoelasticity

## Viscous-liquid+ elastic behaviour

- Found in materials which respond to an applied stress by both recoverable and permanent deformations, which are time dependent
- Very common in non-crystalline organic polymers
- Time-dependent permanent deformation is called viscous flow
- In elastic deformation, the rate of strain or strain is not important



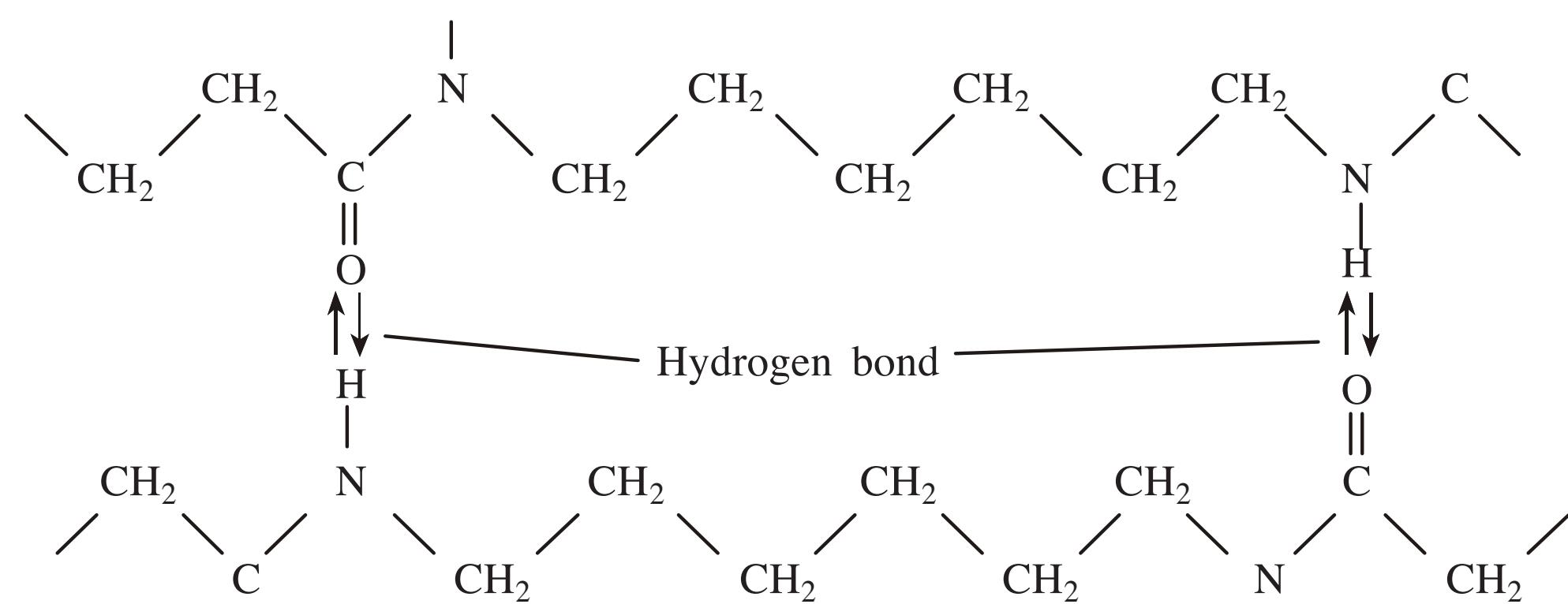
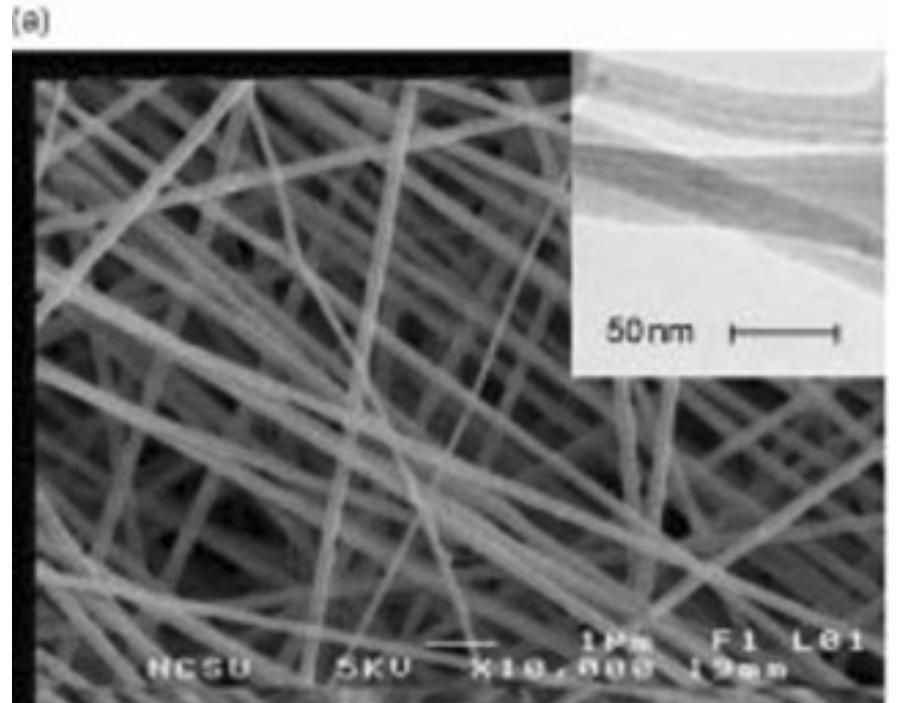
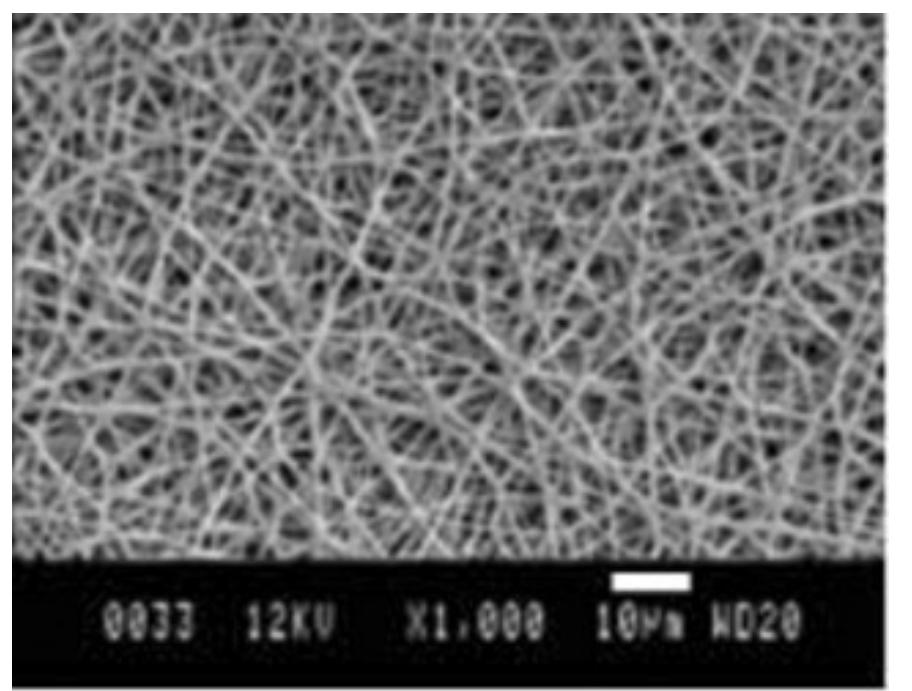
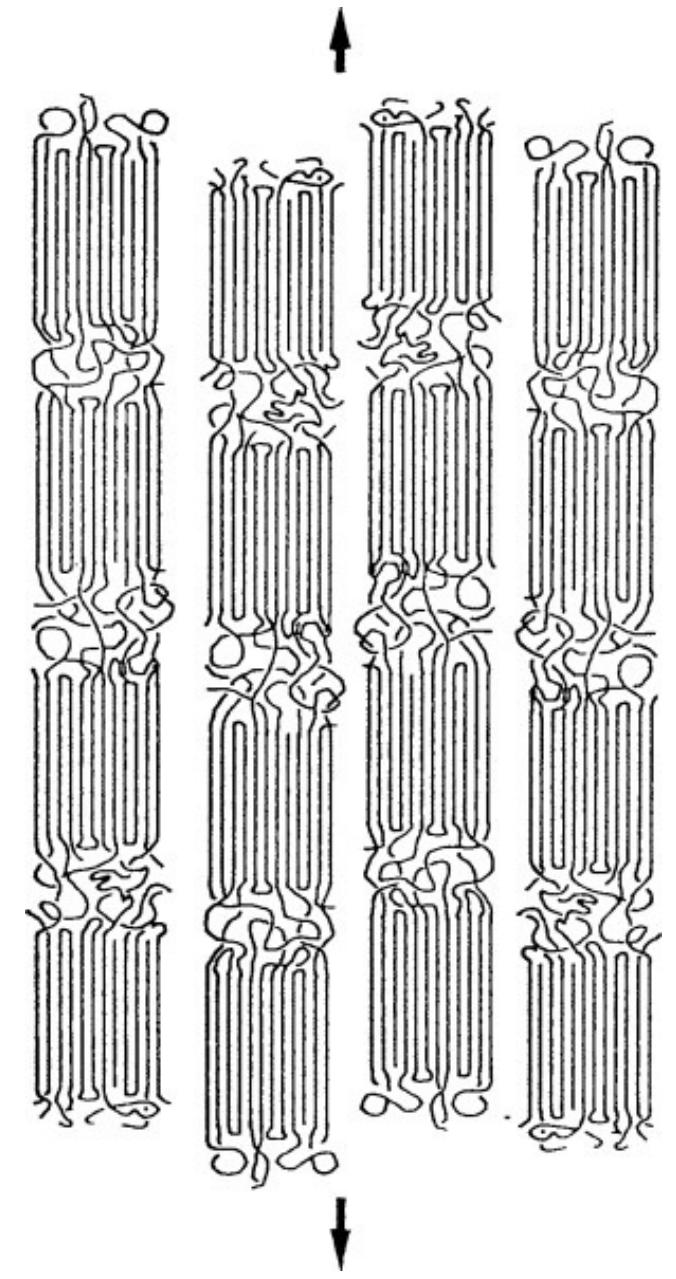
### Amorphous material:

- Glass at low temperatures: not all molecular motion is frozen
  - Rubbery solid above glass transition temperature: conformational changes
  - Viscous liquid at high temperature: segments between entanglements can recover
- 
- At low temperature: elastic (Hooke's law)
  - At high temperature: viscous liquid-like behaviour
  - At intermediate temperatures: combined mechanical characteristics:

### Viscoelasticity

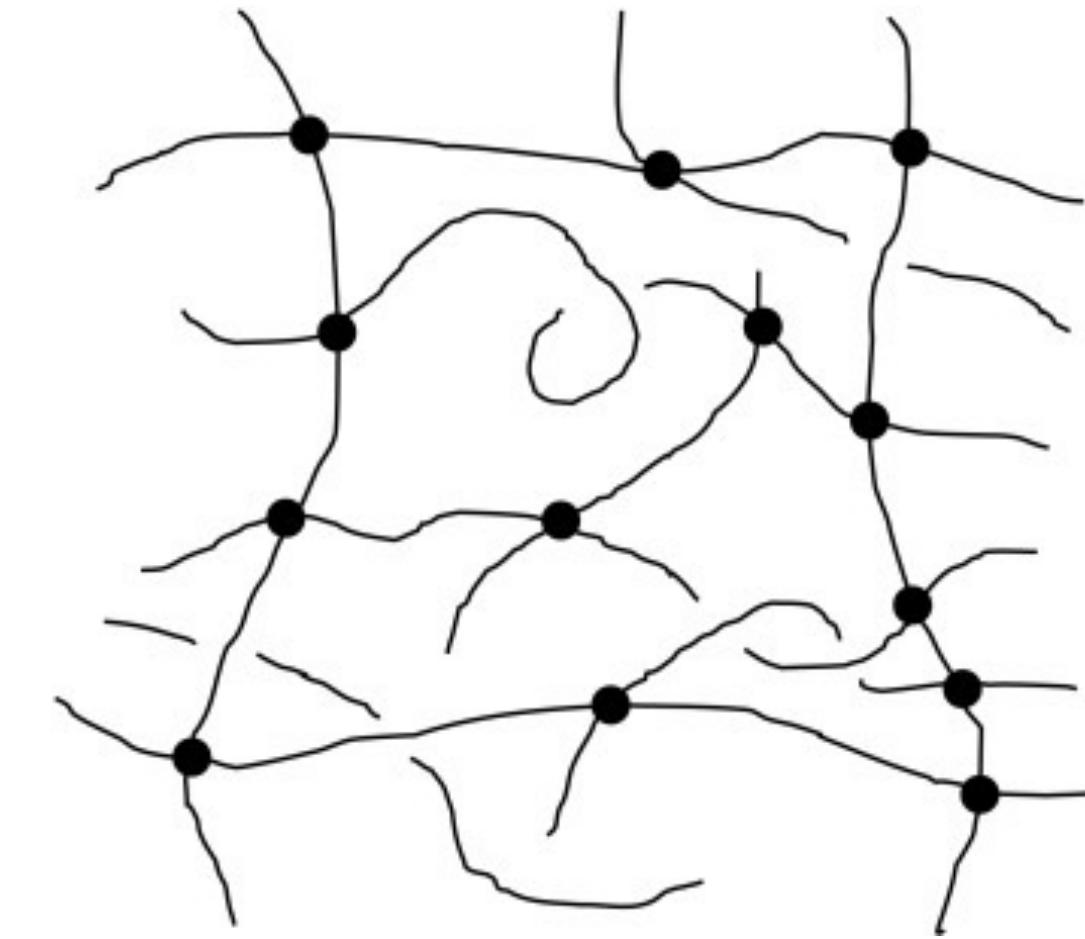
# Fibers

- Polymers are capable of being drawn into long filaments having at least a 100:1 length-to-diameter ratio.
- All the chains are more or less aligned in the long direction of the fibre
- High elastic modulus: Their strength and elastic modulus in a direction parallel to the fibre length are an order of magnitude larger as compared to the nonaligned structure.
- High degree of crystallinity leads to high tensile strength: linear and unbranched polymer chains, polar groups increase inter-chain intermolecular forces
- Examples: Nylon– polyamide fiber



# Elastomers

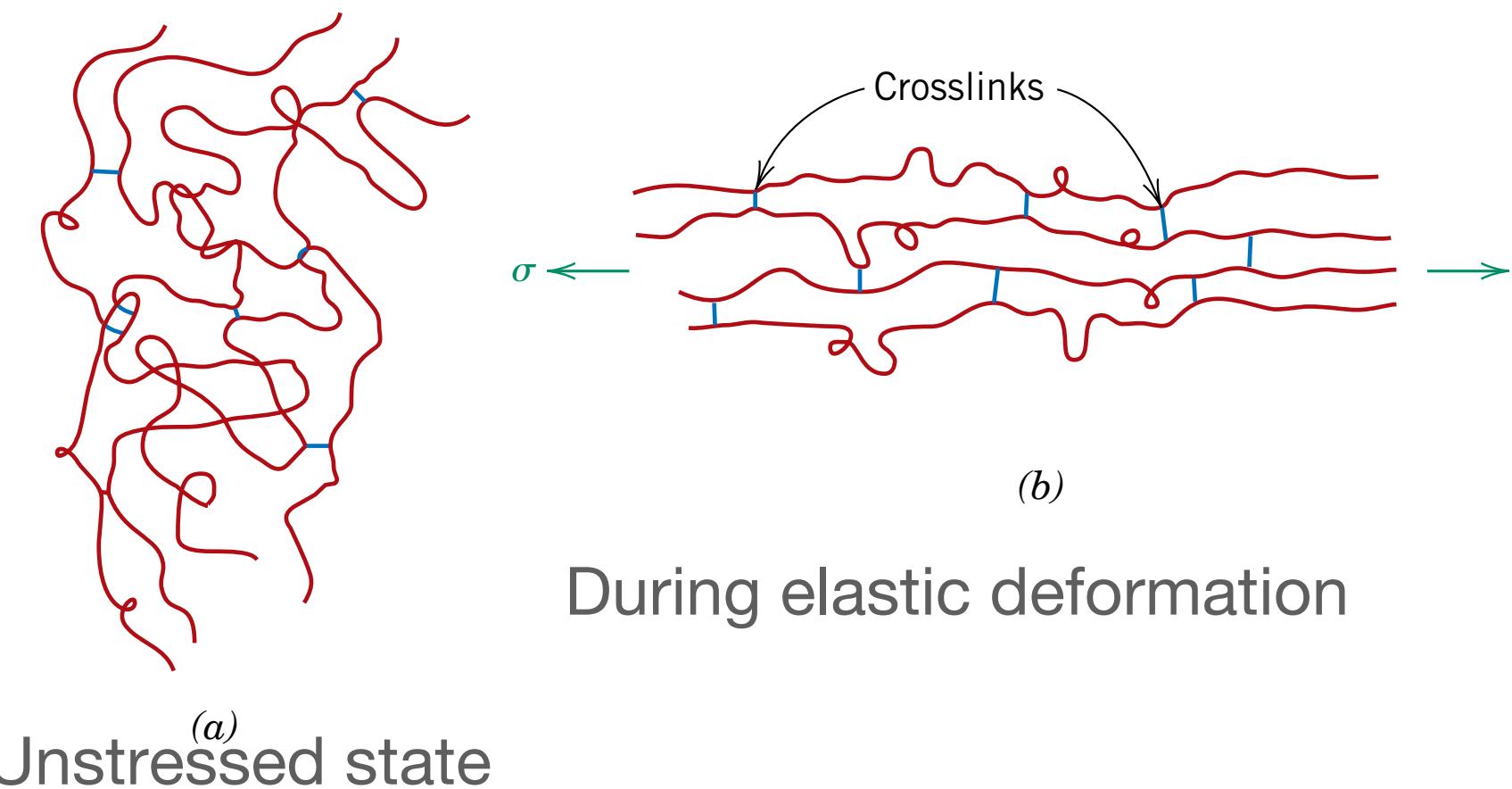
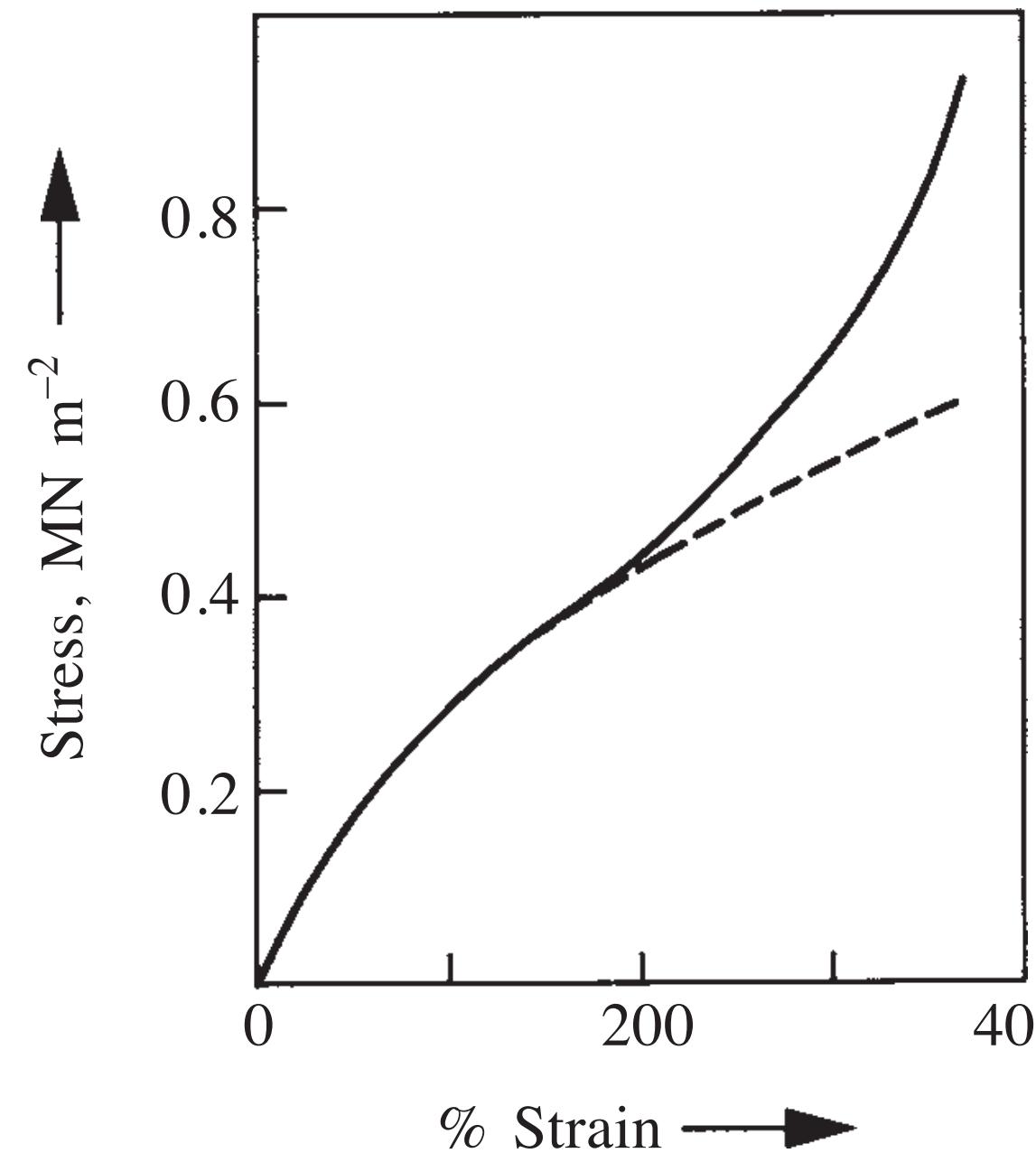
## Rubber-like elasticity



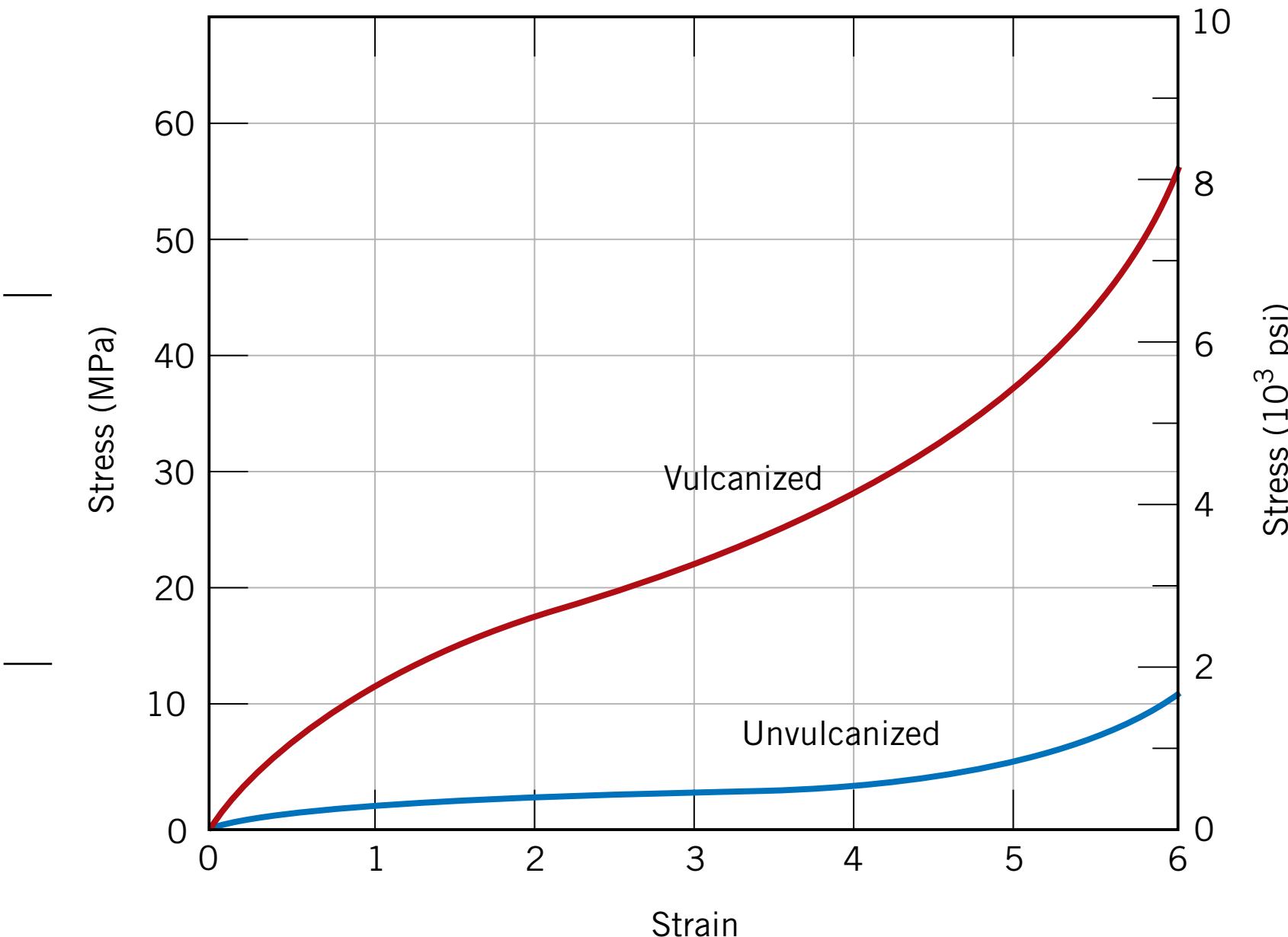
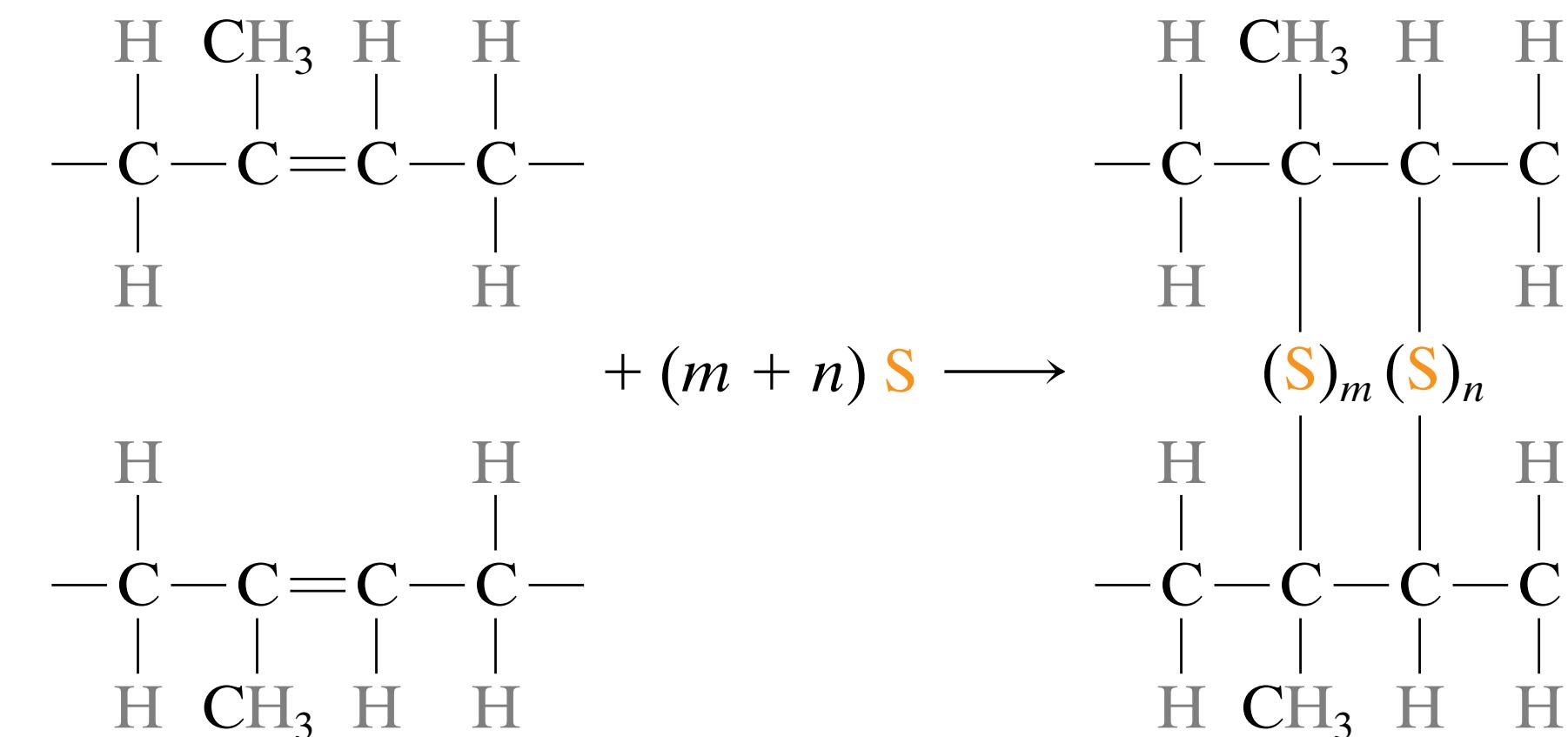
- Materials which undergo recoverable deformation of *a few hundred per cent* are called *elastomers* and exhibit rubber-like elasticity.
- The stress is not proportional to strain in these materials, in contrast to ordinary elastic materials.
- Long chain polymers with some *cross-linking* between the chains.
- This feature is what keeps the molecules from slipping past one another permanently during stretching
- After cross-linking, the translational motion of chains gets restricted to segmental mobility between cross-linking points. When a stress is applied to an elastomer, equilibrium in the molecular configuration is established fairly quickly so that we can ignore the time dependent aspects of stretching as a first approximation.
- Do not easily crystallize
- Amorphous
- Onset of plastic deformation is delayed: restricting the motions of chains

# Elastomers

## Stress-strain curve



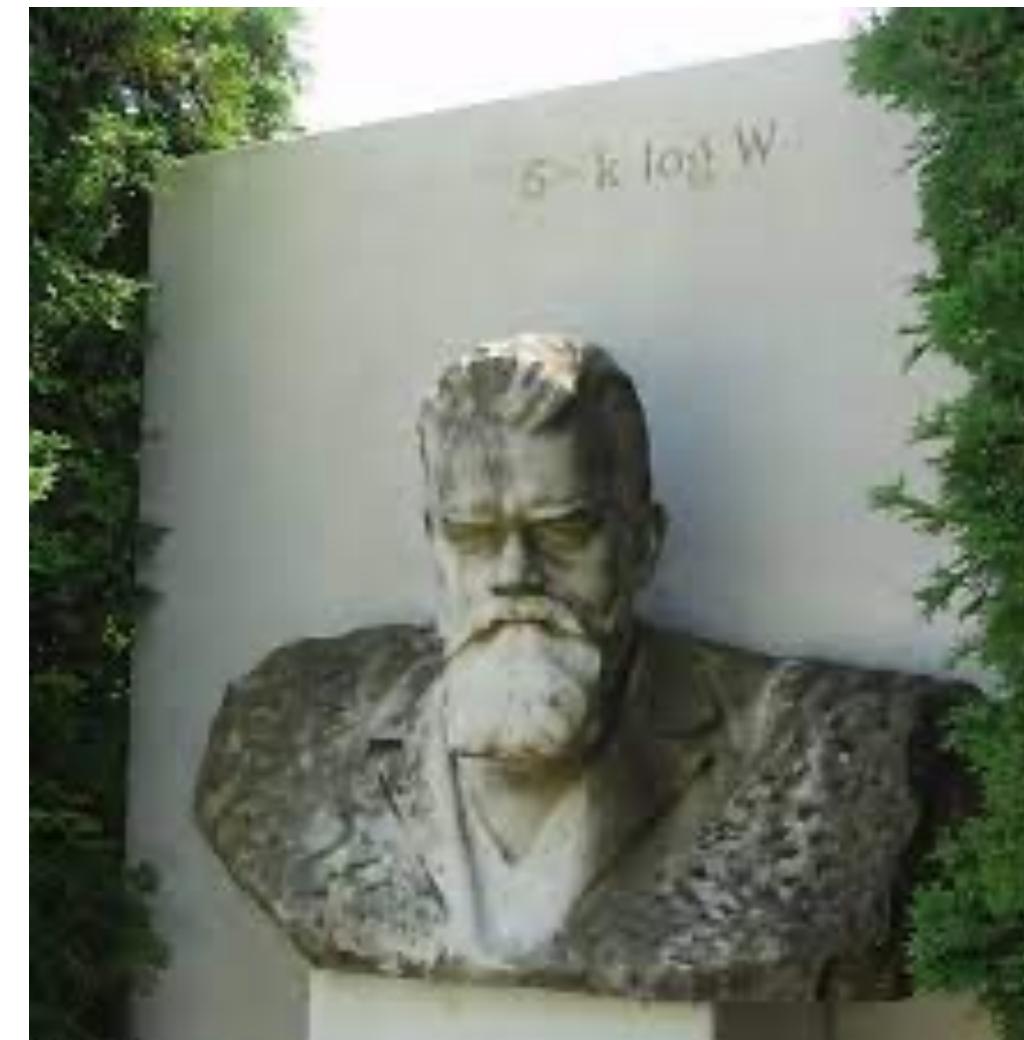
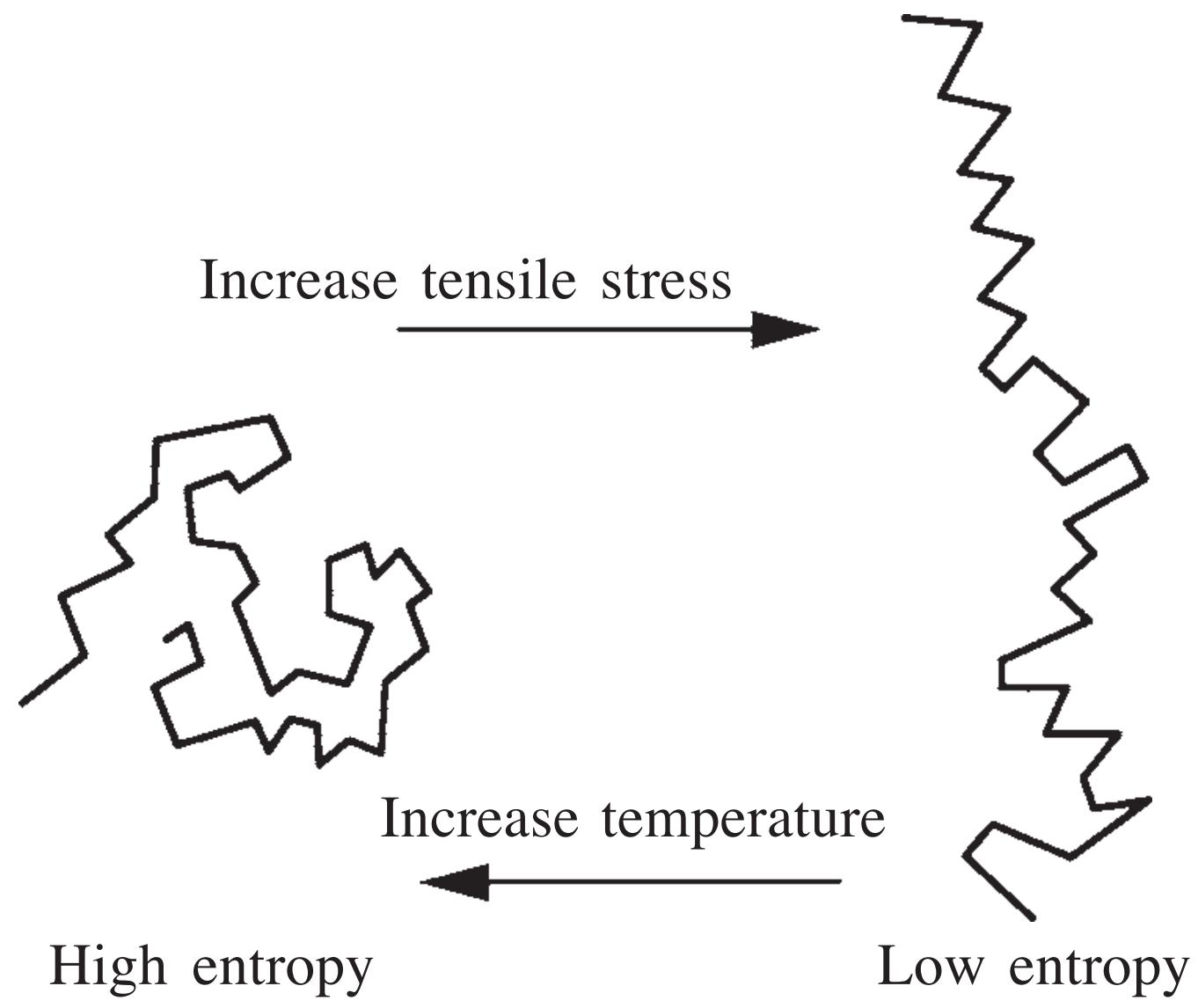
**Vulcanization:** crosslinking process in elastomers



- Sulfur compounds are added to the heated elastomer; chains of sulfur atoms bond with adjacent polymer backbone chains and crosslink them
- Unvulcanized rubber, which contains very few crosslinks, is soft and has poor resistance to abrasion.
- Elastic modulus increases with increasing temperature.
- Magnitude of elastic modulus  $\propto$  density of cross-links.

# Driving force for elastic deformation in elastomer is entropy

## Thermodynamics



A new definition of entropy  
 $S = k \log W$

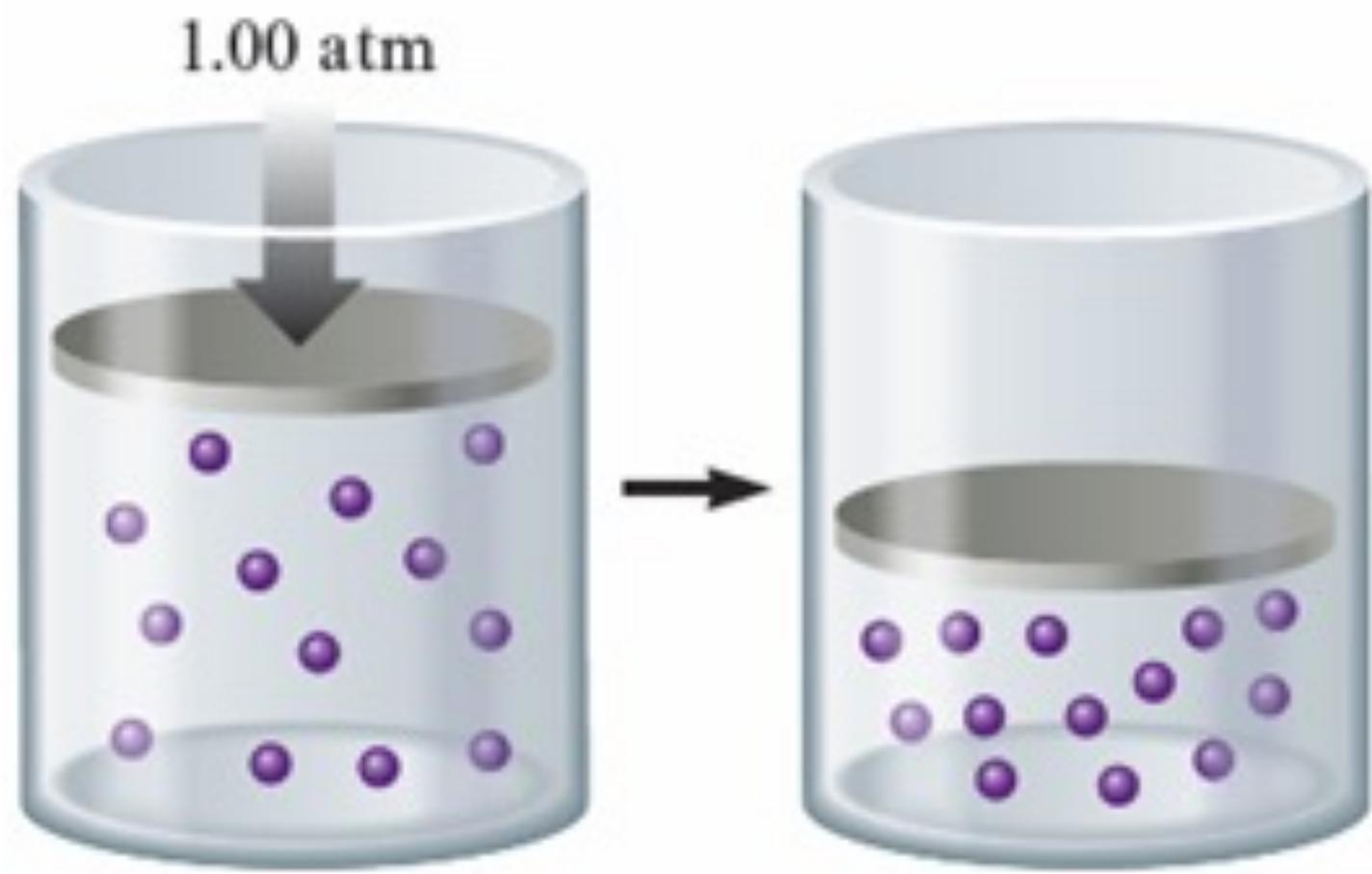
Ludwig Boltzmann

The stretching process merely uncoils the coiled molecules, but does not change the bond lengths or bond angles. This behaviour is in contrast to what happens in an ordinary elastic material, where bond lengths are clearly changed

$W$ = number of ways of arrangement of molecules  
 $S$ = Entropy is a measure of the possible number of ways in which the energy of the system can be distributed among the molecules.

Good reads: "Anxiety and Equation" by Eric Johnson  
"Entropy Demystified" by A. Ben Naim

# Food for thought..



Why does gas in a container expand spontaneously?

**Why does not the gas contract on its own spontaneously?**

Why does a hot coffee mug get cold spontaneously on keeping for sometime?

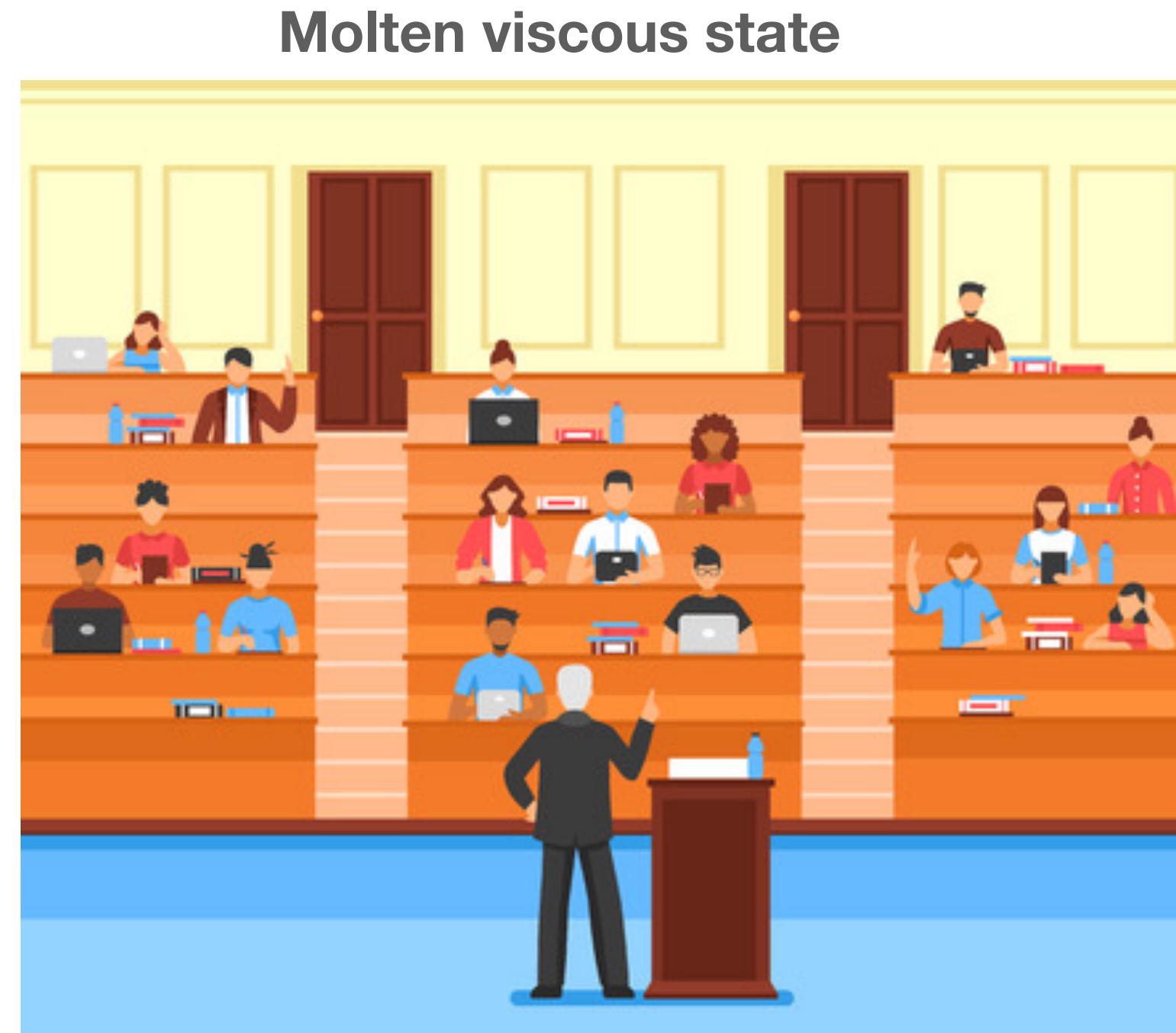
**If you keep a cold coffee mug on table, why doesn't it get hot on its own spontaneously?**

**Dispersal of energy (*distribution of energy*) → spontaneity → entropy**

# The statistical or *molecular* definition of Entropy...

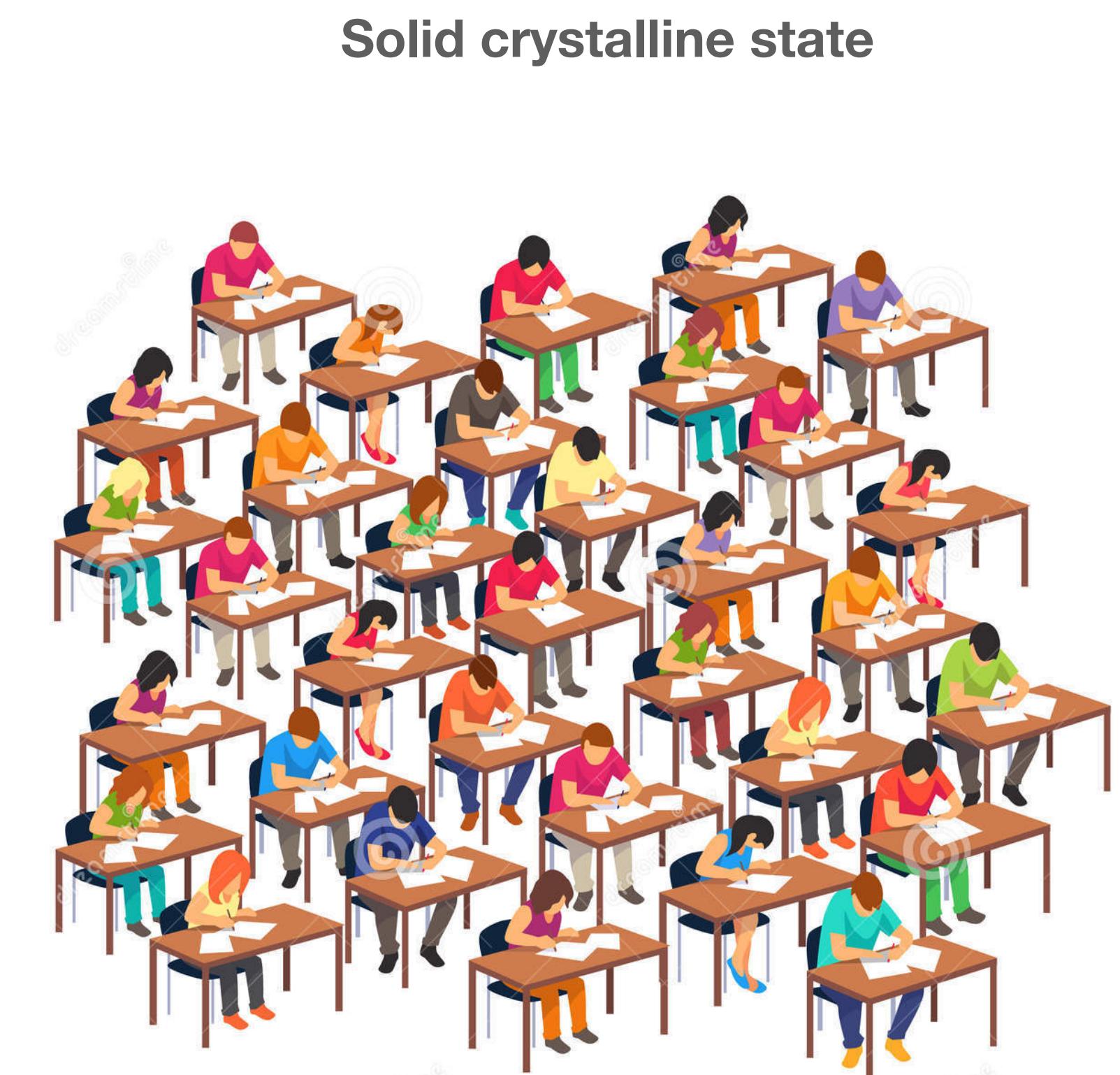


On a "random" lecture day



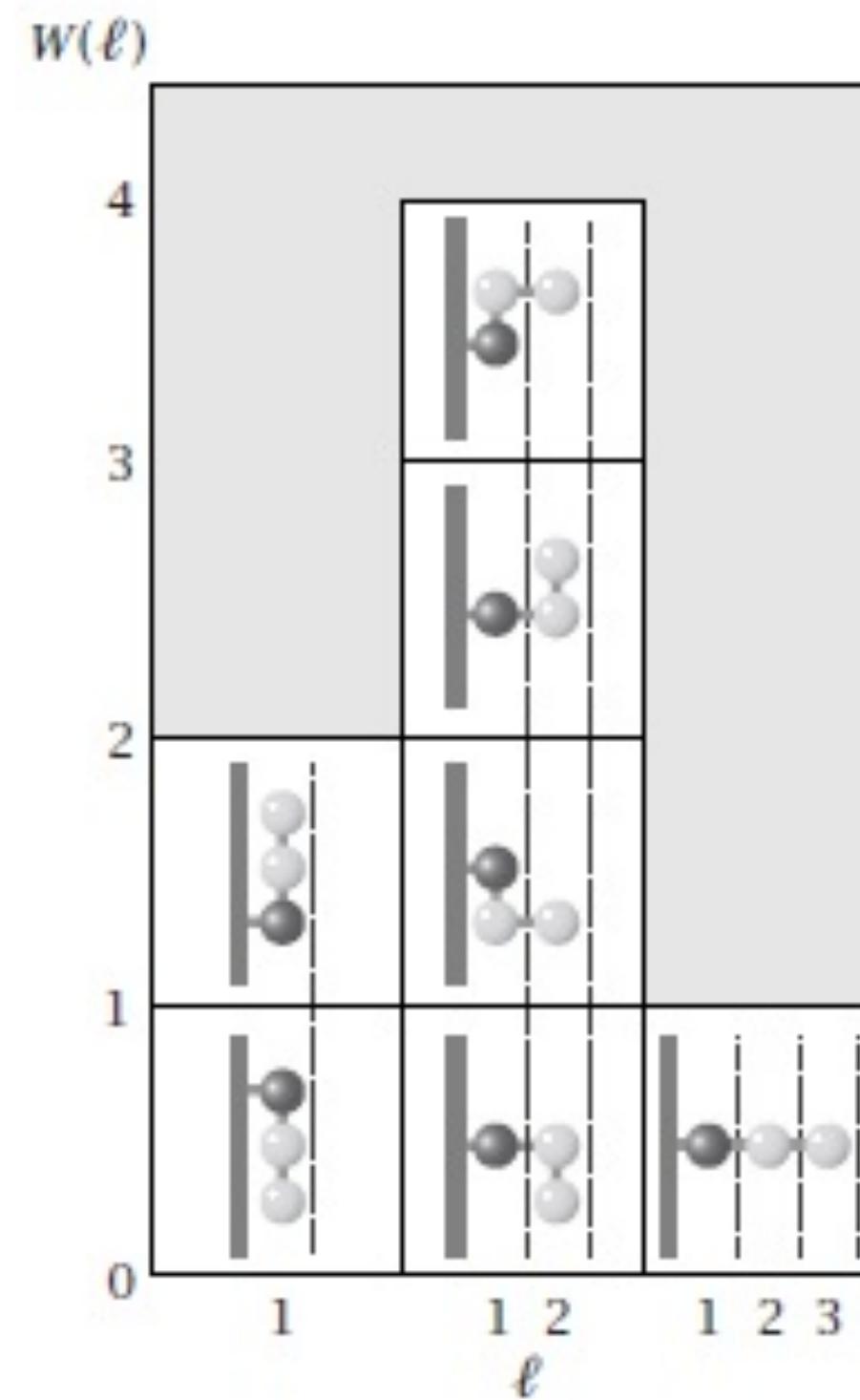
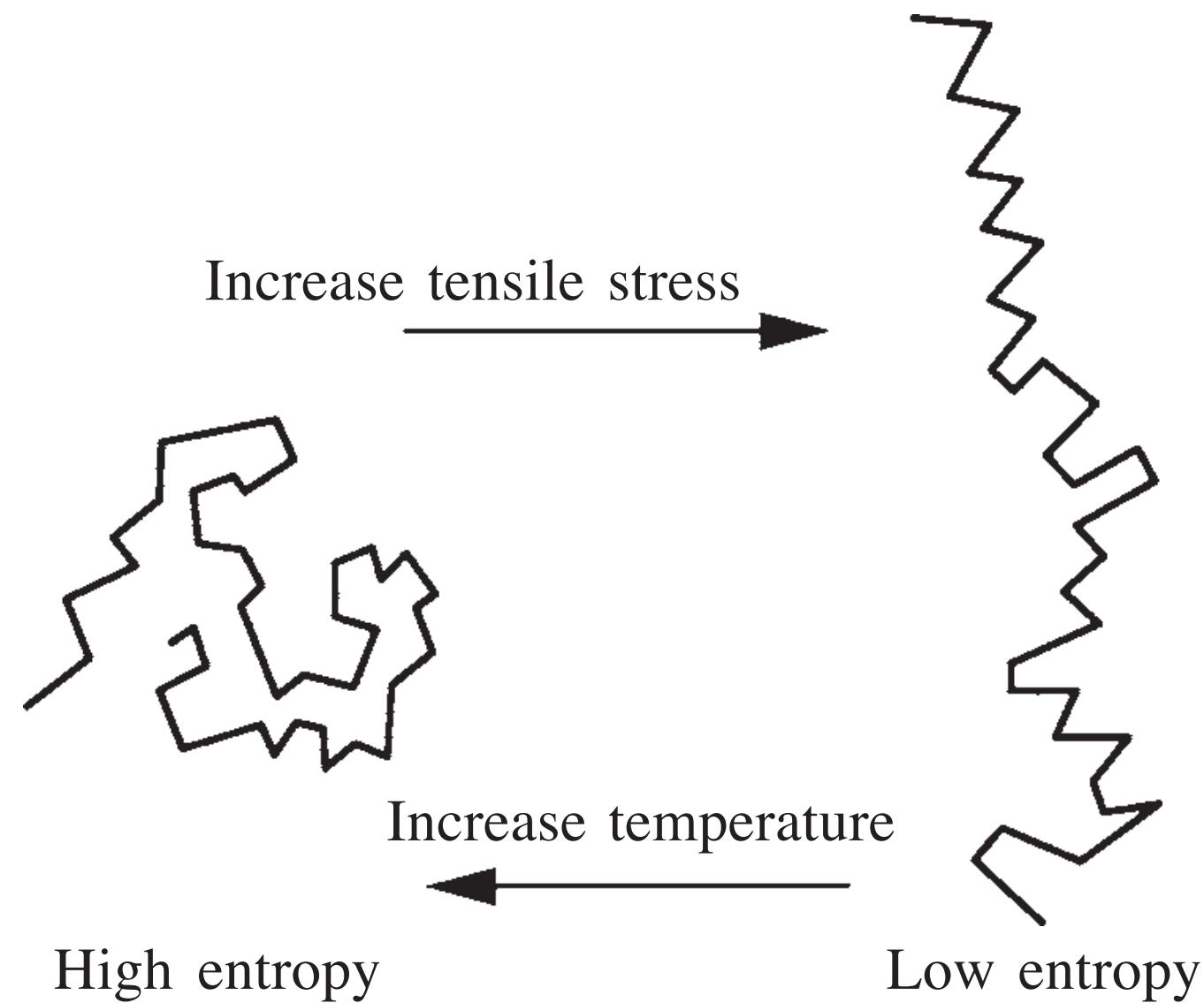
When students *prefer* to choose  
their company..

*Decreasing Entropy*



On "exam" day:  
Perfectly ordered arrangement

# Driving force for elastic deformation is entropy



# Stretchability in rubber

# Which state will have higher entropy?

Case	Left	Right
A		
B		
C		

Permeable Barrier →

# Diffusion in materials



# Lecture 30

**Defects in solids**

*Why things are weak?*

Prof. Divya Nayar

Department of Materials Science and Engineering

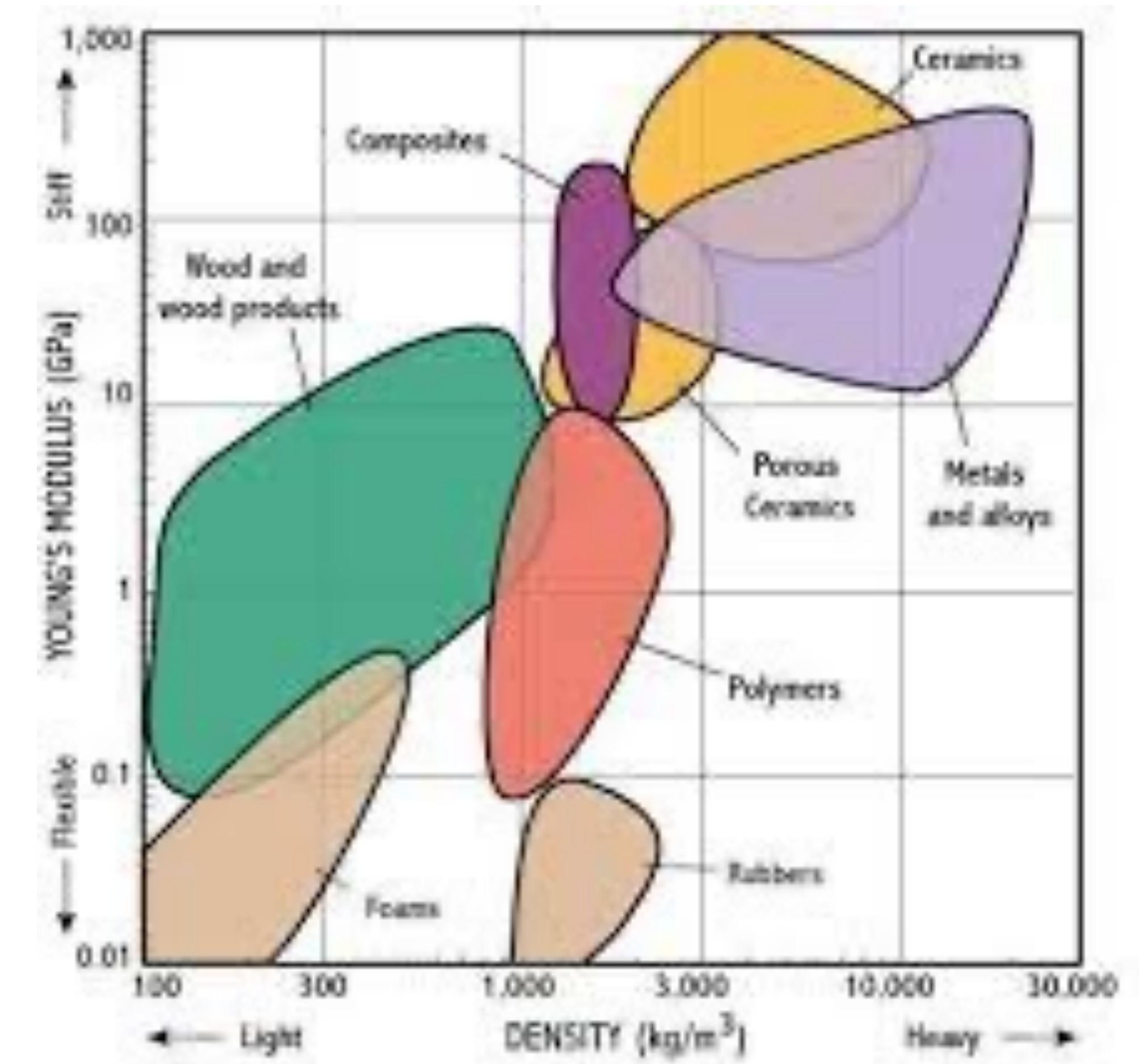
[divyanayar@mse.iitd.ac.in](mailto:divyanayar@mse.iitd.ac.in)

# Previous lectures..

- *Why don't all solids have same strength?*
- *Why do they have any strength at all?*
- *When do we call them strong?*

## In the coming two lectures:

- *Why aren't they much stronger?*
- *Why materials are weak?*
- *Why and how do materials fail?*



# An important engineering problem

## Blades of wind turbine



Ice forming on wind blades



Bugs infesting the blades

Blowing at the blades at 100 mph!



*Light, strong, sustain wind speed:  
balance of elastic-plastic  
deformation!!*

# Defects in solids

## Based on dimensionality

- Point defects (0-D): vacancies (interstitial)
- Line defects (1-D): Dislocations
- Surface defects (2-D): free surface, grain boundaries, twin boundaries, stacking fault
- Volume (or bulk) defects (3-D): pores, cracks, foreign inclusions.

# Dislocations

A **dislocation** is a linear or one-dimensional defect around which some of the atoms are misaligned

Three types of dislocations:

1. **Edge dislocation:** This imperfection is associated with the insertion of an extra half-plane of atoms or removal of half-plane of atoms

2. **Screw dislocation:** associated with a shearing deformational shift along a regular plane.

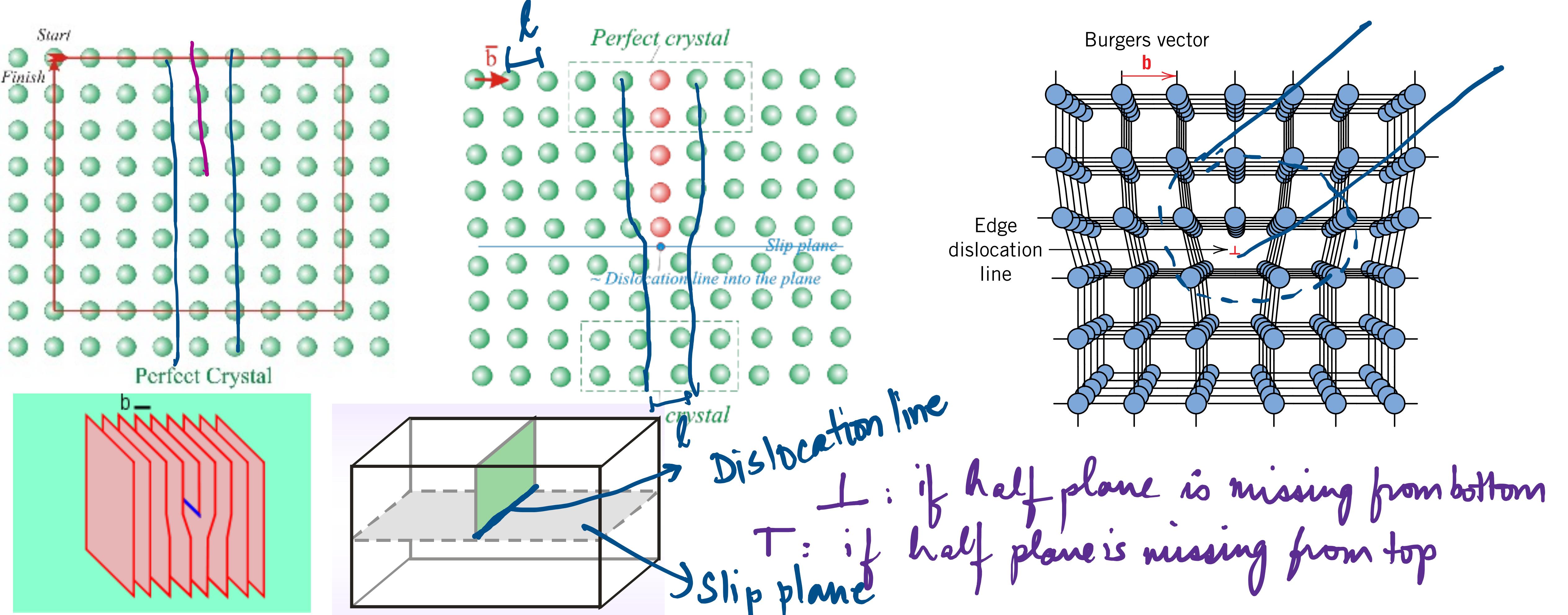
3. **Mixed dislocation:** combination of both edge and screw dislocation.

- Plastic deformation corresponds to the motion of large numbers of dislocations.
- They prevent the synchronized breakage of bonds between atoms in materials and cause gradual deformation by making the one-by-one breakage of single bonds possible.

# Edge dislocation

L or T

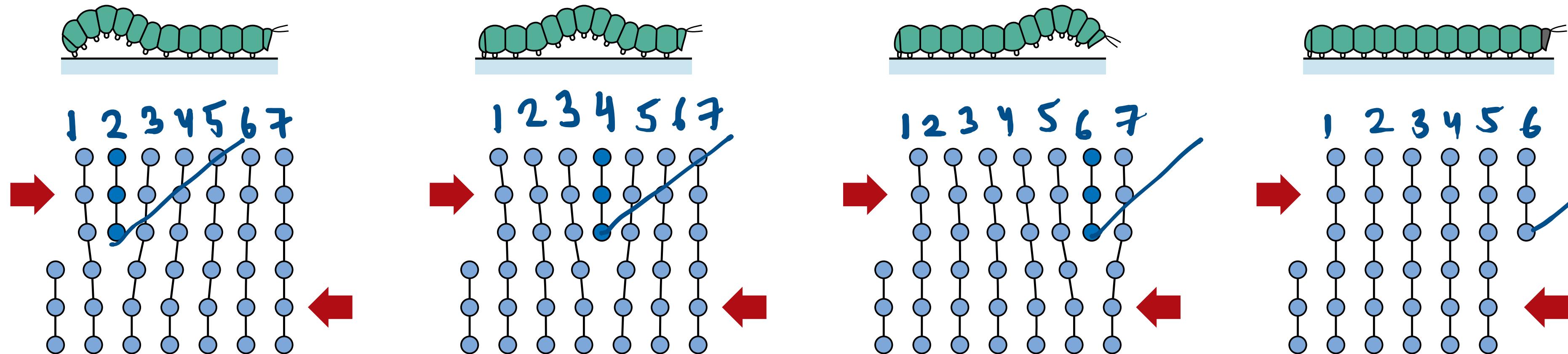
- **Edge dislocation:** it is a linear defect that centers around the line that is defined along the end of the extra half-plane of atoms.
- **Dislocation line:** For an edge dislocation, the intersection of the extra half-plane of atoms with the slip plane defines the dislocation line



# Edge dislocation: slip

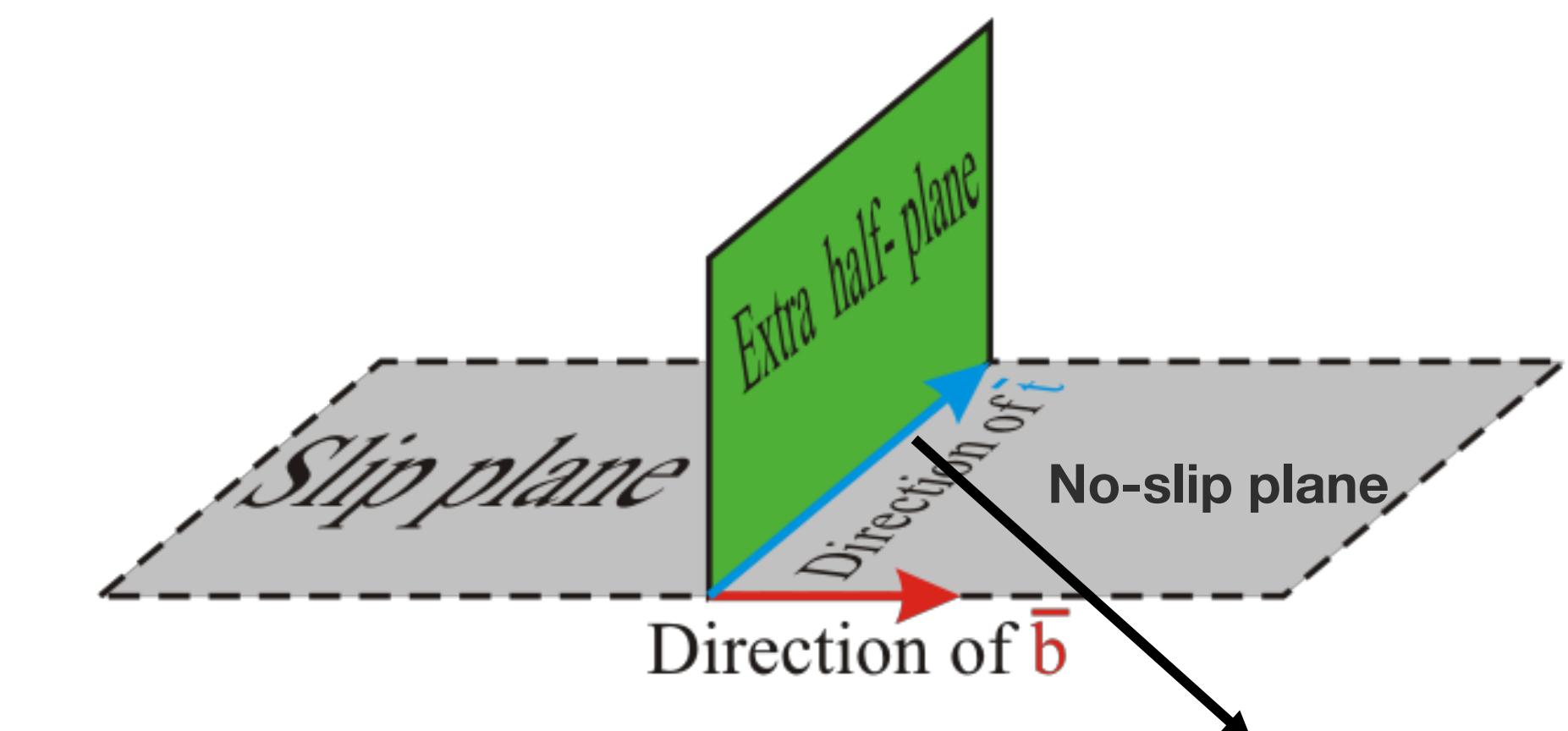
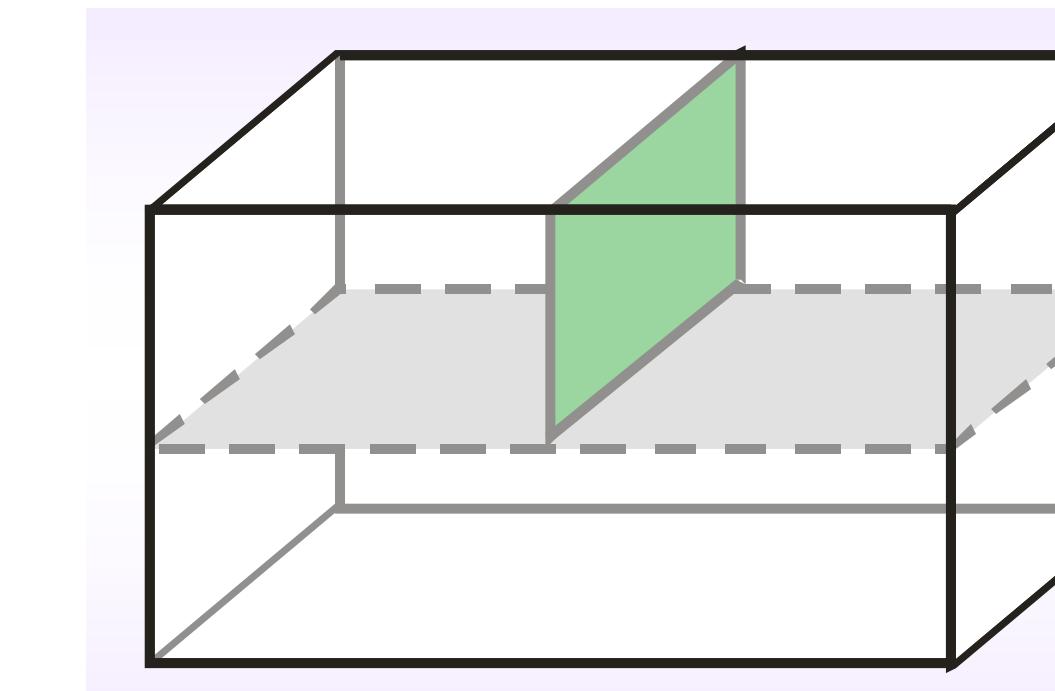
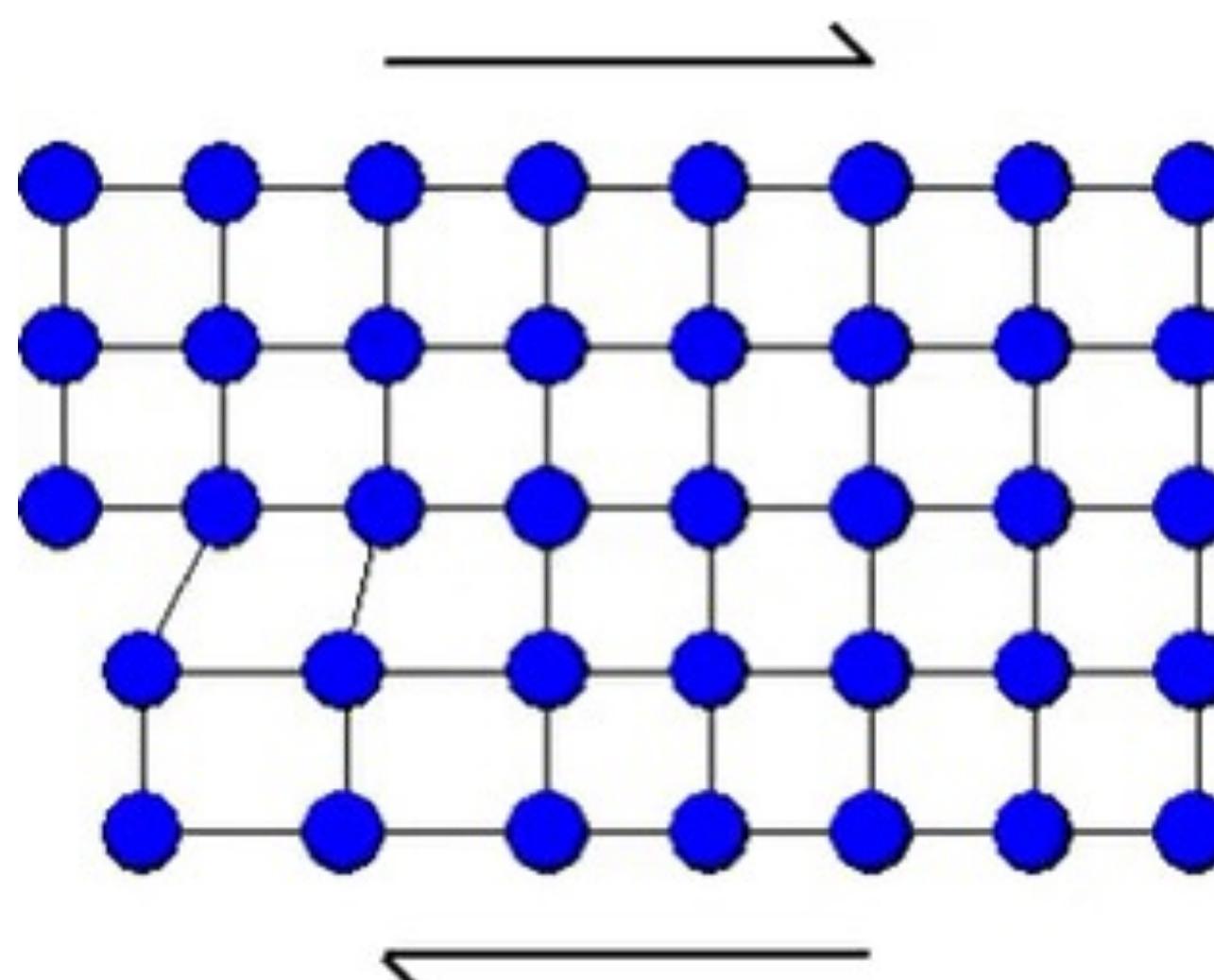
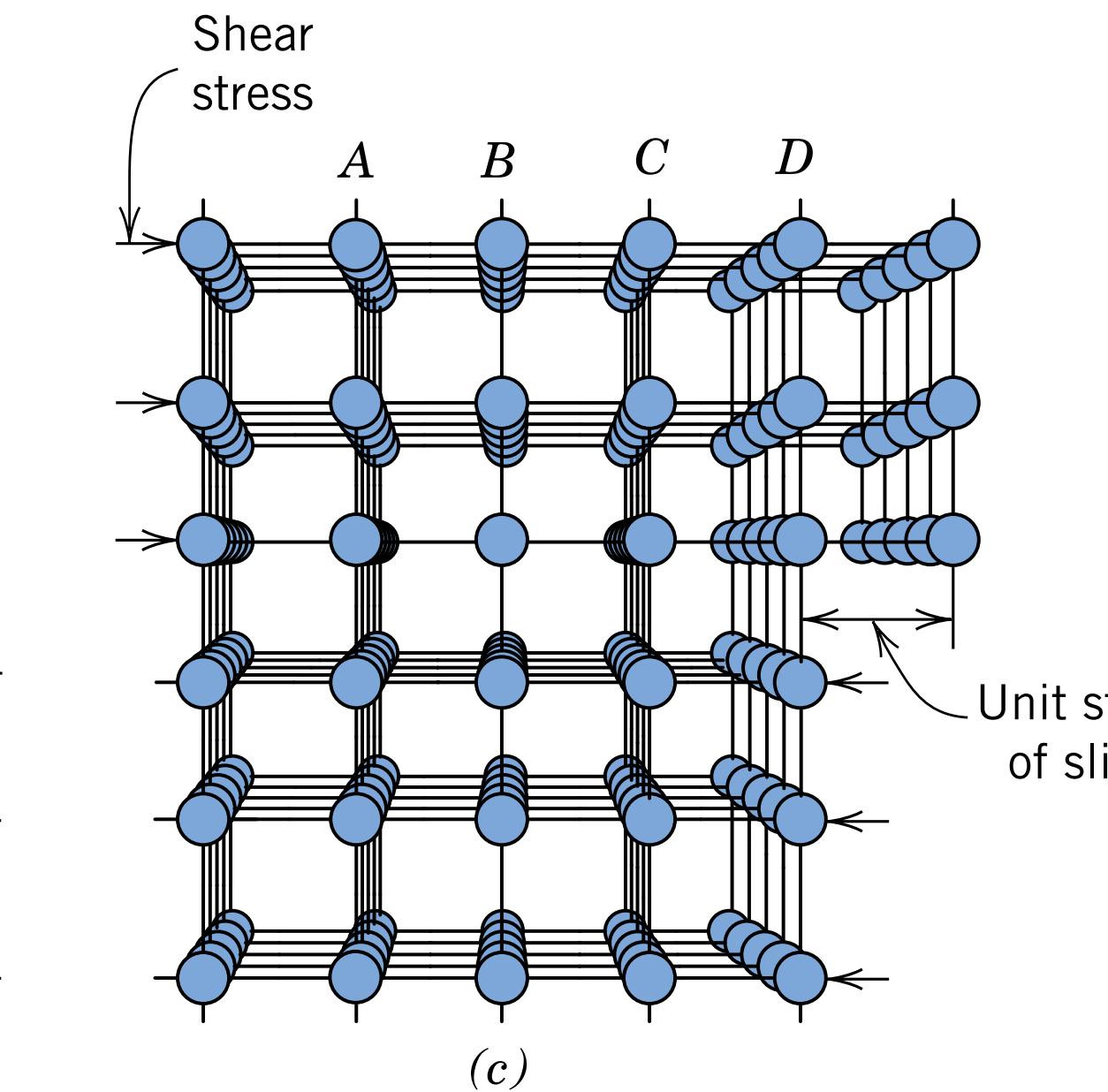
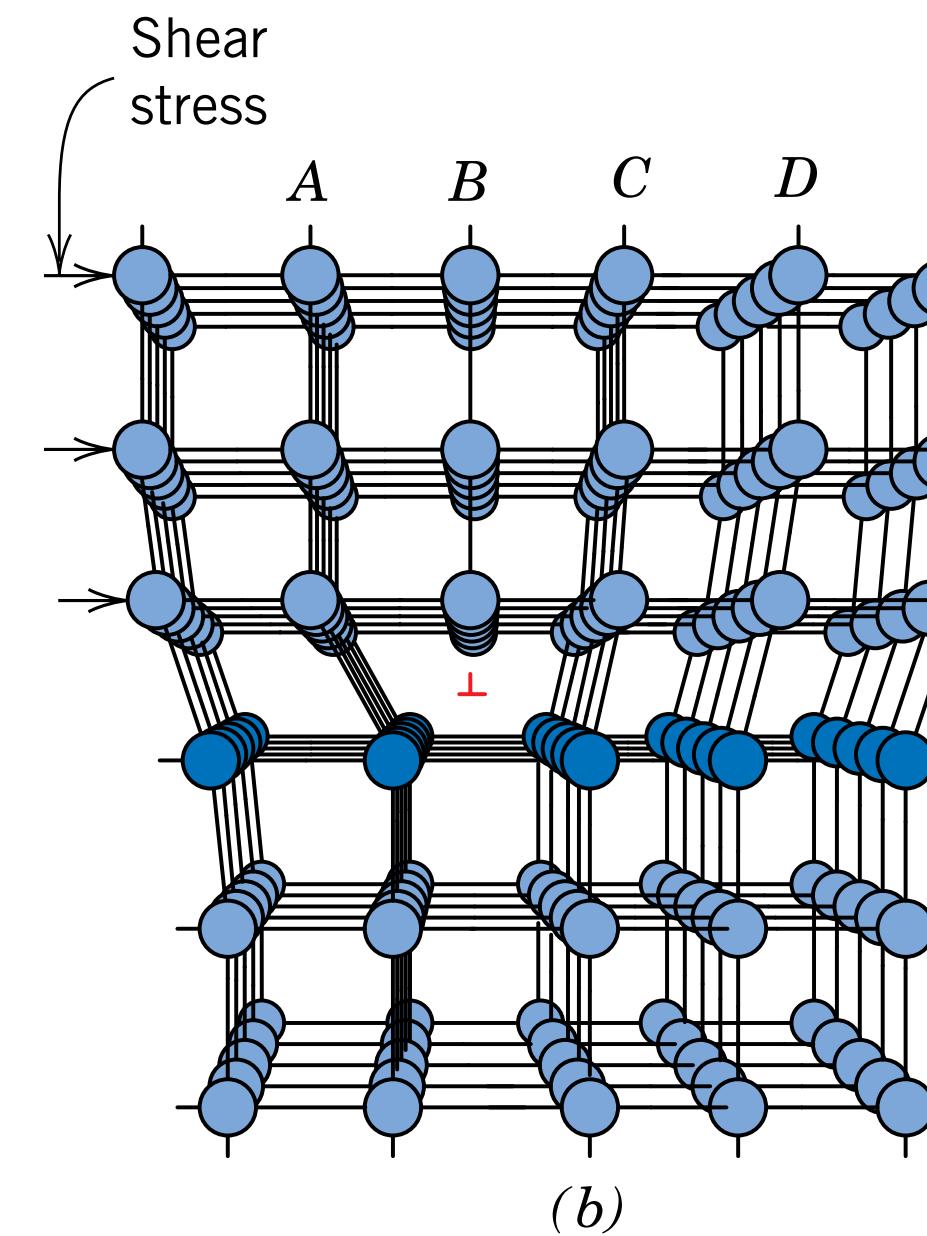
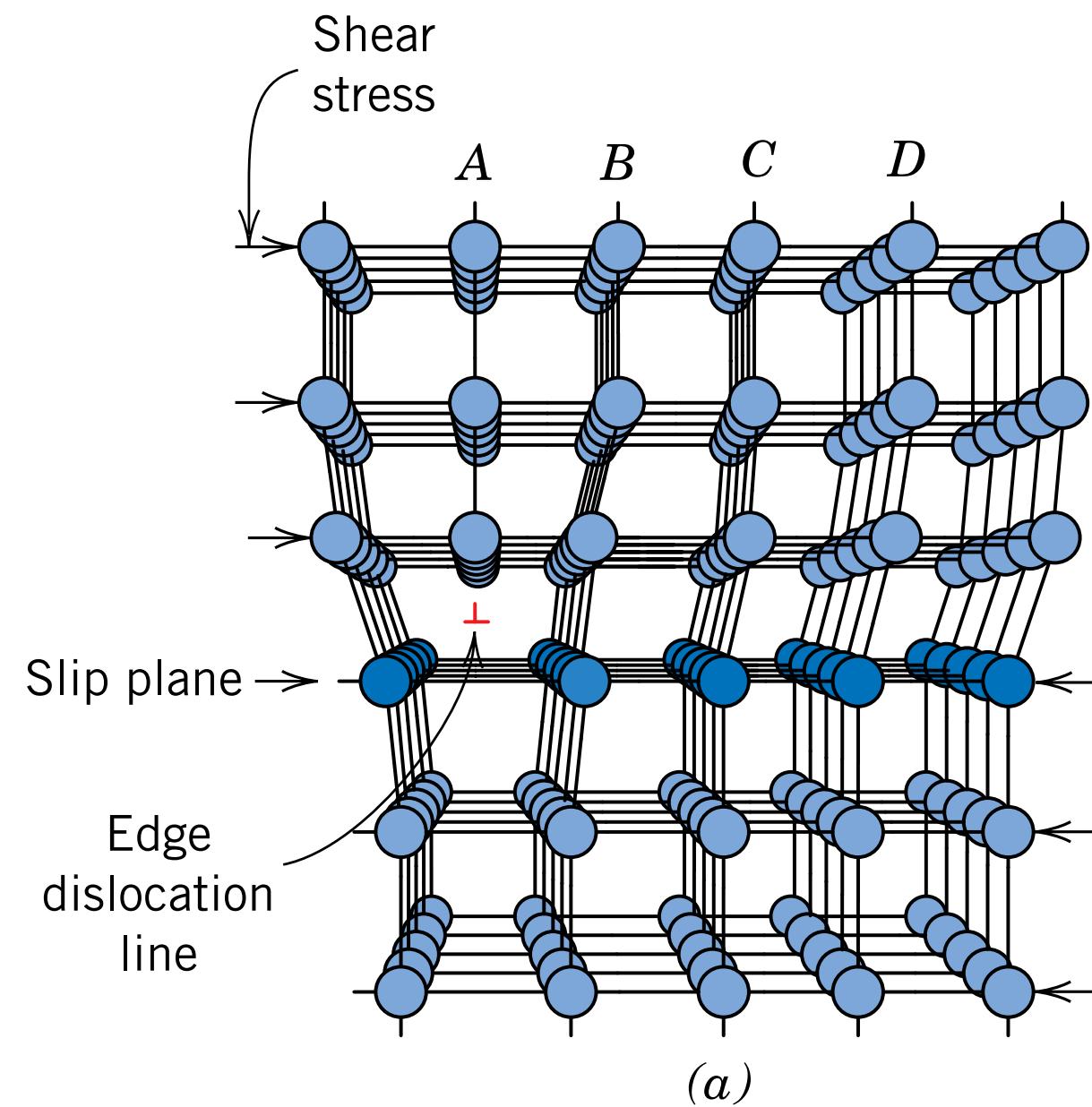
The process by which plastic deformation is produced by dislocation motion is termed **slip**

- An edge dislocation moves in response to a shear stress applied in a direction perpendicular to its line.
- This process is subsequently repeated for the other planes, such that the extra half-plane, by discrete steps, moves from left to right by successive and repeated breaking of bonds and shifting by interatomic distances of upper half-planes.
- Only during the passage of the extra half- plane that the lattice structure is disrupted.
- Ultimately this extra half-plane may emerge from the right surface of the crystal, forming an edge that is one atomic distance wide.
- The crystallographic plane along which the dislocation line traverses is the **slip plane**.
- **Dislocation line** can be considered as the boundary between the slipped and the unslipped parts of the crystal lying over a slip plane.



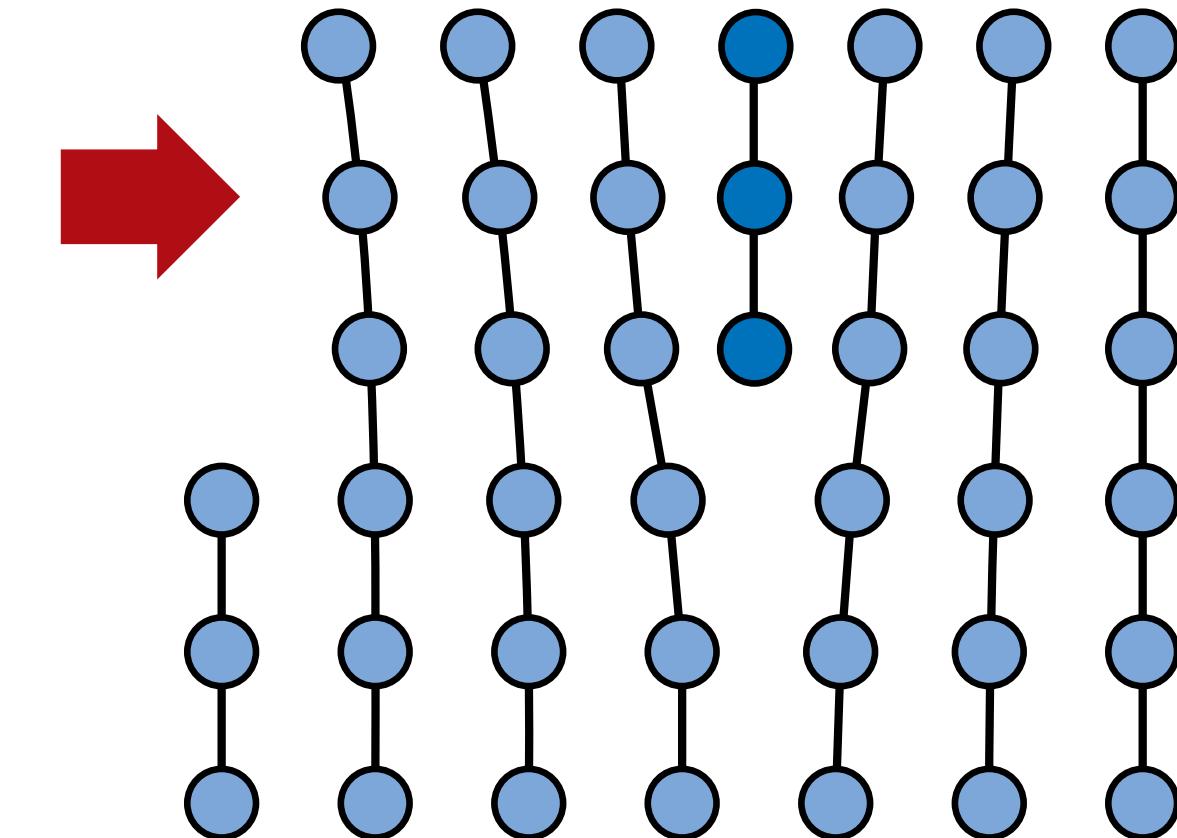
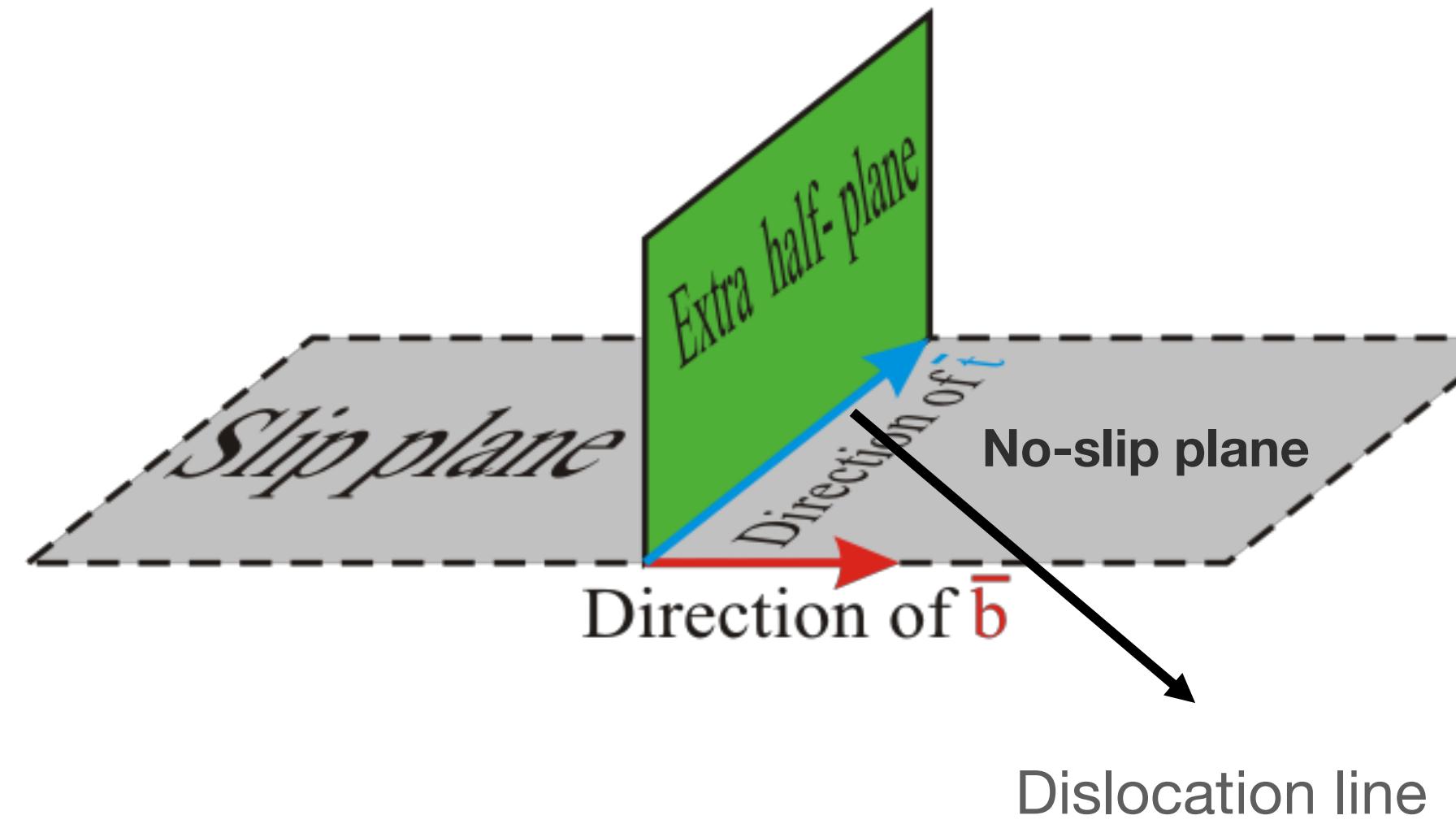
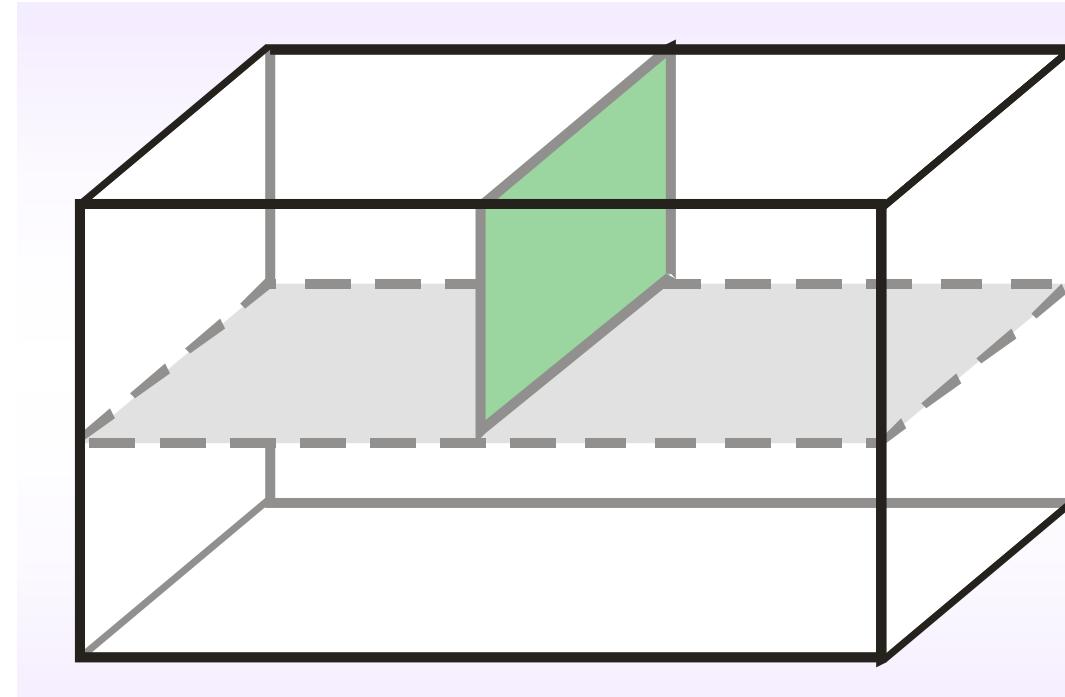
Dislocations prevent the synchronized breakage of bonds between atoms in materials and cause gradual deformation by making the one-by-one breakage of single bonds possible

# Edge dislocation: Slip



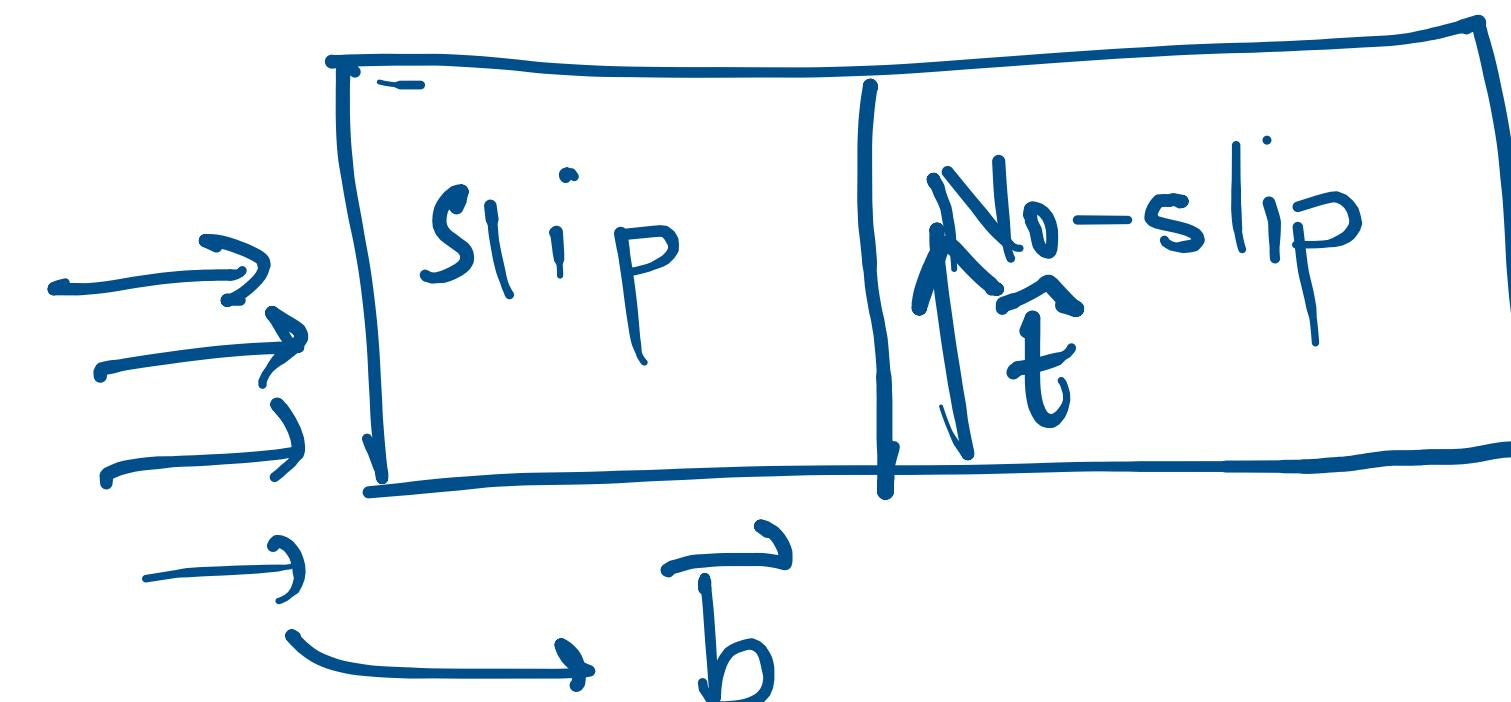
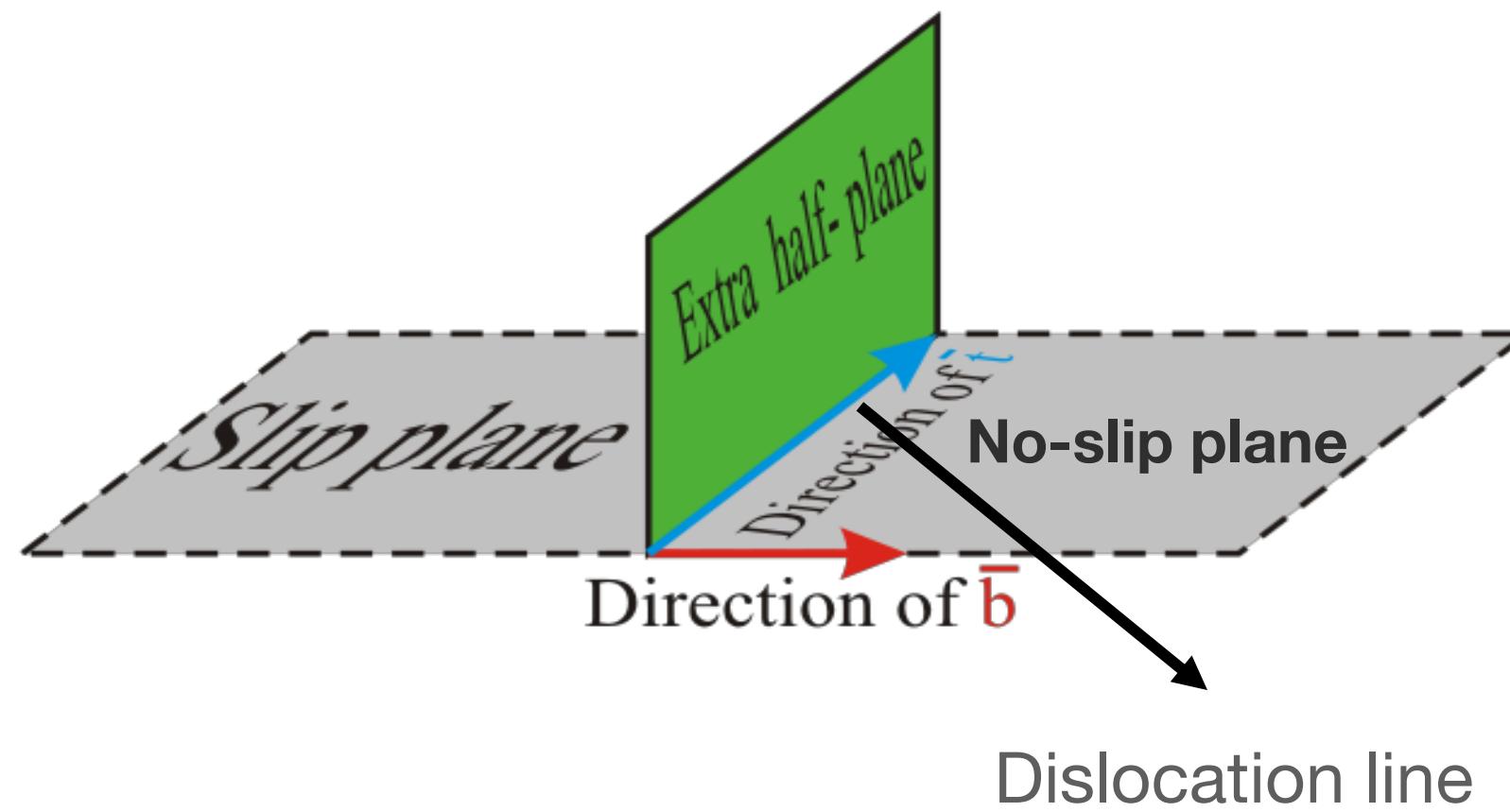
Dislocation line

# Vectors characterizing dislocation

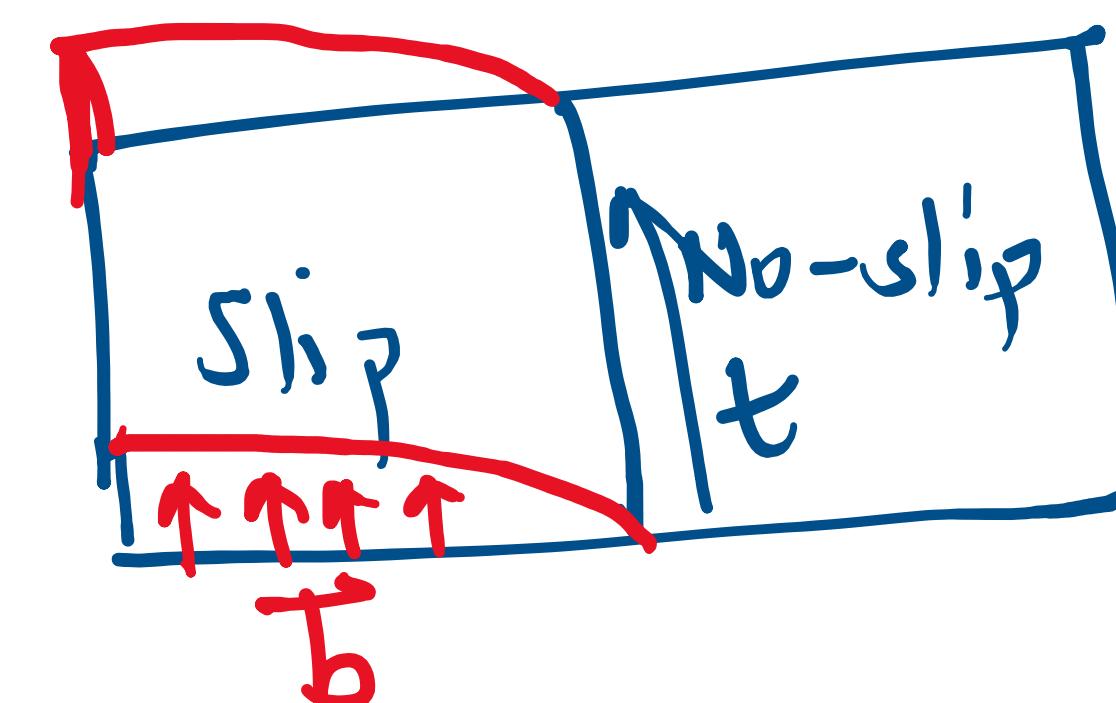


Tangent vector  $\hat{t}$ : unit vector parallel or tangent to the dislocation line  
Burgers vector  $\bar{b}$ : magnitude & direction of slip

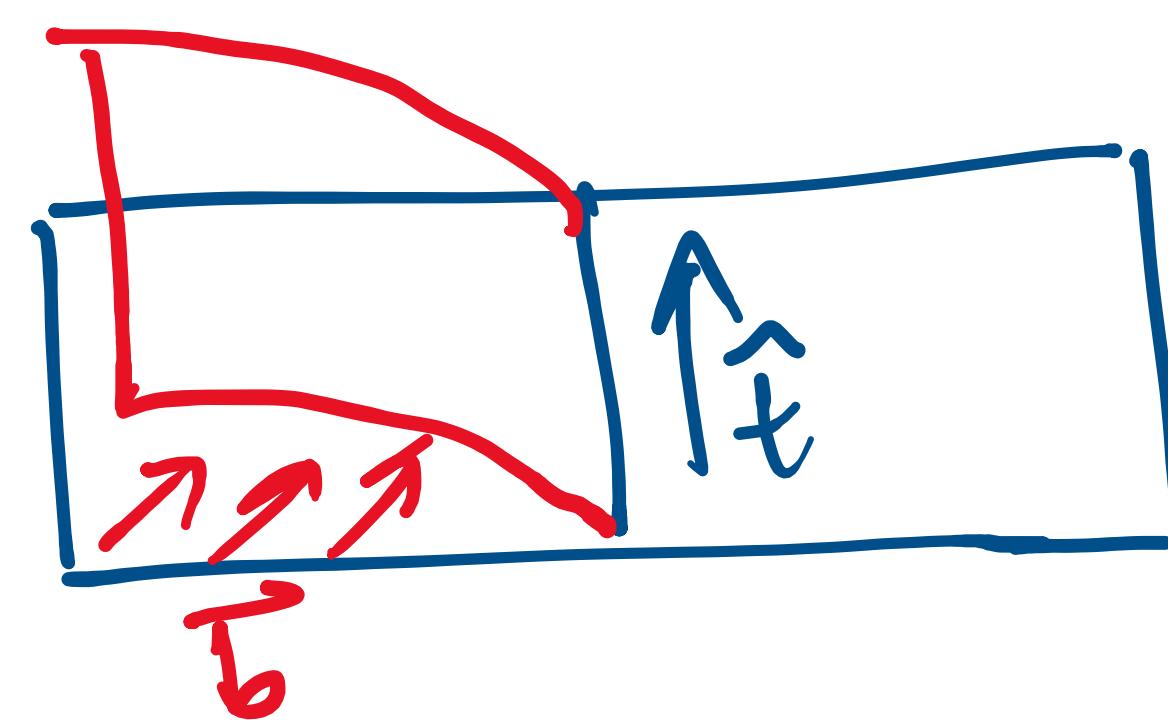
# Edge, screw and mixed dislocation



$\bar{b} \perp \hat{t}$  : Edge dislocation

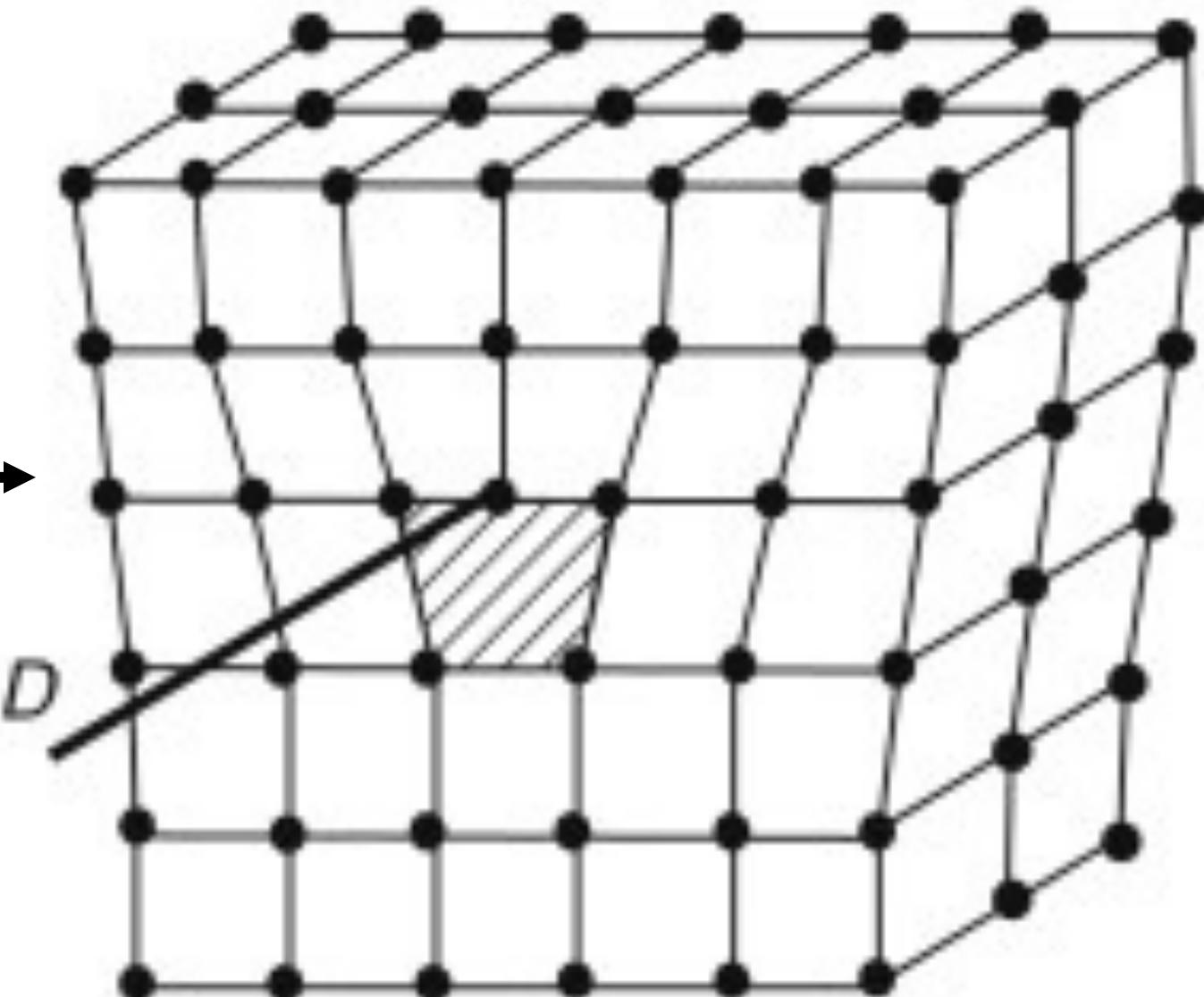


$\bar{b} \parallel \hat{t}$  : Screw dislocation

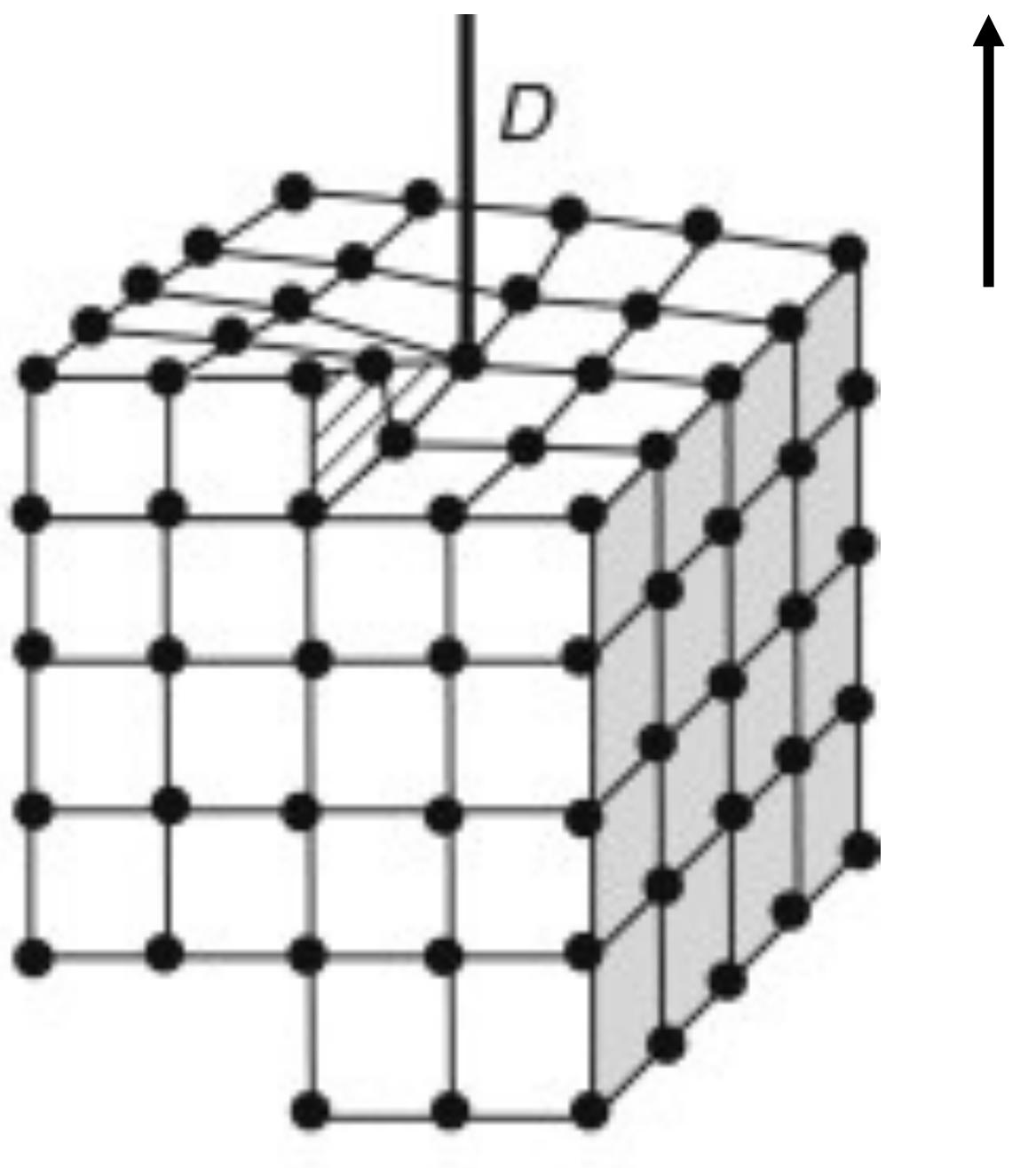


$\bar{b} \times \hat{t}, \bar{b} \not\parallel t$  : Mixed dislocation

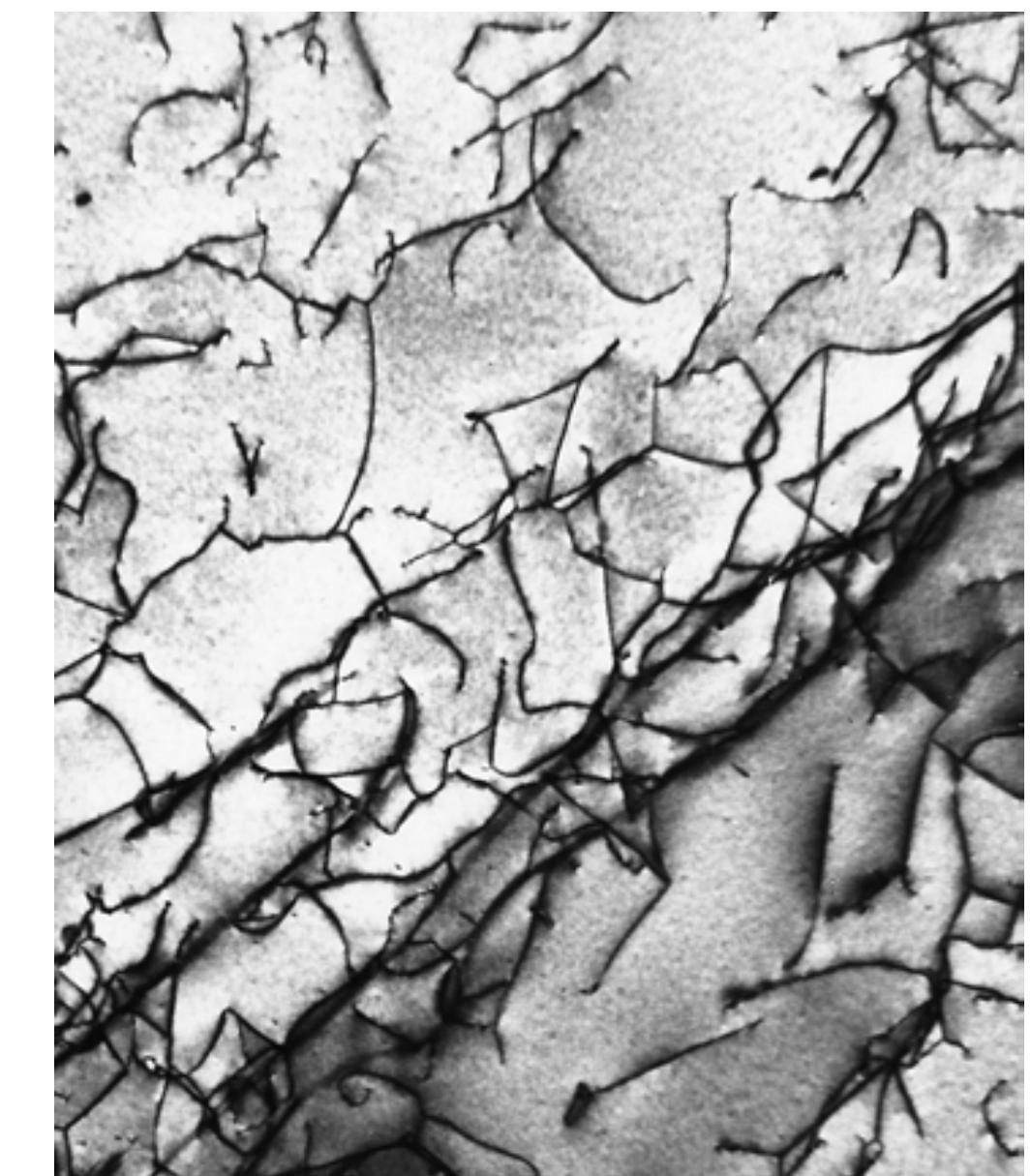
# Edge and screw dislocation



(Edge Dislocation)



(Screw Dislocation)



A transmission electron micrograph  
of a titanium alloy in which the  
dark lines are dislocations. 51,450X

# **Lecture 31**

**Surface defects**

**Strengthening mechanisms-Plastic deformation**

**Prof. Divya Nayar**

**Department of Materials Science and Engineering**

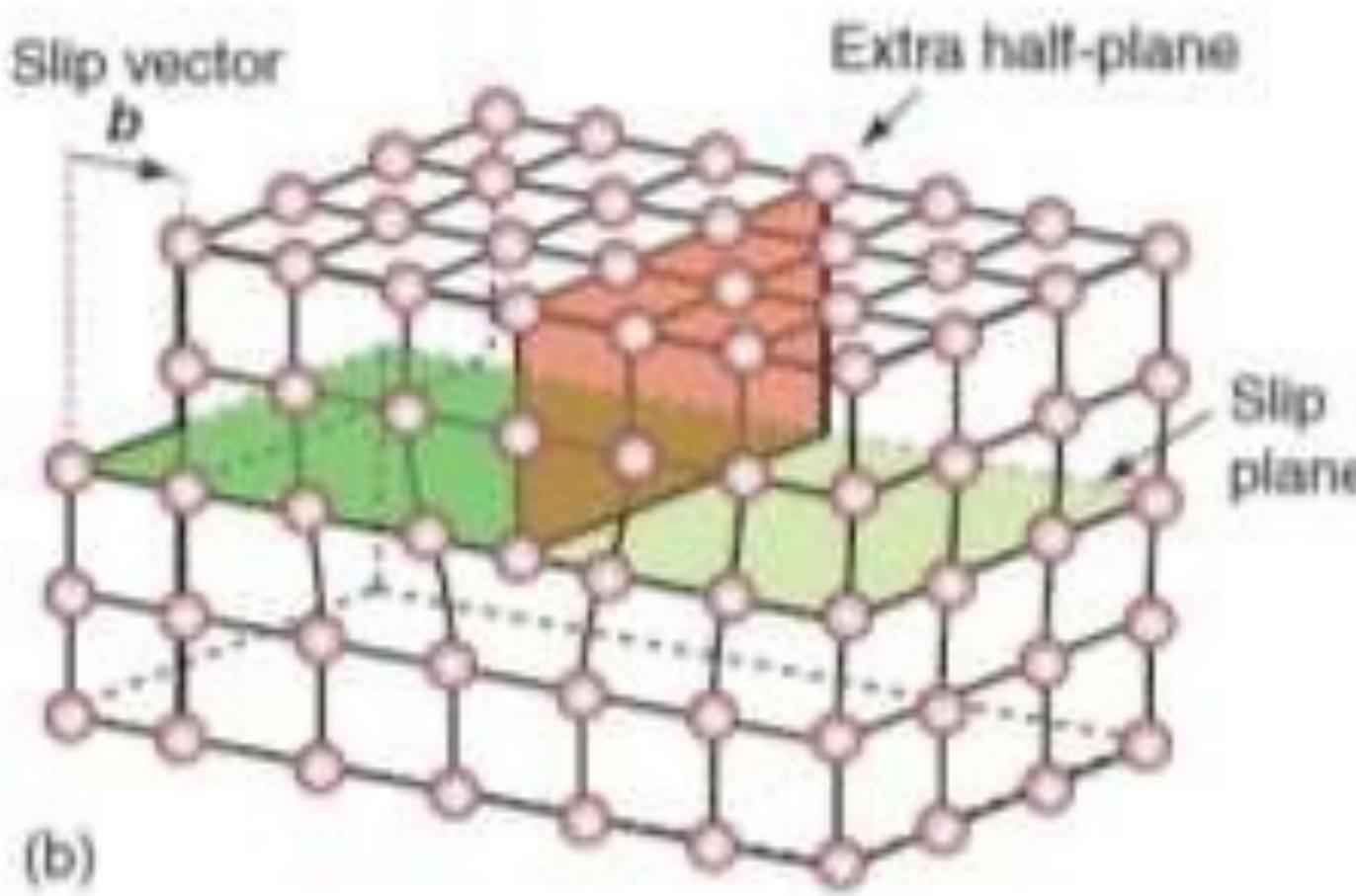
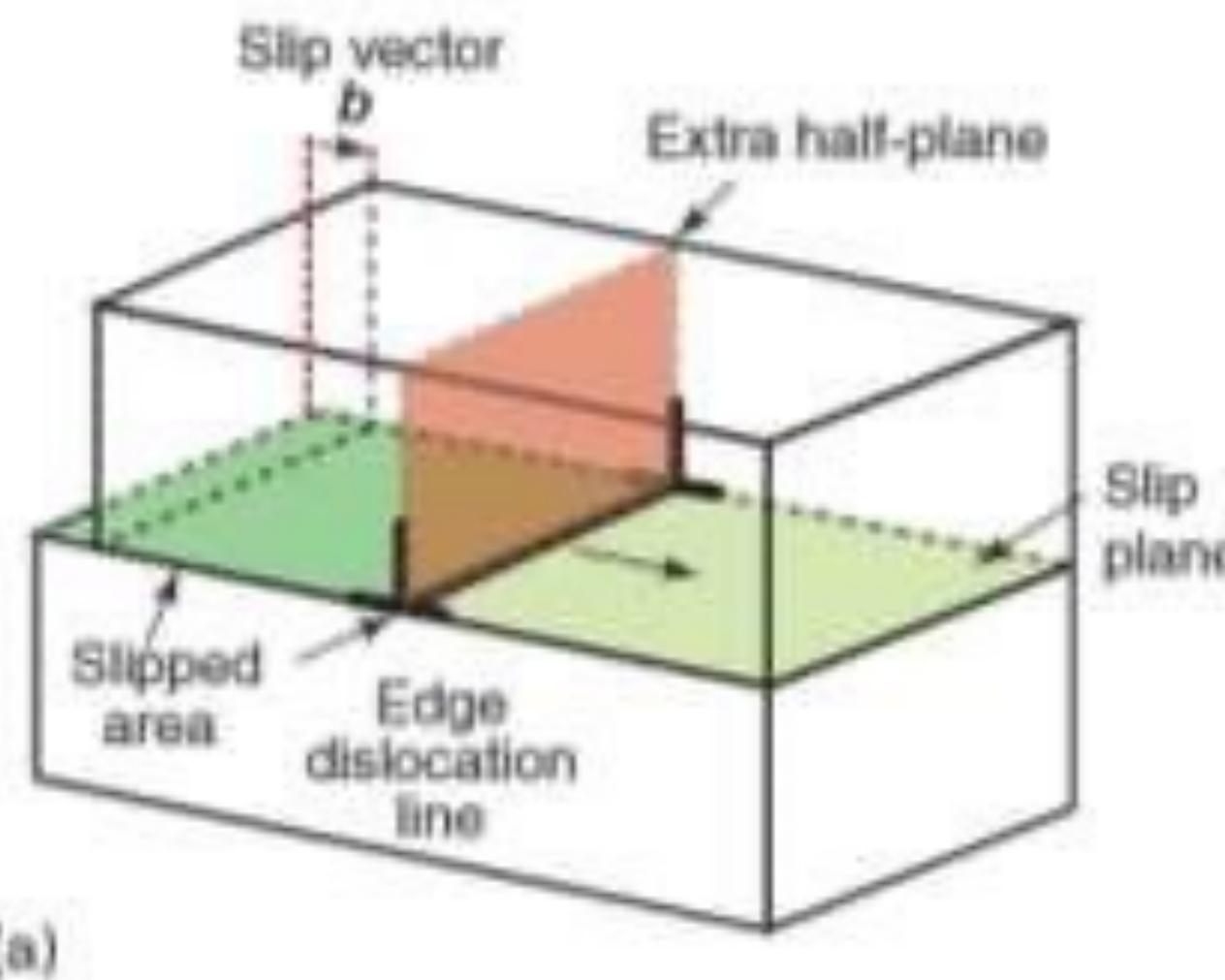
**[divyanayar@mse.iitd.ac.in](mailto:divyanayar@mse.iitd.ac.in)**

# Recap...

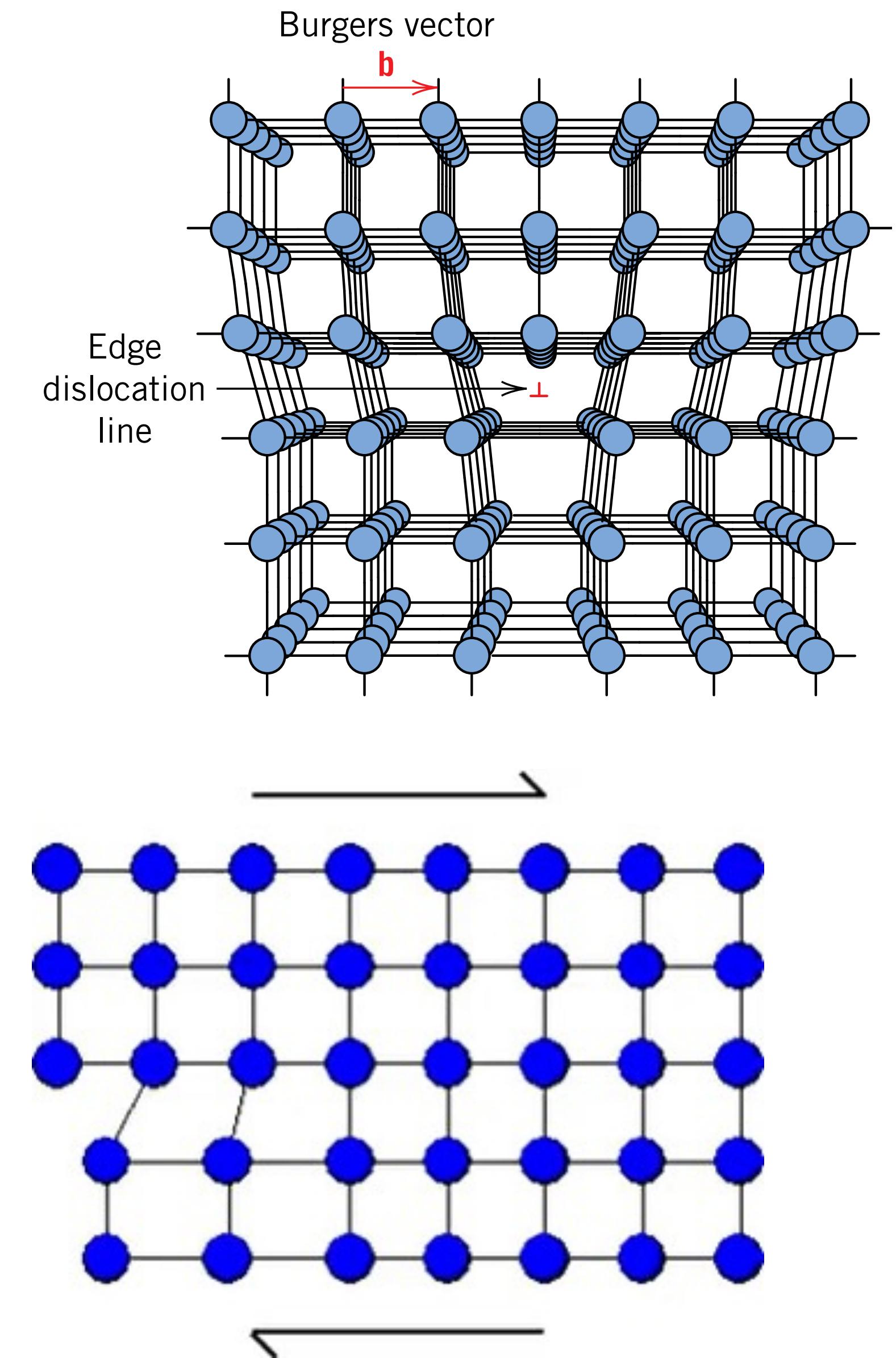
- Defects in solids
- Line defect: Dislocations
- Slip: Edge dislocation

# Dislocation

Motion of dislocation in a slip plane is called glide

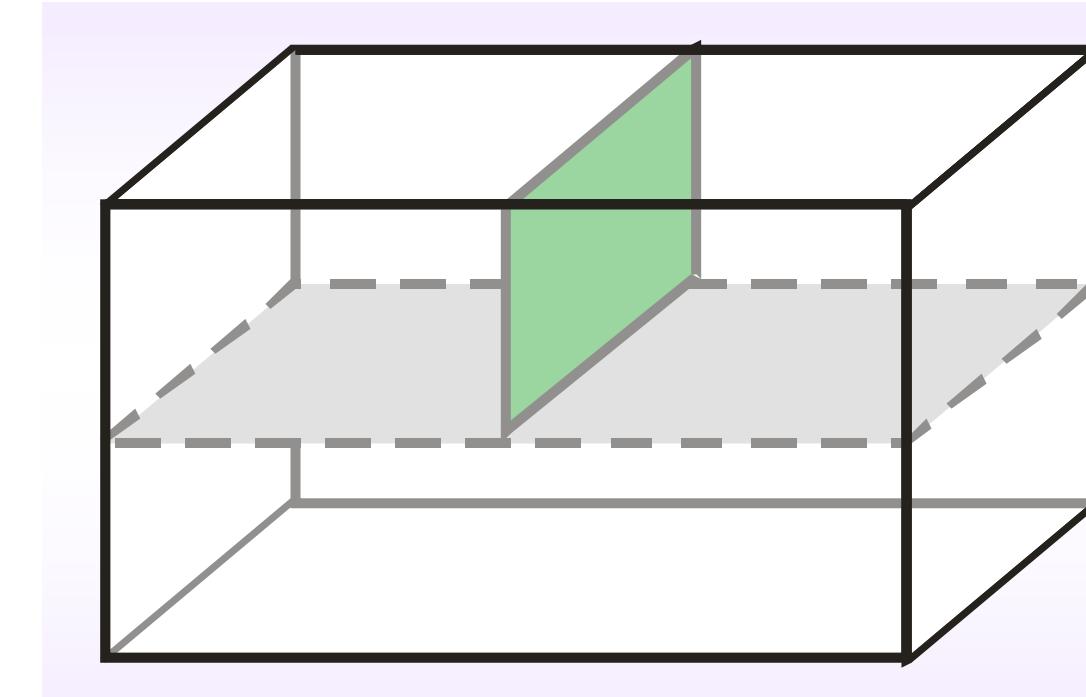
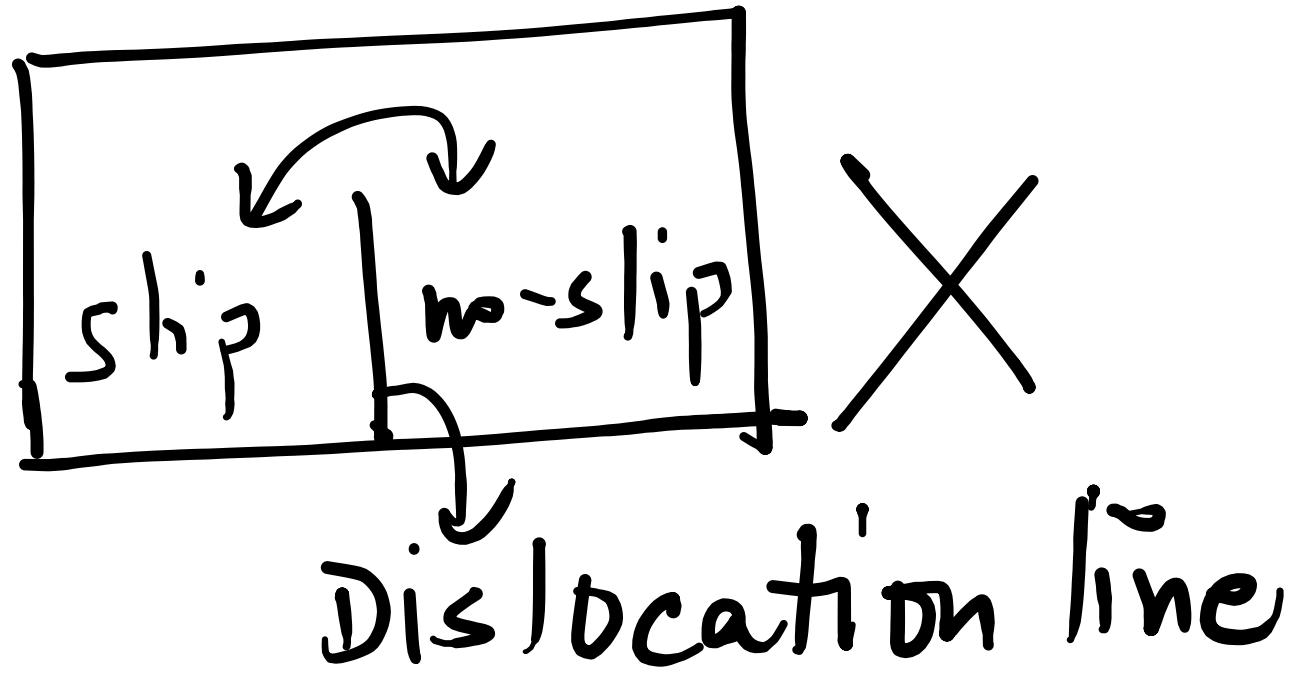
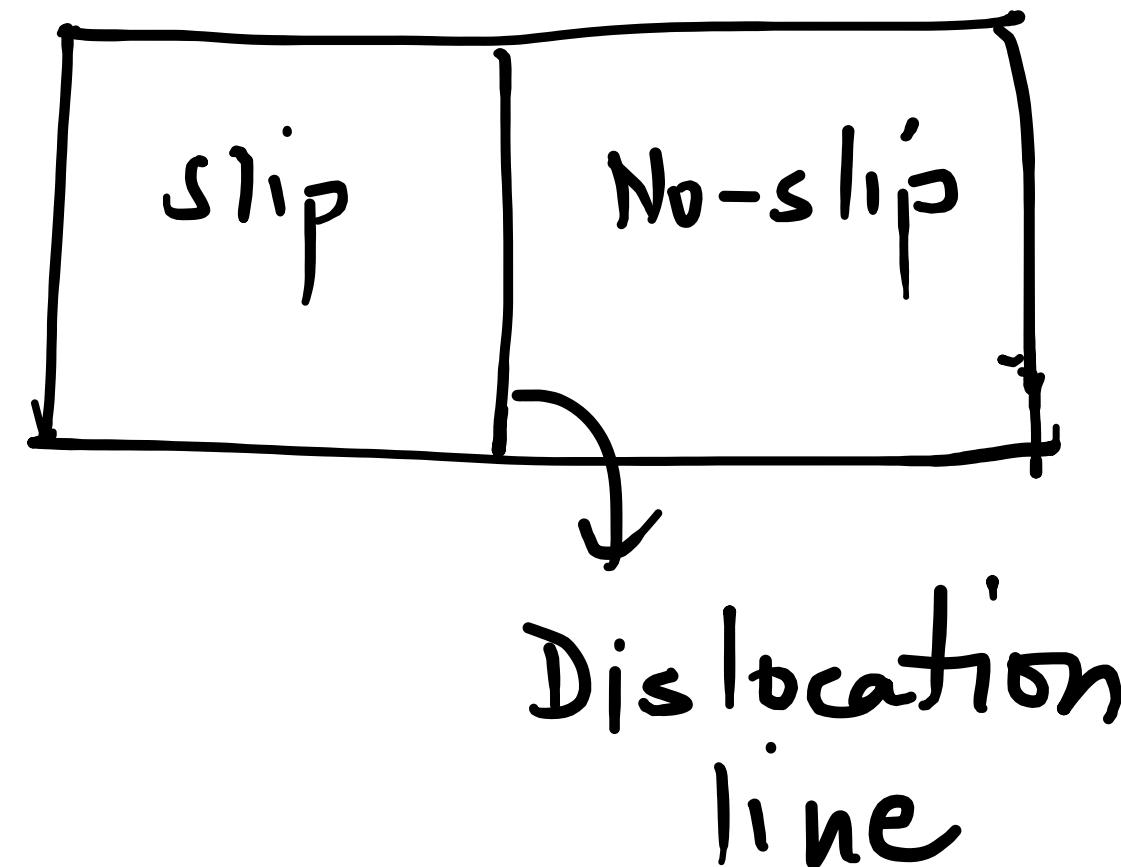


Glide

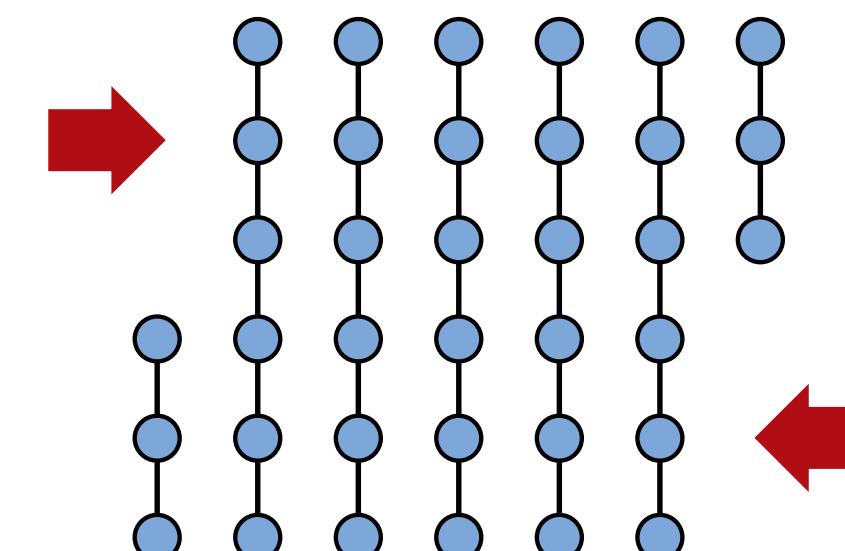


# Surface Defects

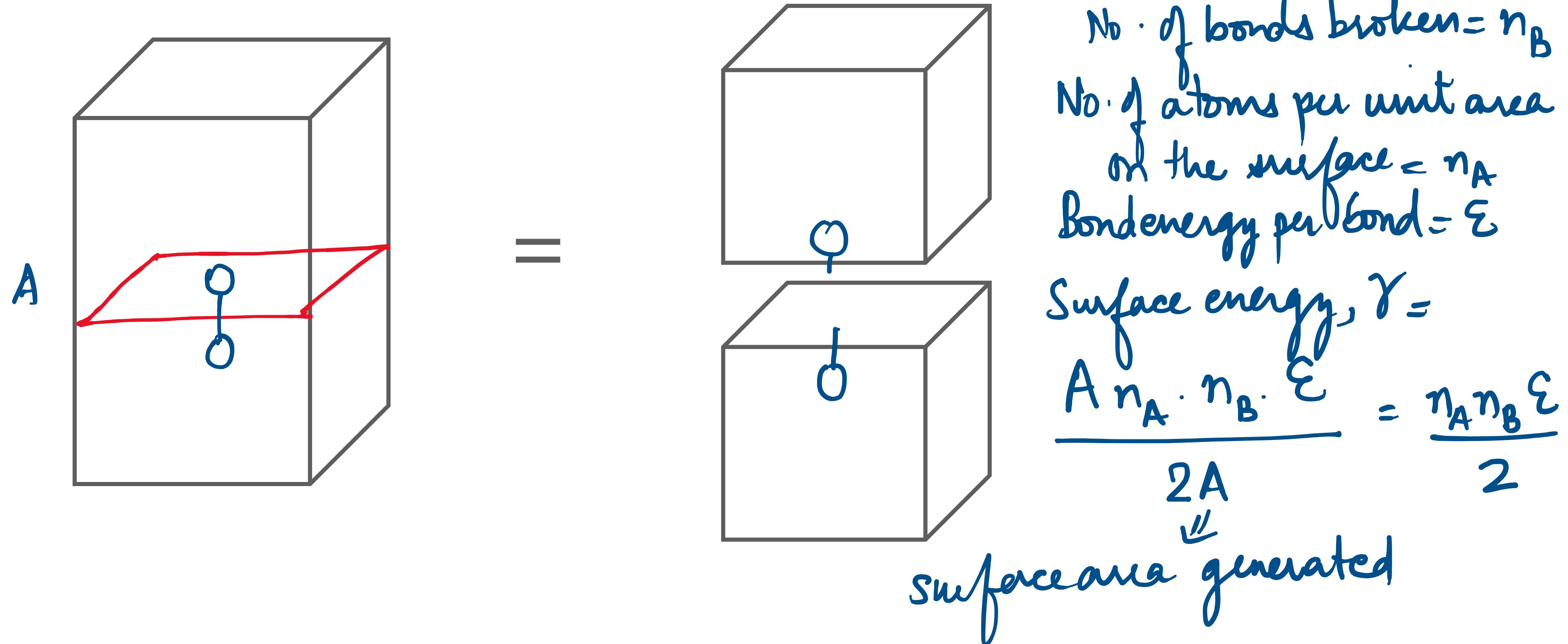
Interfacial defects are boundaries that have two dimensions and normally separate regions of the materials that have different crystal structures and/or crystallographic orientations



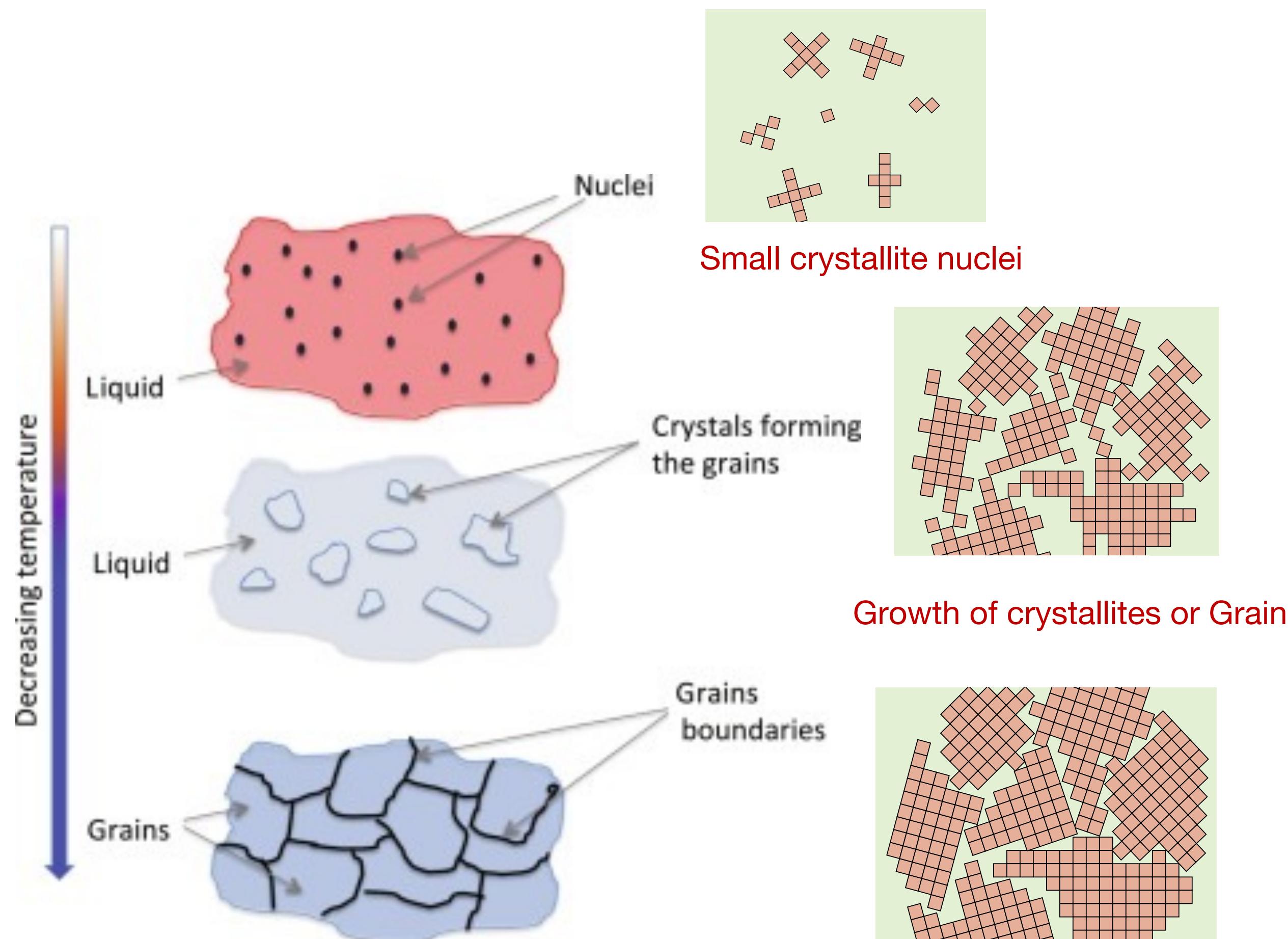
- The dislocation cannot end abruptly inside a crystal. It can end on:
  - Free surfaces (external)
  - Grain boundaries (internal)
  - Other dislocations (nodes)
  - Itself (continuous loop)
- **Free surface:** One boundary is the external surface, along which the dislocation line terminates.
- The bonds of these surface atoms that are not satisfied give rise to a surface energy, expressed in units of energy per unit area ( $J/m^2$  ).



# Surface energy

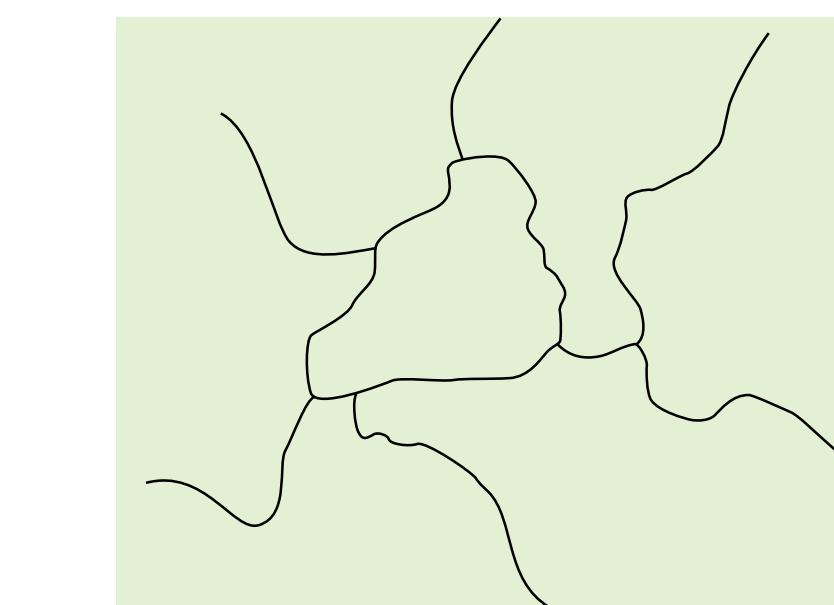


# Grains and grain boundaries



Upon completion of solidification,  
grains having irregular shapes  
have formed.

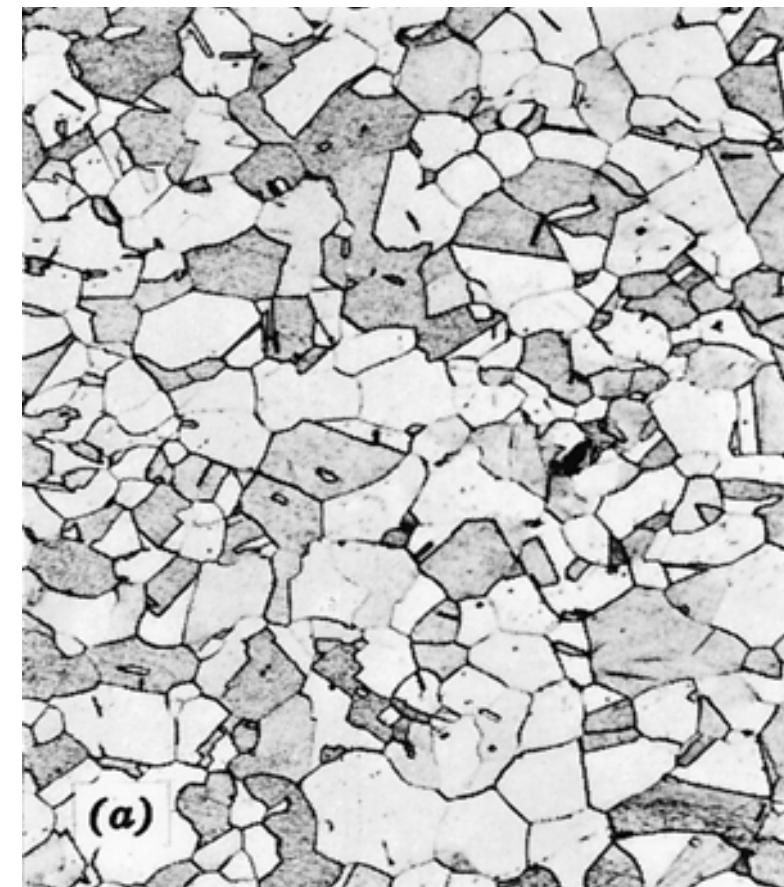
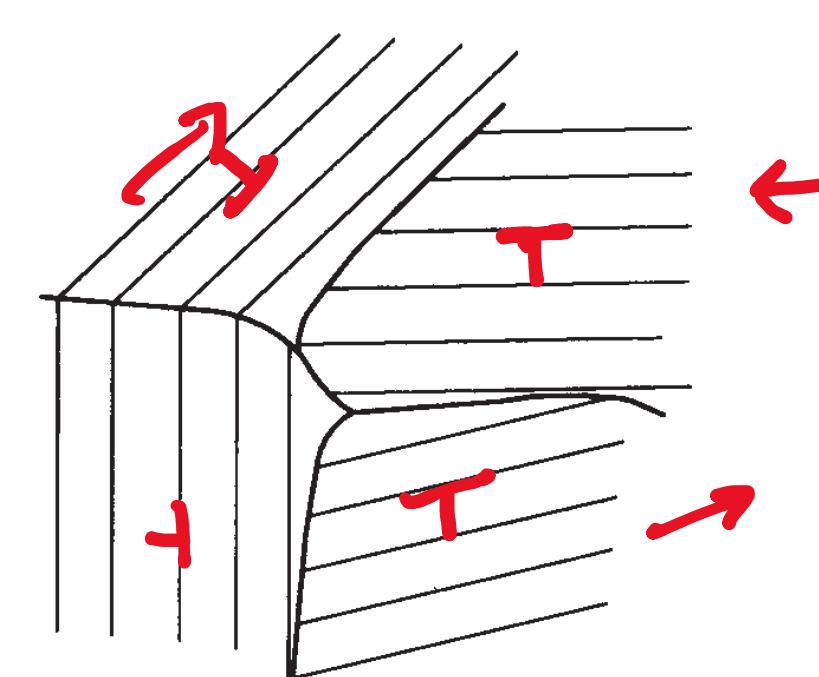
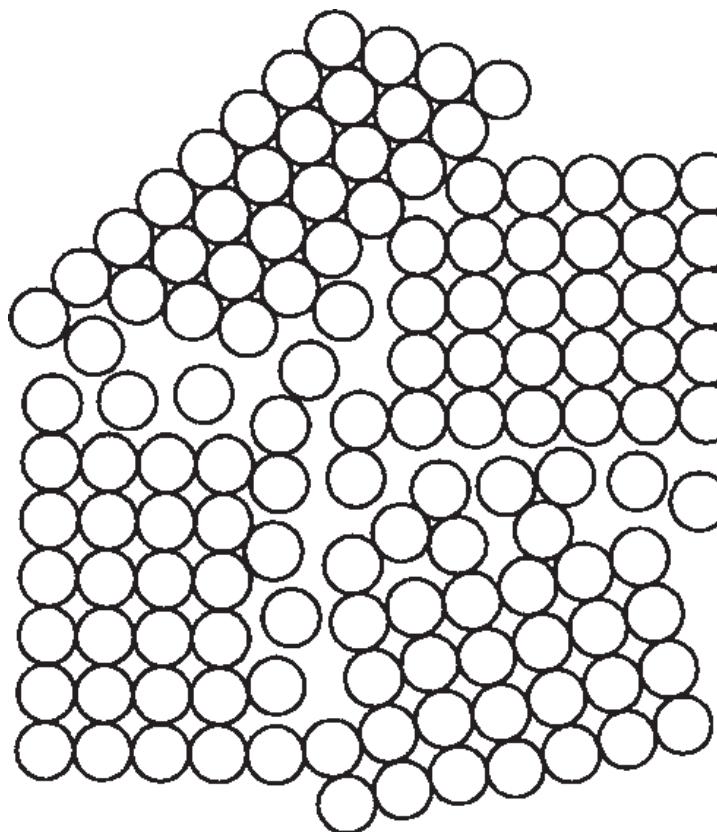
- Polycrystalline materials, the crystallographic orientations of the individual grains are totally random.
- each grain may be anisotropic, a specimen composed of the grain aggregate behaves isotropically.



The grain structure as it would appear under the microscope;  
dark lines are the grain boundaries.

# Grain boundaries

**Boundary separating two small grains or crystals having different crystallographic orientations in polycrystalline materials**



Before plastic deformation



The deformation has produced elongated grains

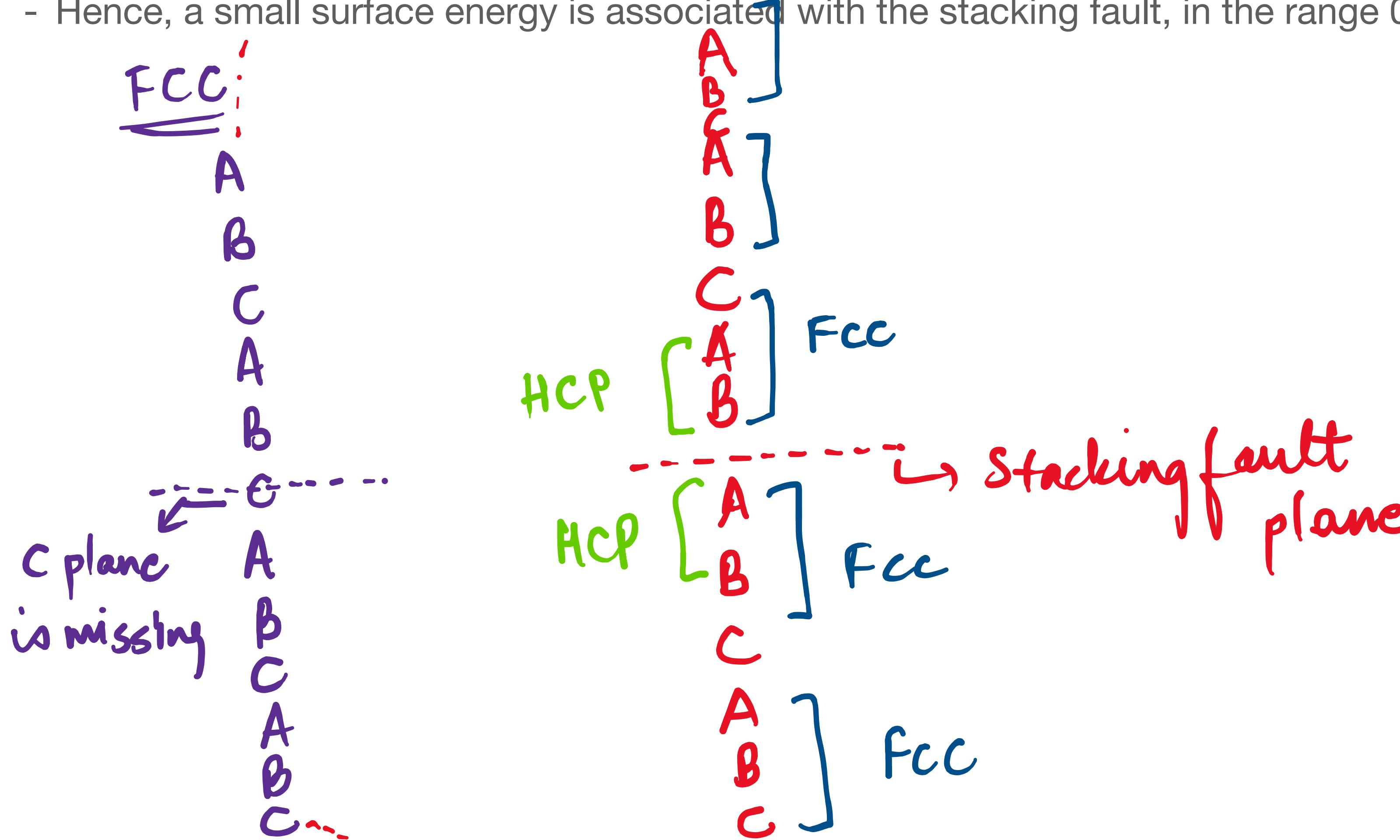
- There is some atomic mismatch in a transition from the crystalline orientation of one grain to that of an adjacent one.
- Various degrees of crystallographic misalignment between adjacent grains are possible
  - (a) When this orientation mismatch is slight, less than 10 degrees, then the term *small- (or low- ) angle grain boundary* is used
  - (b) When the orientation difference is greater than 10 to 15°, the grain boundaries are also known as *high angle boundaries*.
- Planes in grain do not cross the grain boundaries.
- **Half-planes do not cross grain boundaries and thus, dislocation line ends on the grain boundary.**
- **Dislocations are stopped by a grain boundary and pile up against it.**

During plastic deformation:

- grain boundaries usually do not come apart or open up.
- each individual grain is constrained, to some degree, in the shape it may assume by its neighboring grains.

# Stacking Faults

- Planar surface imperfections created by a fault (or error) in the stacking sequence of atomic planes in crystals.
- There is no change in the orientation of the crystal across the stacking fault
- Long-range structure is not affected.
- The number of nearest neighbours in the faulted region remains 12 as in the perfect regions of the crystal
- But the second nearest neighbour bonds in the faulted region are not of the correct type for the FCC crystal.
- Hence, a small surface energy is associated with the stacking fault, in the range  $0.01\text{--}0.05 \text{ J m}^{-2}$  ( $10\text{--}50 \text{ erg/cm}^2$ )



# Twin boundaries

## Mirror lattice symmetry

:

Perfect FCC structure

A  
B C  
A  
B  
--- G ---  
A  
B C  
A  
B  
C

A  
B C  
A  
B  
--- G ---  
A  
B C  
A  
B  
C

"Twin boundary" → g. b.  
↑  
Mirror plane

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# Summary of the defects

1. 1-D defect: dislocation (slip, edge/screw/mixed disclocation, glide)
2. 2-D defect: free surface, grain boundaries, stacking faults, twin boundaries

# Food for thought...



Blacksmith and his forge

Why Blacksmith hammers the weapon to make it strong?



Dislocation motion and strengthening mechanisms

# **Strengthening mechanisms (in single-phase metals)**

**Plastic deformation depends on *the ability of dislocations to move***

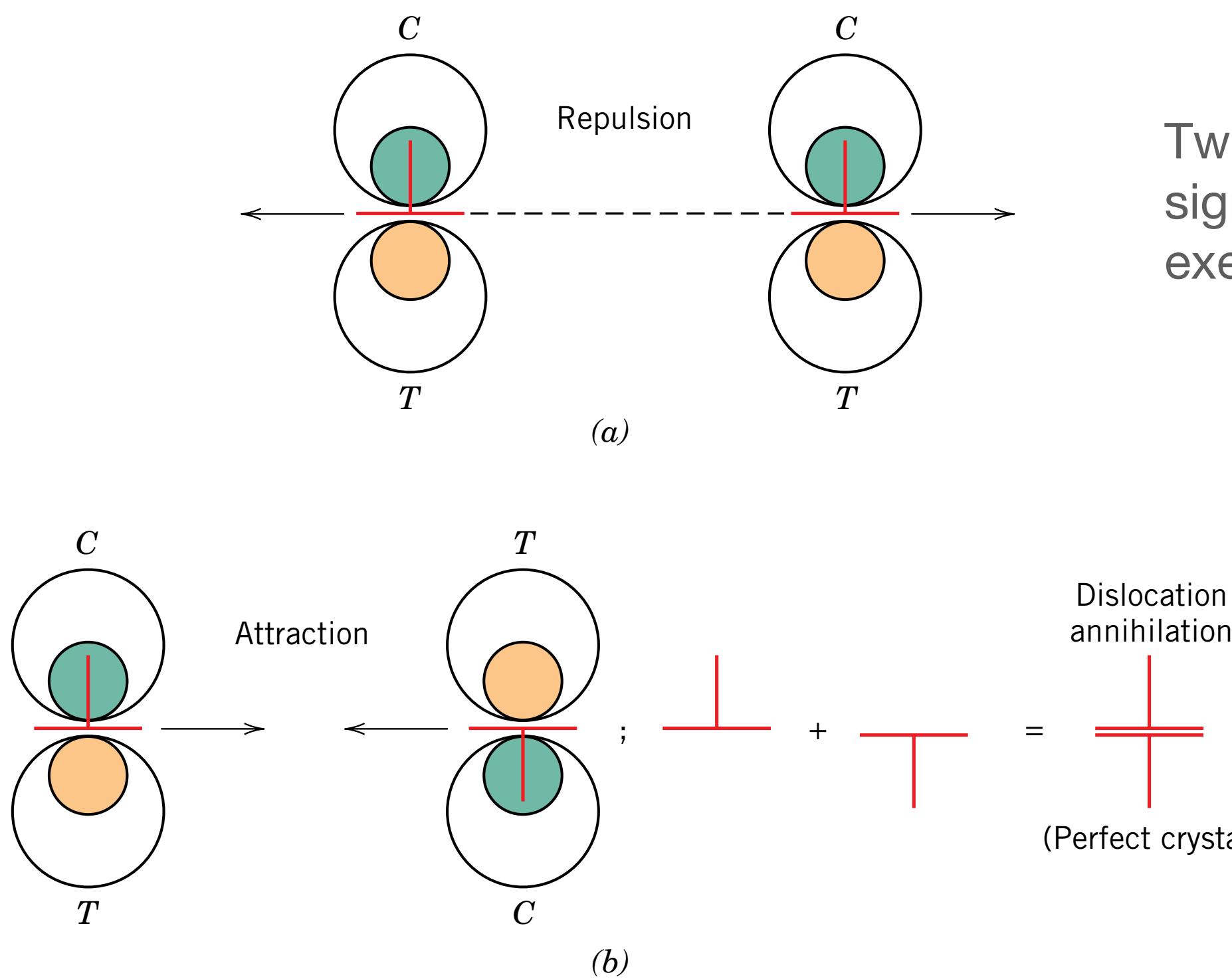
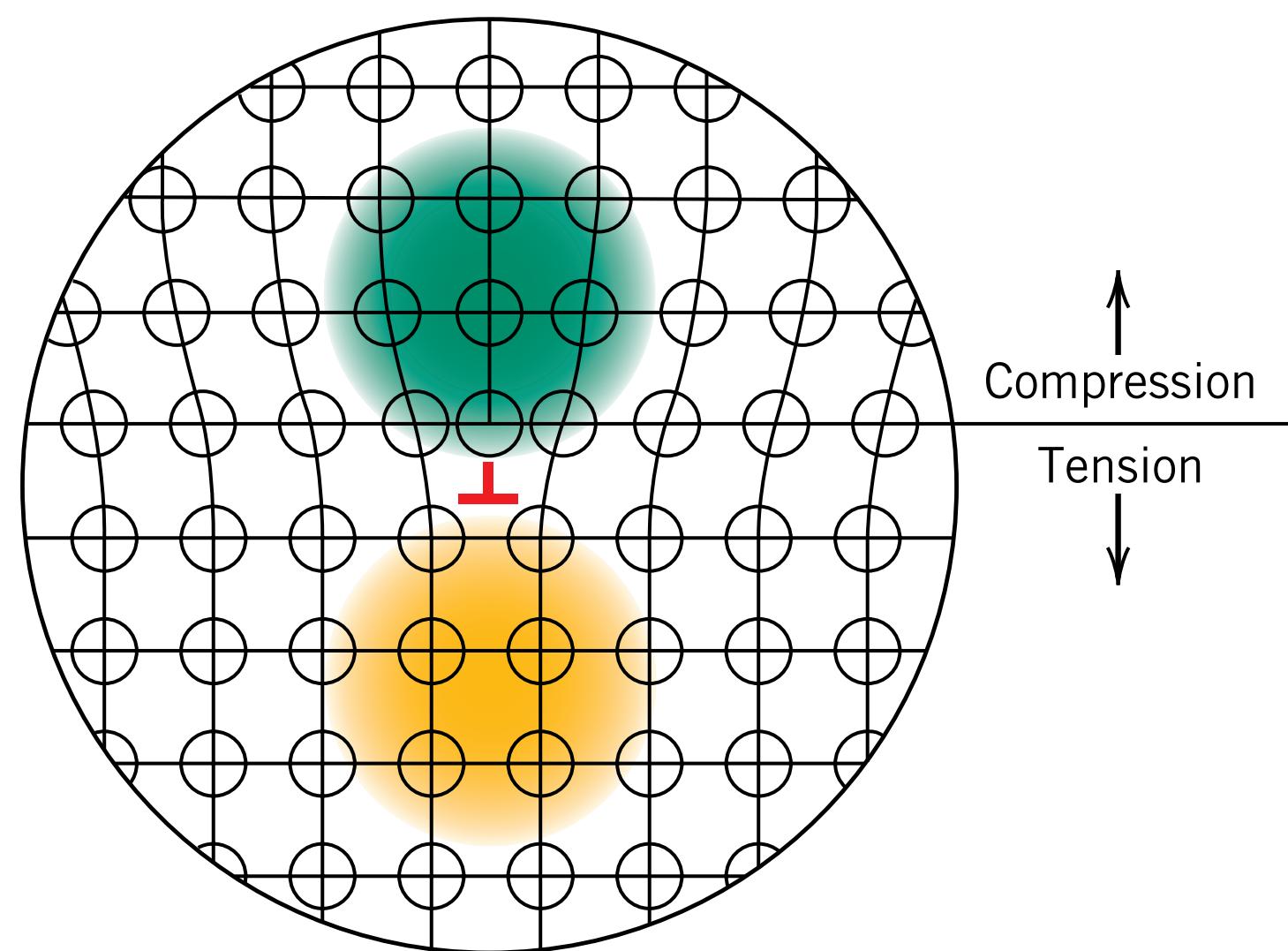
Restricting or hindering dislocation motion renders a material stronger.

- Grain size reduction
- Strain hardening
- Solid solution hardening
- Precipitation hardening

# Lattice strain

## Characteristic of Dislocations

- **Strain energy:** When metals are plastically deformed, some fraction of the deformation energy is retained internally
- Dislocations cause atomic lattice distortion that imposes compressive, tensile, shear strains on neighbouring atoms. e.g. atoms immediately above and adjacent to the dislocation line are squeezed together.
- These lattice distortions may be considered to be strain fields that radiate from the dislocation line. The strains extend into the surrounding atoms, and their magnitude decreases with radial distance from the dislocation.

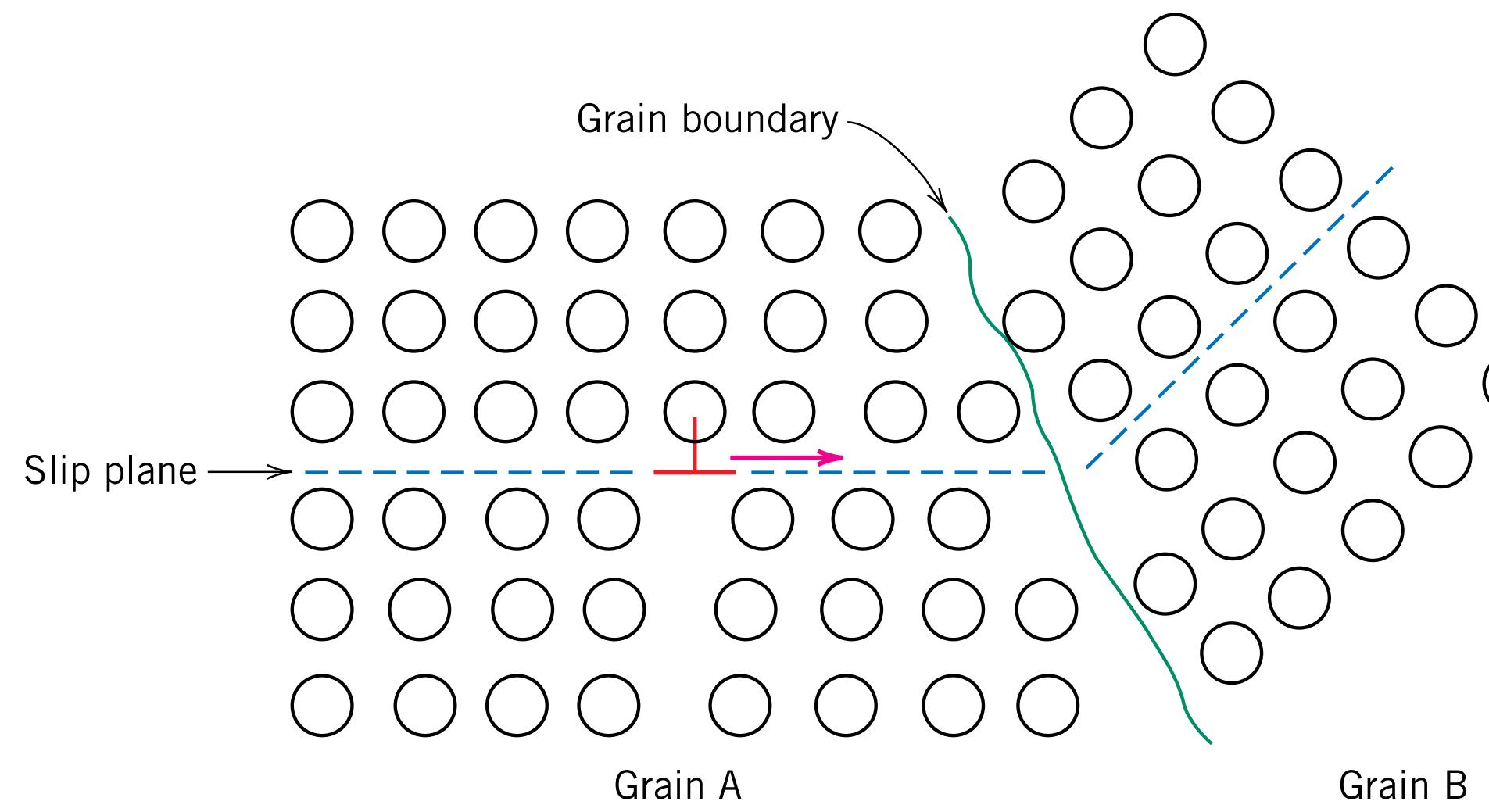


Edge dislocations of opposite sign and lying on the same slip plane exert an attractive force on each other.

Two edge dislocations of the same sign and lying on the same slip plane exert a repulsive force on each other;

# Grain size reduction

The size of the grains, or average grain diameter, in a polycrystalline metal influences the mechanical properties



- The grain boundary acts as a barrier to dislocation motion for two reasons:
  - Since the two grains are of different orientations, a dislocation passing into grain B will have to change its direction of motion; this becomes more difficult as the crystallographic misorientation increases.
  - The atomic disorder within a grain boundary region will result in a discontinuity of slip planes from one grain into the other.
- High-angle grain boundaries: dislocations tend to “pile up” (or back up) at grain boundaries.
- A fine-grained material (one that has small grains) is harder and stronger: greater total grain boundary area to impede dislocation motion.
- grain size which determines the average distance from a dislocation source to the grain boundary
- **The smaller is the grain size, the more frequent is the pile up of dislocations.**

Larger the grain size → distance of dislocation from g.b. is higher → less piling up of dislocations → plastic deformation is easy

# Hall-Petch equation

## Dependence of yield strength on grain size

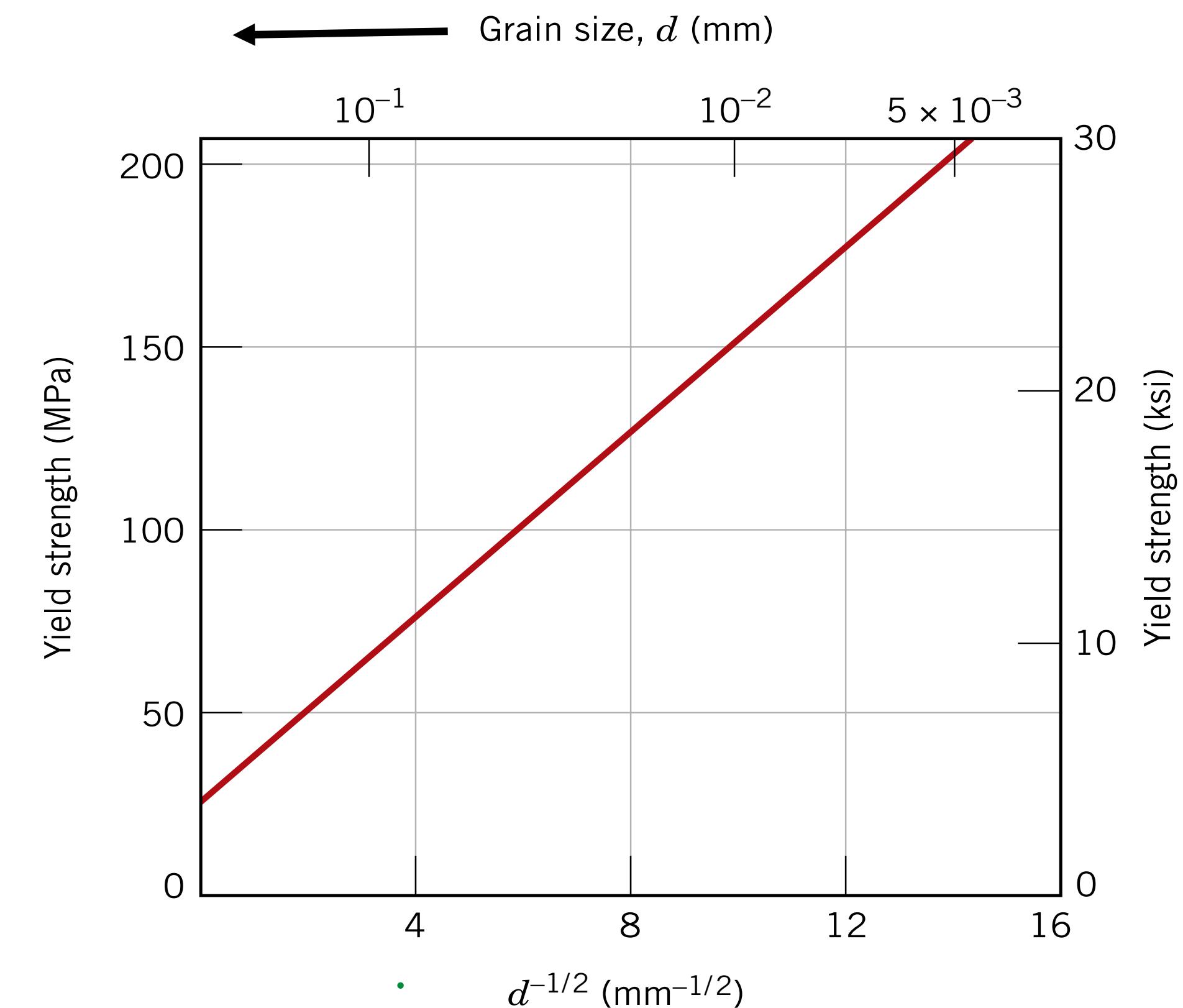
$$\boxed{\sigma_y = \sigma_0 + k_y d^{-1/2}}$$

$d$ : average grain diameter

$k_y$ : constant for a material

$\sigma_0$ : yield stress for crystal of same material with no grain boundaries

[Not valid for both very large (coarse) grain and extremely fine grain polycrystalline materials]



The influence of grain size on the yield strength of a 70 Cu-30 Zn brass alloy.

# **Lecture 32**

## **Failure in materials- Creep**

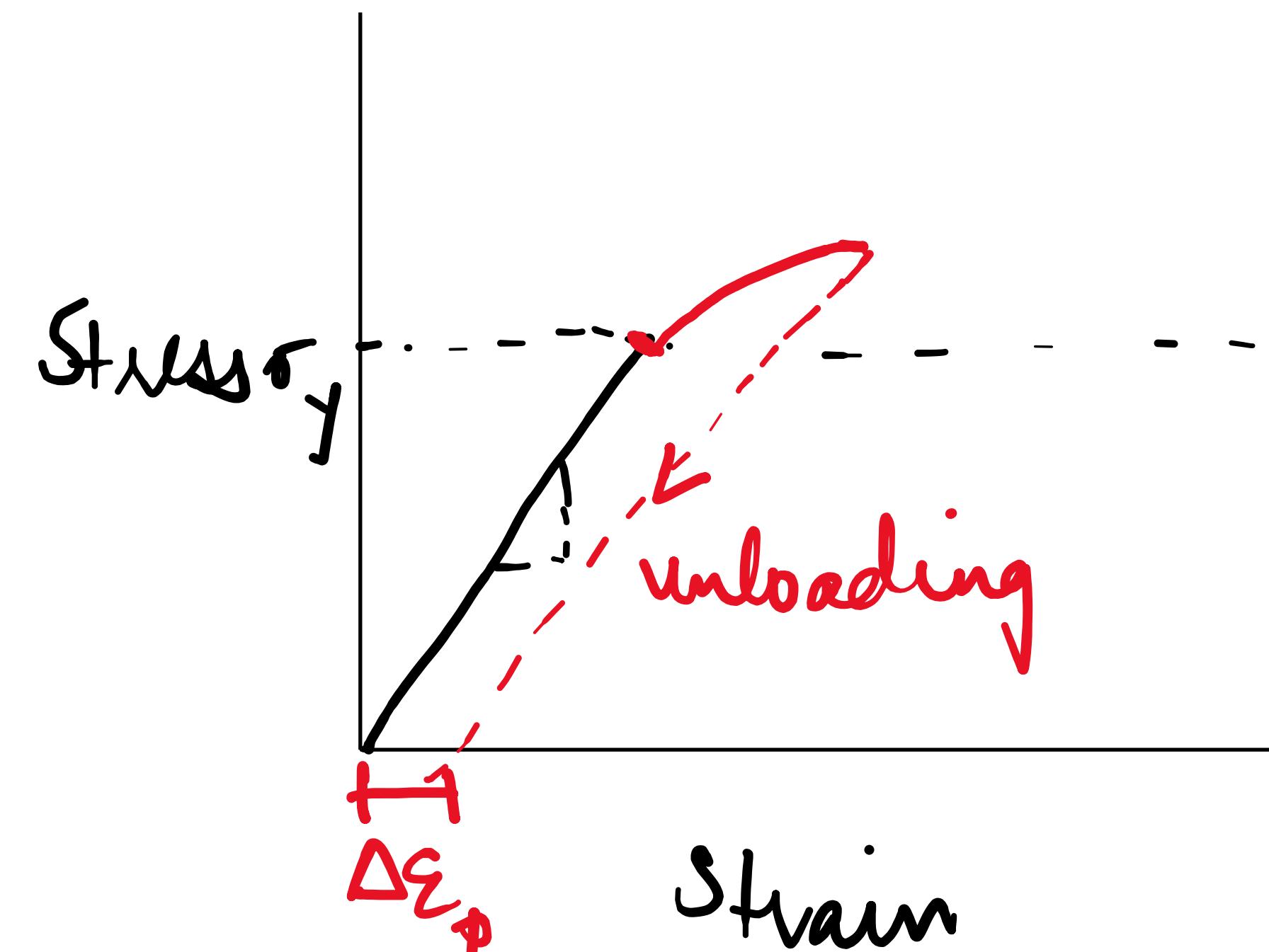
**Prof. Divya Nayar**  
**Department of Materials Science and Engineering**  
**[divyanayar@mse.iitd.ac.in](mailto:divyanayar@mse.iitd.ac.in)**

# Recap...

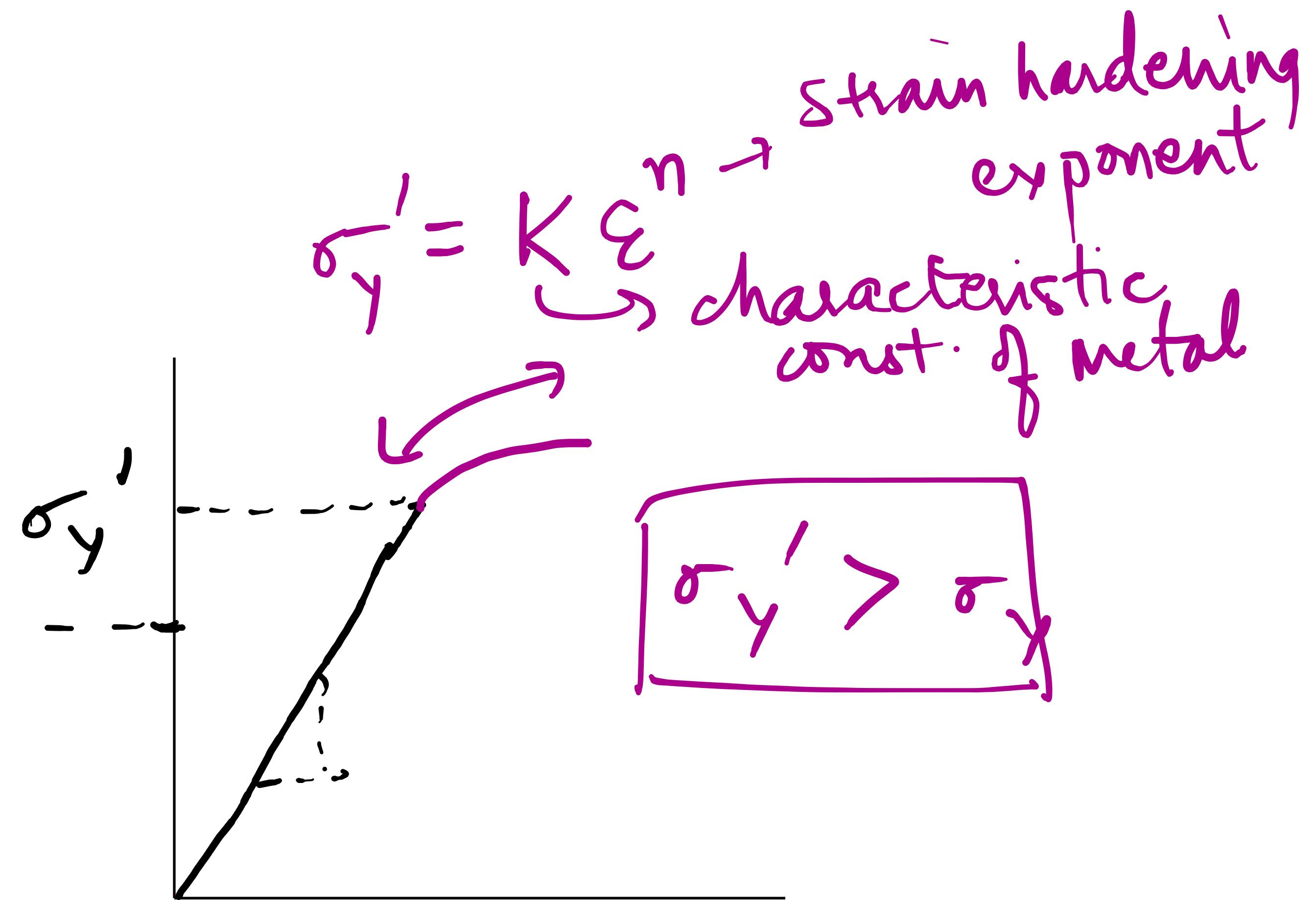
- Surface defects: free surface, grain boundaries, stacking faults, twin boundary
- Lattice strains
- Strengthening mechanisms: grain size reduction

# Strain hardening

Work hardening or cold working



(strained  
unloaded  
specimen)



# Strain hardening

## Dislocation-dislocation interactions

- **Strain hardening:** A ductile metal becomes harder and stronger as it is plastically deformed.
- The temperature at which deformation takes place is “cold” relative to the absolute melting temperature of the metal, **cold working**.
- Most metals strain harden at room temperature.

The dislocation density in a metal increases with deformation



The average distance of separation between dislocations decreases



Resistance to dislocation motion by other dislocations becomes more pronounced.



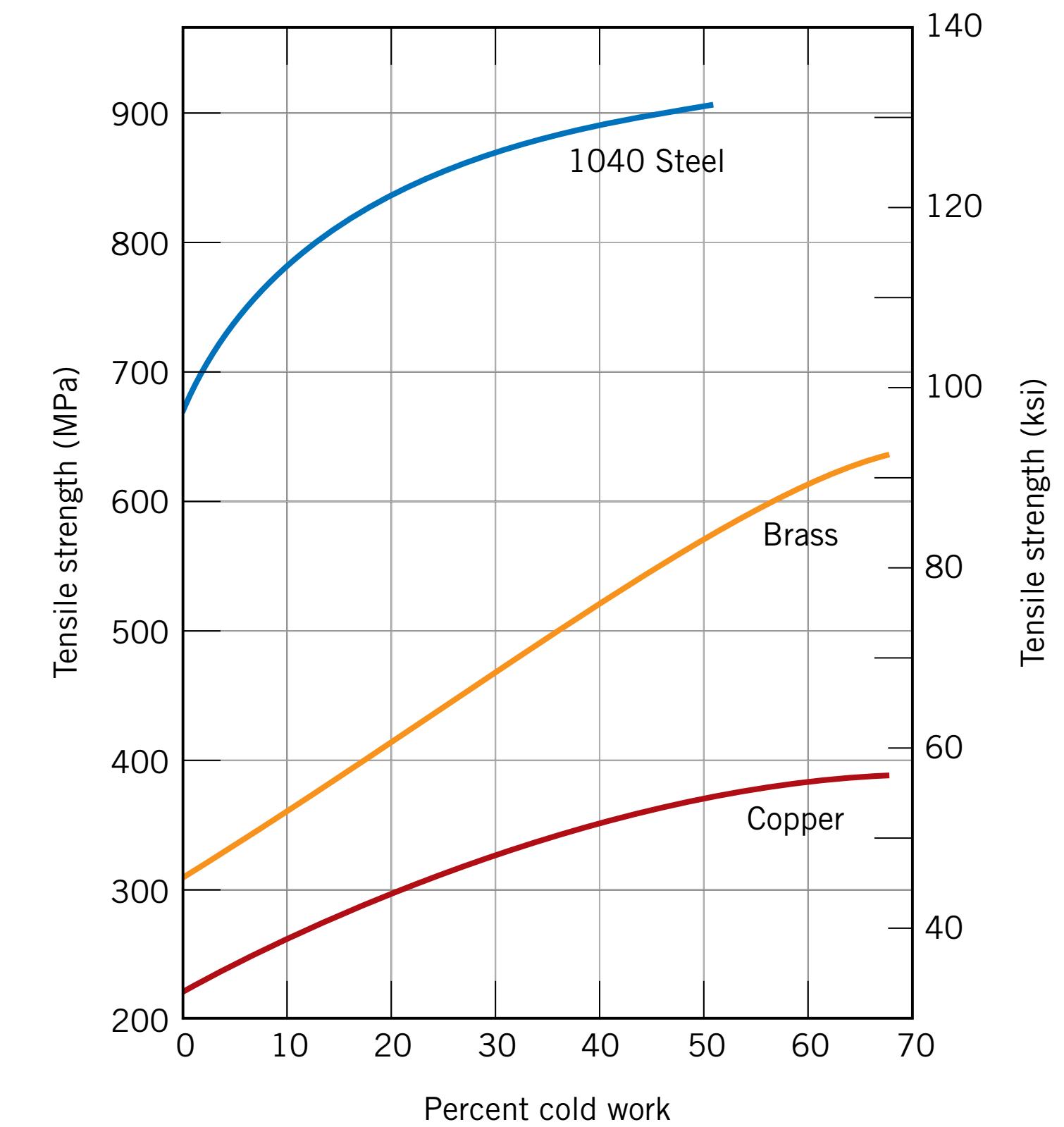
The imposed stress necessary to deform a metal increases with increasing cold work

Degree of plastic deformation as “percent cold work” (%CW)

$$\%CW = \left( \frac{A_0 - A_d}{A_0} \right) \times 100$$

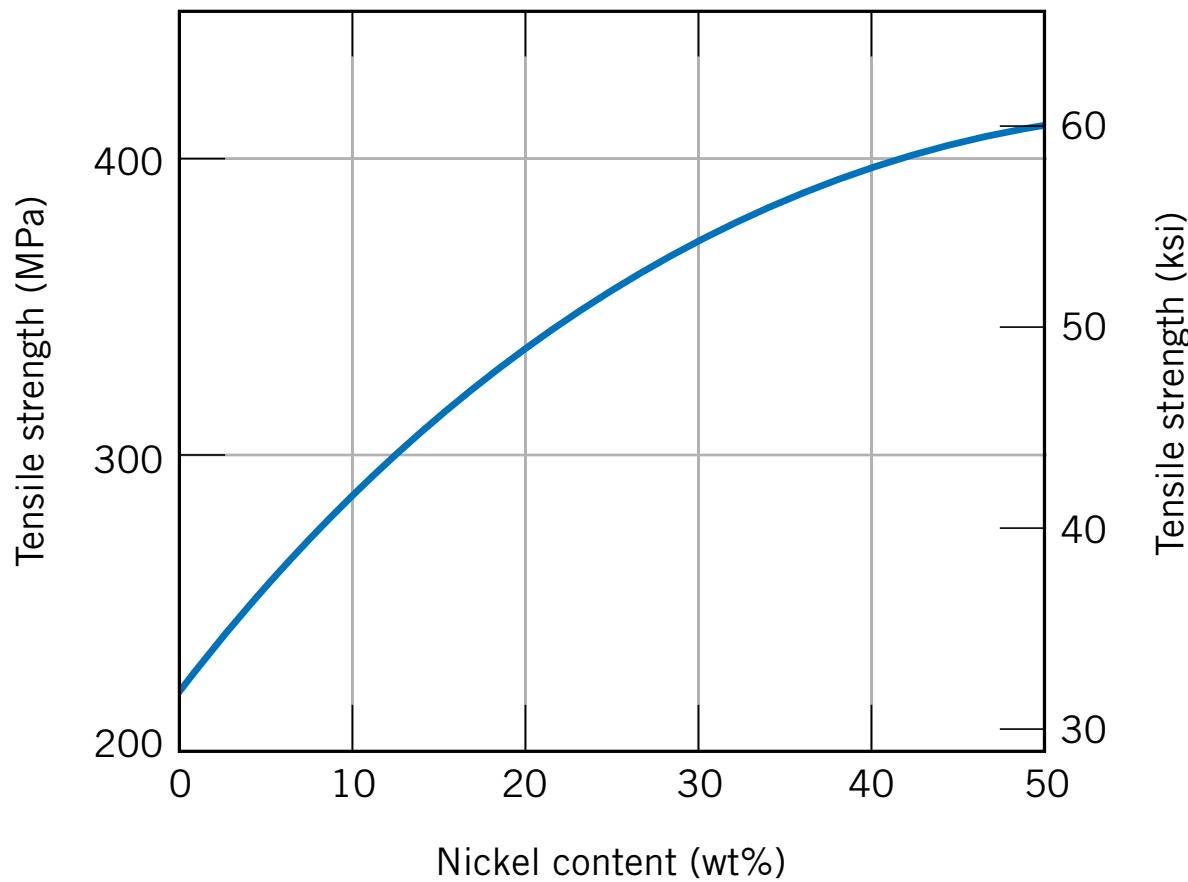
where,  $A_0$  : original cross-section area

$A_d$  : area after deformation



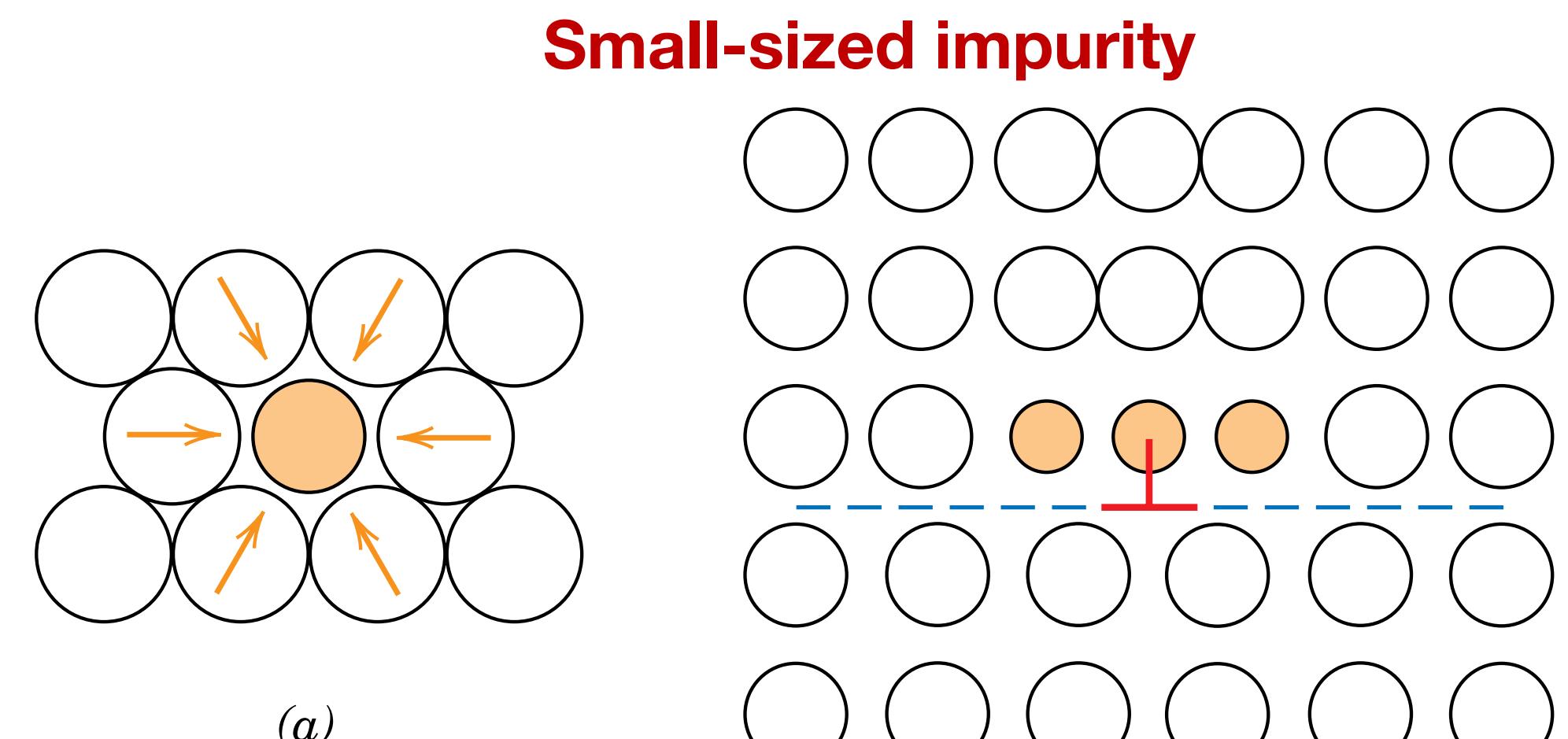
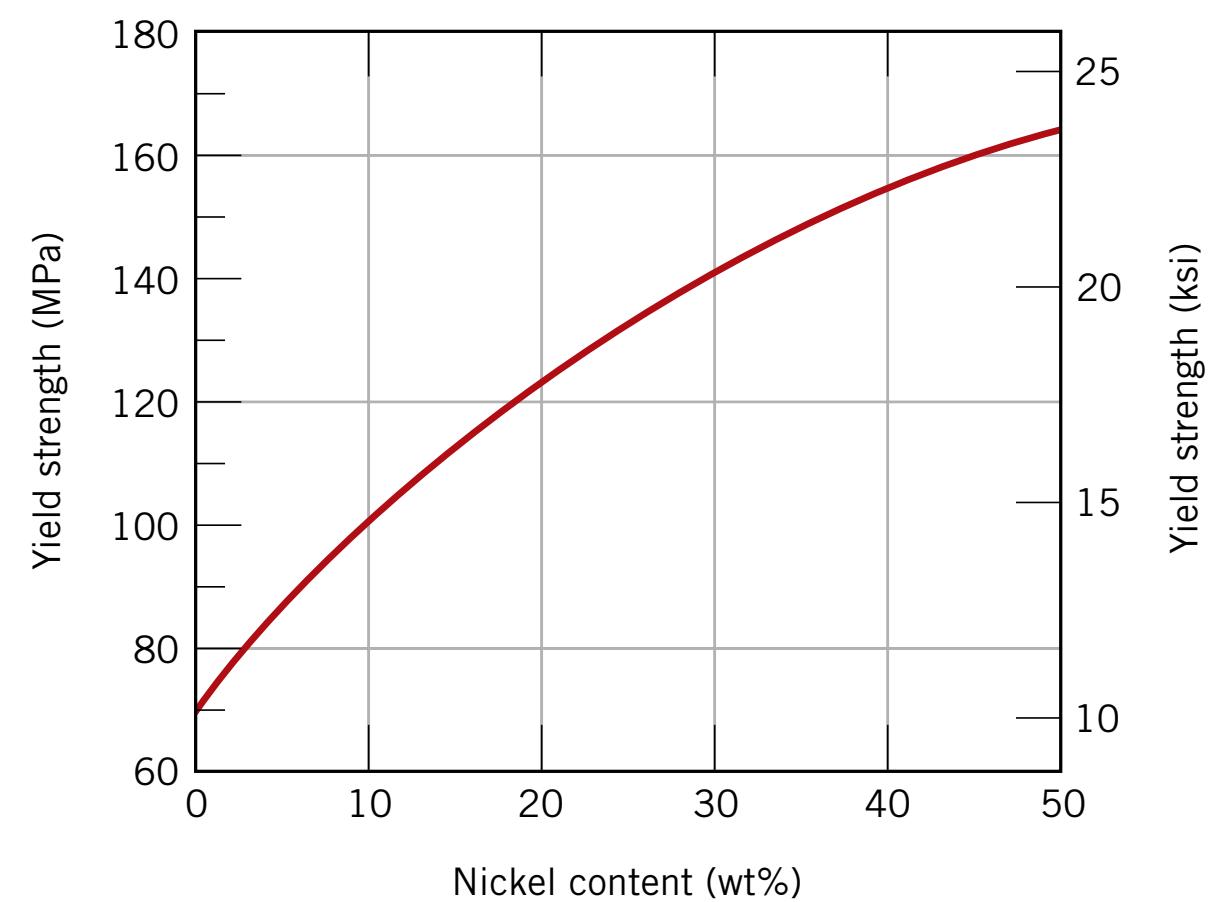
# Solid solution hardening

Strengthen the metals by alloying with impurity atoms that go into either substitutional or interstitial solid solution



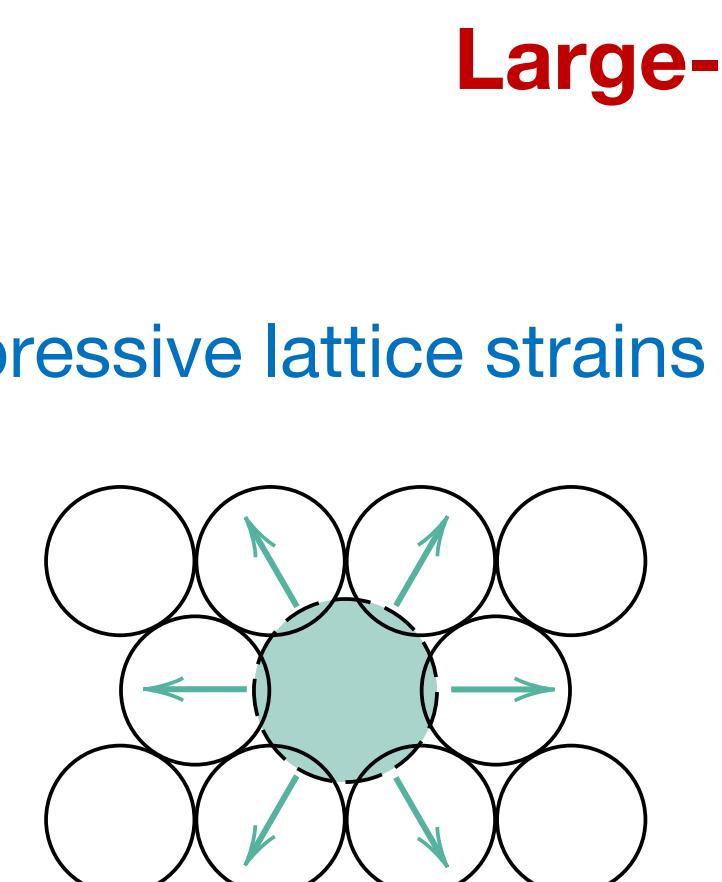
Alloys are stronger than the pure metals

- Alloys are stronger than pure metals because impurity atoms that go into solid solution ordinarily impose lattice strains on the surrounding host atoms.
- Lattice strain field interactions between dislocations and these impurity atoms result, and, consequently, dislocation movement is restricted.

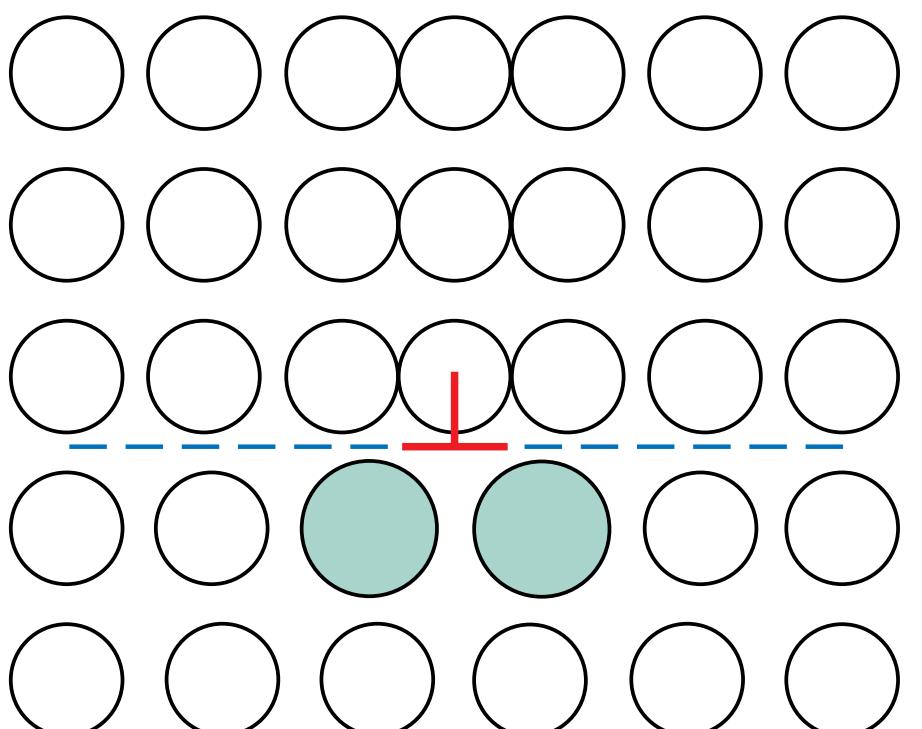


tensile lattice strains imposed on host atoms

Possible locations of smaller impurity atoms relative to an edge dislocation: cancellation of lattice strains



Compressive lattice strains



# Failure in materials

- Creep
- Fracture
- Fatigue

Strengthening mechanisms

- Grain size reduction
- Strain hardening
- Solid sol<sup>n</sup> hardening
- Precipitation hardening

# Food for thought...

Wood bends by weight of fruit but steel bridges do not

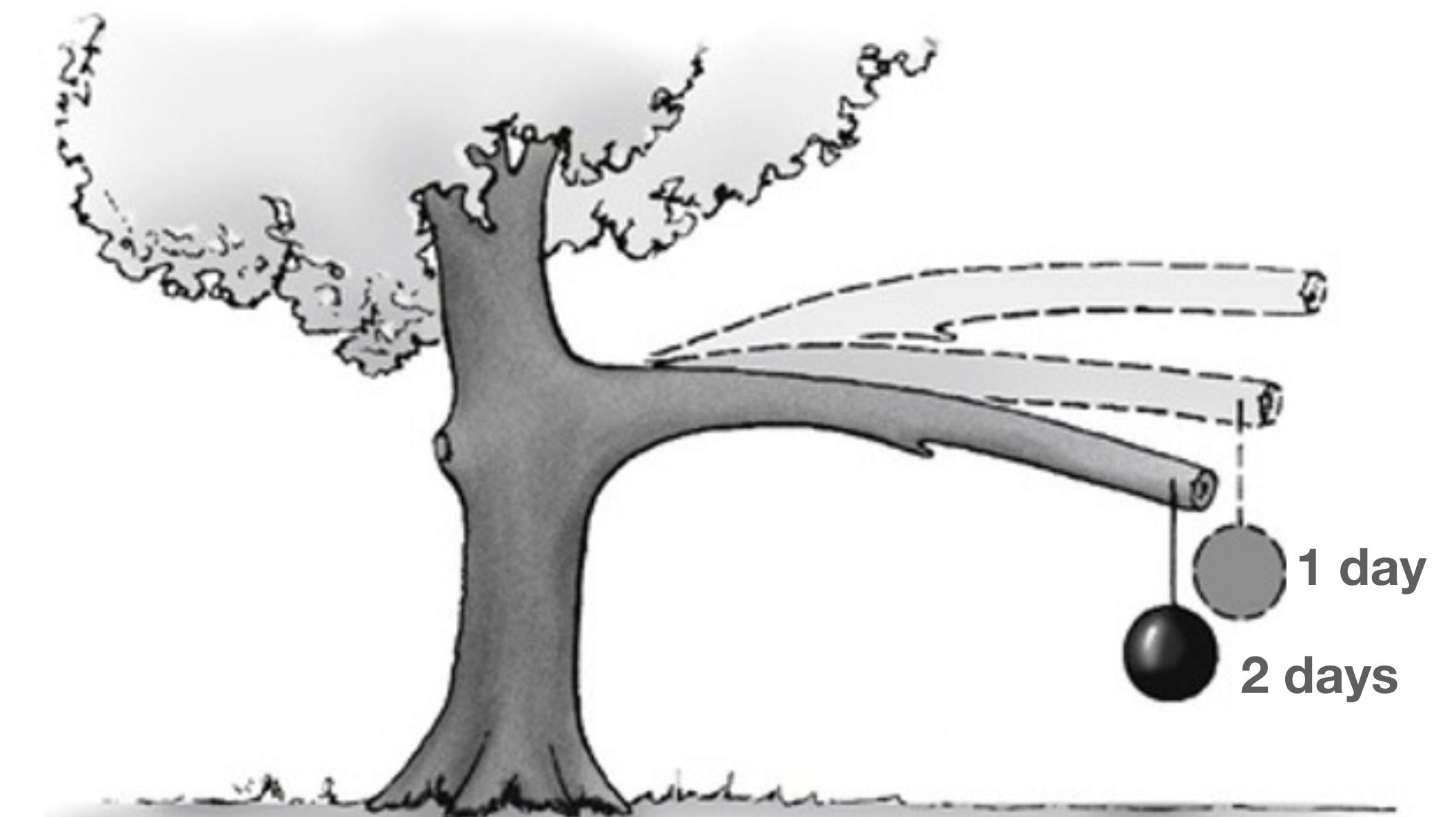
Young's modulus of timber : 150-200 GPa



Young's modulus of steel:  
200 GPa



Similar Young's modulus!



?

# Creep

## ***Cold flow***



Failure of Turbine rotors in jet engines



Creep in concrete bridges

*High temperatures, static mechanical stresses*

# Creep

Materials are often placed in service at **elevated temperatures** and exposed to static mechanical stresses

- The stress in elastic deformation is time-independent.
- Creep is the **time-dependent** and permanent plastic deformation of materials when subjected to a constant load or stress.
- Amorphous polymers, which include plastics and rubbers, are especially sensitive to creep deformation
- **Creep test** consists of subjecting a specimen to a *constant load or stress* while maintaining the temperature constant; deformation or strain is measured and plotted as a function of elapsed time.
- Thermally activated process.

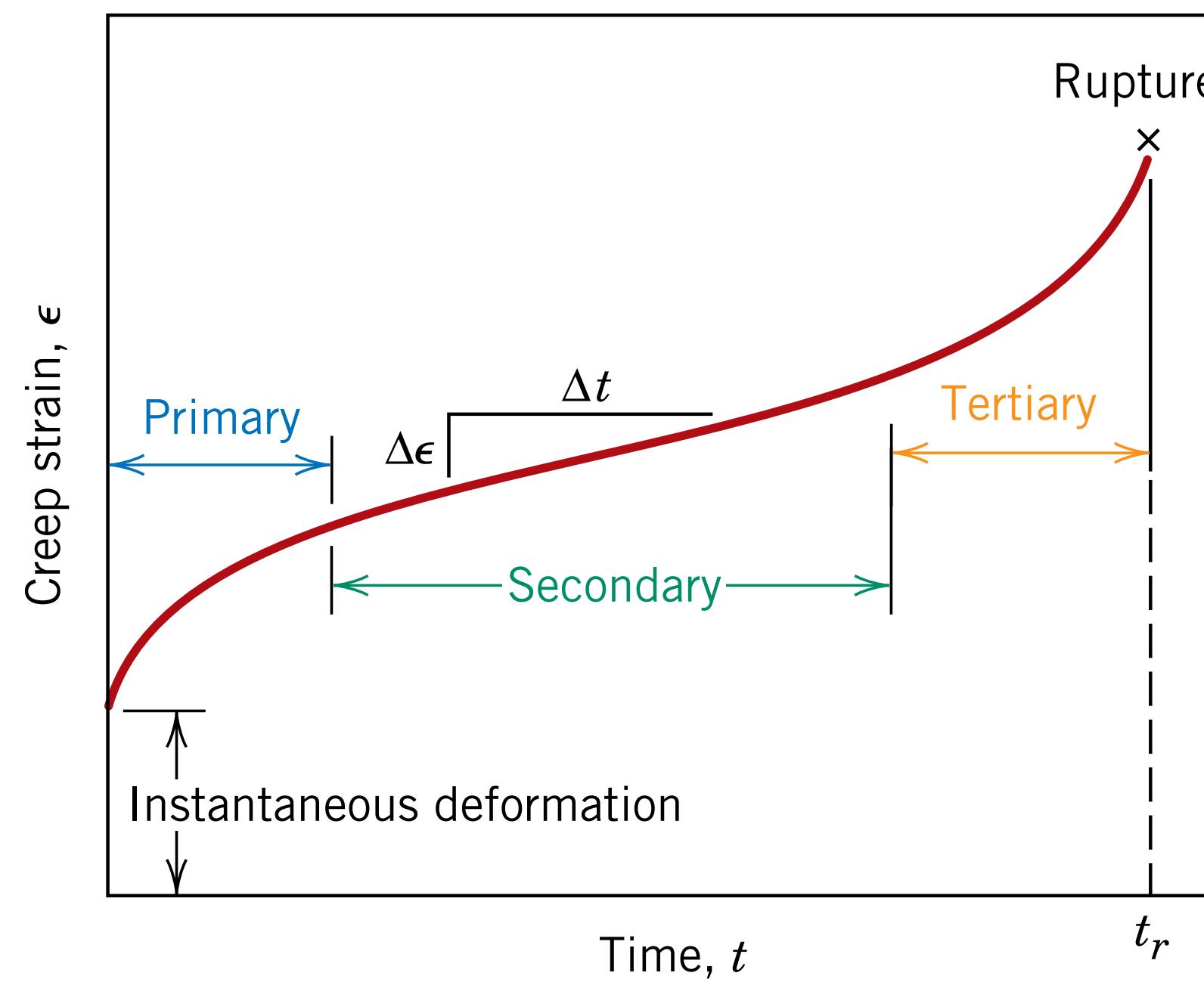
Creep is observed only at  $T > 0.4T_m$   
( $T_m$  = melting point)

Find  $\frac{T}{T_m}$  and check!

e.g. room T for Fe is  $0.16T_m$ , Cu is  $0.22T_m$ : No creep at room T  
room T for Pb is  $0.5T_m$ : Creep observed at room T.

# Creep Test

Creep strain vs. time: conducted in uniaxial tension using a specimen having the same geometry as for tensile tests



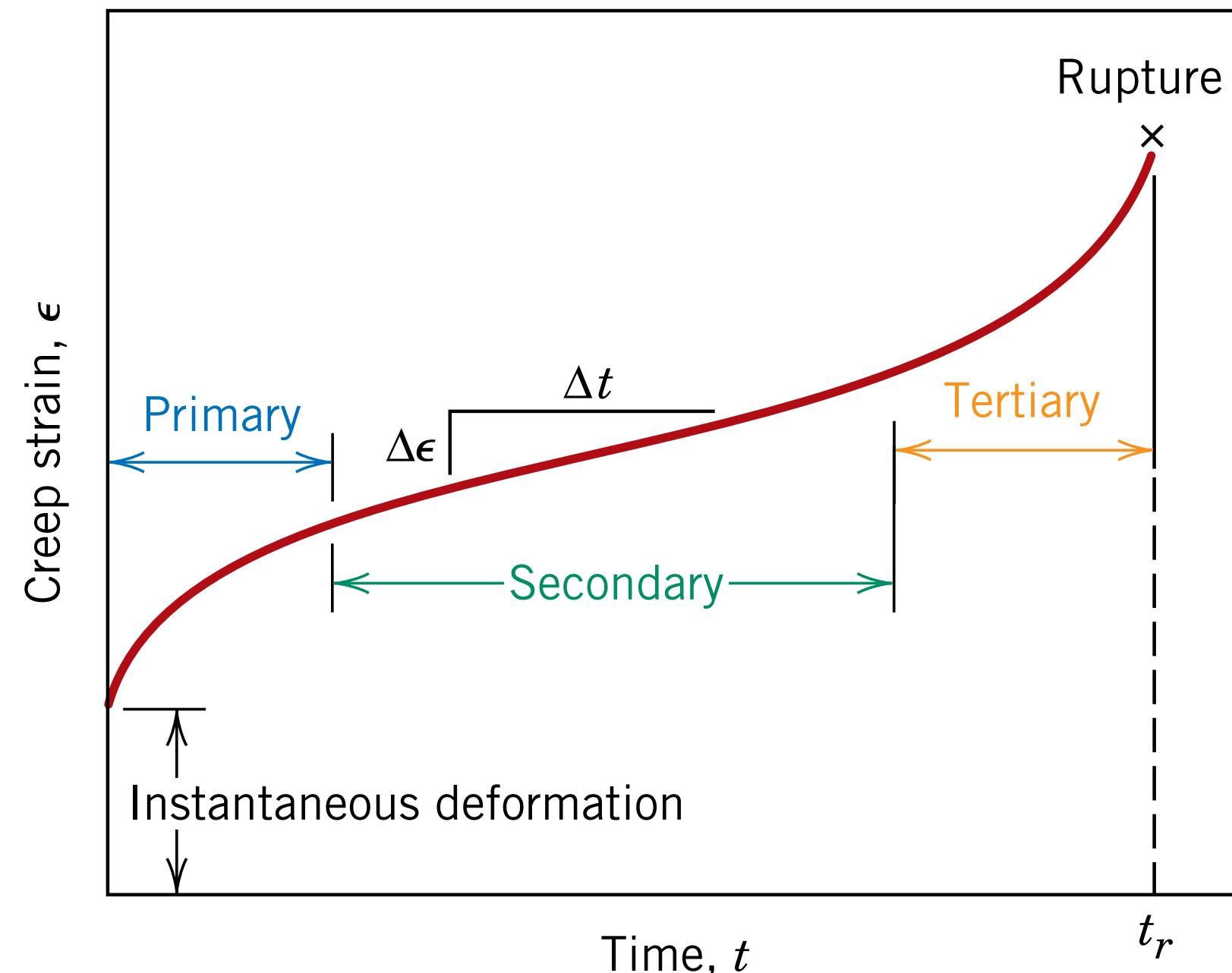
Three stages:

1. Primary
2. Secondary
3. Tertiary

Minimum creep rate:  $\dot{\epsilon}_{ss} = \frac{d\epsilon}{dt}$  (slope) [Also, called steady-state creep rate]  
rupture lifetime,  $t_r$ : total time to rupture

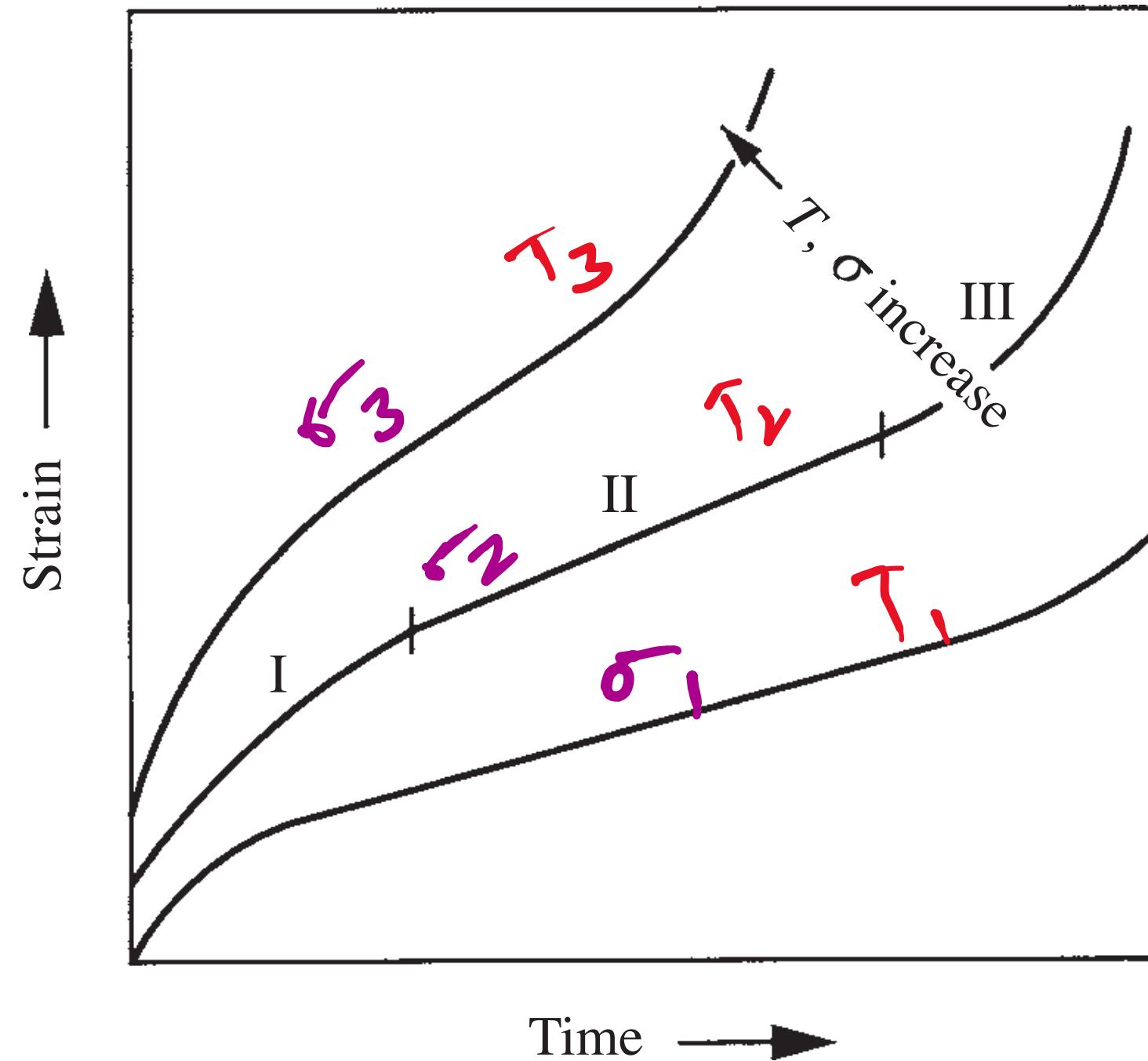
# Creep Test

1. **Primary or transient creep:** The creep rate continuously decreases i.e. the slope of the curve diminishes with time. Increase in creep resistance or strain hardening.
2. **Secondary creep or steady-state creep:** the rate is constant; the plot becomes linear. This is often the stage of creep that is of the longest duration. Balance between the competing processes of strain hardening and recovery. **Recovery** is the process whereby a material becomes softer and retains its ability to experience deformation.
3. **Tertiary creep:** there is an acceleration of the rate and ultimate failure. This failure is frequently termed **rupture** and results from microstructural and/or metallurgical changes; for example, grain boundary separation, and the formation of internal cracks, cavities, and voids.



# Stress and temperature dependence on Creep

$$T_1 < T_2 < T_3, \sigma_1 < \sigma_2 < \sigma_3$$



$$\dot{\epsilon}_{ss}(T, \sigma) = C \sigma^n \exp\left(-\frac{Q}{RT}\right)$$

$\dot{\epsilon}_{ss}$  = steady-state strain rate at  $T$  and  $\sigma$   
 $T$  = test temperature

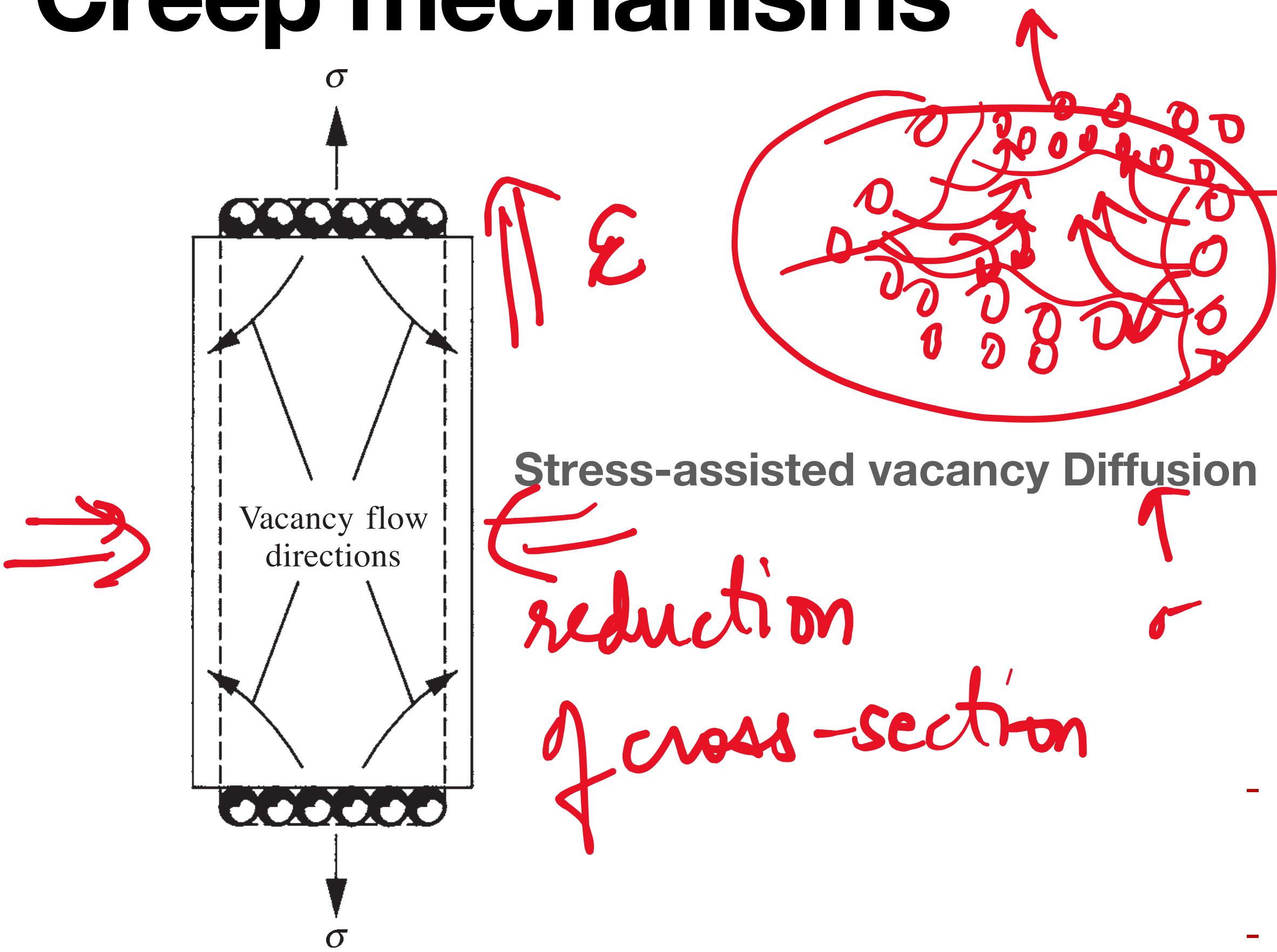
$C$  = a constant

$\sigma$  = test stress

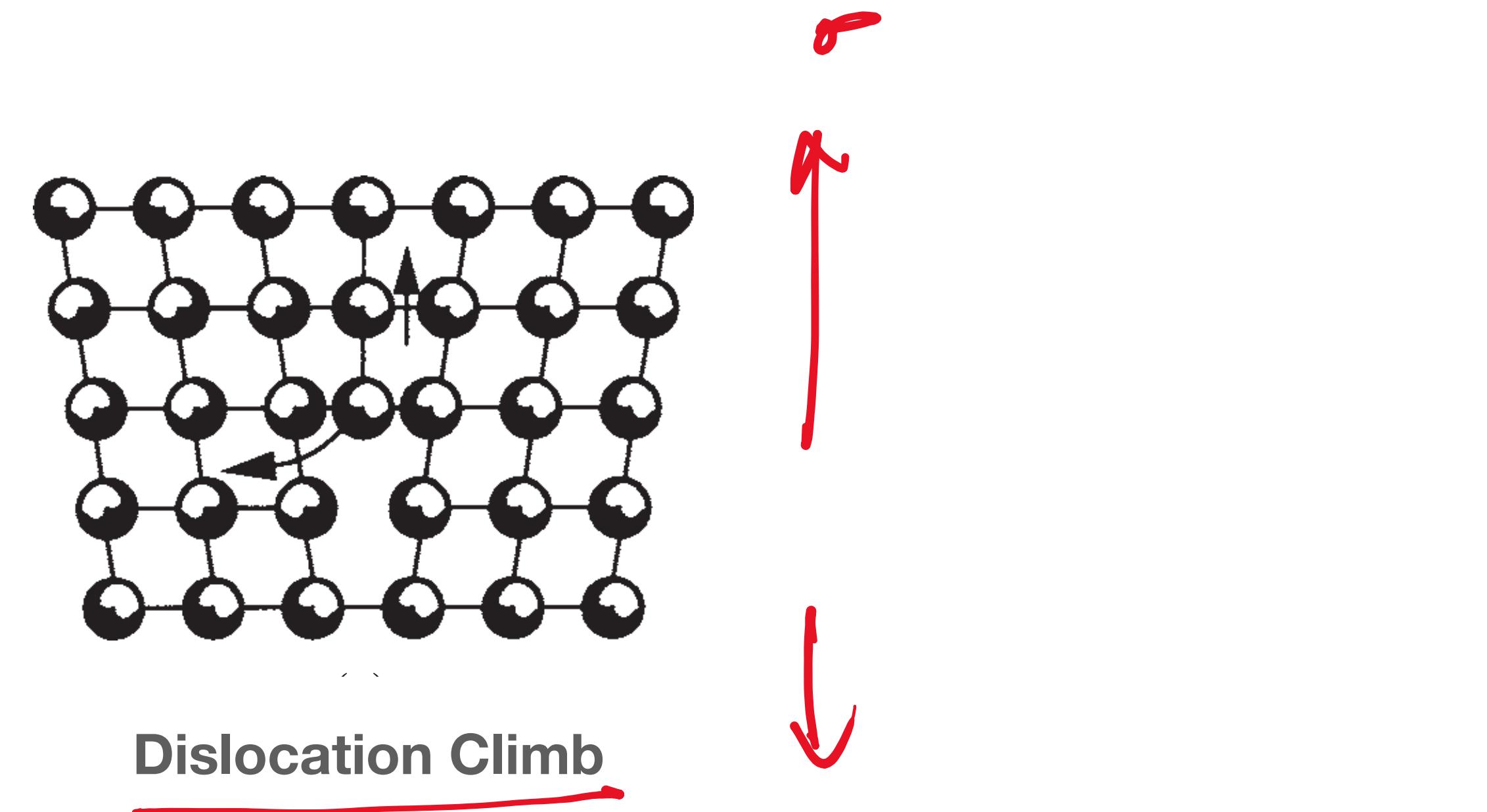
$n$  = stress exponent ( $n \sim 1$  to 8)

$Q$  = activation energy

# Creep mechanisms

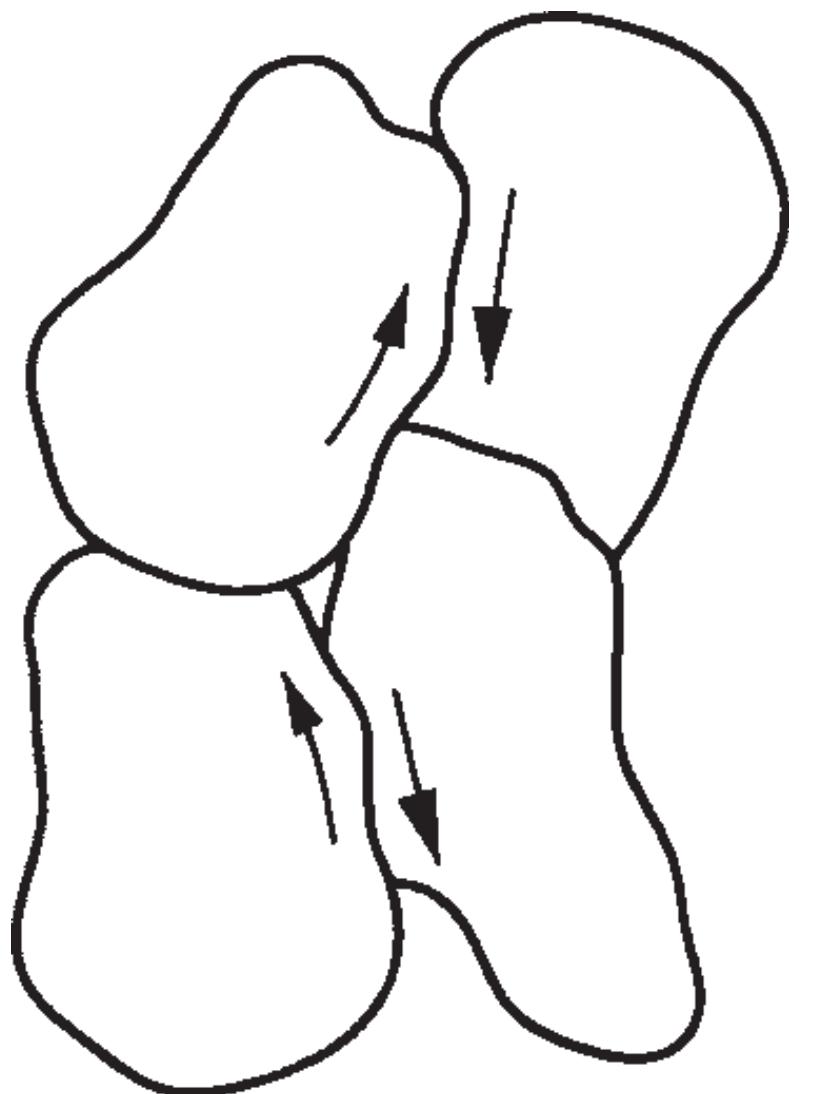


- Vacancies move in response to the applied stress from surfaces of the specimen perpendicular to the stress axis to the surfaces that are parallel to the stress axis.
- Over a period of time, this movement would elongate the specimen in the direction of the stress axis and contract it in the transverse direction resulting in creep.



- Thus edge dislocations piled up against an immobile dislocation can move to other parallel slip planes by climb and continue their motion in response to the stress.
- *The rate controlling step in the climb process is the diffusion of vacancies.*
- The measured activation energy for creep agrees with the activation energy for self-diffusion by the vacancy mechanism in a number of materials.

# Creep mechanisms



- Grain boundaries lose their strength at a lower temperature than the grains themselves.
- At temperatures above  $0.5 T_m$ , the viscosity of the grain boundaries is small enough for them to behave like a very viscous liquid separating the neighbouring grains and allowing them to slide against each other.
- At high temperatures, the grain boundaries facilitate the deformation process by sliding, whereas at low temperatures, they increase the yield strength by stopping the dislocations.

## Grain boundary sliding

### Creep resistant materials:

- *Cold working or strain hardening cannot be used for creep resistance.* At temperatures above  $0.4T_m$ , recrystallization will occur quite readily and the cold-worked strength will be lost on recrystallization. *Recrystallization* is the process of nucleation and growth of new, strain-free crystals, which replace all the deformed crystals of the worked material. It starts on heating to temperatures in the range of  $0.3\text{--}0.5T_m$ , which is above the recovery range.
- *Solid solution hardening can be used for better creep resistance.*
- *Fine-grained materials should be avoided at high T as grain boundary sliding can add to creep deformation.*
- Minimizing grain boundary sliding.
- Using high melting point material.

# The online experience so far...

**Expectations!!!**

**What students have  
actually felt!**

How to attend Online Class :

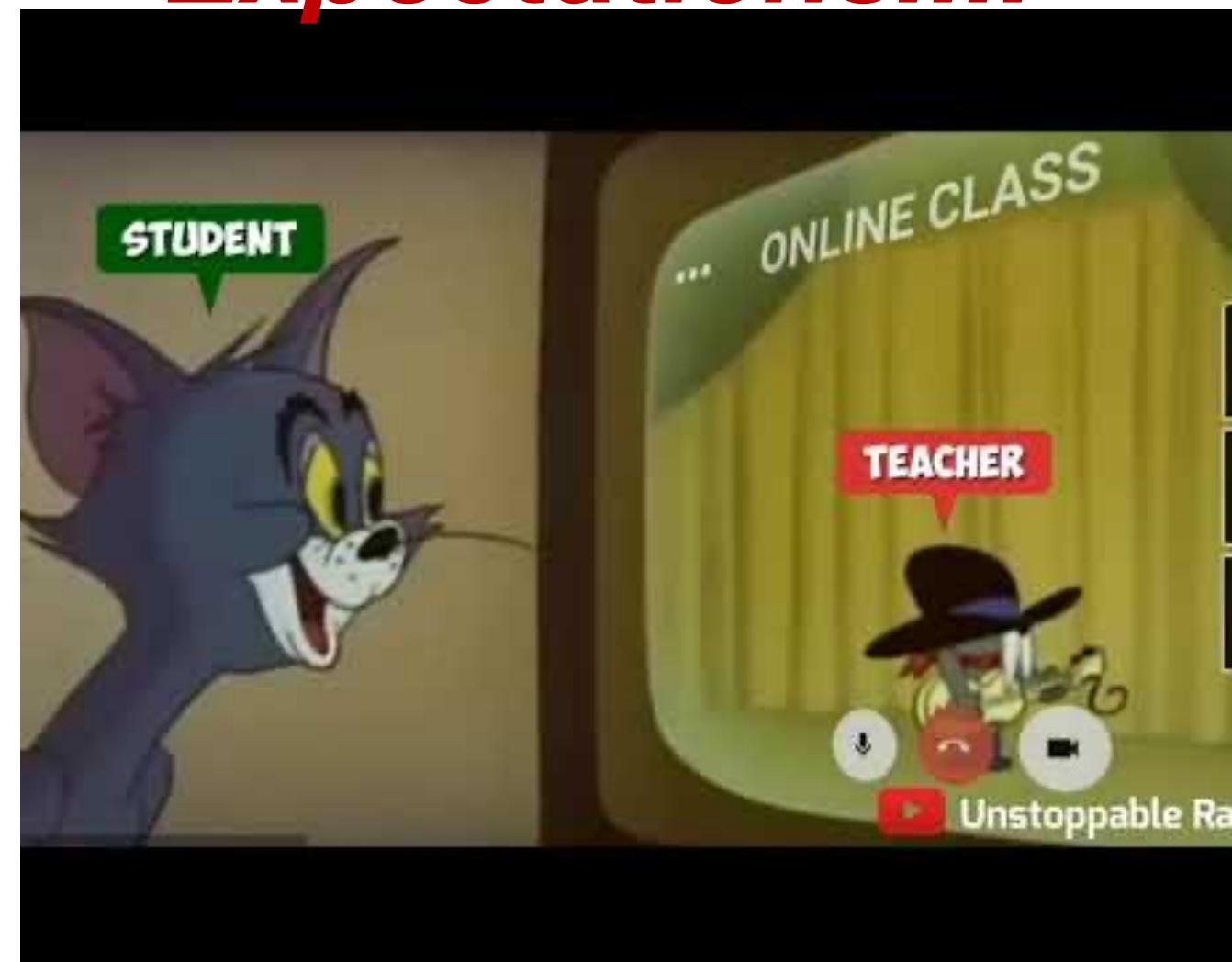
Step 1 :

Step 2 :

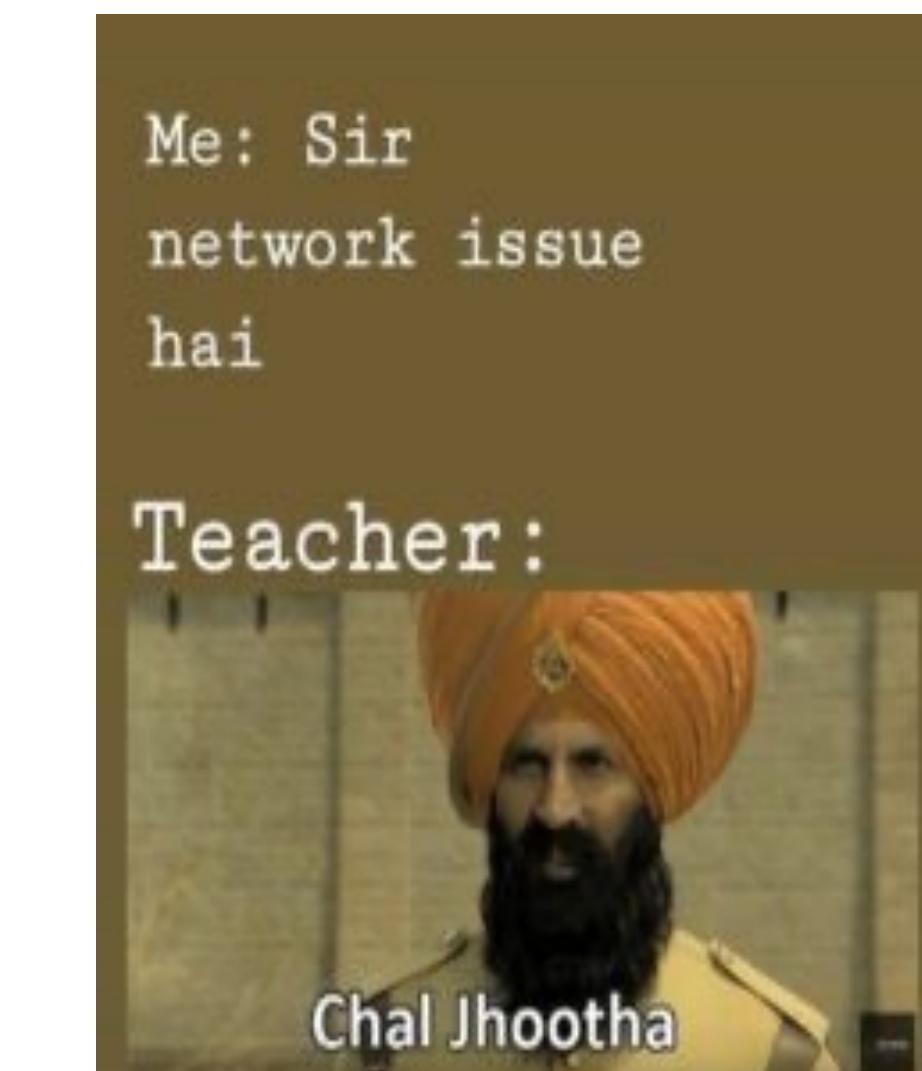
Step 3 :



**Me during online classes**



When the teacher asks us a question  
online and no one knows the answer  
Me :



Me: Sir  
network issue  
hai

Teacher:

Chal Jhootha

**What Teachers have  
actually felt!**

**"HOW WAS ONLINE TEACHING?"**



**Teacher In Offline Class**



**Teacher In Online Class**



Please Say Something Guys

# What COVID era has taught us?



We got connected to  
ourselves



We found out our hidden talents and hobbies



We got closer to our families

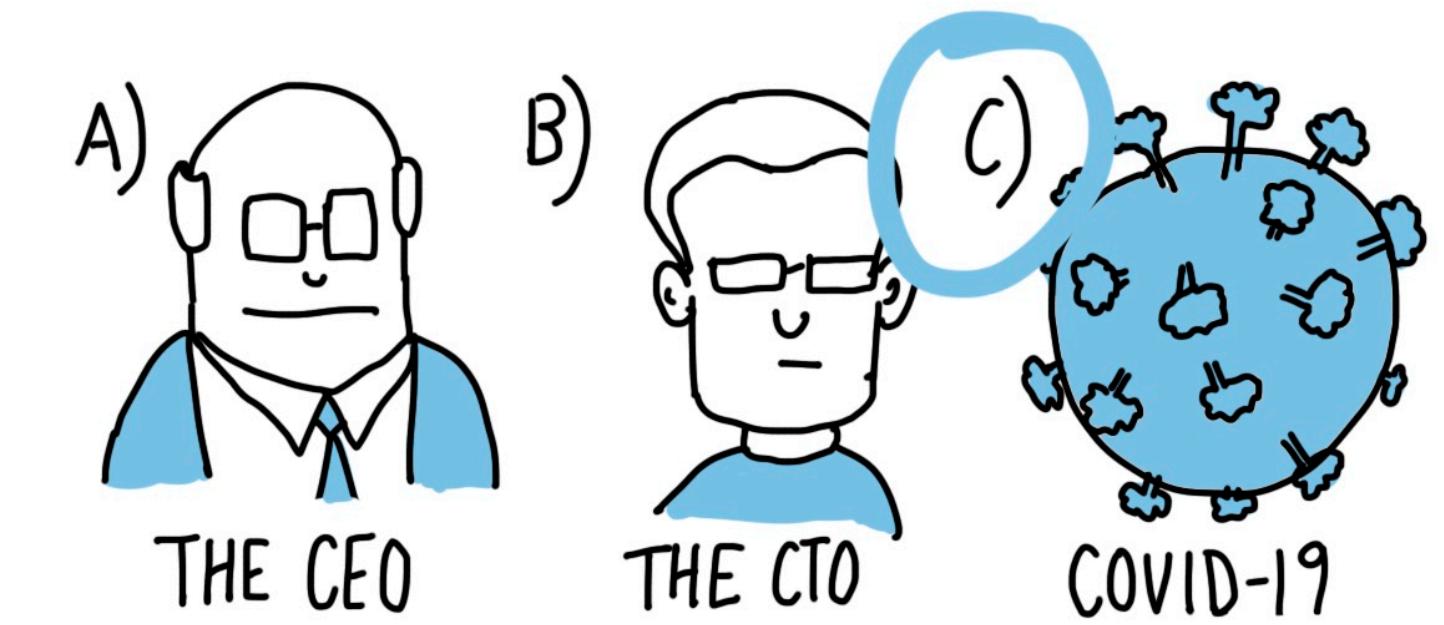
Travel agents: "Yeah, we're good!" 😂

Thanks for your patience during this trying time!



We got more patient

WHO LED THE DIGITAL TRANSFORMATION  
OF YOUR COMPANY ?



We got more DIGITAL

**Welcome to the Offline lectures!**

# Lecture 33

## Computational modeling of materials- An introduction

### Textbooks:

- Computational Materials Science: J. Gunn Lee
- Understanding Molecular Simulations: D. Frenkel and B. Smit
- Molecular Modelling Principles and Applications: Andrew Leach

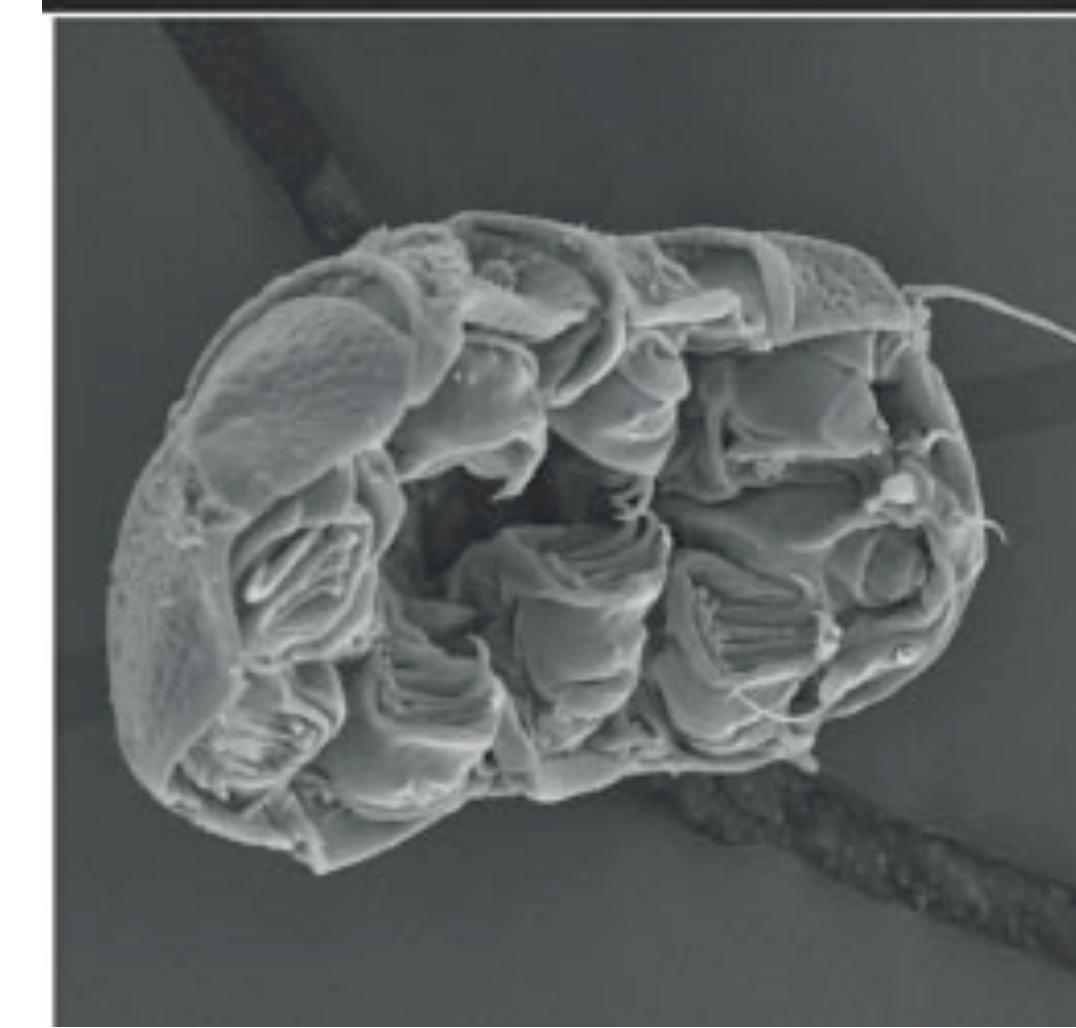
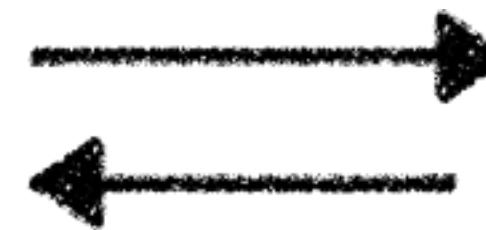
**Prof. Divya Nayar**  
Department of Materials Science and Engineering  
[divyanayar@mse.iitd.ac.in](mailto:divyanayar@mse.iitd.ac.in)

# What we will cover in three lectures?

- Introduction to computational materials science
- Molecular modeling: the basics
- Multiscale modeling
- Molecular simulations methods: molecular dynamics
- Examples of simulations of materials

.

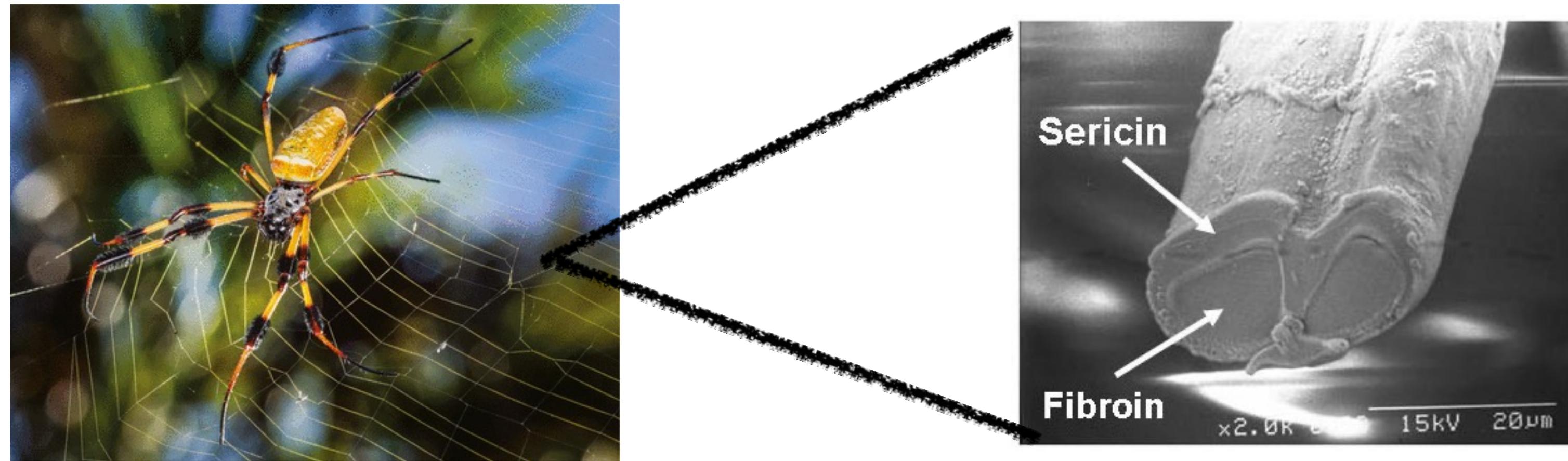
# Tardigrade: Water Bear



Microscopic animals that can survive extreme conditions:  
high altitudes, deep sea, exposure to radiation including space!

Can survive in dehydrated state for several weeks because of sugar present in cells !

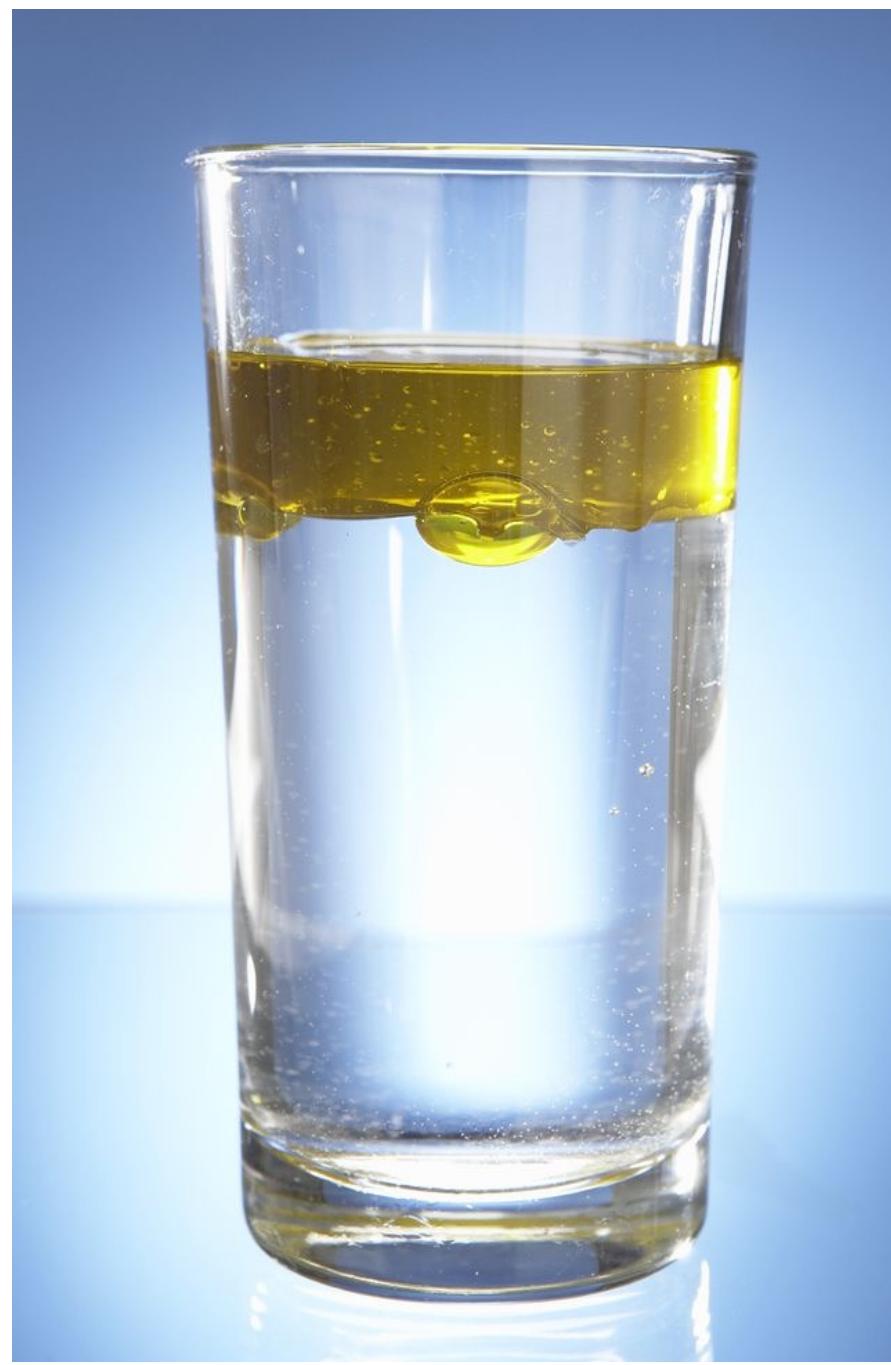
*Can we understand how sugar protects this organism?*



Spider Silk: tensile strength  
5 times more than steel !

Protein called Fibroin  
(fibril structure)

Can we design materials with the strength of spider silk ?



Water and oil don't mix!



Yet water clogs natural (methane) gas pipelines under sea by forming solid hydrates

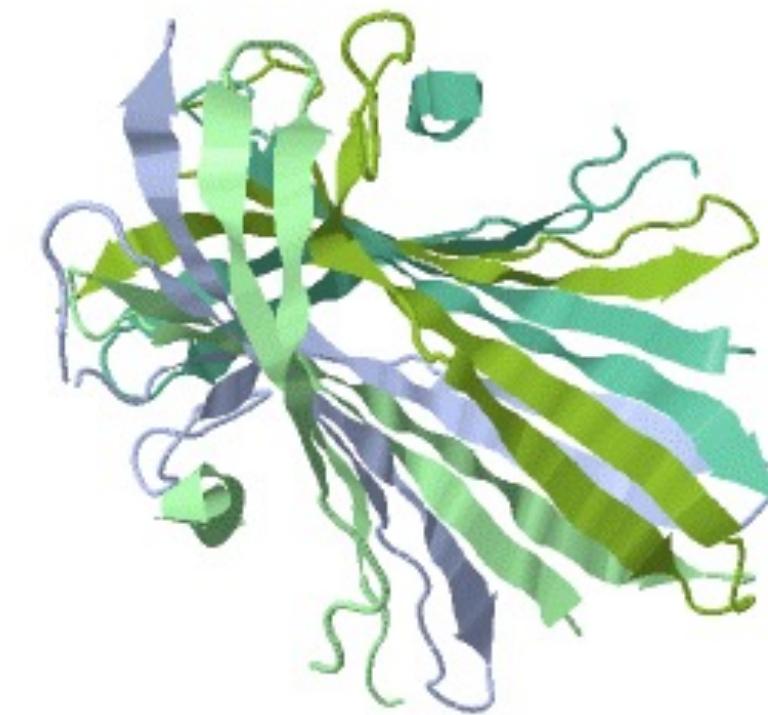
Why water does not mix with oil in one case but forms solid hydrates in natural gas pipelines in the other case?

# Computational Experiments!

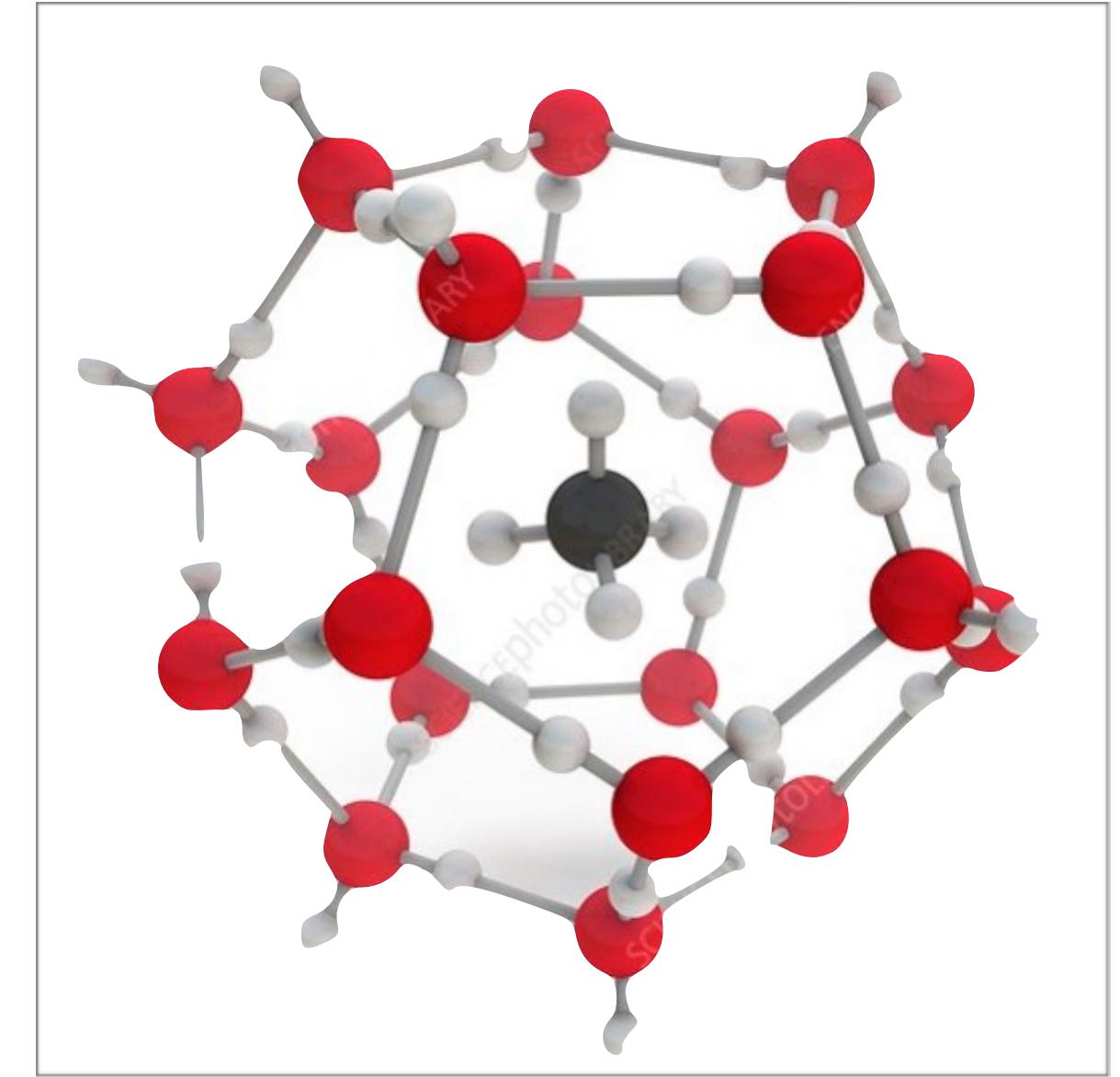
## Molecular Modeling



Trehalose sugar



Fibroin protein



Methane gas hydrate

<https://proteopedia.org/wiki/index.php/Fibroins>

<https://www.chemistryworld.com/news/water-trapped-in-a-sugar-crystal/3004284.article>

<https://www.sciencephoto.com/media/568364/view/methane-hydrate-molecule-artwork>

# Computational Materials Science

## Modeling and Simulations: *Not just an extra tool!*

- Can act as a bridge between theory and experiments
- Can help in validating a theory
- Can help in understanding problems under extreme conditions where experiments are not feasible
- Can provide additional insights into experiments
- Can help in designing and predicting new materials: motivating new experiments

# Three pillars of science



The Nobel Prize in Chemistry 2013  
Martin Karplus, Michael Levitt, Arieh Warshel

## The Nobel Prize in Chemistry 2013



© Harvard University  
Martin Karplus



Photo: © S. Fisch  
Michael Levitt



Photo: Wikimedia Commons  
Arieh Warshel

The Nobel Prize in Chemistry 2013 was awarded jointly to Martin Karplus, Michael Levitt and Arieh Warshel "for the development of multiscale models for complex chemical systems".

# The ingredients

Computer, Programming, Models, Simulation...



Ada Lovelace  
(1815-1852)

Ada Lovelace broke gender barriers like never before and went on to discover computer programming 175 years ago, an industry still dominated by men.

## ADA LOVELACE FIRST COMPUTER PROGRAMMER

**The Analytical Engine**

Lovelace's program turned a complex formula into simple calculations that could be encoded on punched cards and fed into Charles Babbage's Analytical Engine, a mechanical computer that he designed but never built. She published it in 1843, a century before the modern computer age.

$$\frac{x}{e^x - 1} = \frac{1}{1 + \frac{x}{2} + \frac{x^2}{2 \cdot 3} + \frac{x^3}{2 \cdot 3 \cdot 4} + \&c.}$$

*"I want to put in something about Bernoulli's Number, in one of my Notes, as an example of how an explicit function may be worked out by the engine, without having been worked out by human head and hands first."*

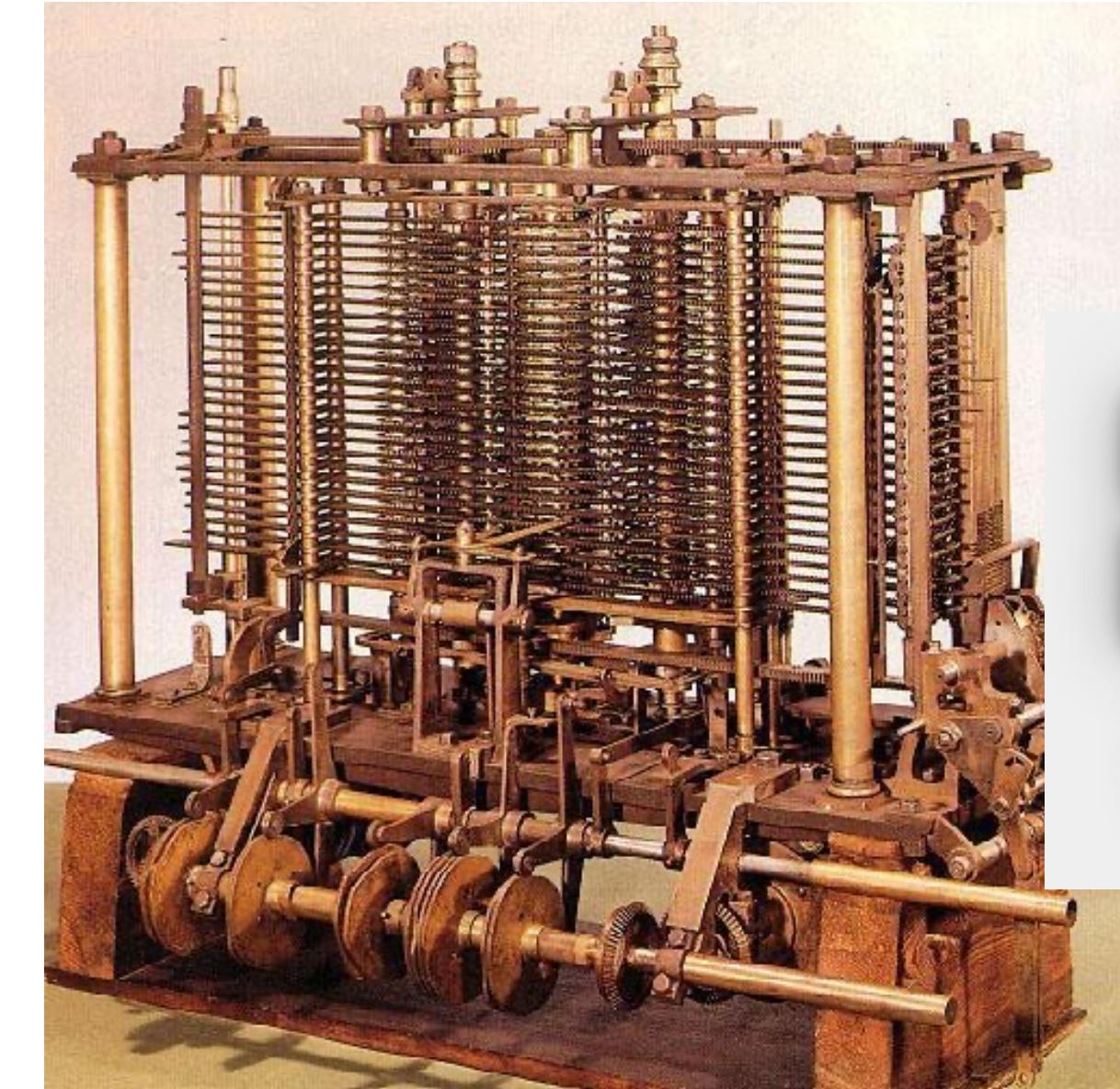
**A Universal Computer**

Lovelace did more than write the first computer program. She was also the first person to realise that a general purpose computer could do anything, given the right data and instructions.

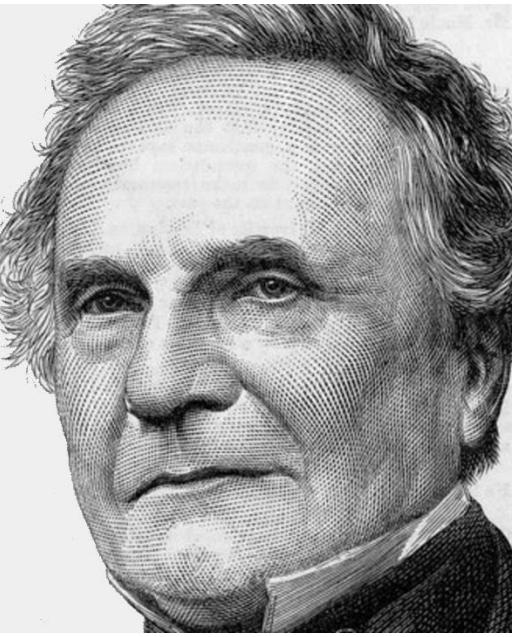
*"The Analytical Engine weaves algebraic patterns just as the Jacquard loom weaves flowers and leaves."*

**Augusta Ada King, Countess of Lovelace**  
Born: 10 December 1815  
Died: 27 November 1852

Ada Lovelace Day  
FindingAda.com

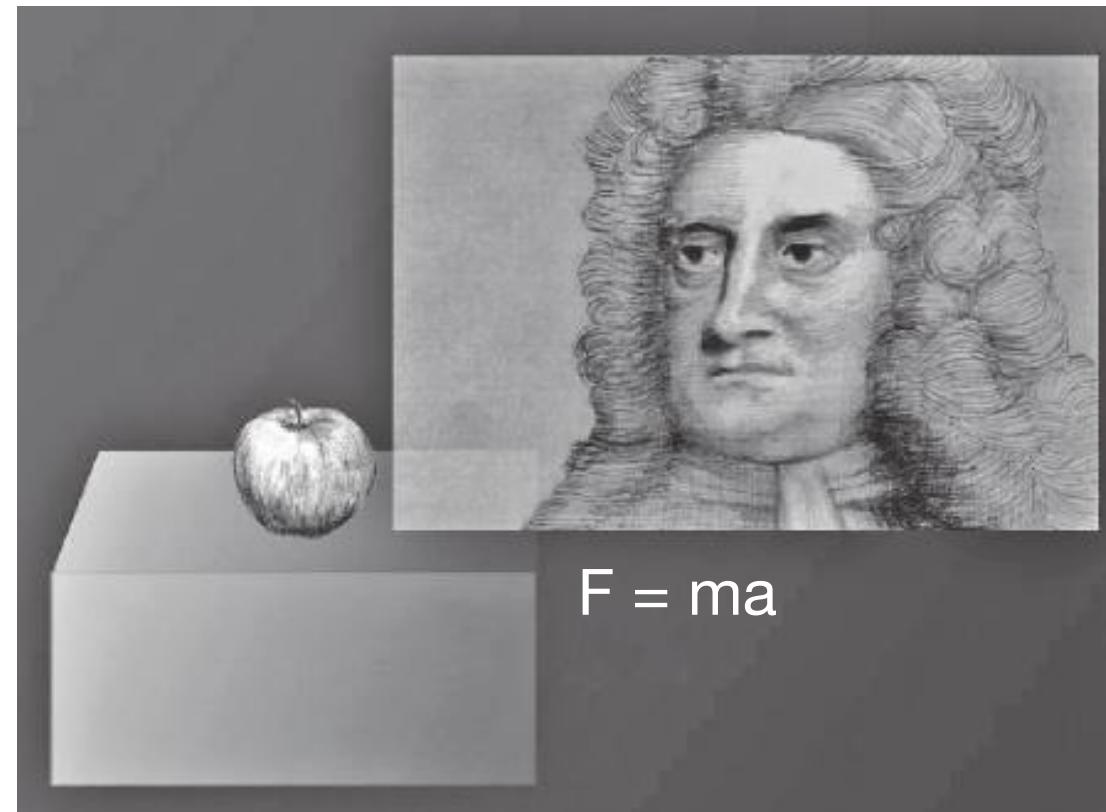


CHARLES  
BABBAGE  
1791-1871

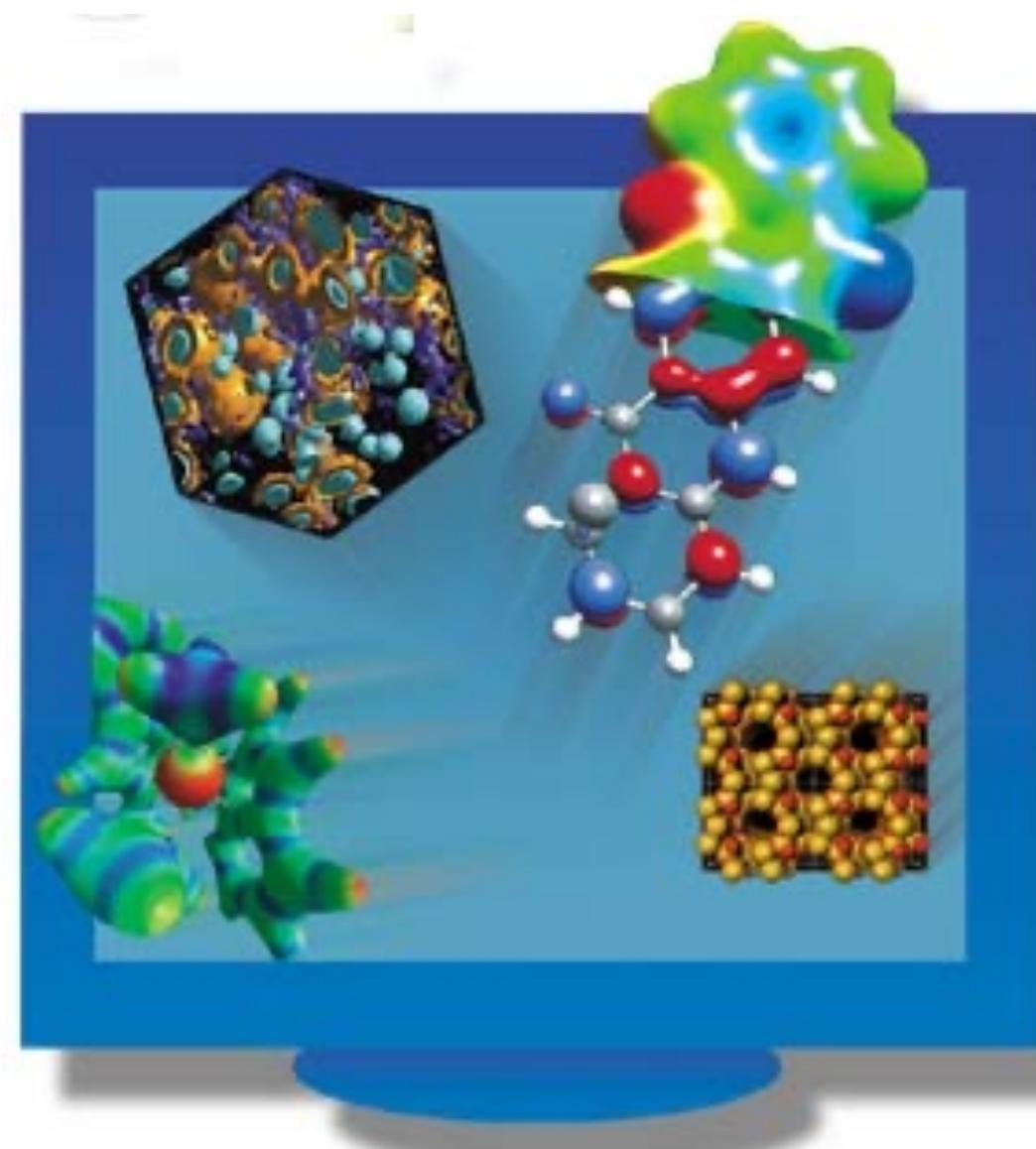


Analytical Engine: First computer

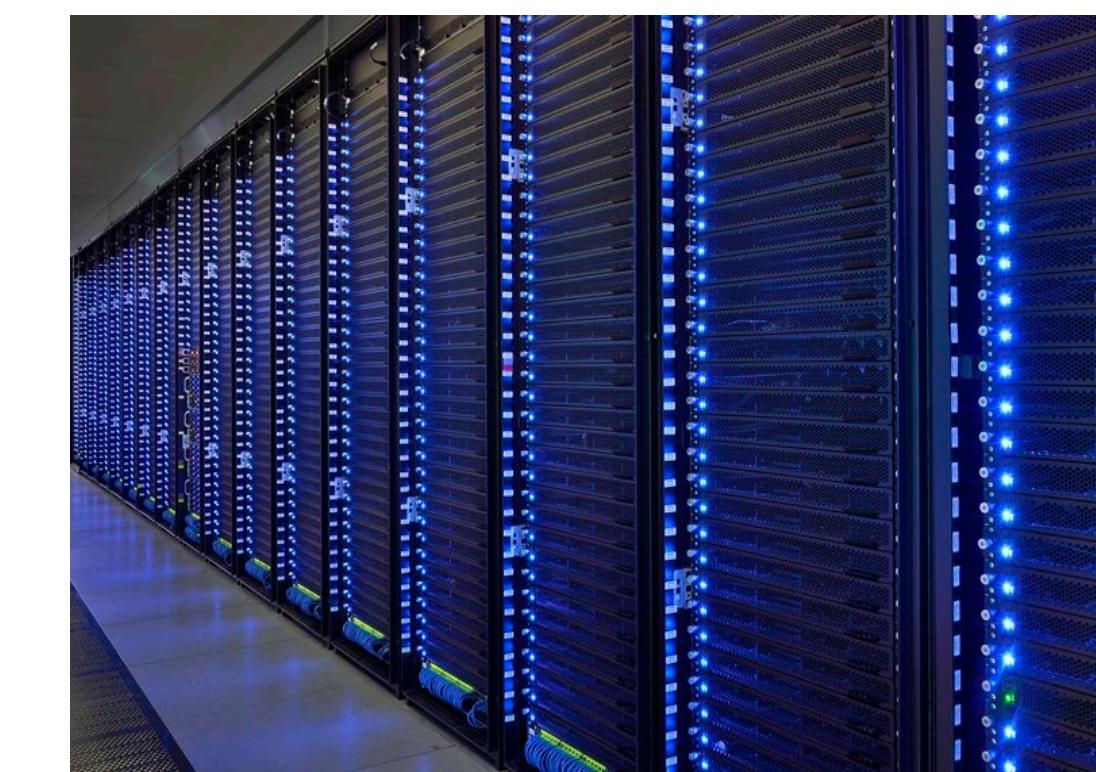
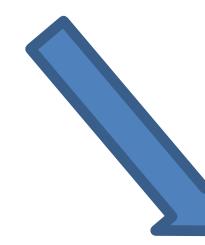
# Computational Materials Science



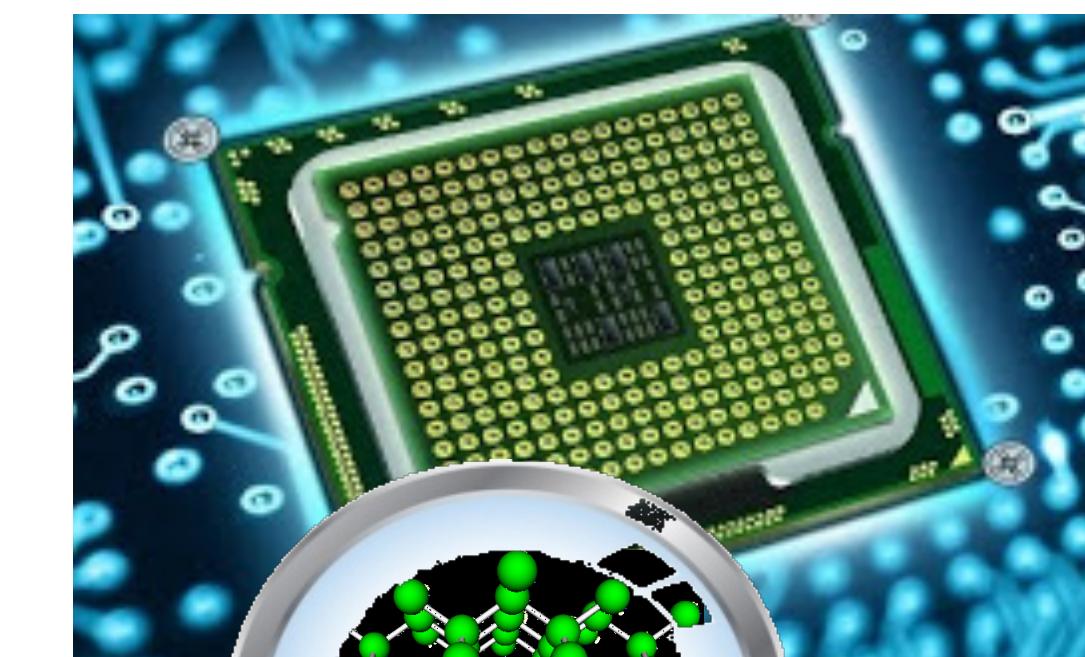
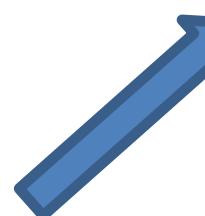
*Theory*



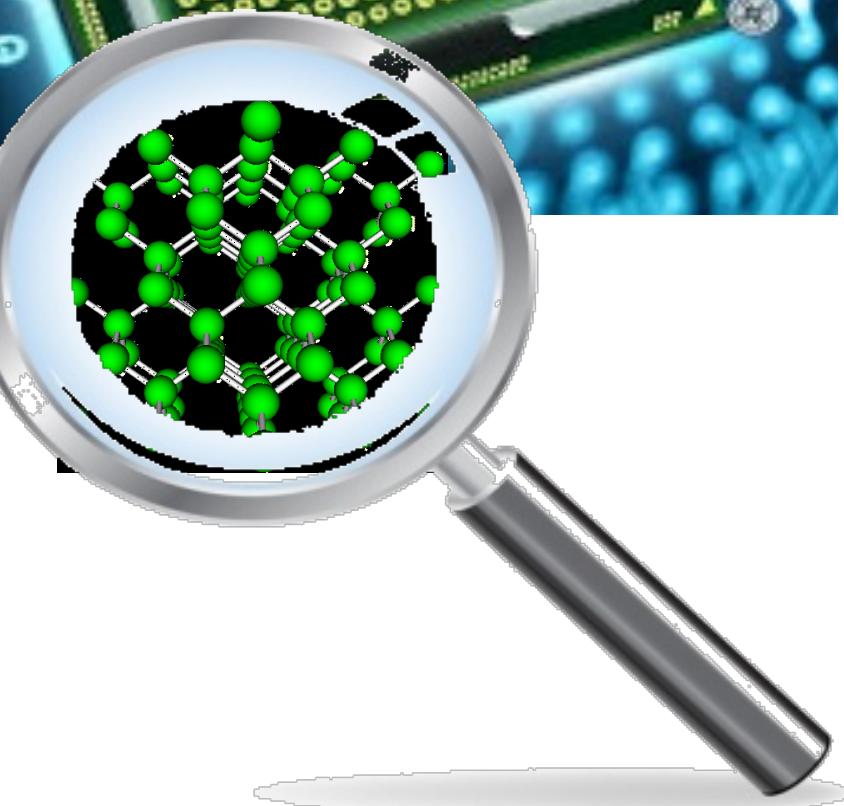
*Modeling and simulations*



*High Performance Computing*

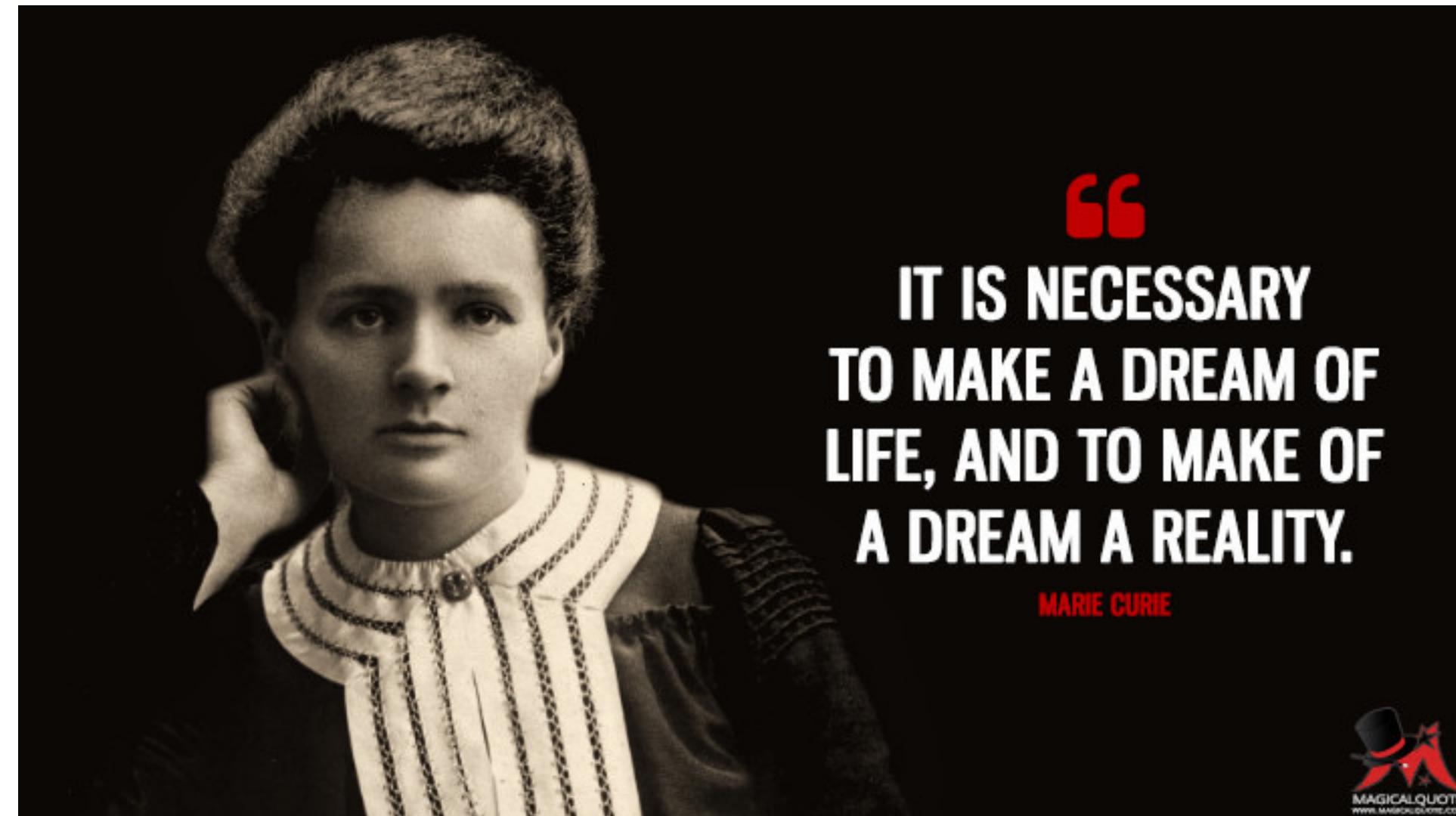


*Computational microscope !*



*Dream*

Decipher, Design, Discover... *Develop*



# ***A computational experiment***

## **The Recipe**

- Define the problem
- Make a MODEL (that represents the real system properly)
- Select the relevant rules (THEORY)
- Write a code or use a software to do the job
- Run the SIMULATION
- Analyze the data produced

**What is *modeling* in computational “experiments”?**

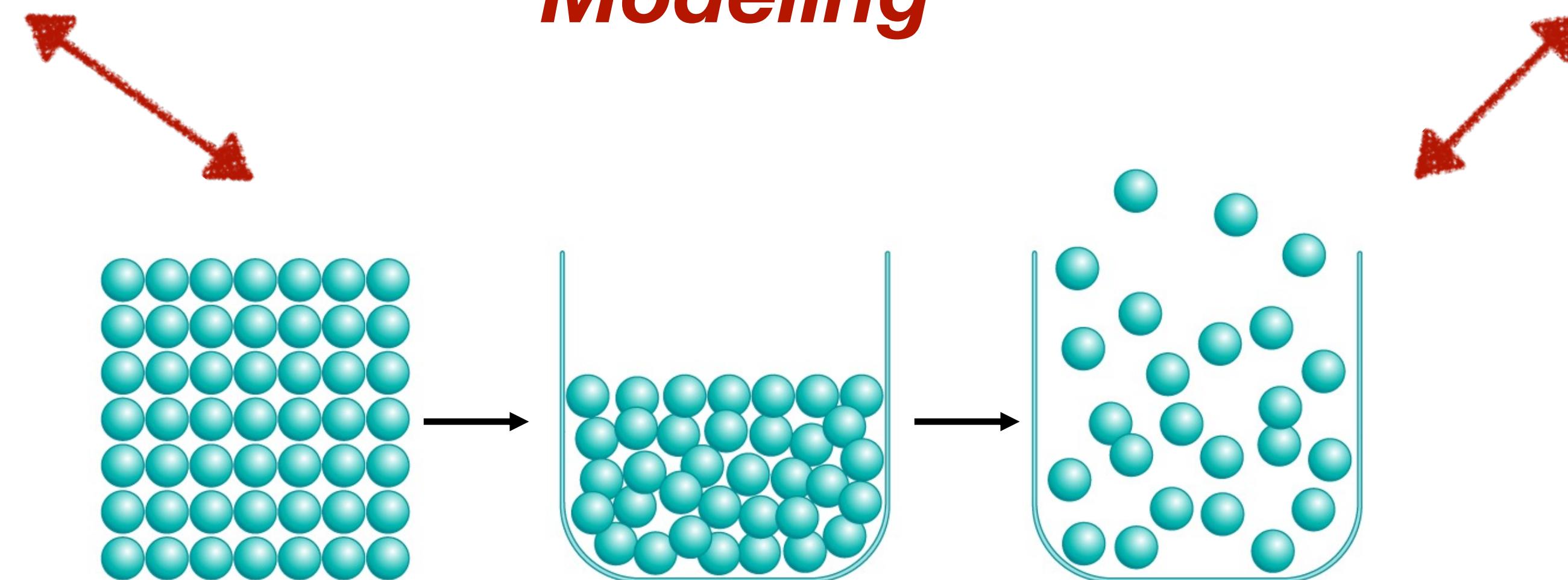
# A model describes the *nature* of the system

Even if it may not describe the system completely

## Experiment



## Modeling



## Theory

Latent heat of fusion and  
Vaporisation

# Create a *model* to study the pollution levels in different areas of Delhi

Whole city

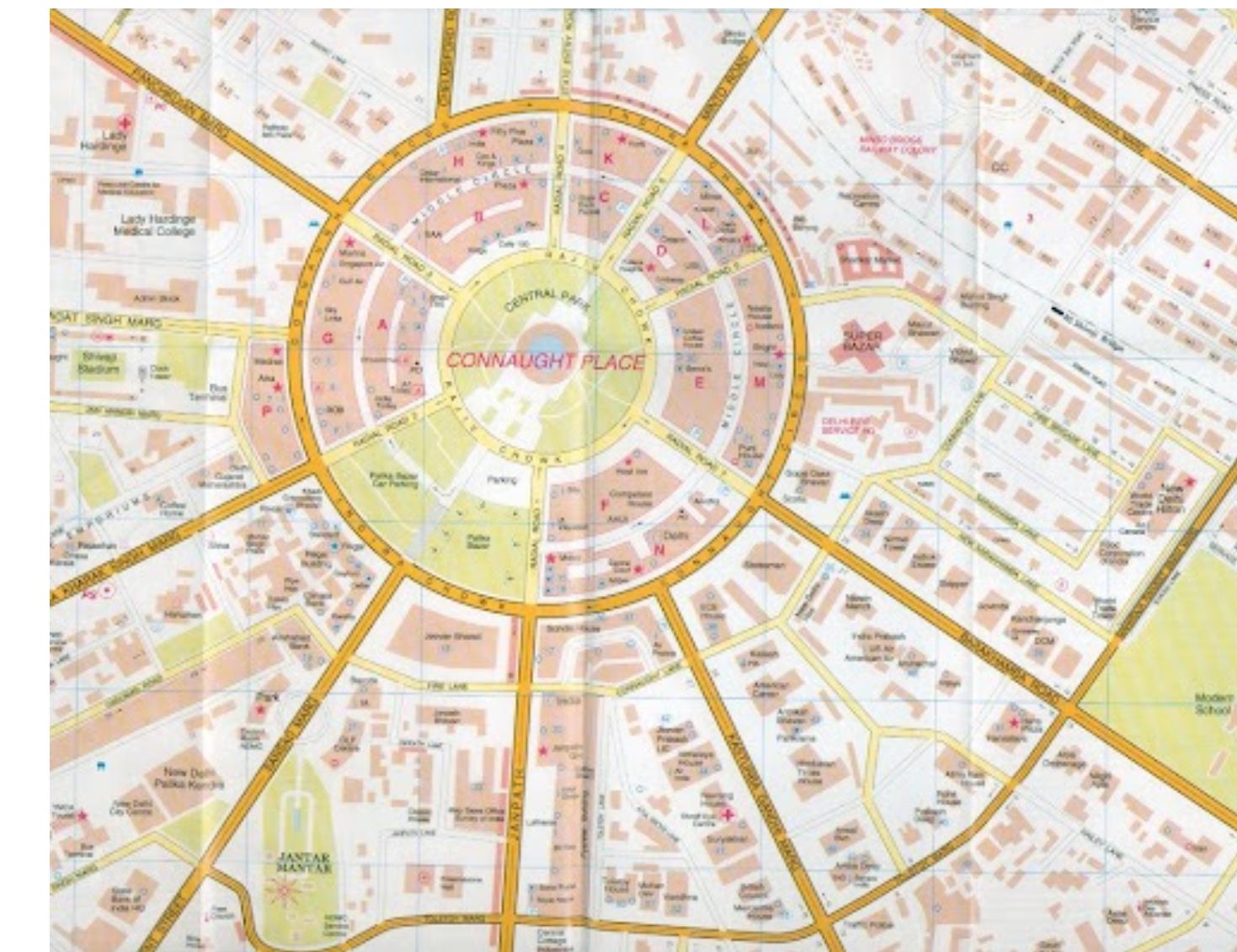


Study the map of the whole city

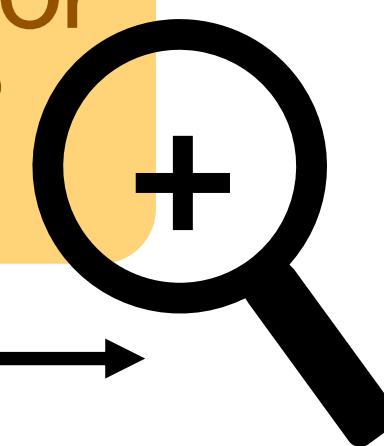


Scale!

A busy area of the city e.g. Connaught Place

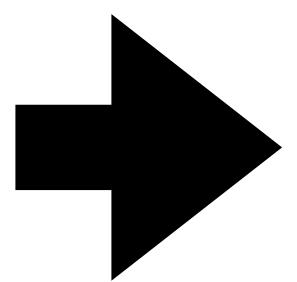


Which part of the city?: Whole? Or only the central/outskirt area?

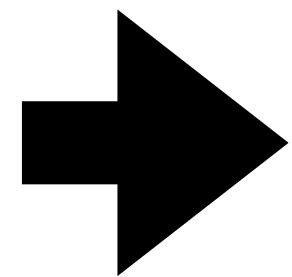


# Pollution levels in the *whole* city

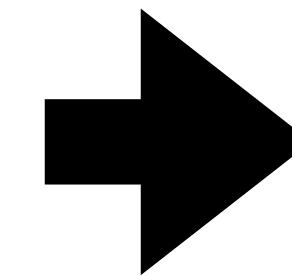
The BIG Picture



The Scale



The Details



The Connections

Create a model of  
Delhi



Study the map of the  
city



Major regions of Delhi:  
S, N, E, W

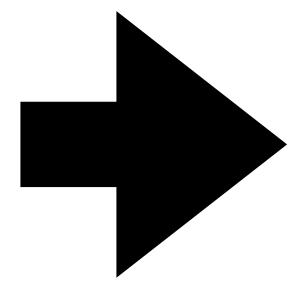
Google images



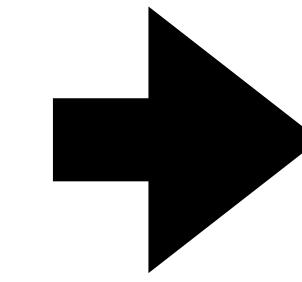
Roads, Metro...

# Pollution levels in a part of the city

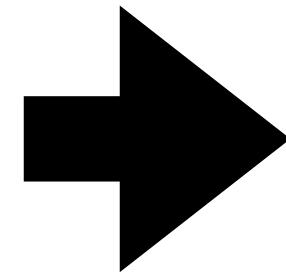
The BIG Picture



The Scale



The Details



The Connections

Create a model of a commercial area of Delhi

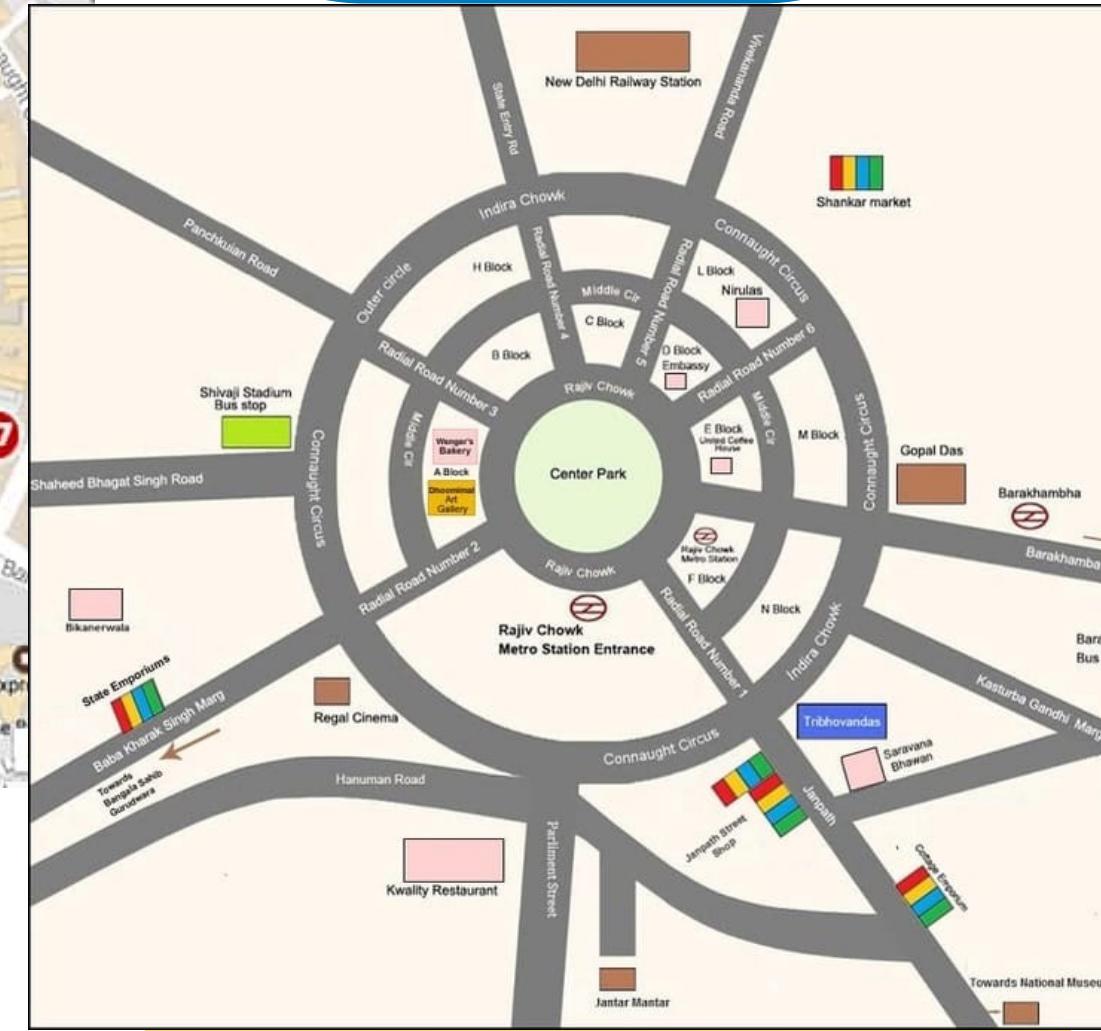


Which part of the city?: Whole?  
Or only the central/outskirt area?

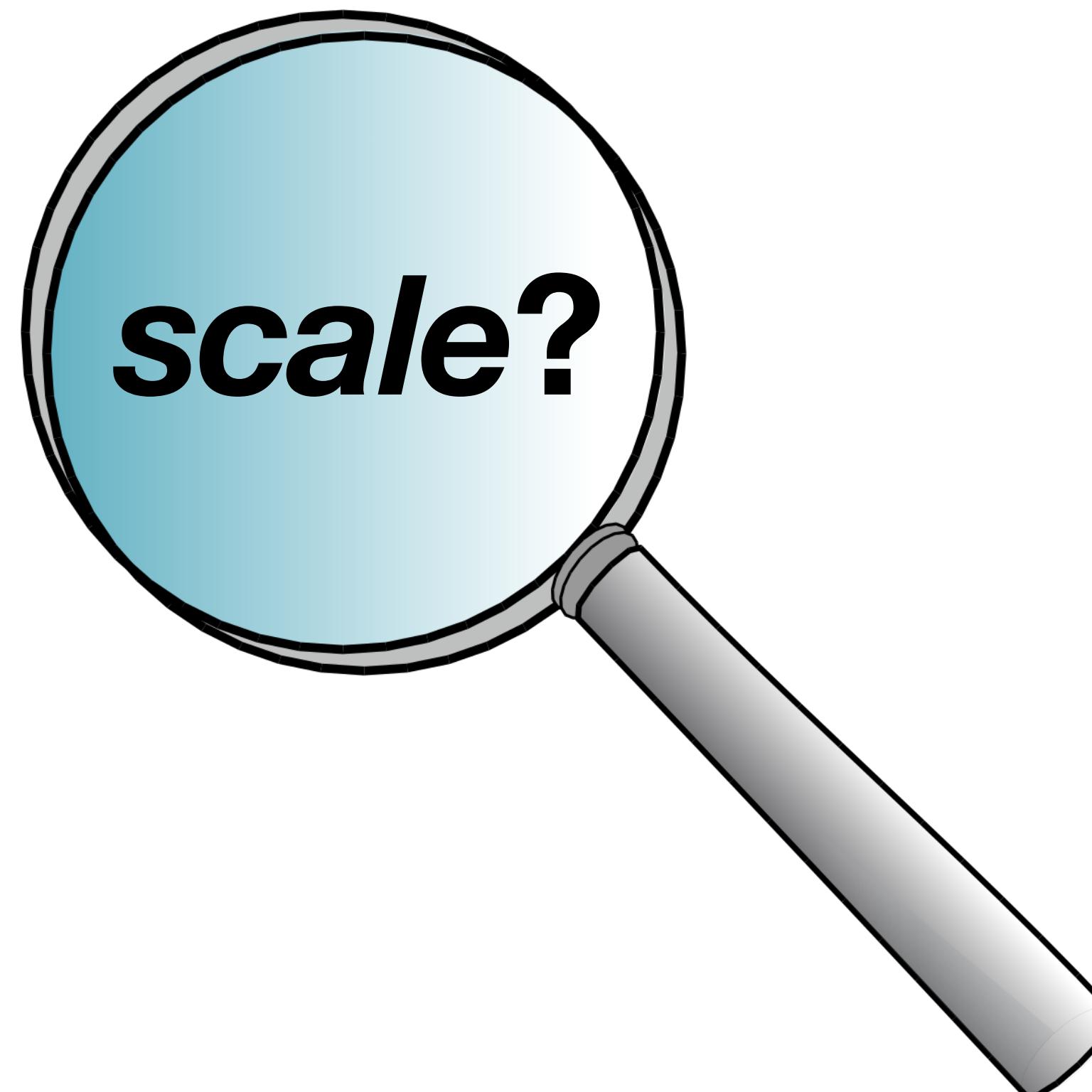
- 01. Barbeque Nation
- 02. Boombox Cafe
- 03. Cafe OMG
- 04. Farzi Cafe
- 05. Hotel Palace Heights
- 06. House of Commons
- 07. Jungle Jamboree
- 08. Kinbuck-2
- 09. Kitchen Bar
- 10. Lord of the Drinks
- 11. Luggage Room
- 12. My Bar HQ
- 13. Office Canteen Bar
- 14. Open House Cafe
- 15. Public Connection
- 16. TC Bar & Restaurant
- 17. Teddy Boy Restaurant
- 18. The Niche Restaurant
- 19. The Vault Cafe
- 20. Unplugged Courtyard
- 21. Warehouse Cafe



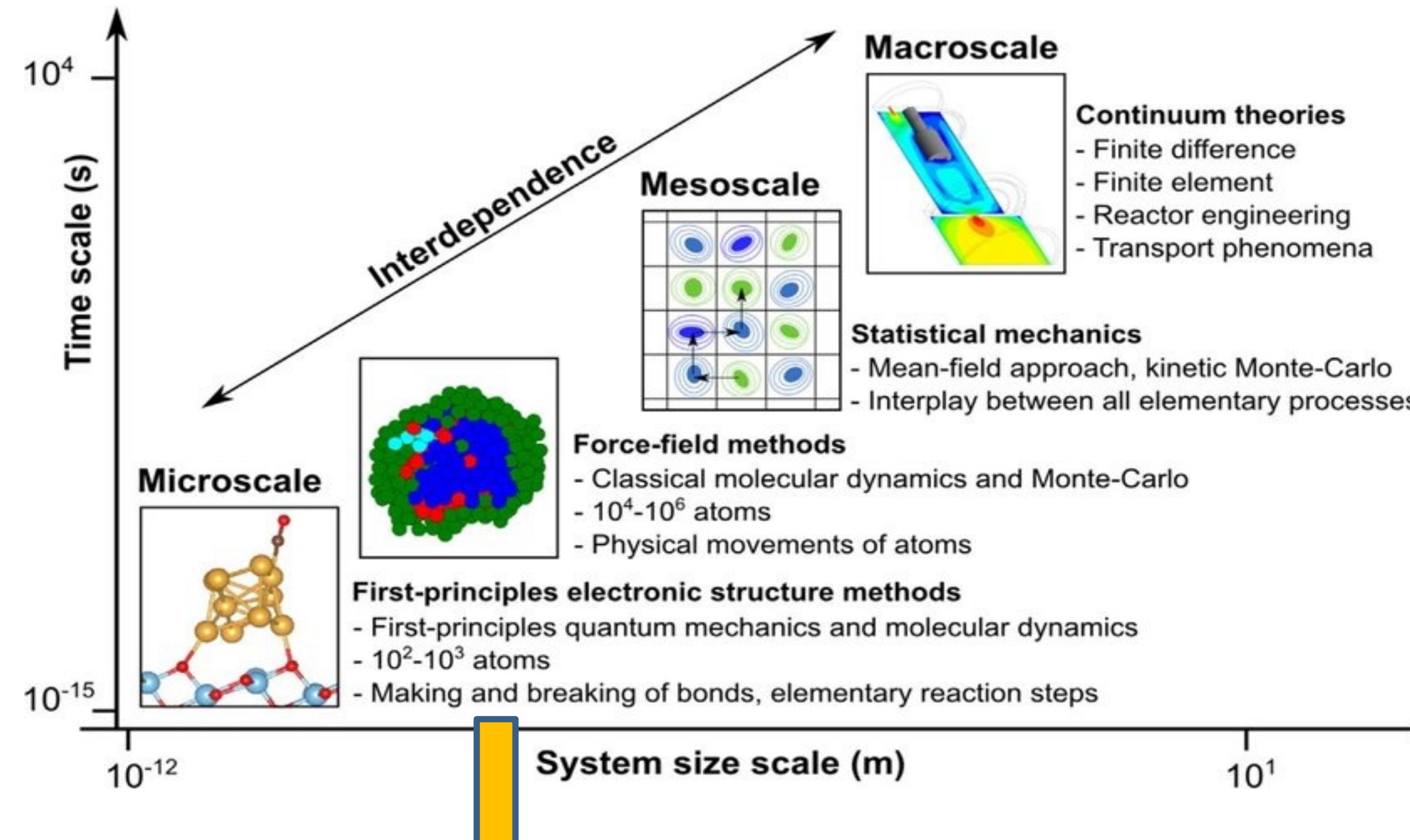
Buildings, blocks, roads, parks, shops, restaurants



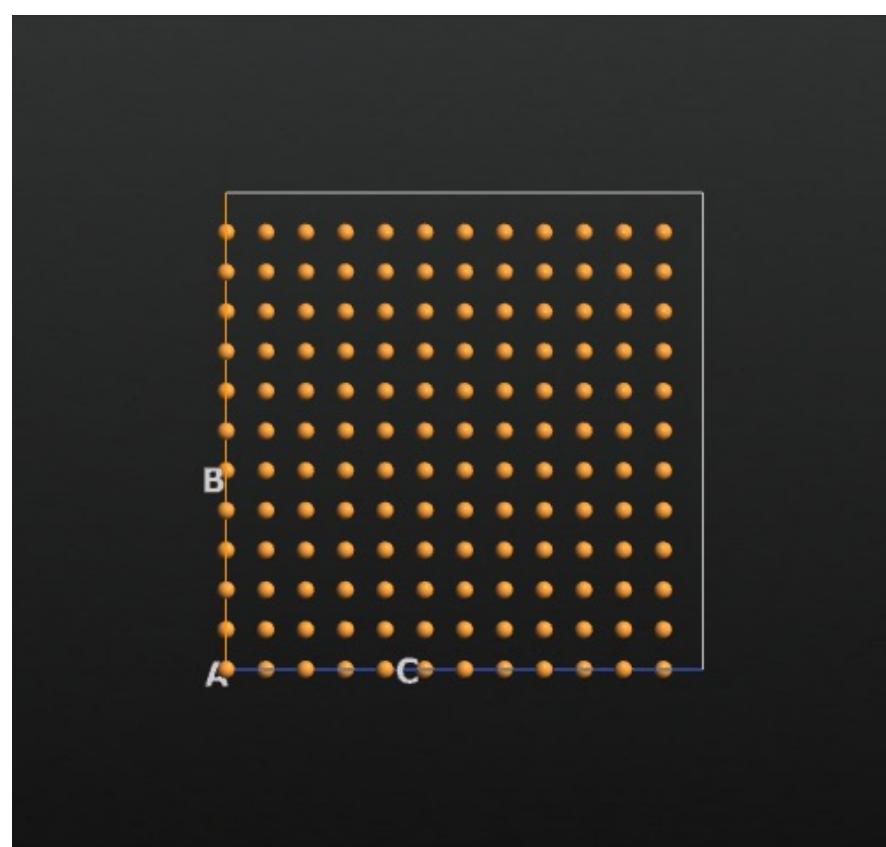
**How to determine the magnification**



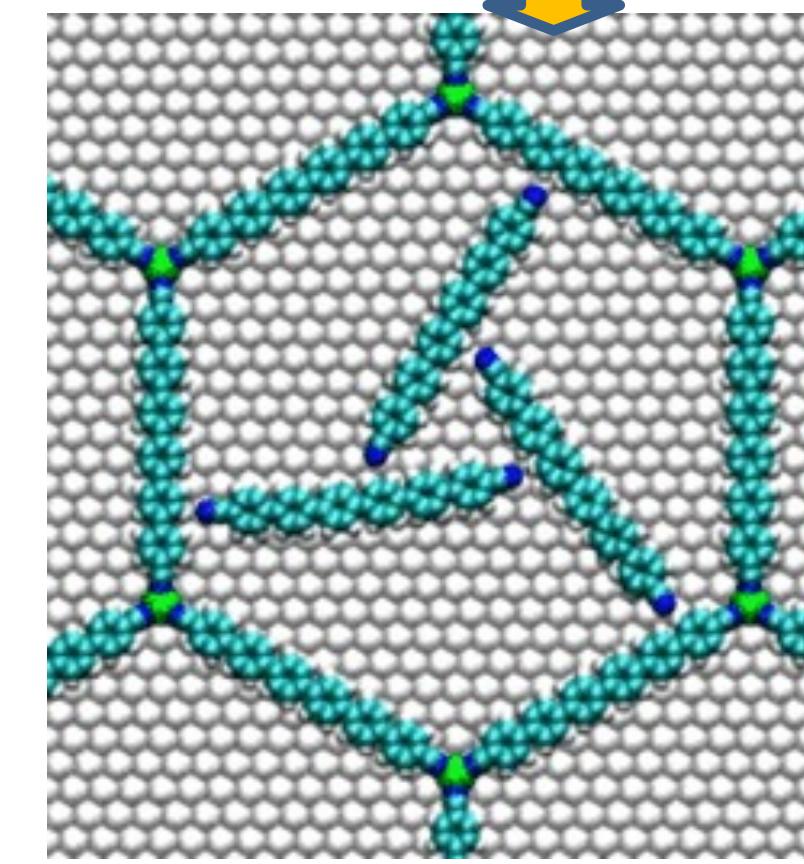
# Materials modeling at different length scales



<http://dx.doi.org/10.1016/B978-0-12-409547-2.14273-8>



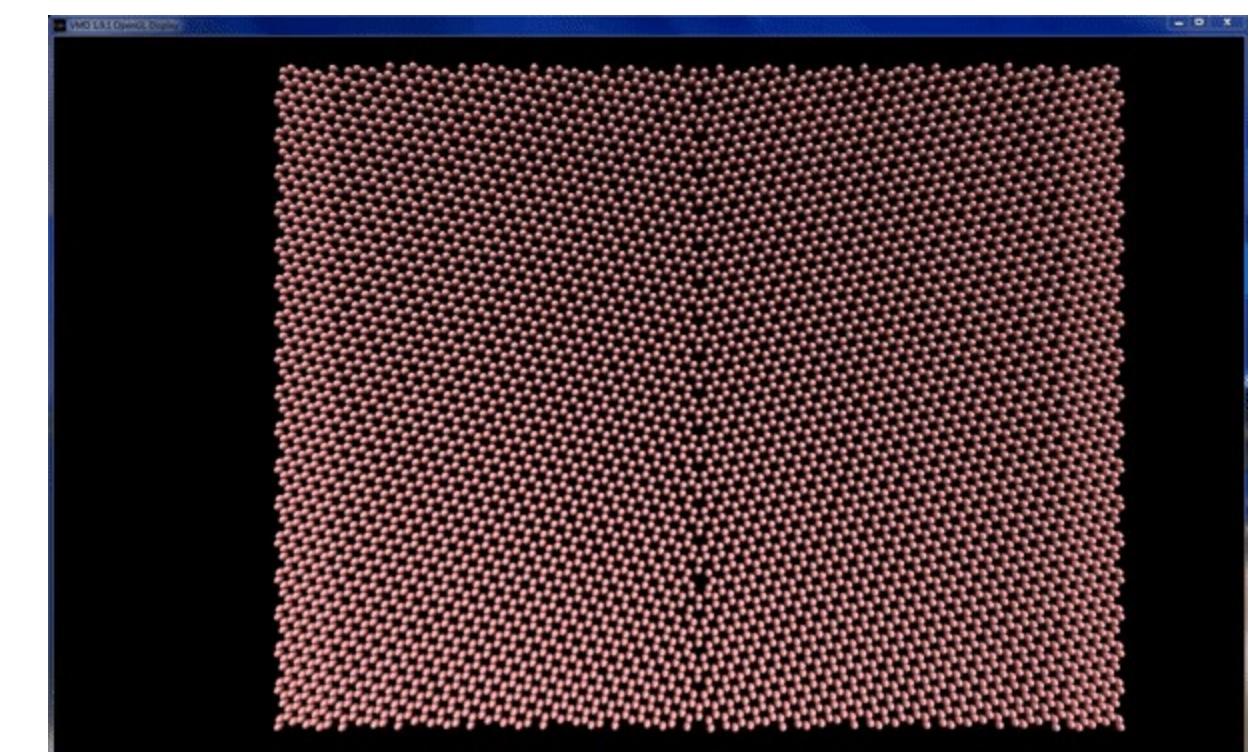
Melting of Cu



Molecular motor in a nanopore

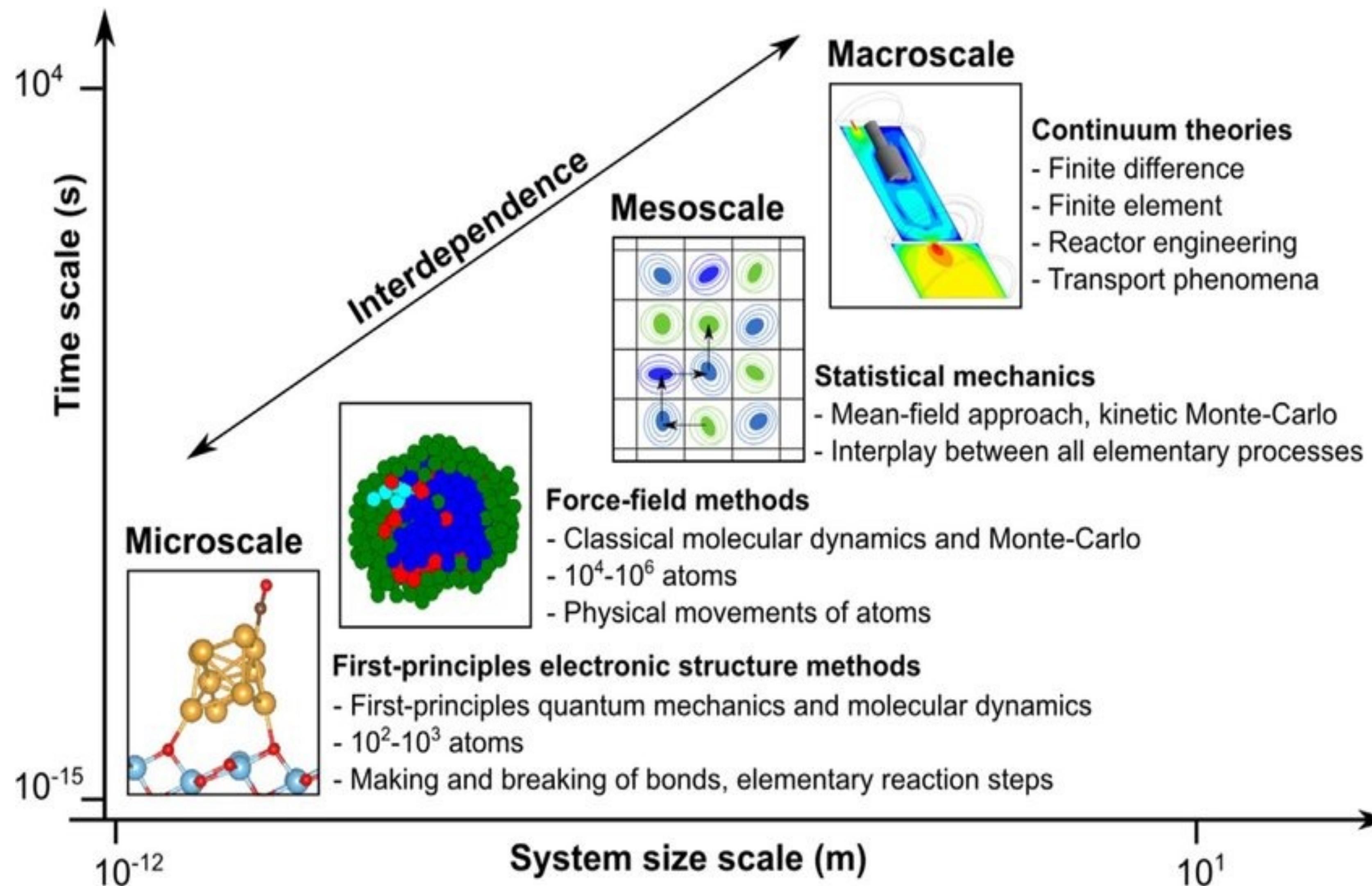


Polymers growth on a surface



Graphene grain boundary failure

# Materials Multi-scale modeling (M<sup>3</sup>)



# Create a model to study the behaviour of water

River



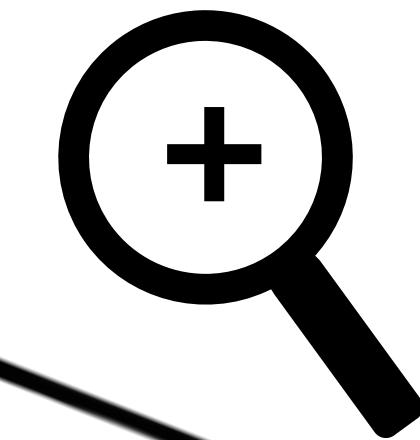
(kms)



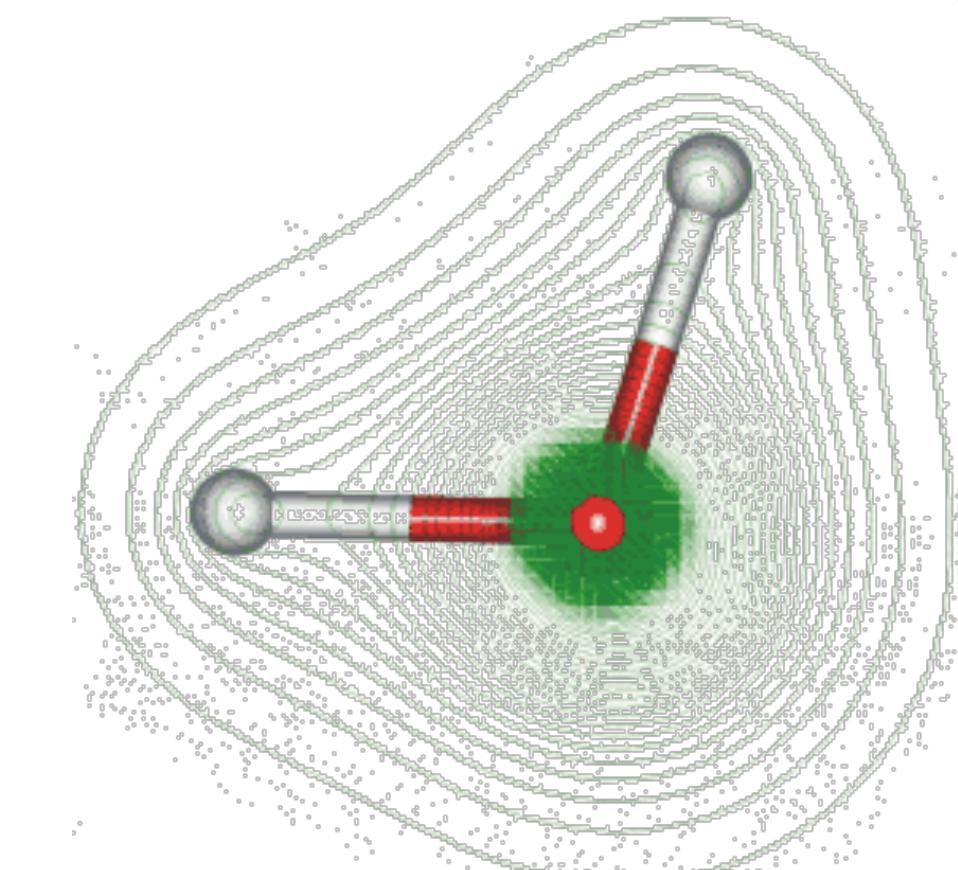
Water pipes  
(Meters)



Glass of water  
(Many molecules)  
(Nanometer= $10^{-9}$  m)



Scale!



Electron density in a water  
molecule (picometer= $10^{-12}$  m)



Google images

[https://water.lsbu.ac.uk/water/water\\_molecule.html](https://water.lsbu.ac.uk/water/water_molecule.html)



# Lecture 34

## Modeling and simulations of materials

### Textbooks:

- Computational Materials Science: J. Gunn Lee
- Understanding Molecular Simulations: D. Frenkel and B. Smit
- **Molecular Modelling Principles and Applications: Andrew Leach (Chapter 4)**

Prof. Divya Nayar

Department of Materials Science and Engineering

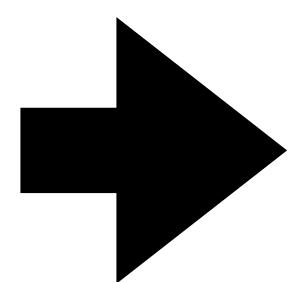
[divyanayar@mse.iitd.ac.in](mailto:divyanayar@mse.iitd.ac.in)

# Recap...

- Computational materials science: Introduction
- Role of simulations
- Modeling in simulations: multi-scale modeling
- Developing a model

# How would you create a *model* of water molecules?

The BIG Picture



The Scale

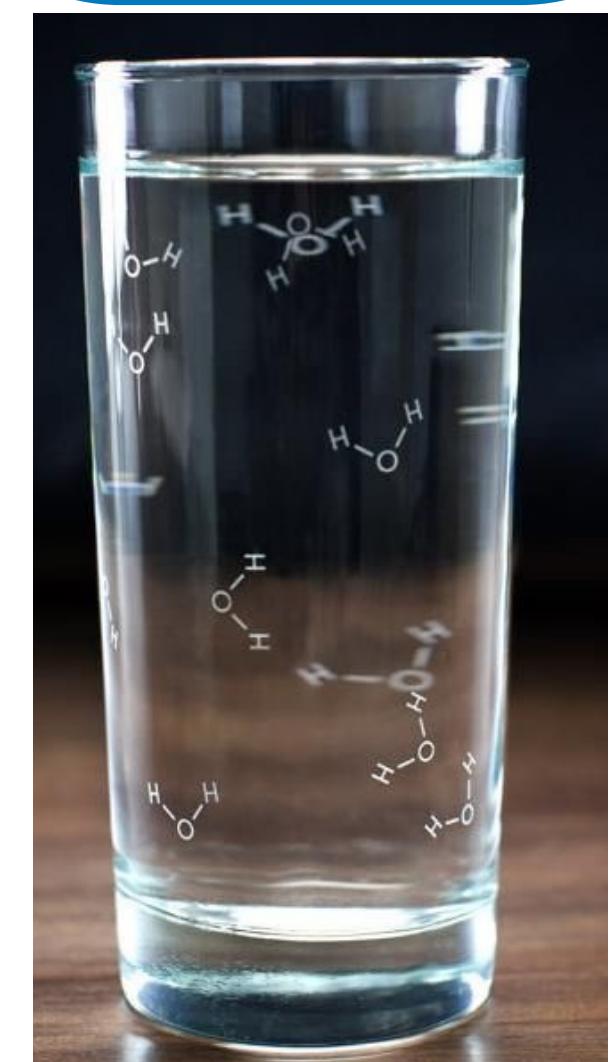


Behaviour of water as a solvent

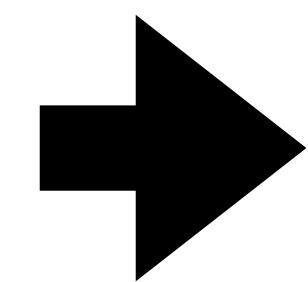
Water as a solvent

Google images

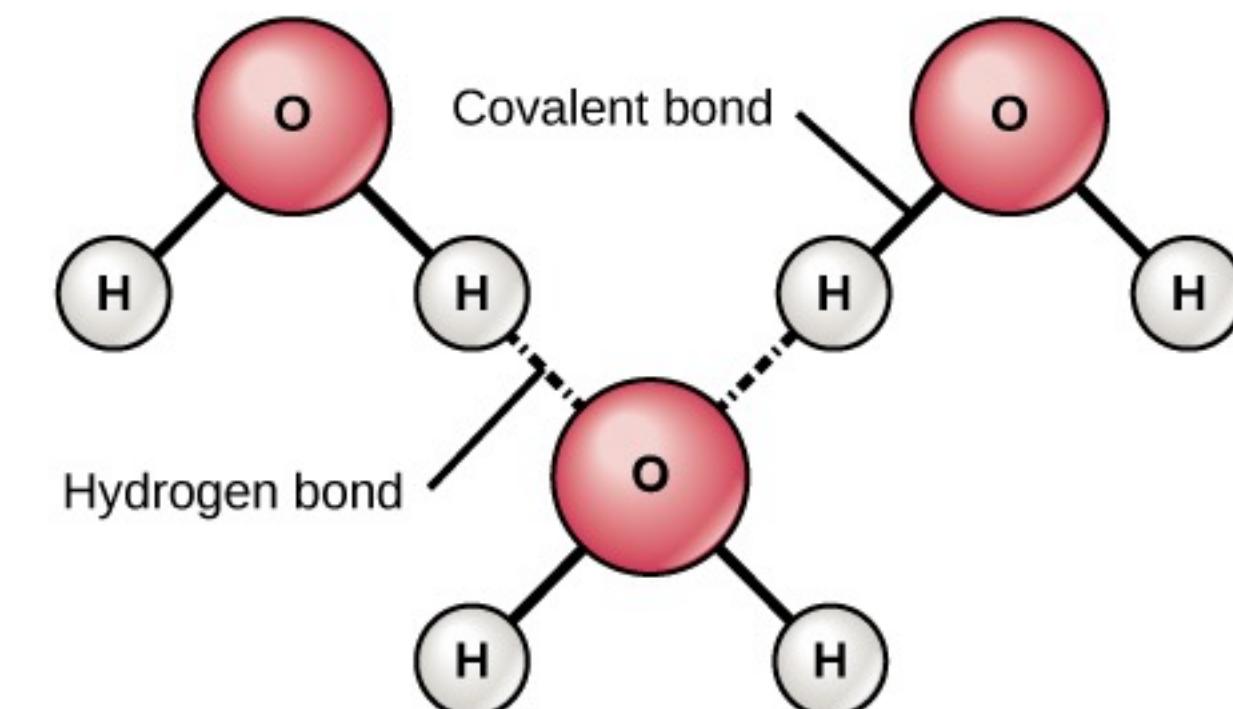
The Details



How do water molecules look inside a glass of water? How many molecules:  $\sim 10^{25}$

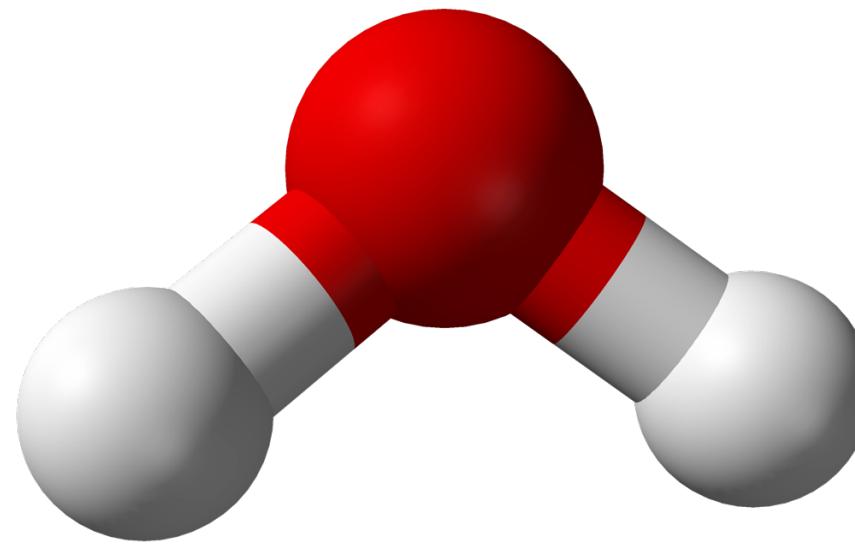


The Connections



How do water molecules interact?

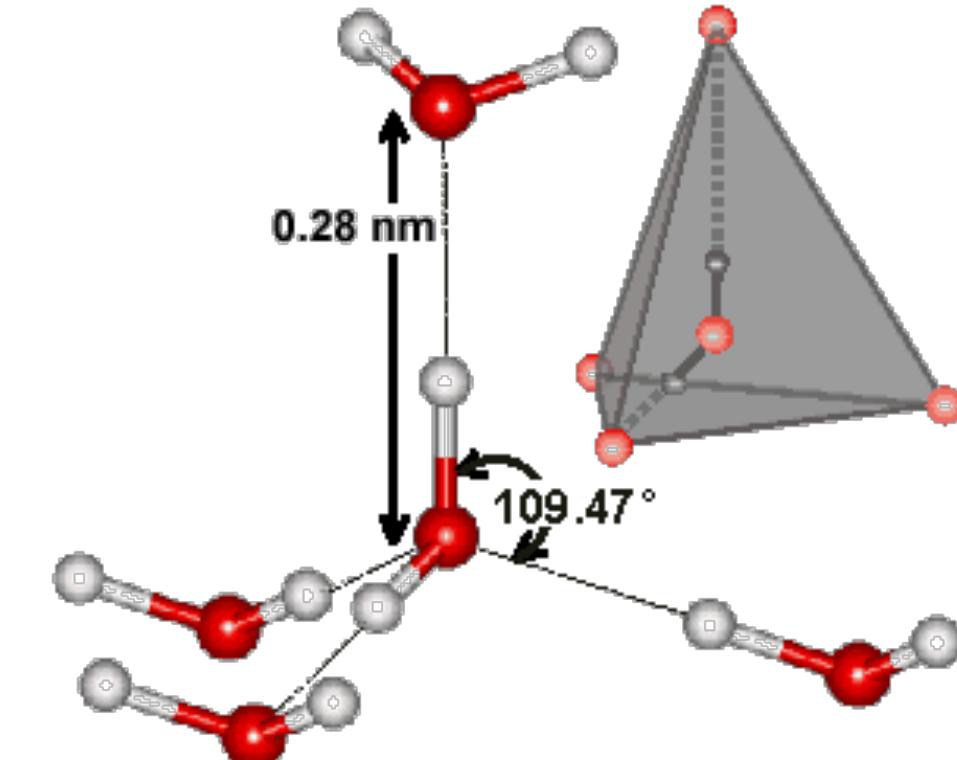
# A meaningful model of water



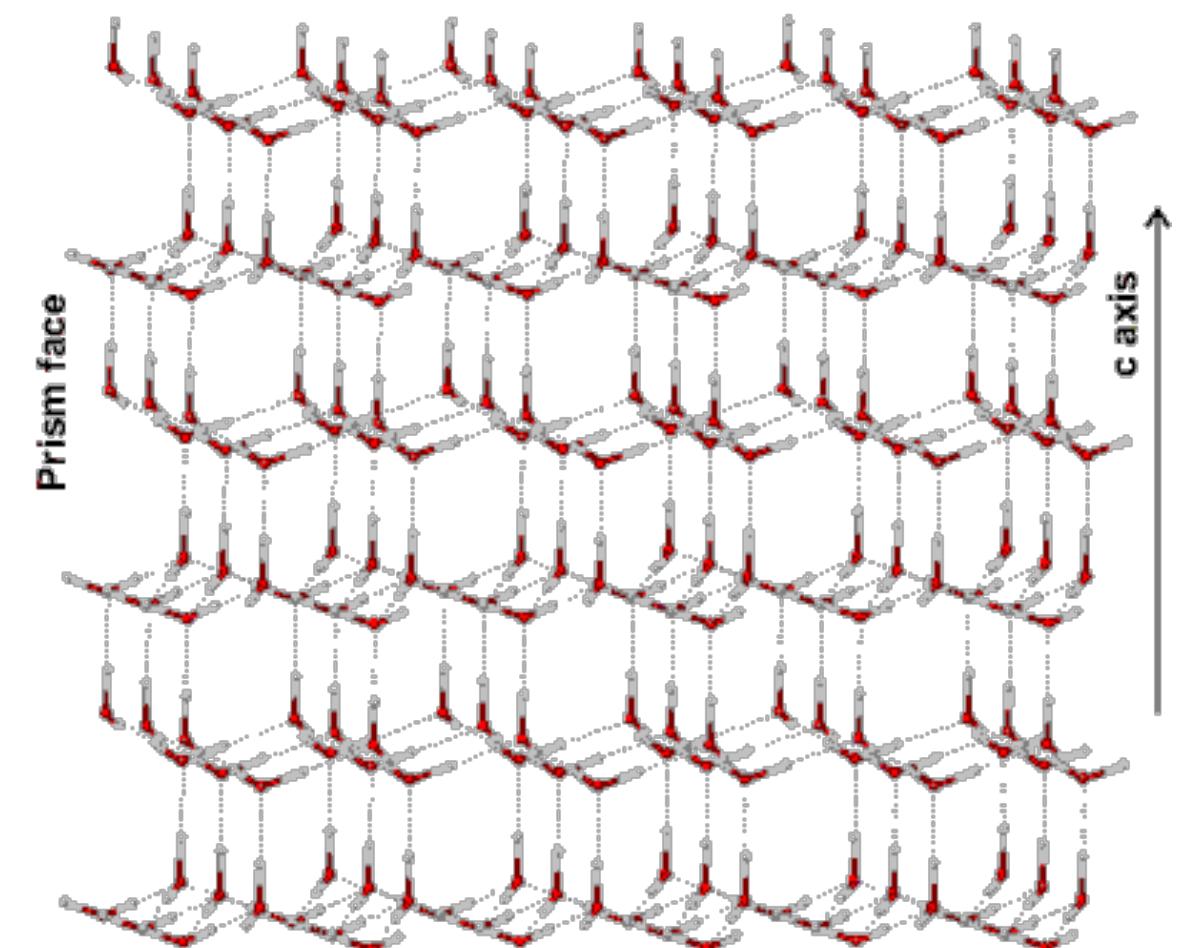
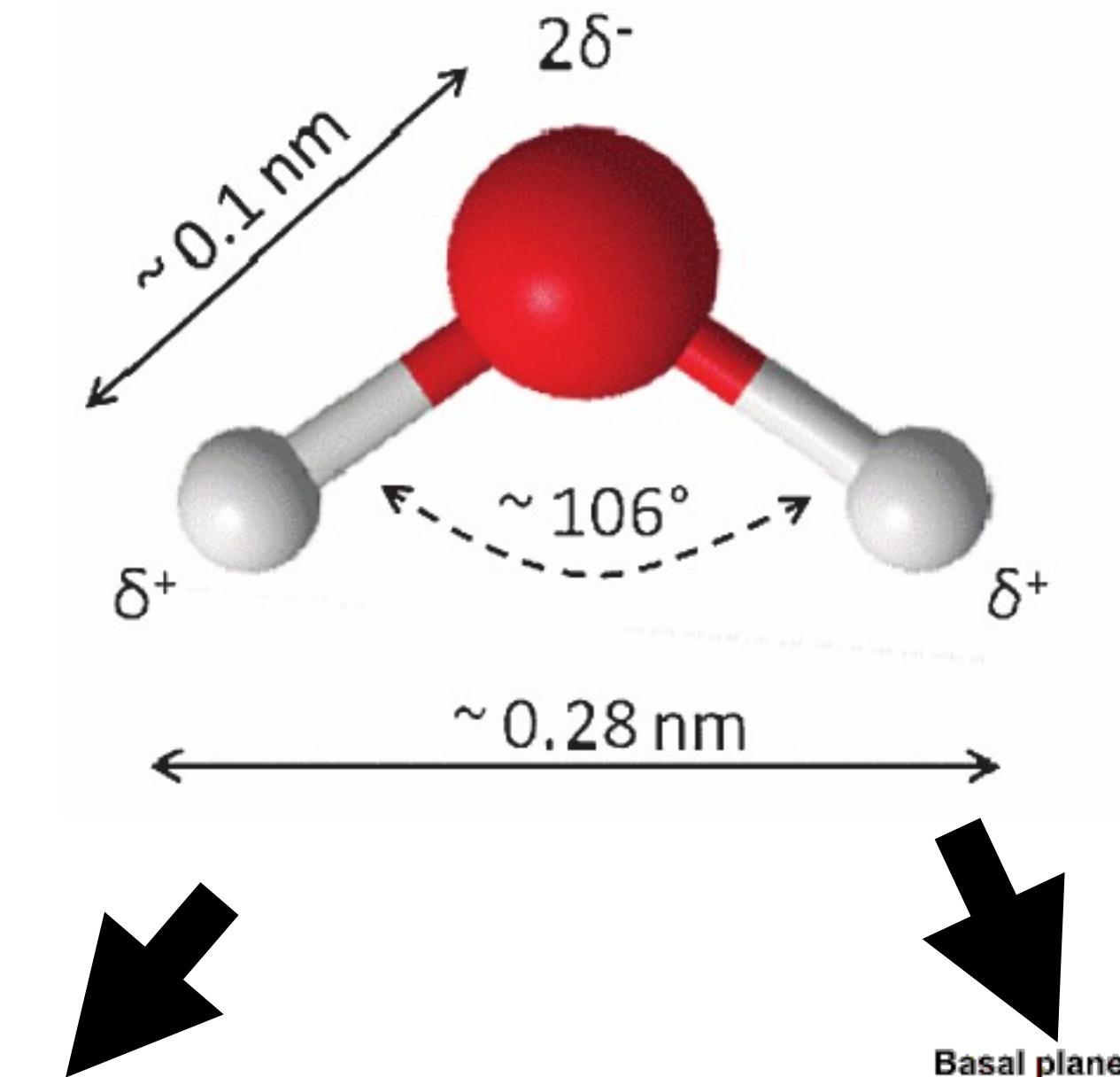
Toy model

*Attractions and repulsions:*

- Bonded interactions
- Electrostatic Interactions
- Dispersive interactions



**Hydrogen bonding in water**



Ice

# *A mathematically meaningful model of water*

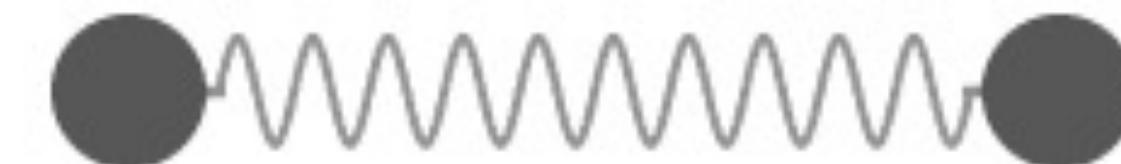
## Molecules undergo vibrations at room temperature



A ball free to move around  
(Monoatomic gas like  
Argon, Neon ..)



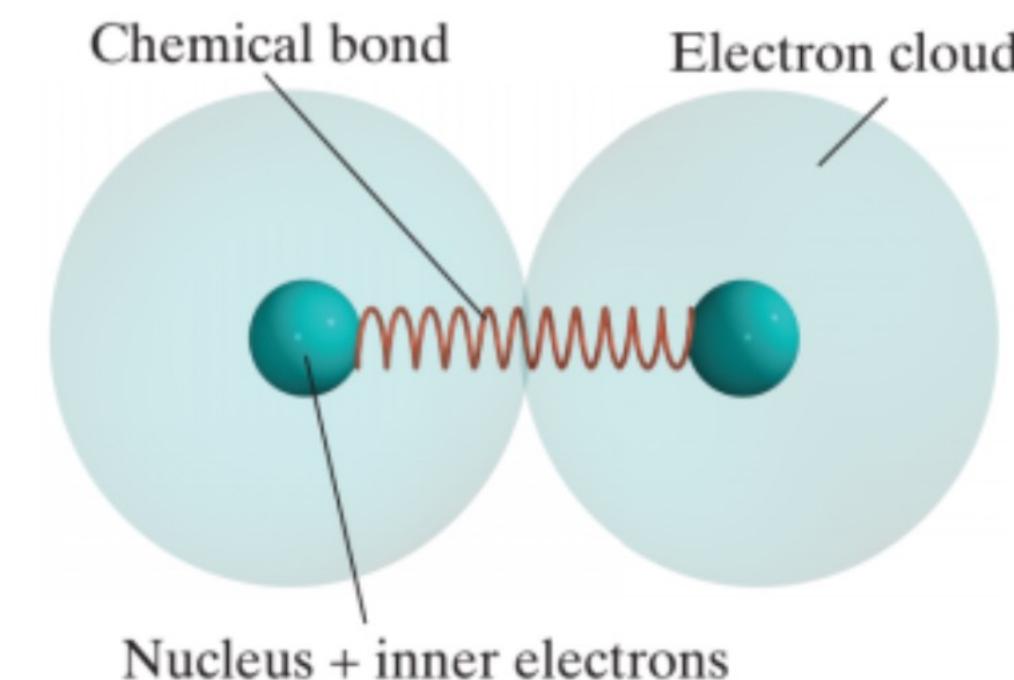
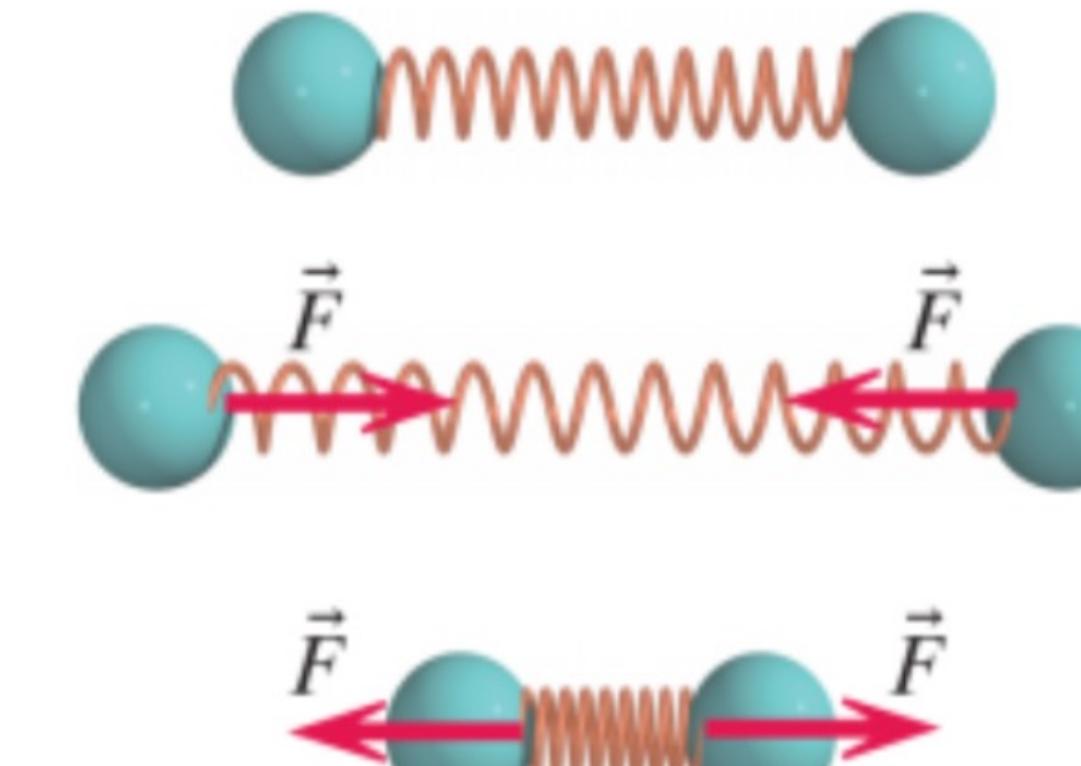
Restricted motion of  
the ball



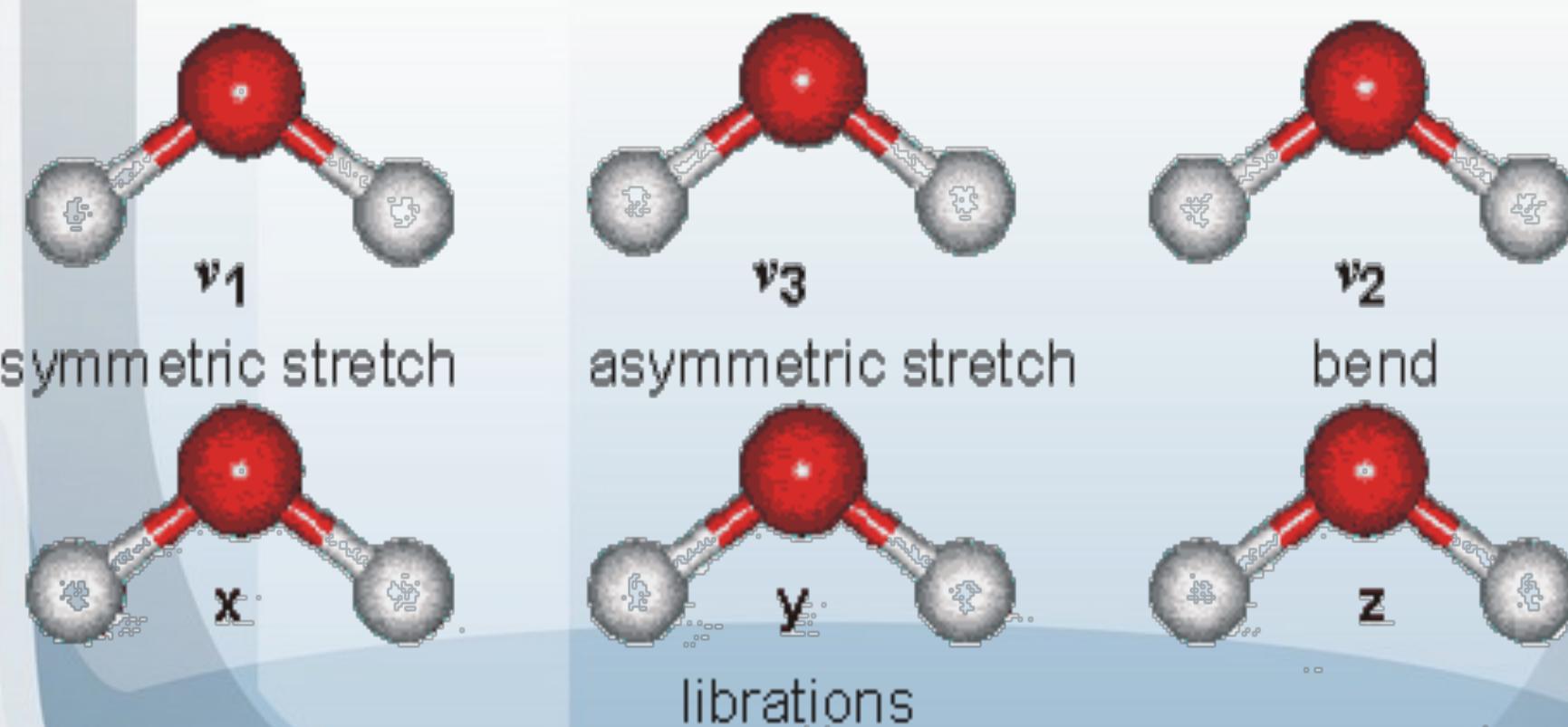
Molecules vibrate, rotate and translate

Hooke's Law

$$F = kx$$



## Vibrations in water molecules



## Model of a molecule (Force-field)

$$U(r) = U_{bonded}(r) + U_{non-bonded}(r)$$

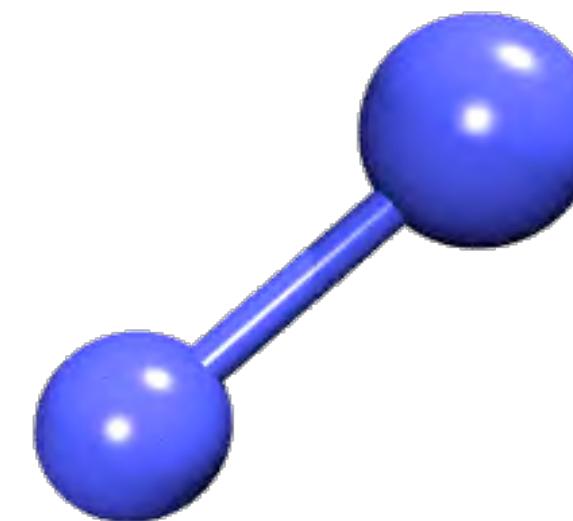
$$U(r) = U_{bond}(r) + U_{angle}(r) + U_{torsions} + U_{dispersion} + U_{electrostatic}$$

**Force-field or Potential energy surface:** Mathematical function that describes the energy of molecules as a function of the geometry/coordinates of molecules.



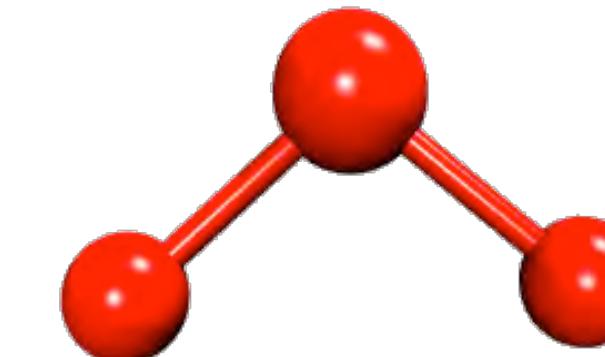
Each vibration (or libration) corresponds to a peak in Infrared spectrum (vibrational spectroscopy)

# Types of Bonded interactions



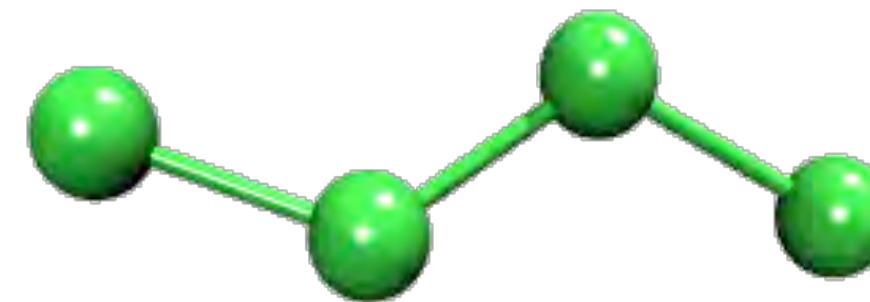
Bond

2-body interaction



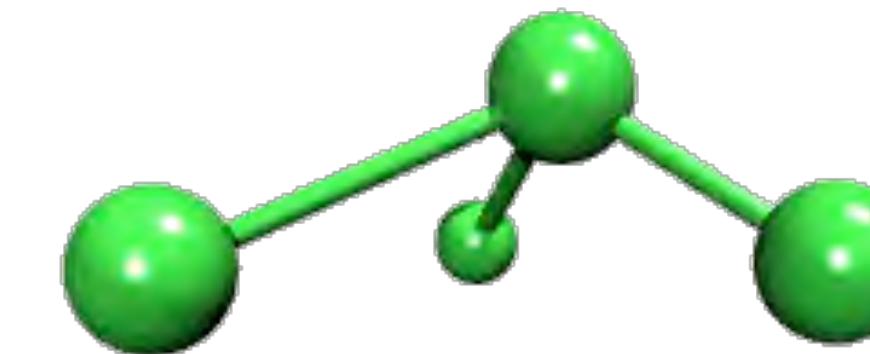
Angle

3-body interaction



Dihedral

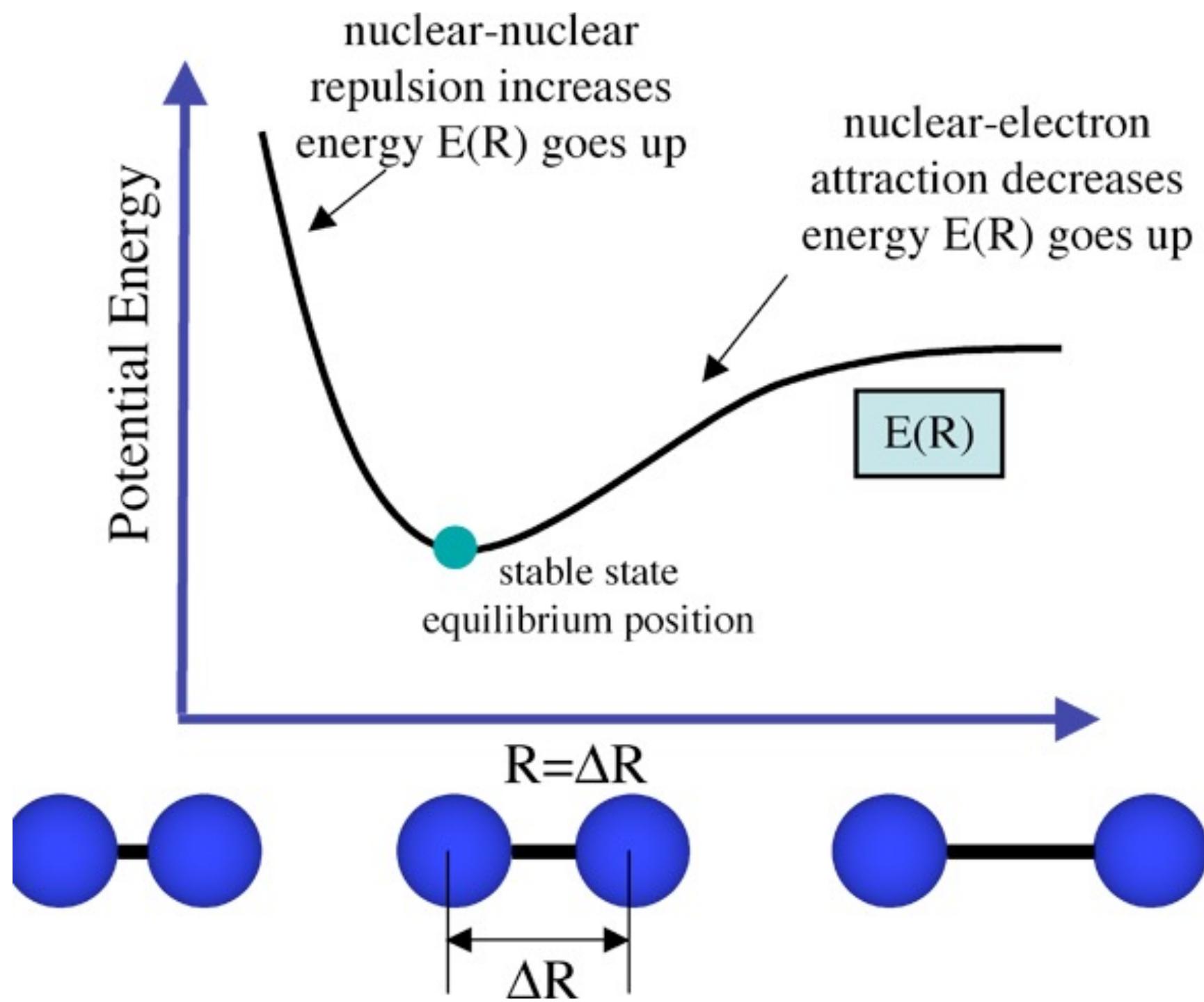
4-body interaction



Improper

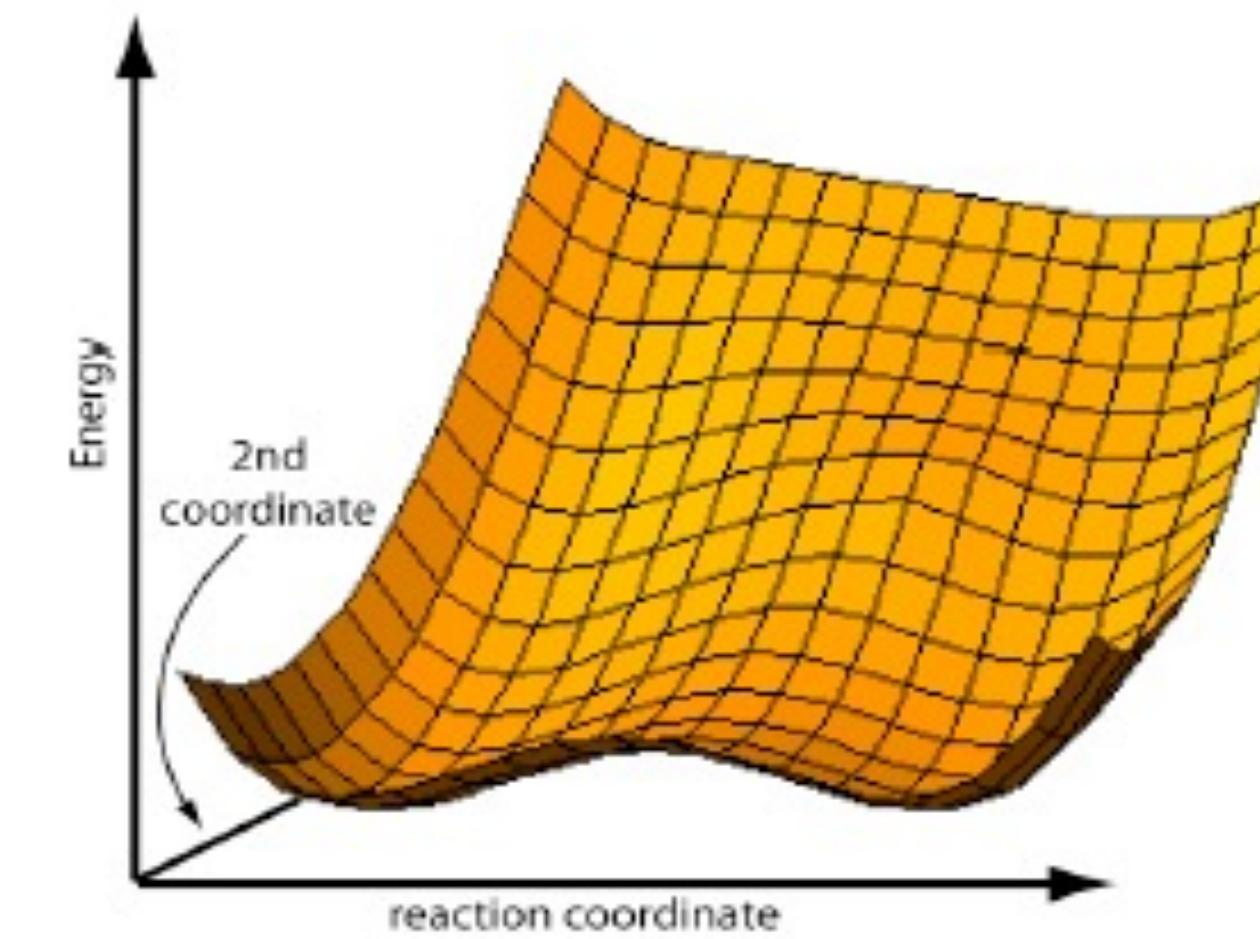
4-body interaction

# PES of a diatomic molecule



## Morse potential

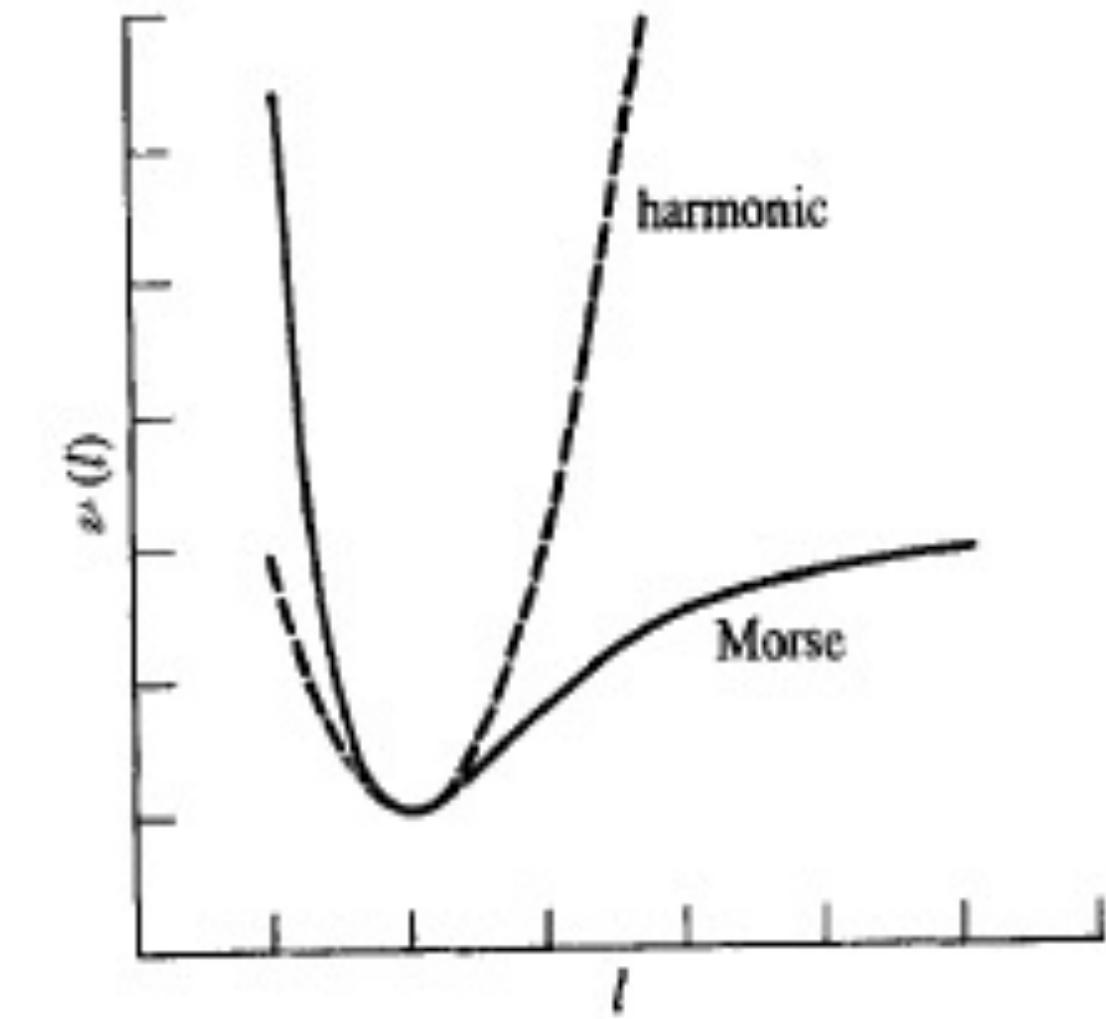
$$V'(r) = D_e (1 - e^{-a(r-r_e)})^2$$



A two-dimensional PES

## Hooke's law

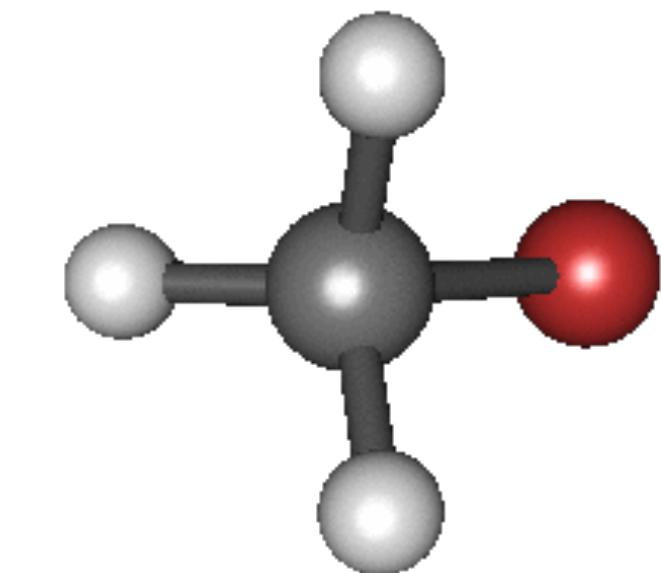
$$\nu(l) = \frac{k}{2} (l - l_0)^2$$



# Modeling the bonded interactions

## Bond stretching

Morse potential  $v(l) = D_e \{1 - \exp[-a(l - l_0)]\}^2$



Hooke's law  $v(l) = \frac{k}{2}(l - l_0)^2$

Bond	$l_0$ (Å)	$k$ (kcal mol <sup>-1</sup> Å <sup>-2</sup> )
Csp <sup>3</sup> –Csp <sup>3</sup>	1.523	317
Csp <sup>3</sup> –Csp <sup>2</sup>	1.497	317
Csp <sup>2</sup> =Csp <sup>2</sup>	1.337	690
Csp <sup>2</sup> =O	1.208	777
Csp <sup>3</sup> –Nsp <sup>3</sup>	1.438	367
C–N (amide)	1.345	719

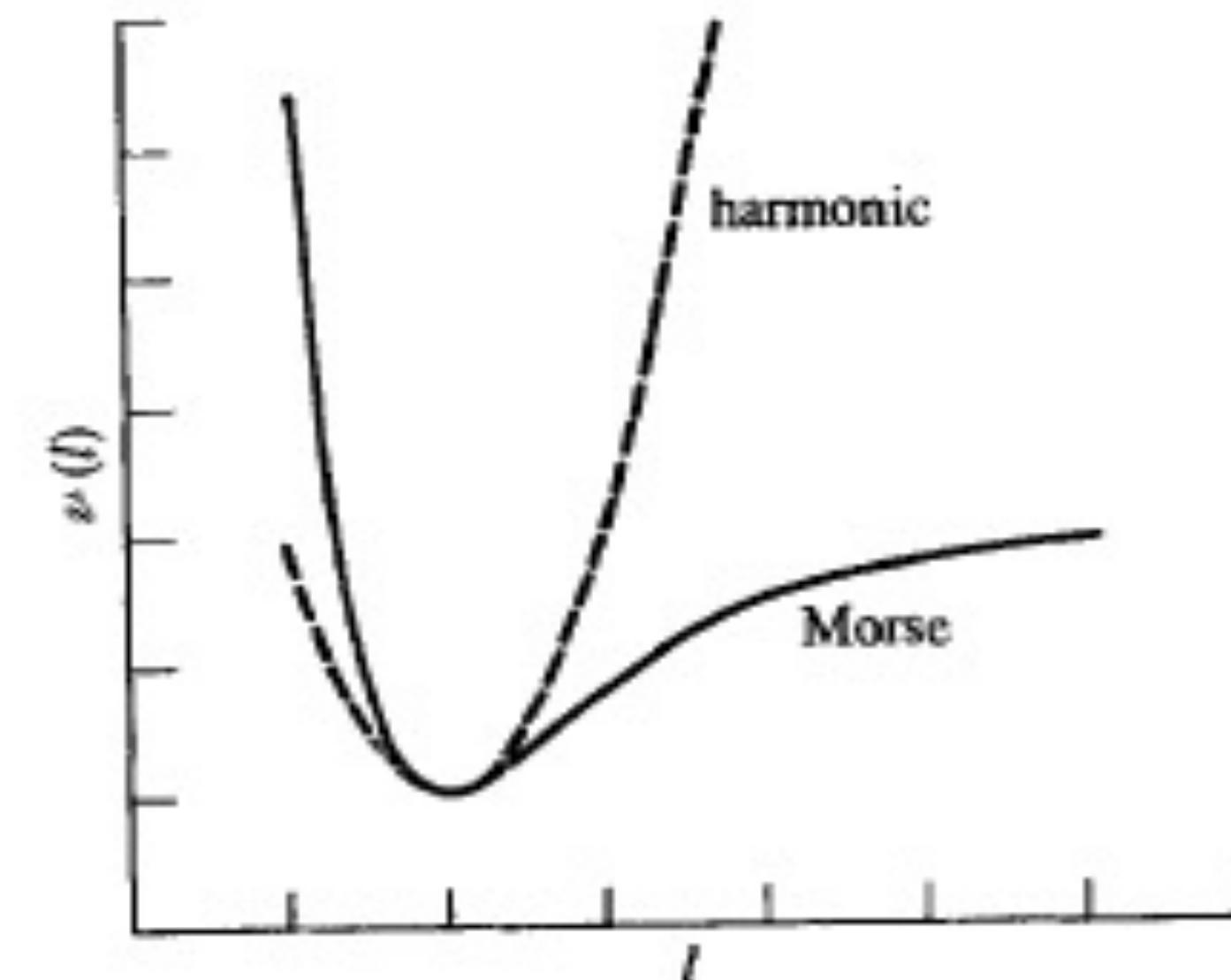


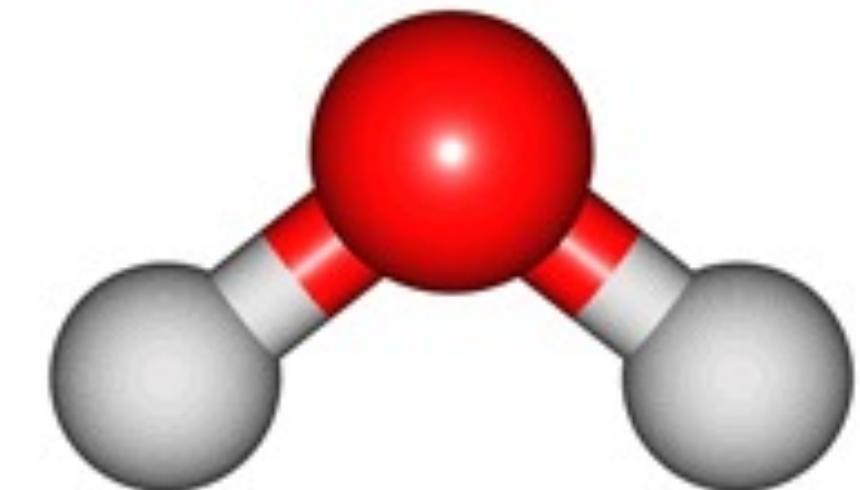
Table 4.1 Force constants and reference bond lengths for selected bonds [Allinger 1977]

# Modeling the bonded interactions

## Angle bending

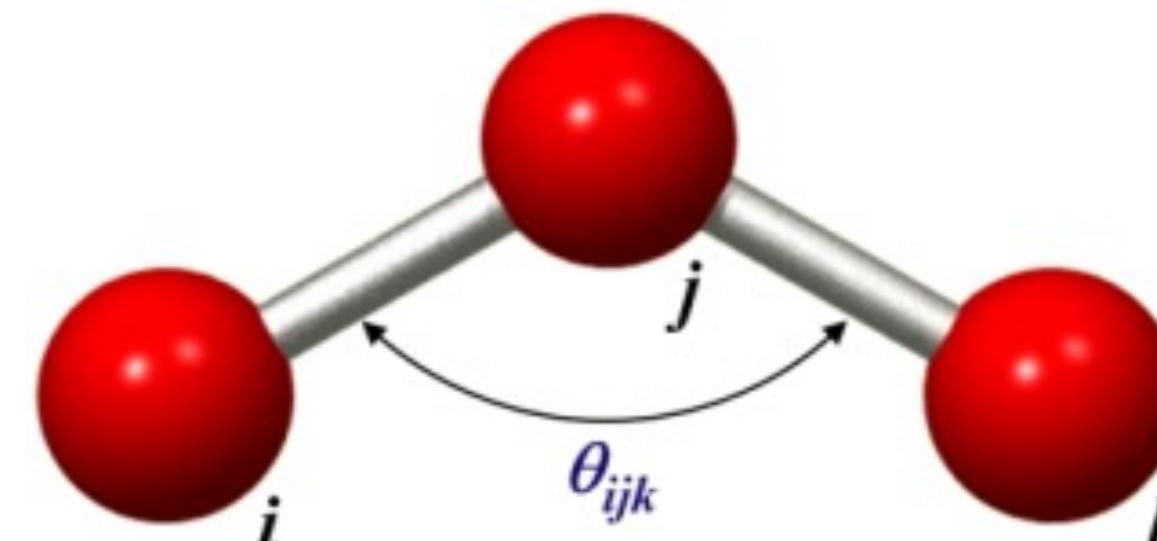
Hooke's law (harmonic potential)

$$v(\theta) = \frac{k}{2}(\theta - \theta_0)^2$$



Angle	$\theta_0$	$k$ (kcal mol <sup>-1</sup> deg <sup>-1</sup> )
Csp <sup>3</sup> –Csp <sup>3</sup> –Csp <sup>3</sup>	109.47	0.0099
Csp <sup>3</sup> –Csp <sup>3</sup> –H	109.47	0.0079
H–Csp <sup>3</sup> –H	109.47	0.0070
Csp <sup>3</sup> –Csp <sup>2</sup> –Csp <sup>3</sup>	117.2	0.0099
Csp <sup>3</sup> –Csp <sup>2</sup> –Csp <sup>2</sup>	121.4	0.0121
Csp <sup>3</sup> –Csp <sup>2</sup> –O	122.5	0.0101

Table 4.2 Force constants and reference angles for selected angles  
[Allinger 1977].

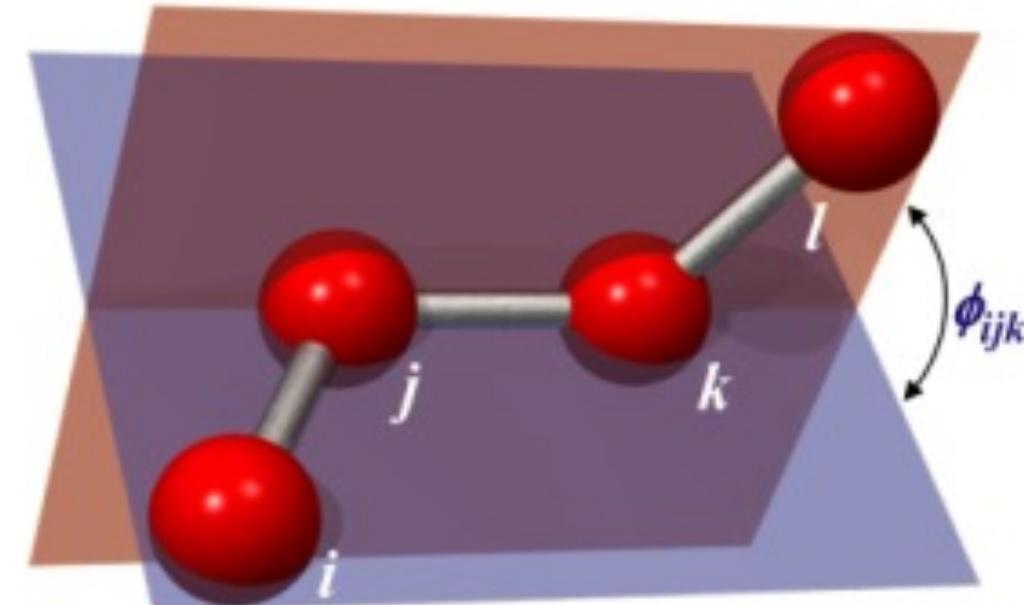


# Modeling the bonded interactions

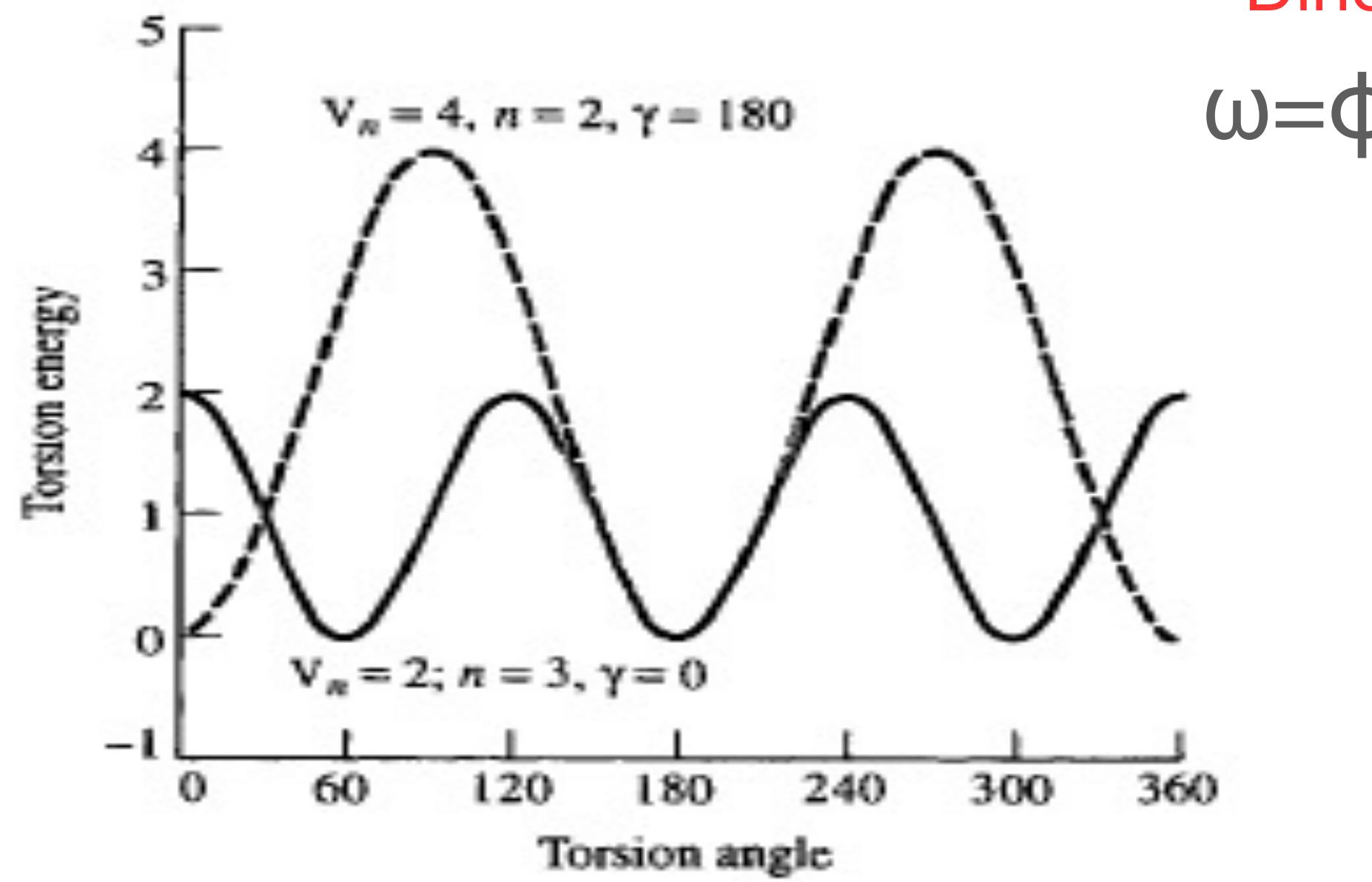
## Torsions (1,4- interactions)

$$v(\omega) = \sum_{n=0}^N \frac{V_n}{2} [1 + \cos(n\omega - \gamma)]$$

$$v(\omega) = \sum_{n=0}^N C_n \cos(\omega)^n$$



Dihedral (Proper torsion)



$$\omega = \phi$$

V<sub>n</sub> = barrier height

n = multiplicity (the no. of minimum points in the function as the bond is rotated through 360 deg)

γ = phase factor (where the torsion angle passes through minimum)

or click on  
an angle

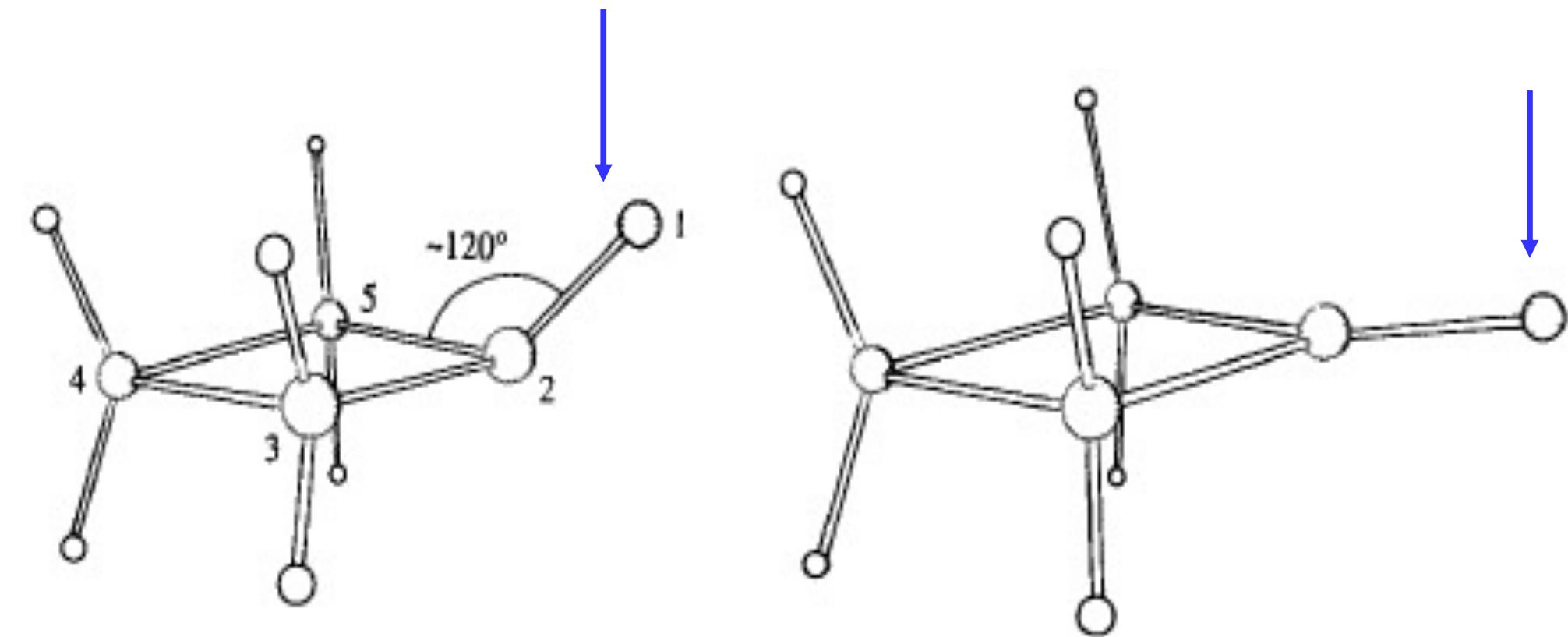


$$\Phi = 0^\circ$$



# Modeling the bonded interactions

## Improper Torsions (1,4- interactions)

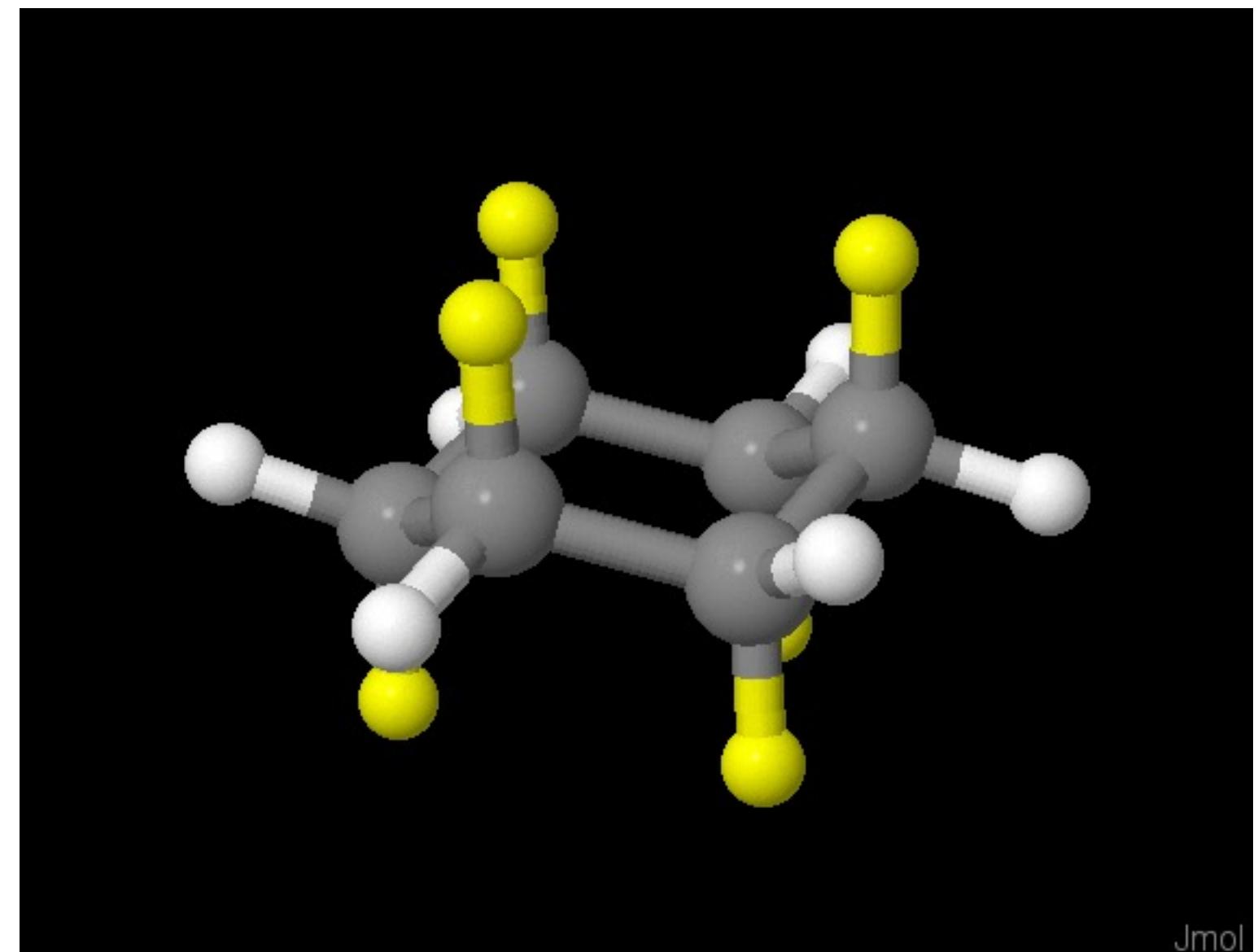
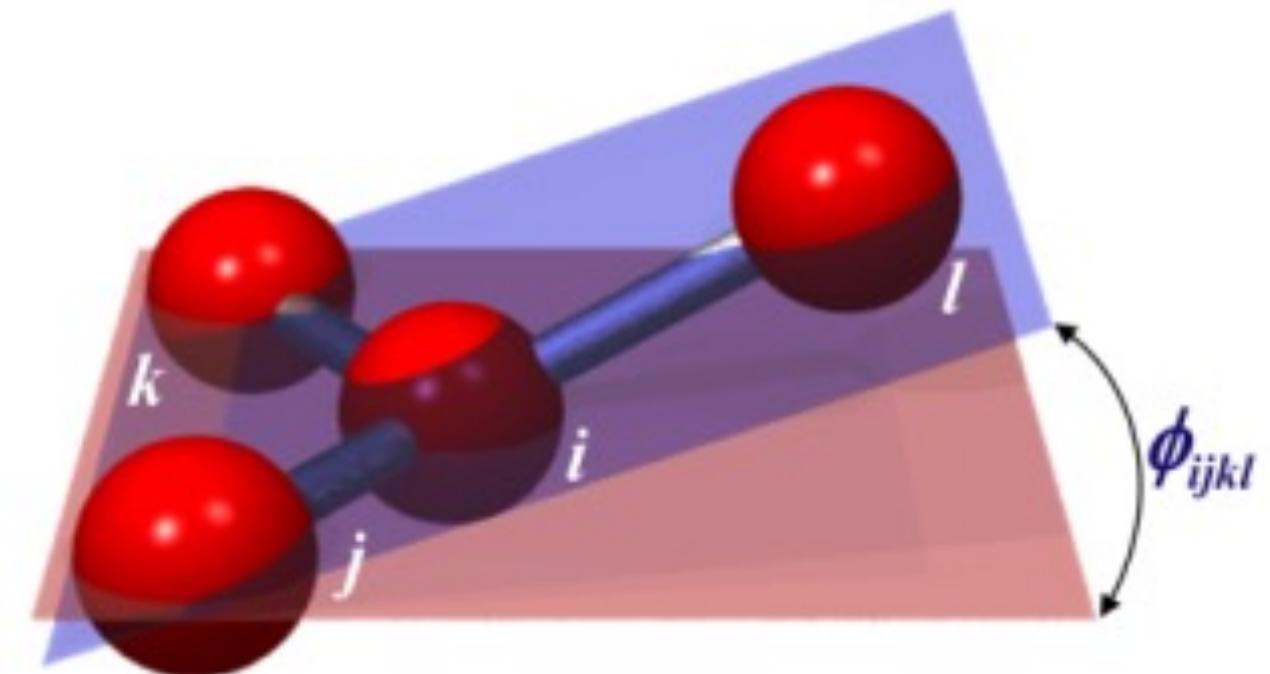


obtained

desired

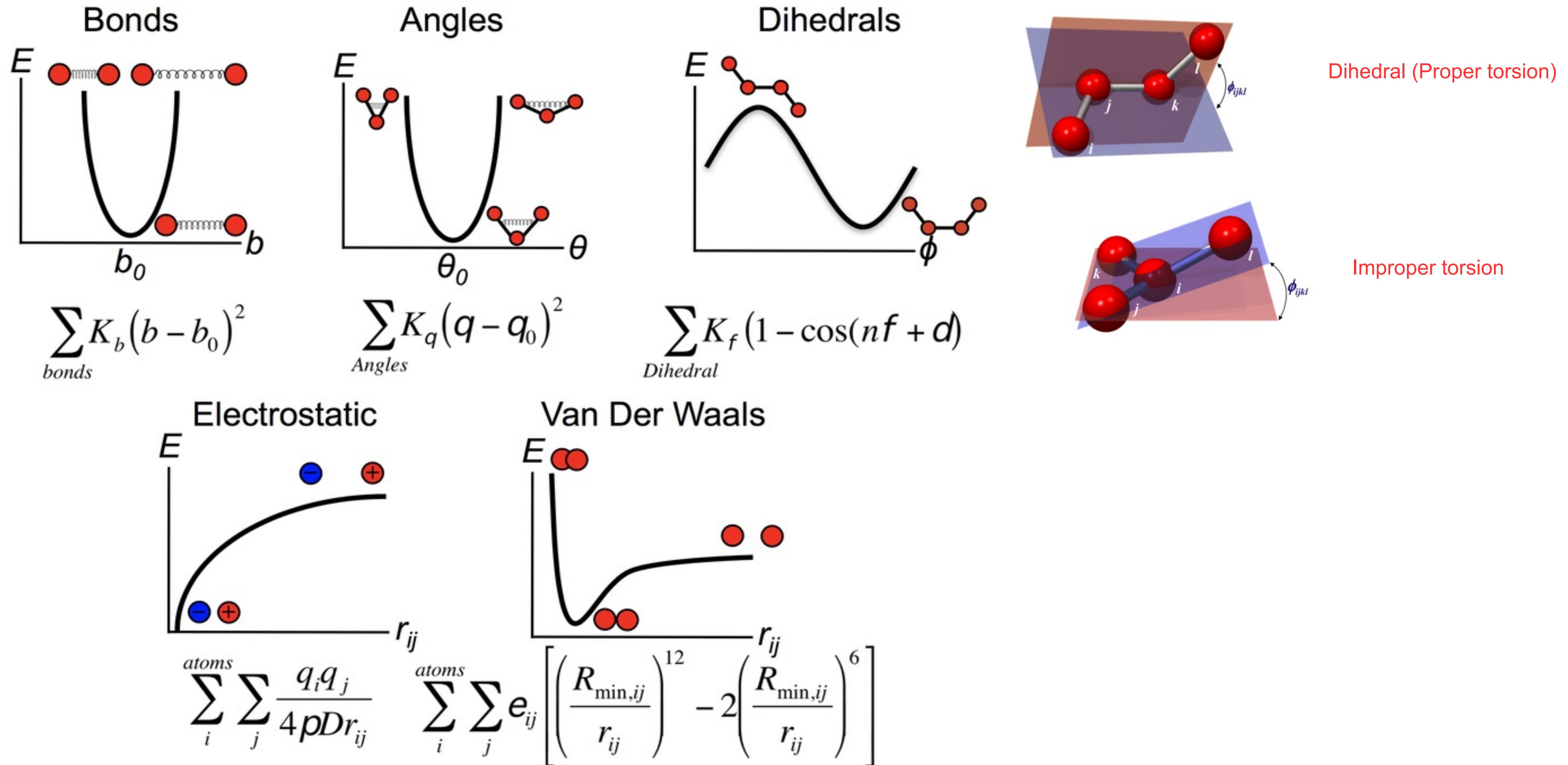
$$v(\omega) = k(1 - \cos 2\omega)$$

(out-of-plane bending term)



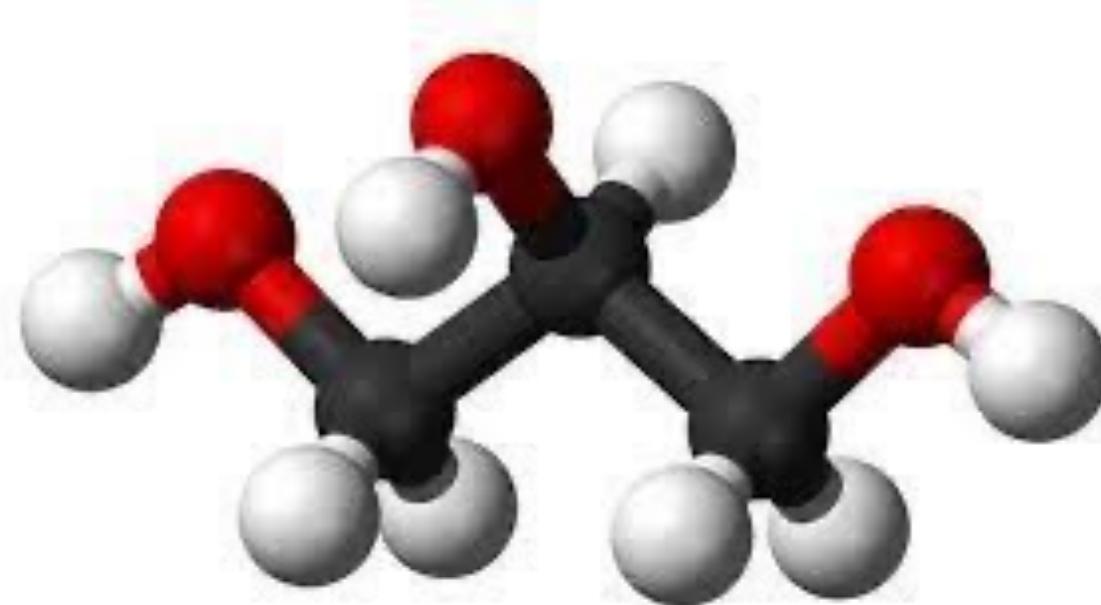
Jmol

# Models of different interactions: Summary

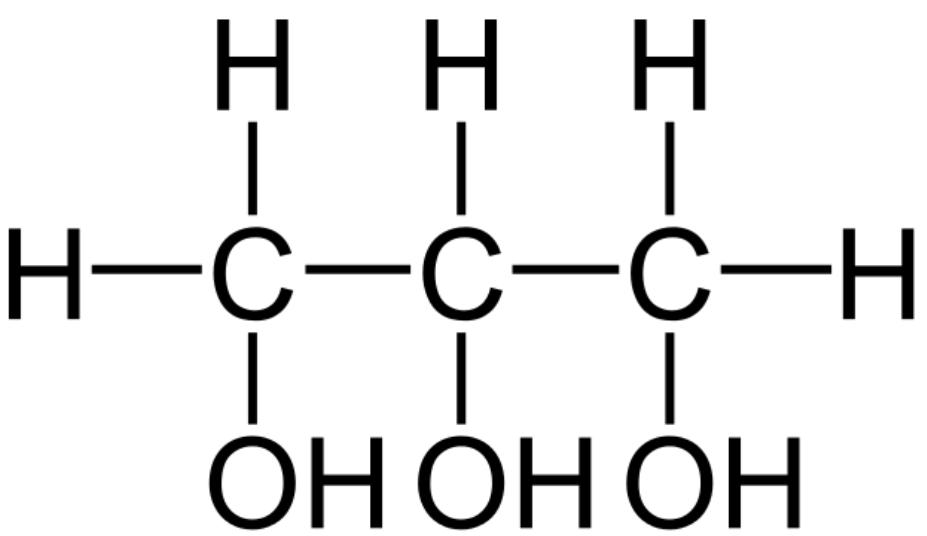


# Potential energy surface: Examples

## Molecular model

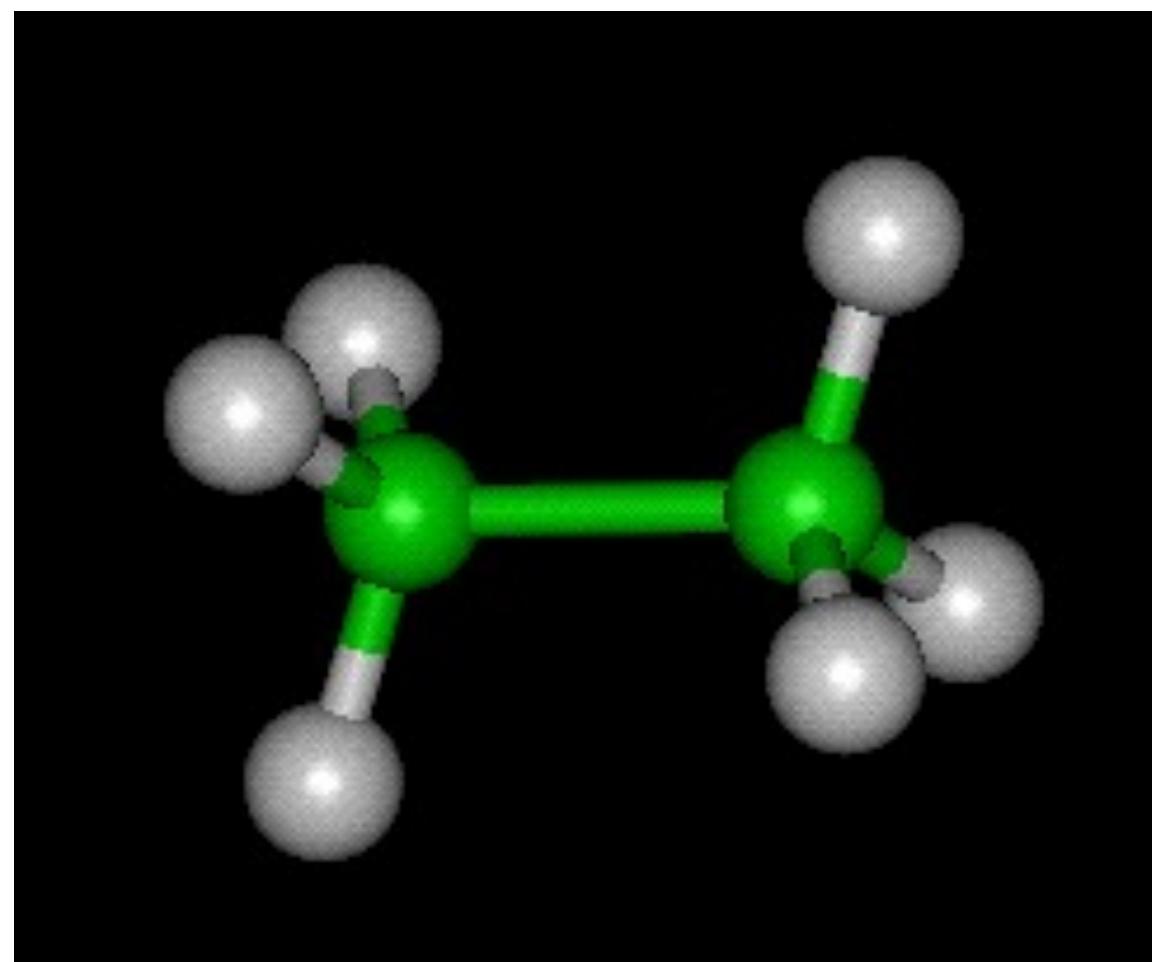


glycerol

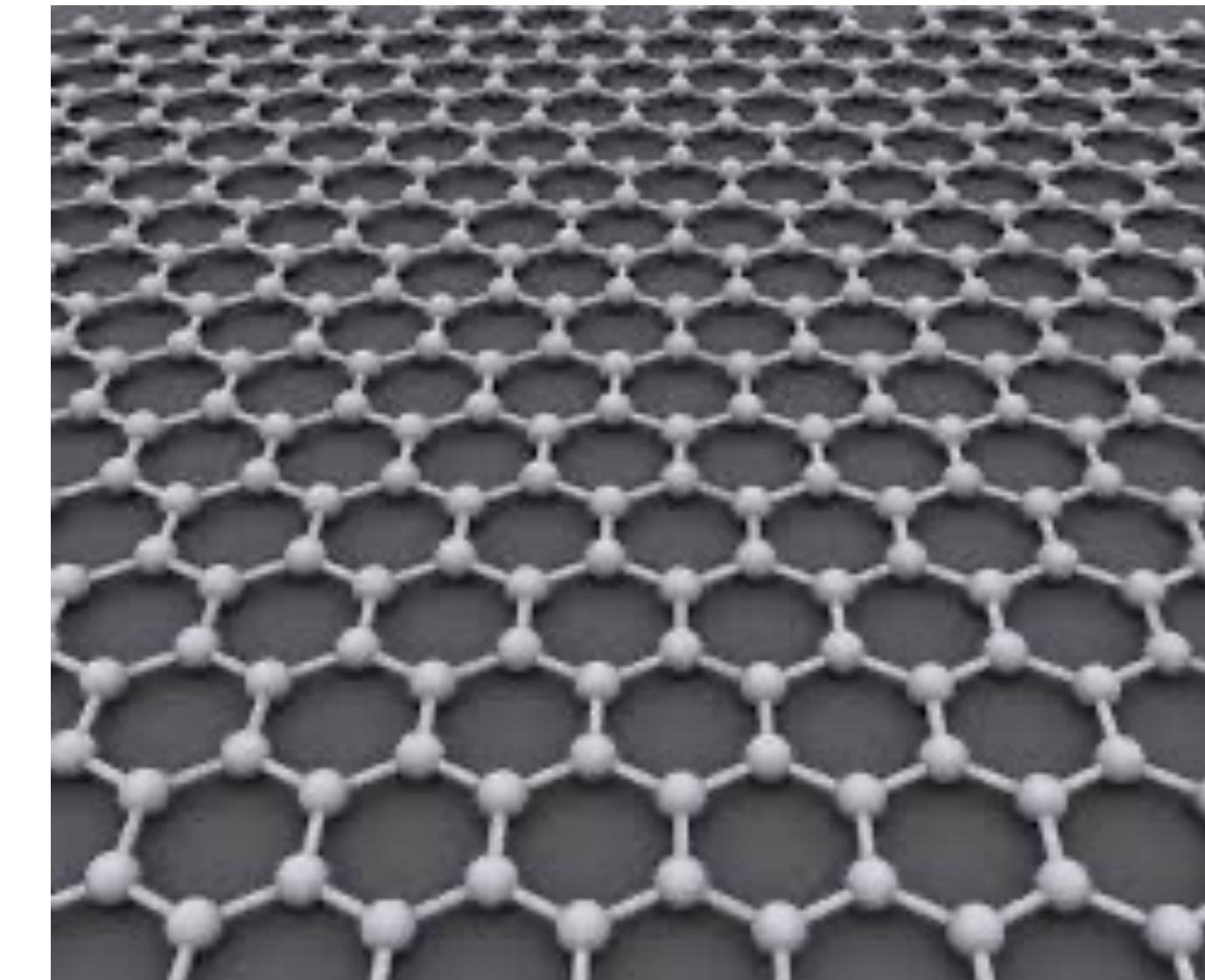


$$U(r) = U_{bonded}(r) + U_{non-bonded}(r)$$

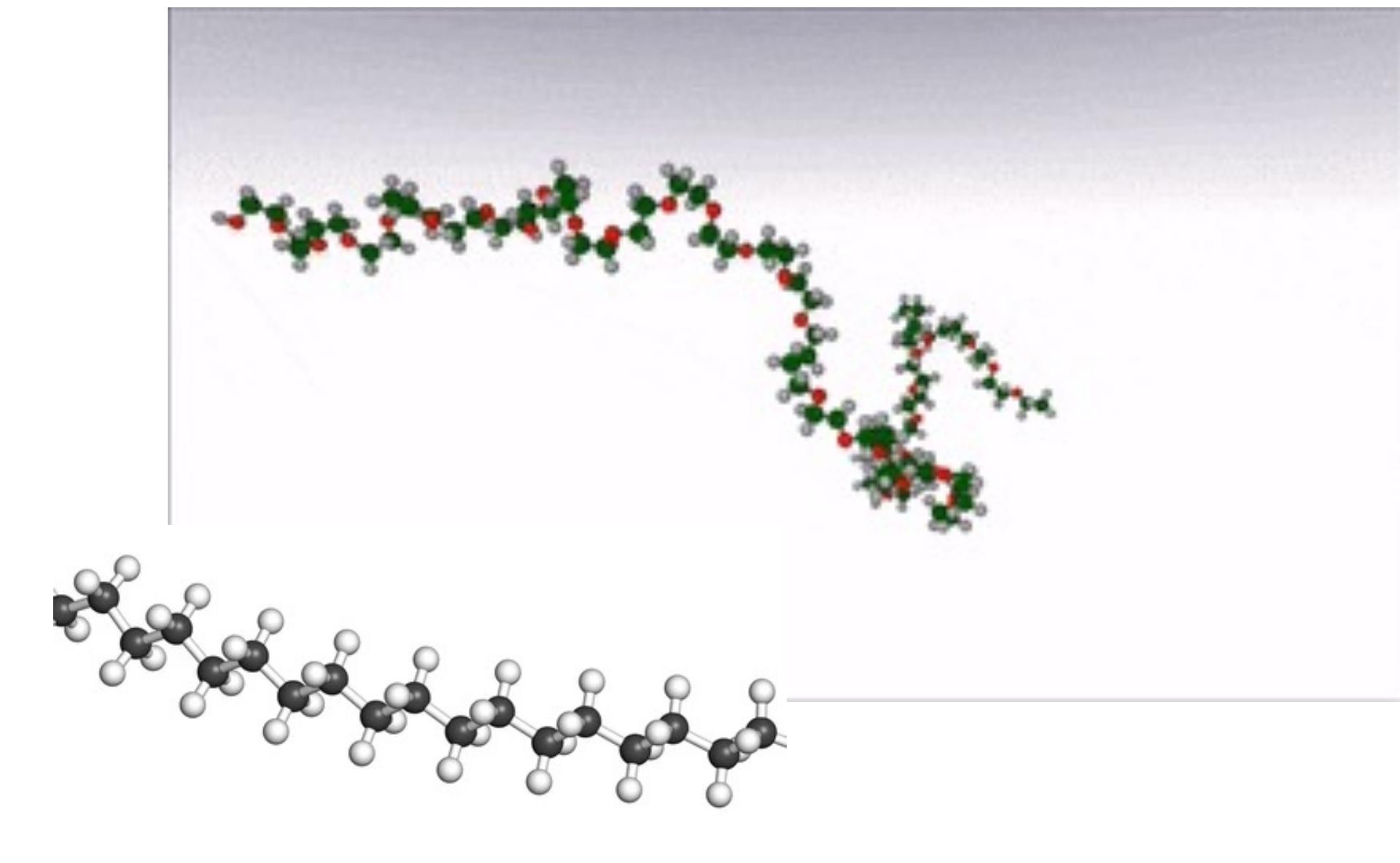
No. of bonds:  
No. of angles:  
No. of dihedrals:



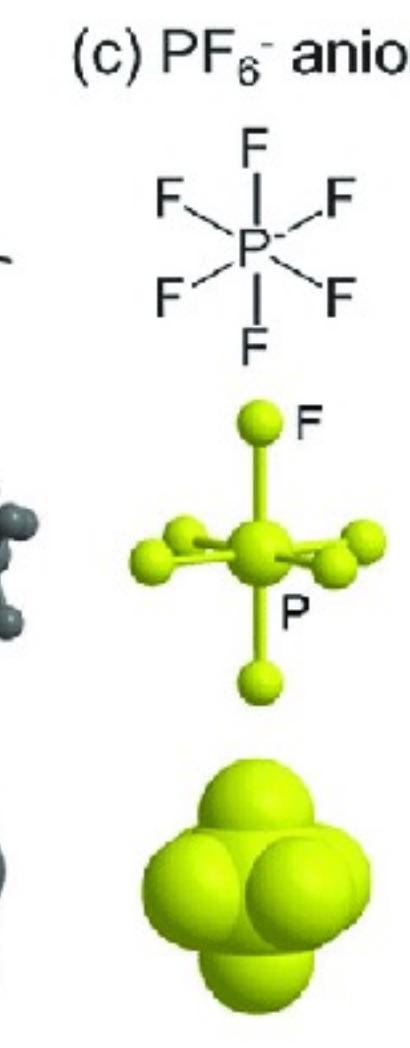
Alkanes



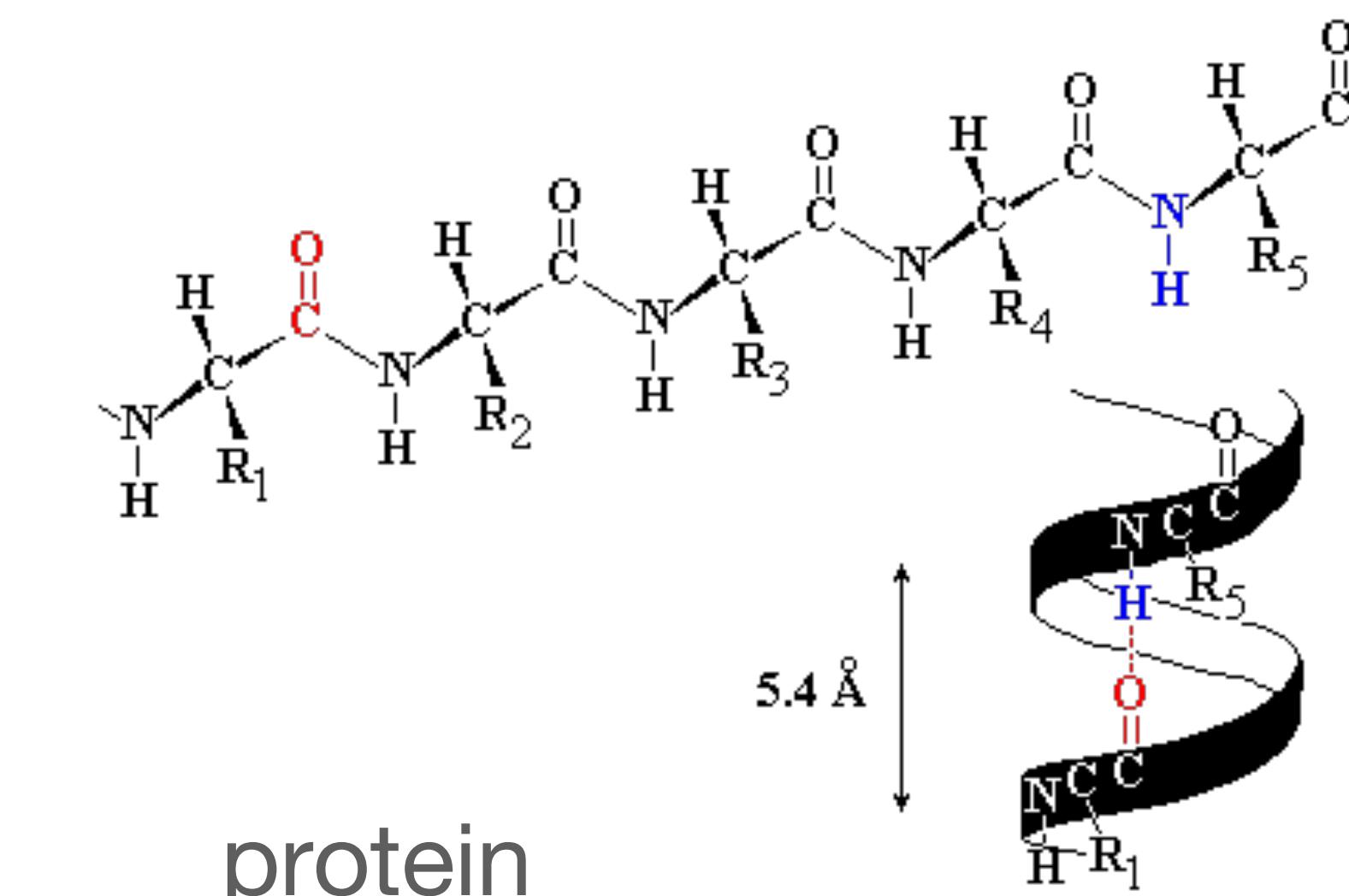
graphene



polymer



Ionic liquid

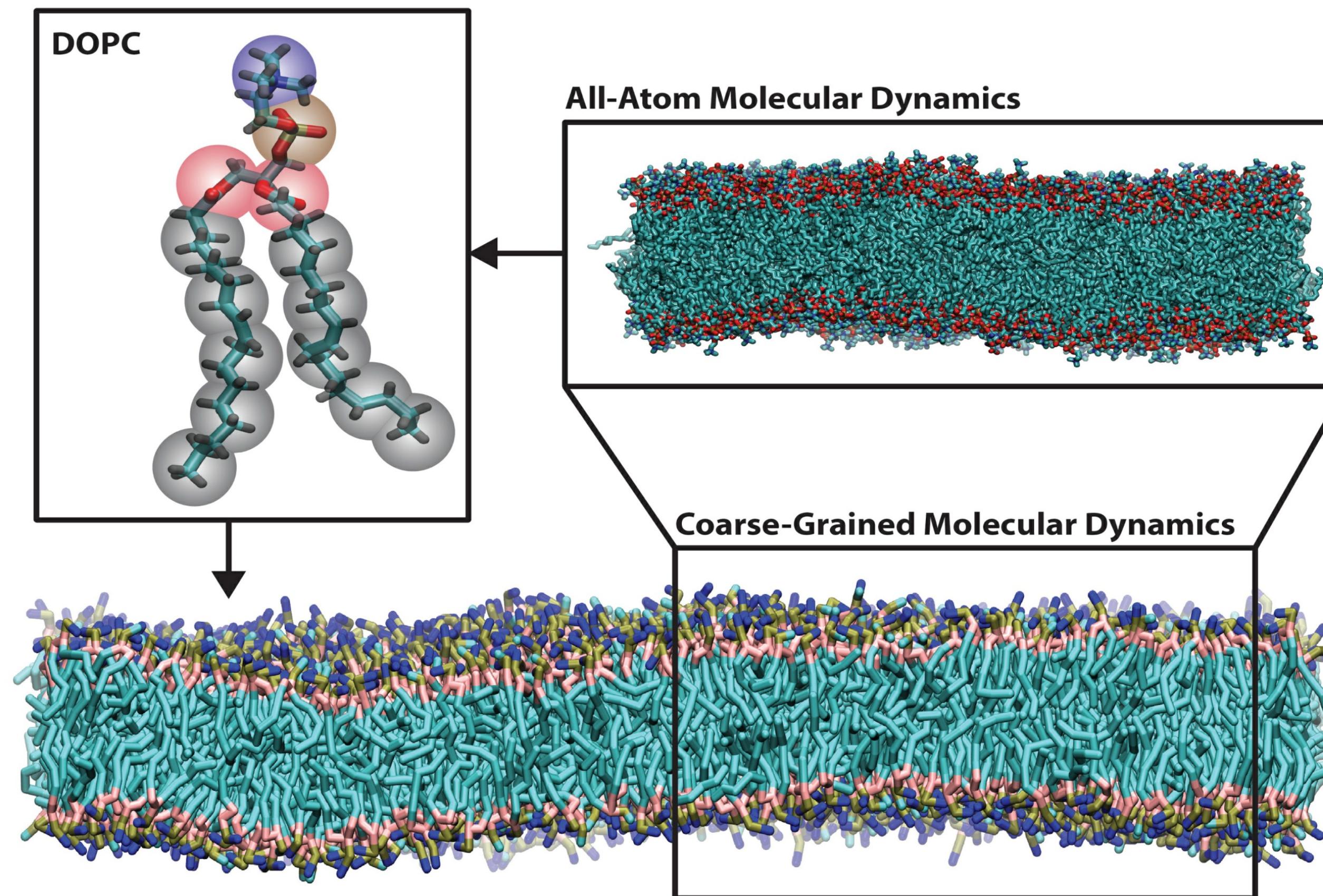


protein

# Parameterisation of force-fields

- Non-bonded and torsional terms most sensitive
- Vibrational frequencies
- Atomic coordinates: X-ray diffraction, neutron scattering
- Inter-atomic distance: NMR
- Quantum mechanics calculations provide data for parameterisation

# Coarse-grained modeling: Membrane modeling

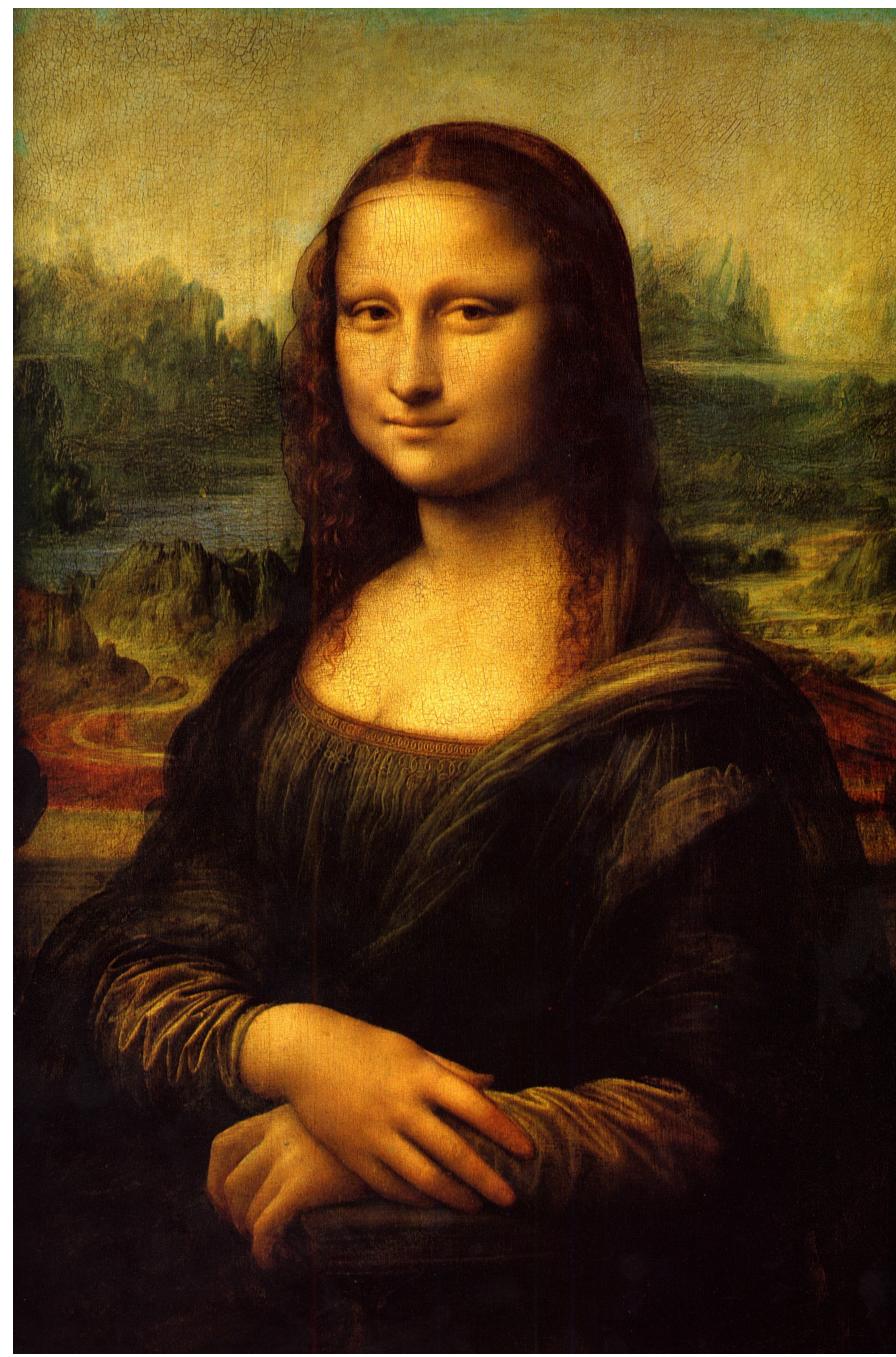


# Coarse-graining: Multi-scale models

- Many complex physical phenomena in liquids, soft materials, and biomolecular systems occur over length and time scales that are well beyond the current capabilities of atomic-level simulation.
- Novel approaches are developed that can access longer time and length scale phenomena : Coarse-graining
  - Group of atoms clustered into new “CG” sites.
  - CG sites interact through more computationally efficient effective interactions.
  - **3 goals:**
    - a.) to develop a computationally cheaper CG model
    - b.) to develop a CG model that has a smoother underlying energy landscape:  
Faster equilibration, larger time steps
    - c.) to represent correct physical behavior



# Louvre Museum, Paris



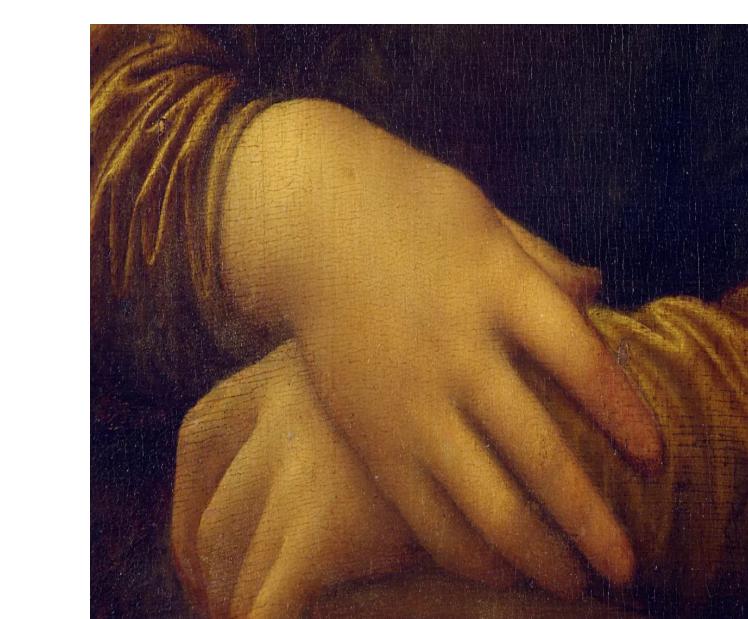
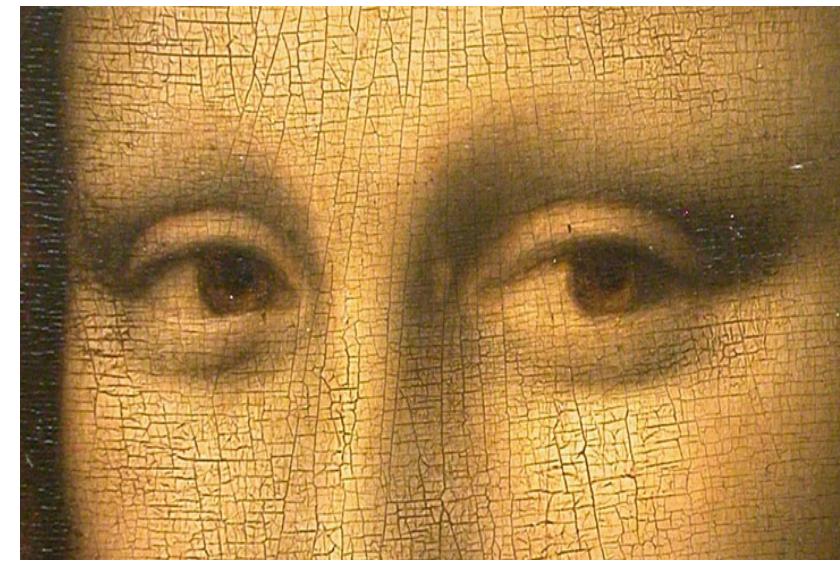
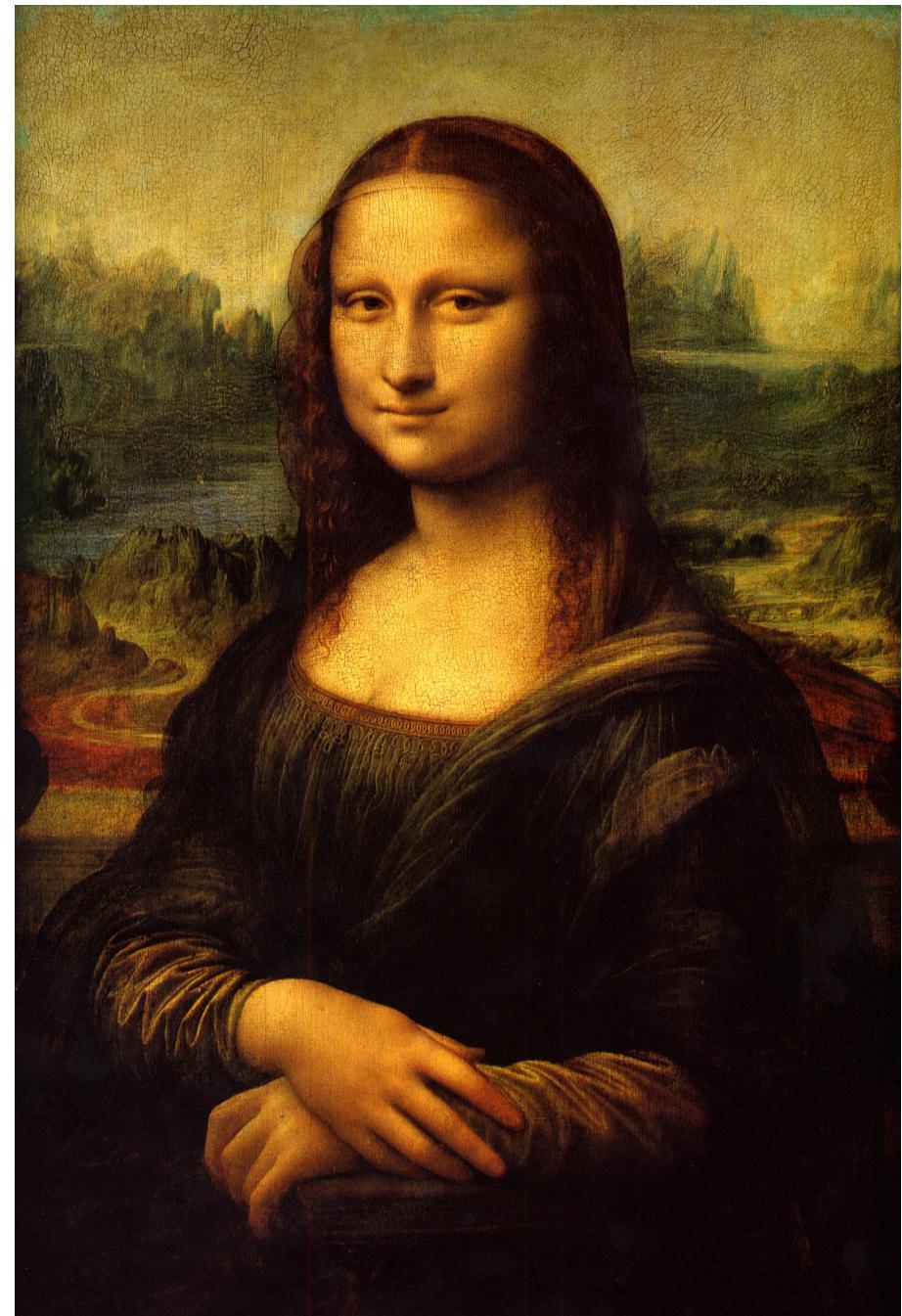
High resolution



Low resolution

“Coarse grained “

# Desired properties determine the level of coarse graining or fine-grained details



X



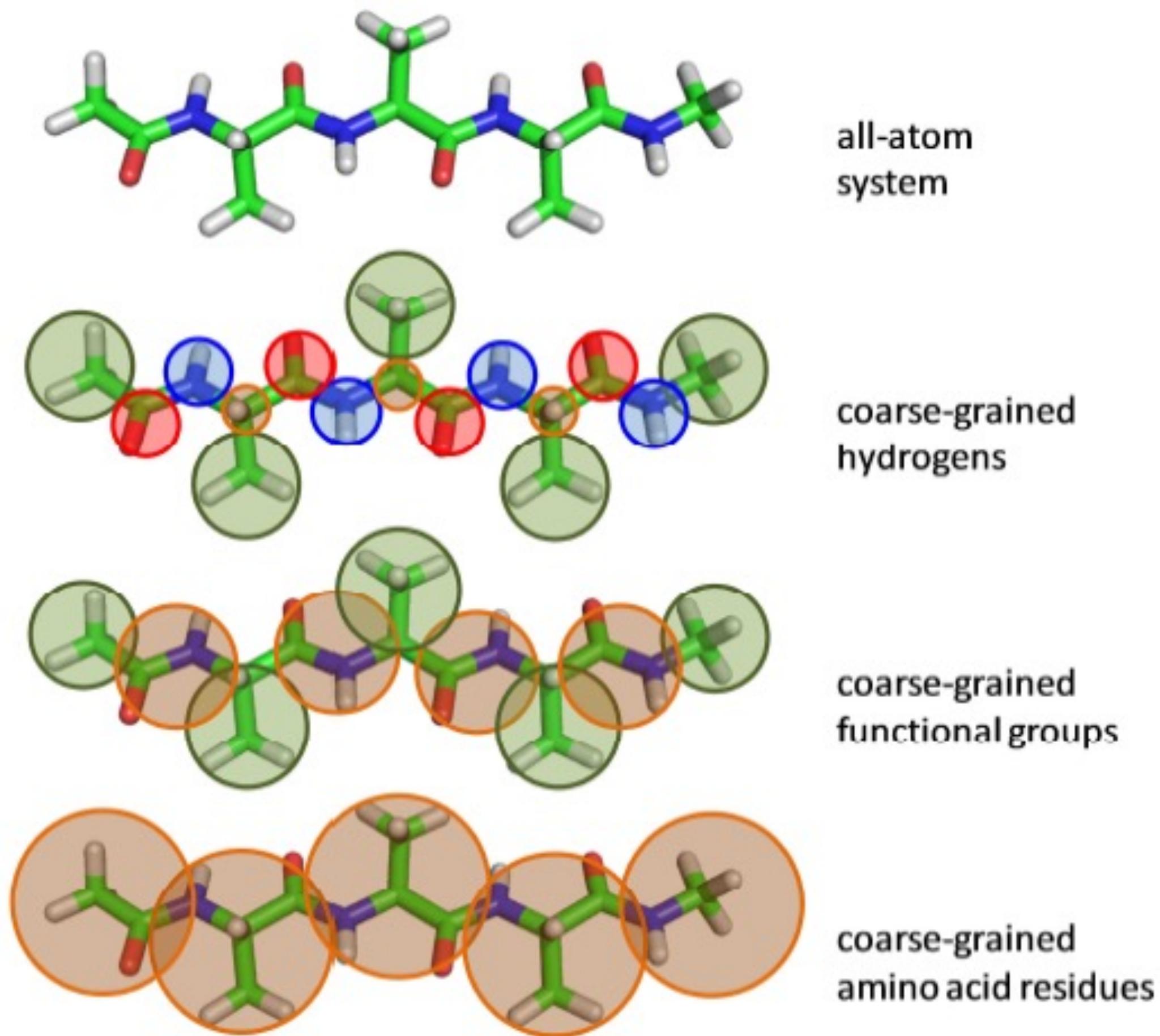
X



The overall properties of the coarse-grained model should remain the same as in fine-grained all-atom model

# Procedure of coarse-graining models

## Mapping scheme



## Fine-grained model

## Mapping scheme

- irrelevant degree of freedom can be lost, important ones should be kept
- there is no way to determine an optimal mapping scheme.

## Coarse-grained model



# Instructions for Major exam

- Major exam: 12<sup>th</sup> April 2022, 2:15 pm-4:15 pm, LH108 and LH521.
- One hour exam on MOODLE in OFFLINE mode.
- Syllabus: Lectures taught after the MINOR exam.
- Please make sure that your laptop battery is working fine and can hold charge upto 1.5 hrs atleast.
- Please ensure that your laptop is able to connect to the IITD network without any hardware issues.
- No excuse of laptop getting discharged or any technical faults will be considered. In such a case, no request for Viva or re-major will be considered. It is your responsibility to ensure that your exam can go smoothly.
- All of you must attempt the exam. No re-major /viva requests will be entertained at any cost.

# Lecture 35

## Molecular dynamics simulations

### Textbooks:

- Computational Materials Science: J. Gunn Lee
- Molecular Modelling Principles and Applications: Andrew Leach (Chapter 4)
- Understanding Molecular Simulations: D. Frenkel and B. Smit (Chapter 4)

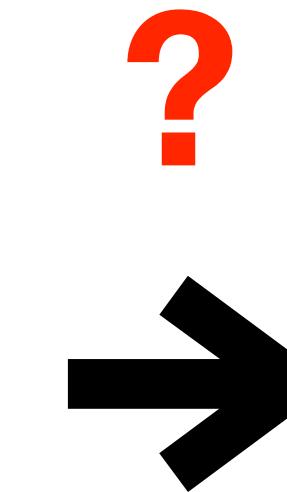
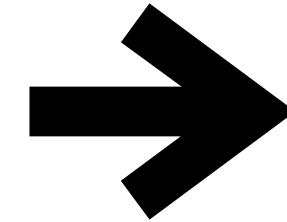
Prof. Divya Nayar  
Department of Materials Science and Engineering  
[divyanayar@mse.iitd.ac.in](mailto:divyanayar@mse.iitd.ac.in)

# Recap...

- Computational materials science: Introduction
- Modeling in simulations: potential energy surface and multi-scale modeling
- Developing a model

# Computational experiment: *Recipe*

## Turning complex ideas into solvable equations



Define a problem

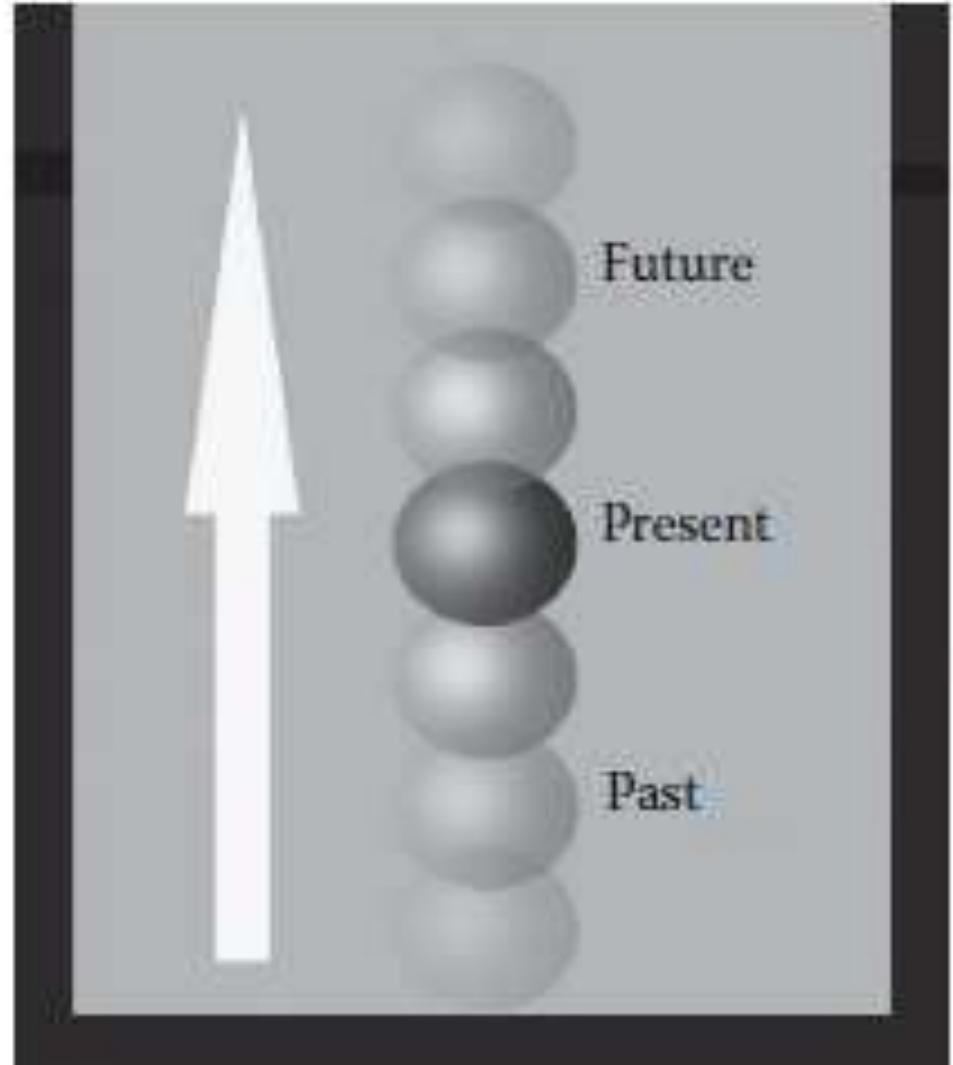


Build a model



- Theory: set of rules to follow
- Simulation: algorithm to solve the problem
- Computer: ???

# Classical Systems



Thermal de Broglie wavelength

$$\Lambda = \frac{h}{2\pi m k_B T}$$

$h$  = Planck's constant

$T$  = temperature

$m$  = mass of particle

$k_B$  = Boltzmann's constant

For a system to be classical, the wavelength should be much lesser than the inter-particle spacing

$$\Lambda \ll d$$

Hamiltonian for electronic systems

$$\hat{H} = \sum_{i=1}^N \left( \frac{-h}{2m_i} \nabla_i^2 + \hat{V}_i \right)$$

Kinetic energy  
operator

Potential energy  
operator

Hamiltonian for classical systems

$$H = \sum_i^N \frac{p_i^2}{2m_i} + U(r_1, \dots, r_N)$$

Kinetic energy Potential energy

*6N-dimensional hypersurface (phase space)*

## Opening lines of "States of Matter", D.L. Goodstein

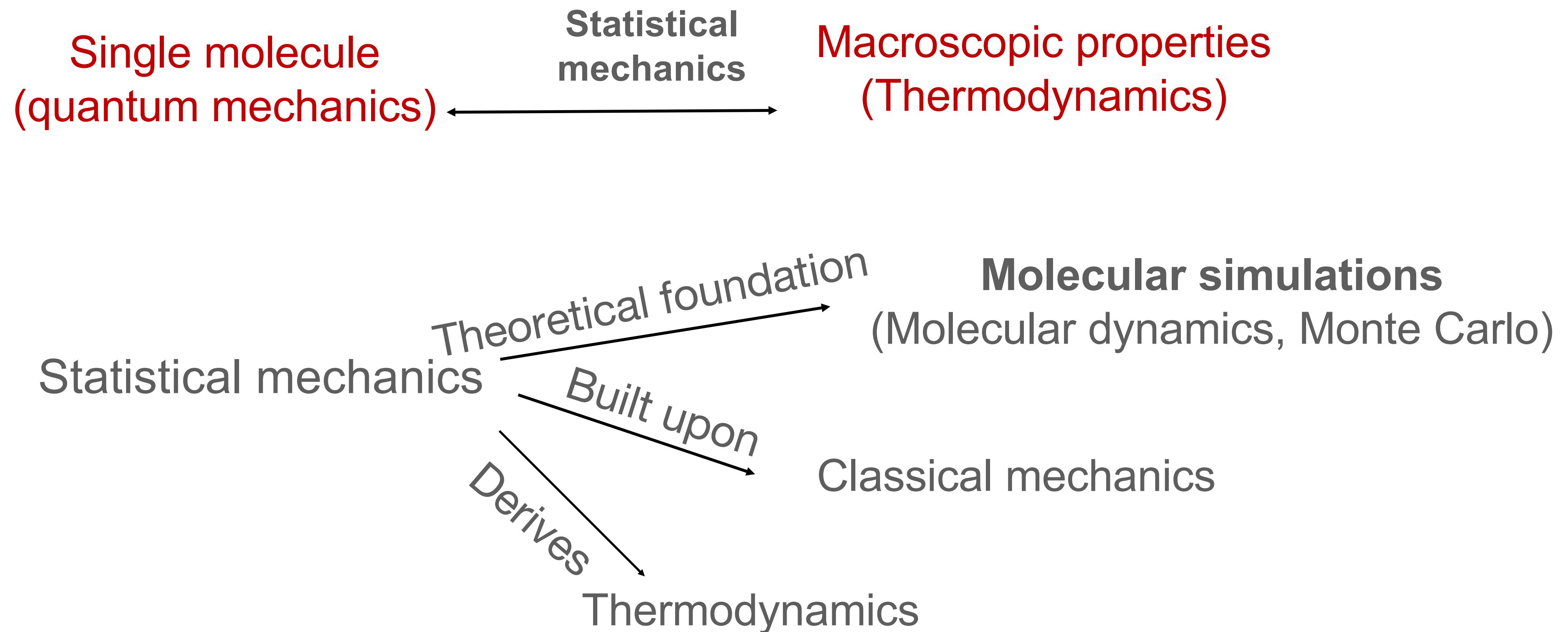
# STATISTICAL MECHANICS

## 1.1 INTRODUCTION: THERMODYNAMICS AND STATISTICAL MECHANICS OF THE PERFECT GAS

Ludwig Boltzmann, who spent much of his life studying statistical mechanics, died in 1906, by his own hand. Paul Ehrenfest, carrying on the work, died similarly in 1933. Now it is our turn to study statistical mechanics.

Perhaps it will be wise to approach the subject cautiously. We will begin by considering the simplest meaningful example, the perfect gas, in order to get the central concepts sorted out. In Chap. 2 we will return to complete

# Statistical Mechanics (The Theory)



# Some definitions

- **Microstate:** A state or configuration of the system in which the constituent elements i.e.  $3N$  position and  $3N$  momentum coordinates are specified.

$$\{ \vec{r}_1, \vec{r}_2, \dots, \vec{r}_N; \vec{p}_1, \vec{p}_2, \dots, \vec{p}_N \}$$

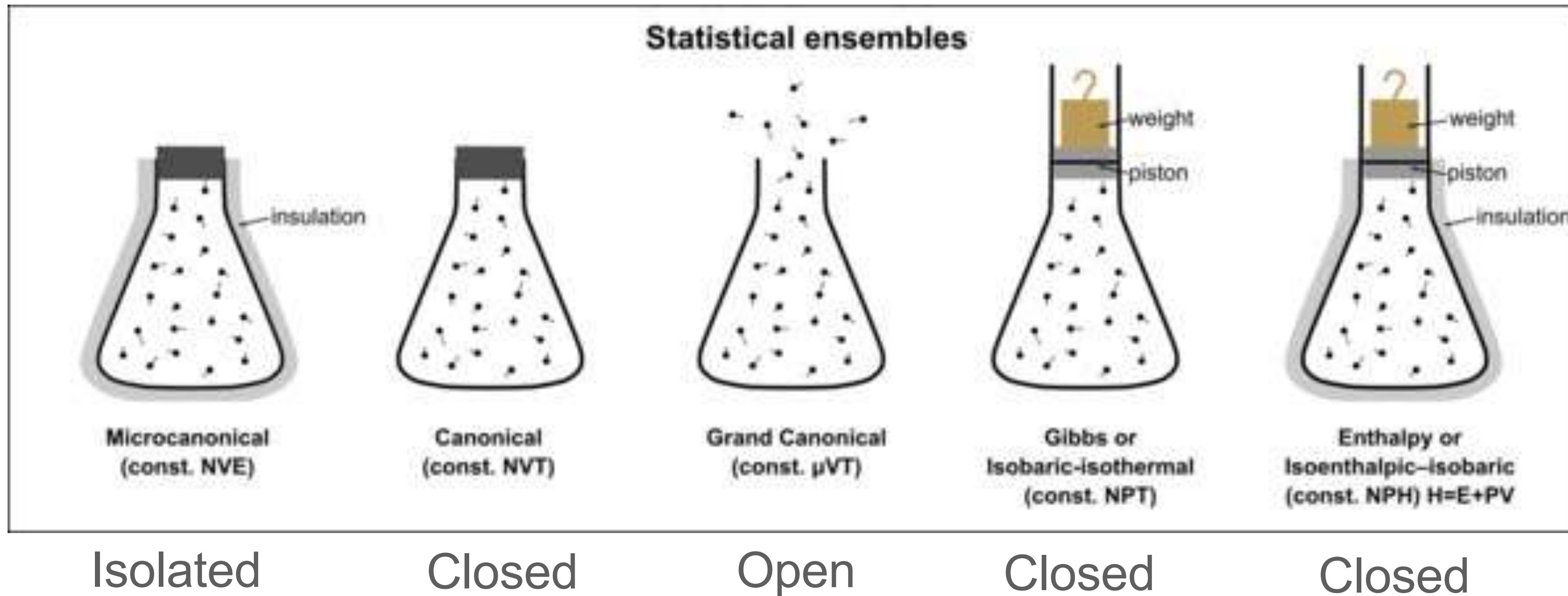
- **Ensemble:** A collection of microstates satisfying some common set of macroscopic constraints.

- **Partition function:** Sum over all possible microstates weighted by probability of occurrence of microstates in the ensemble.

# Ensembles



# Ensembles



N= no. of particles

V= volume of the system

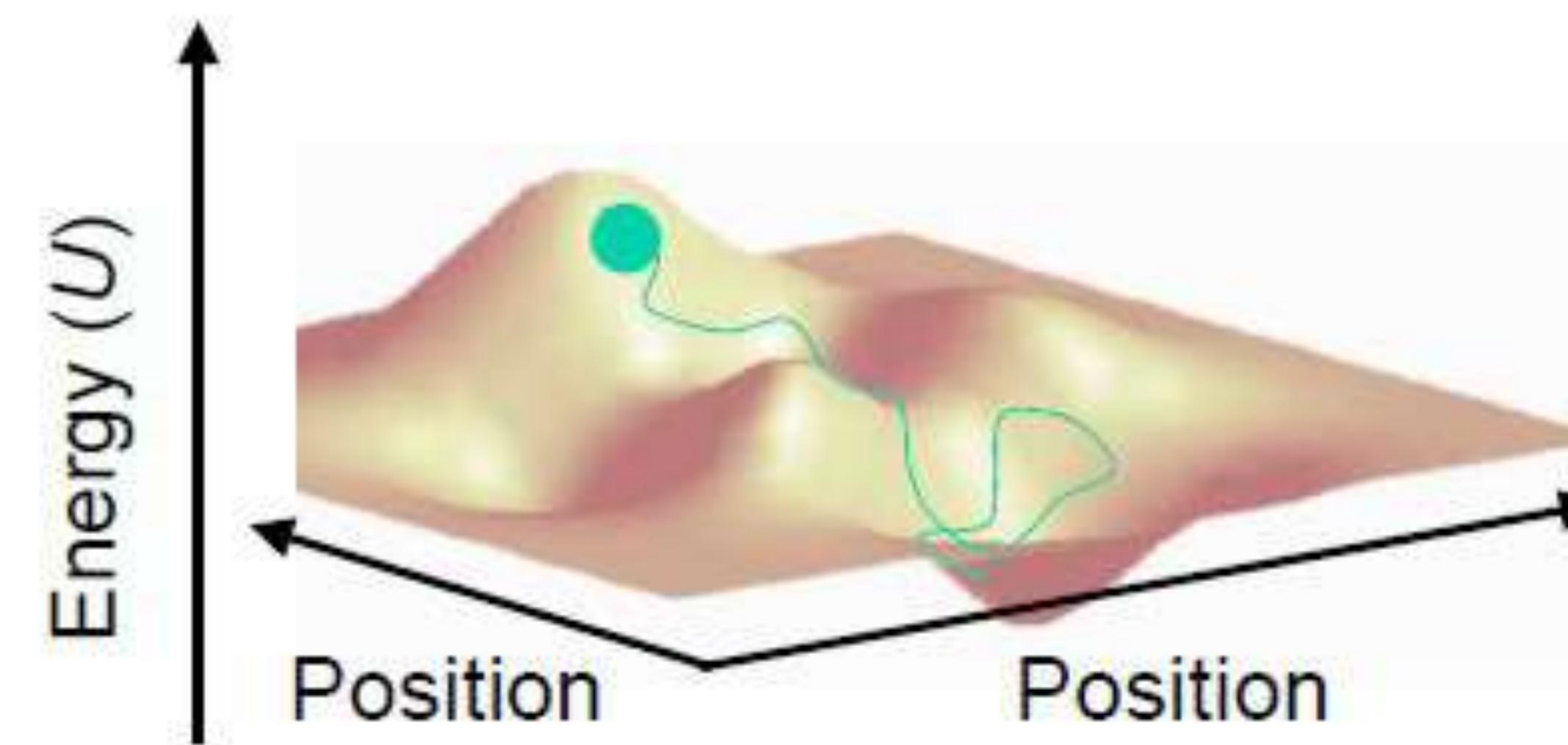
E= total energy of the system

T= temperature

P= pressure

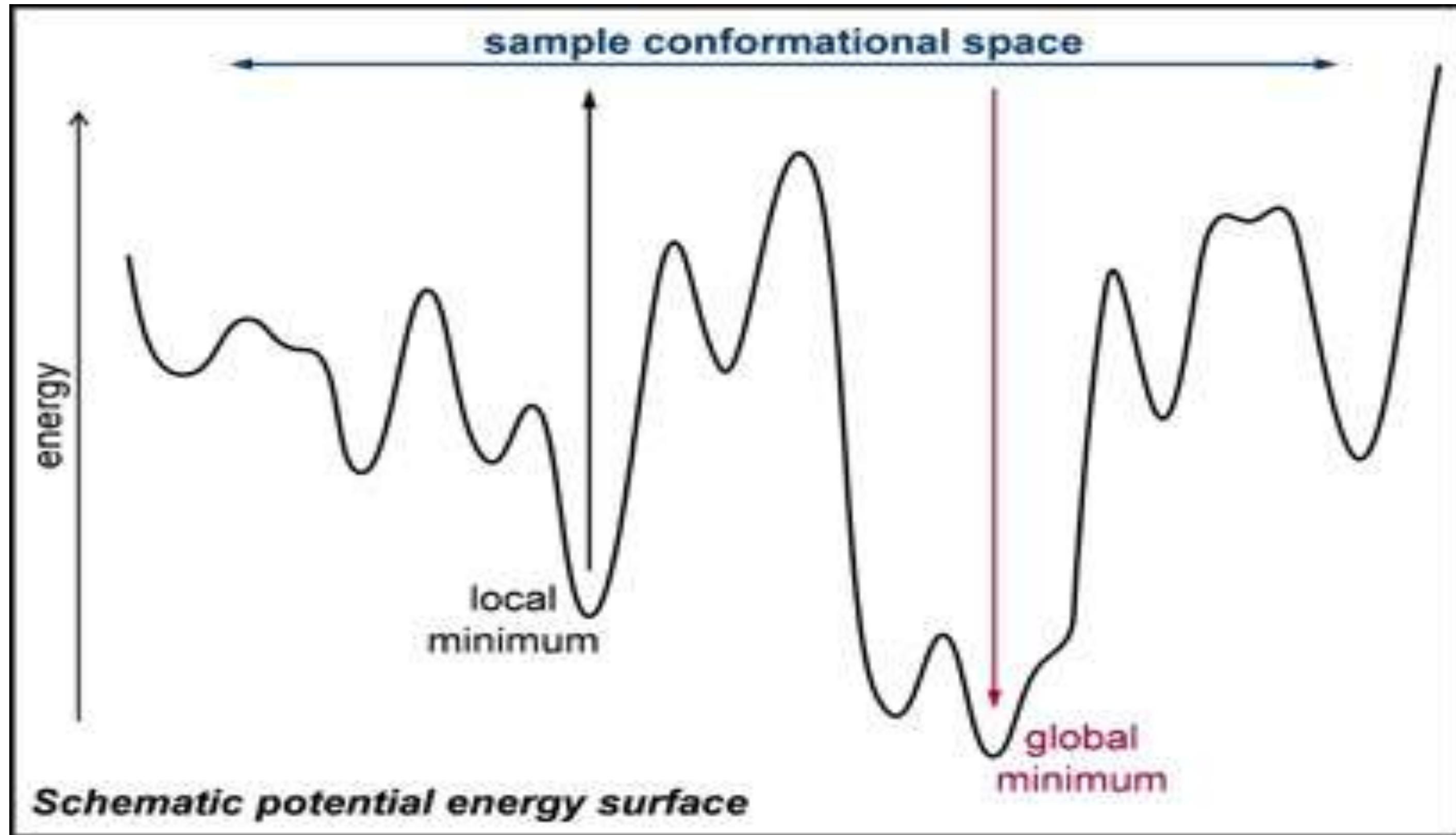
# Basic Idea of molecular dynamics simulation

- Mimic the behaviour of atoms in real systems.
- The potential energy function allows to calculate the force experienced by each atom due to the others.
- Newton's law governs the motion of atoms.
- The average behaviour of the system can be observed by sampling all possible points on this landscape.



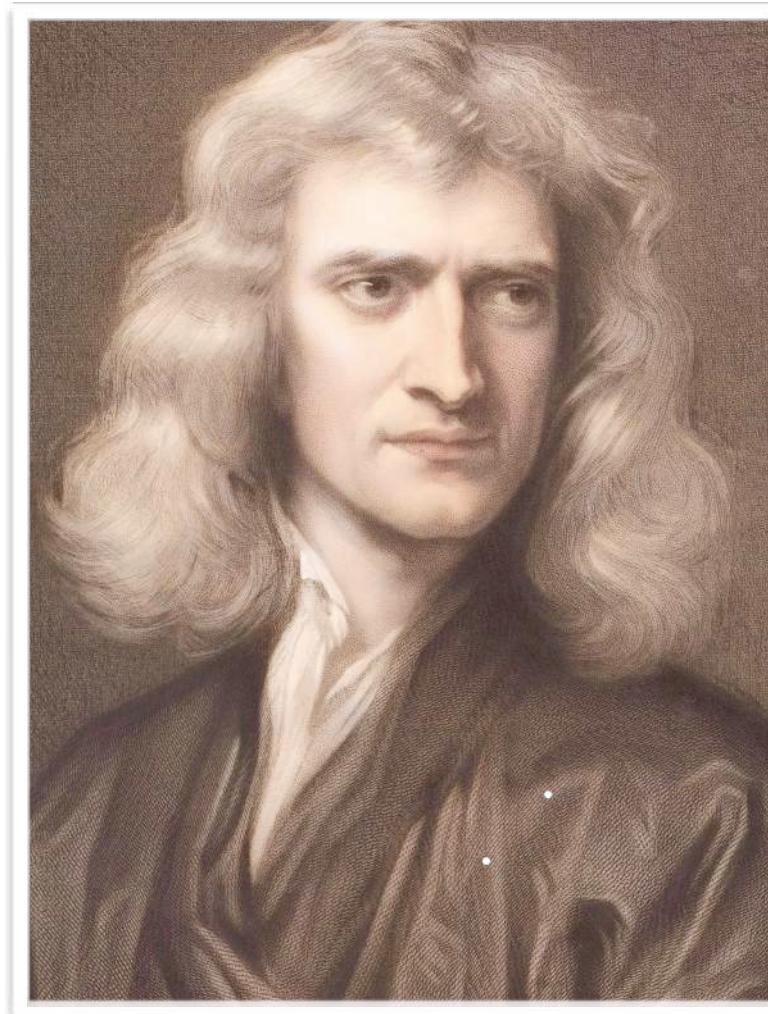
# Potential Energy Surface or Potential Energy Landscape

- Each point in the energy landscape corresponds to a “microstate” or configuration of the system
- Target is to sample as many microstates or configurations as possible to obtain an average behaviour or property of the system.



# Molecular dynamics simulations

## Newton's second law of motion



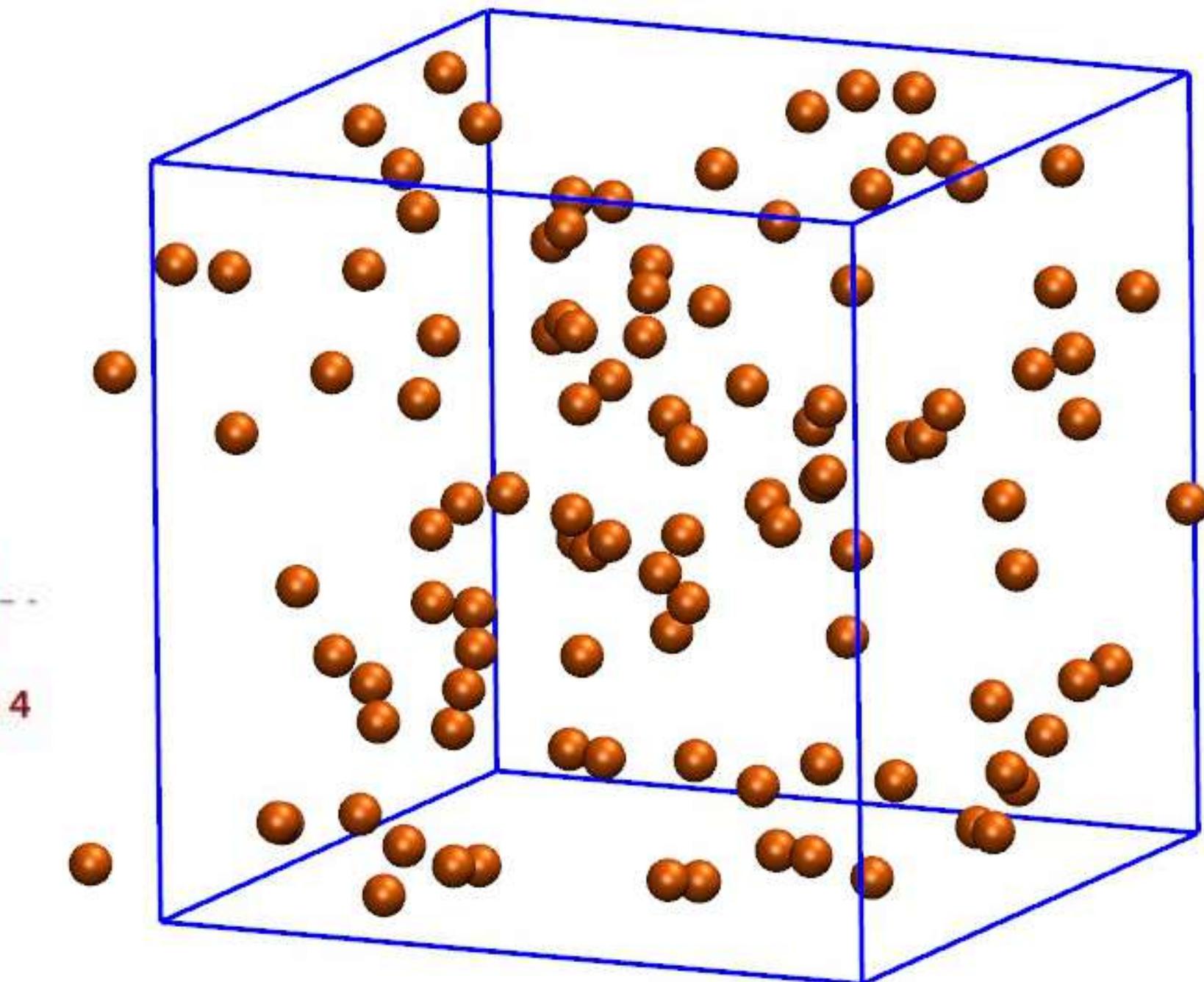
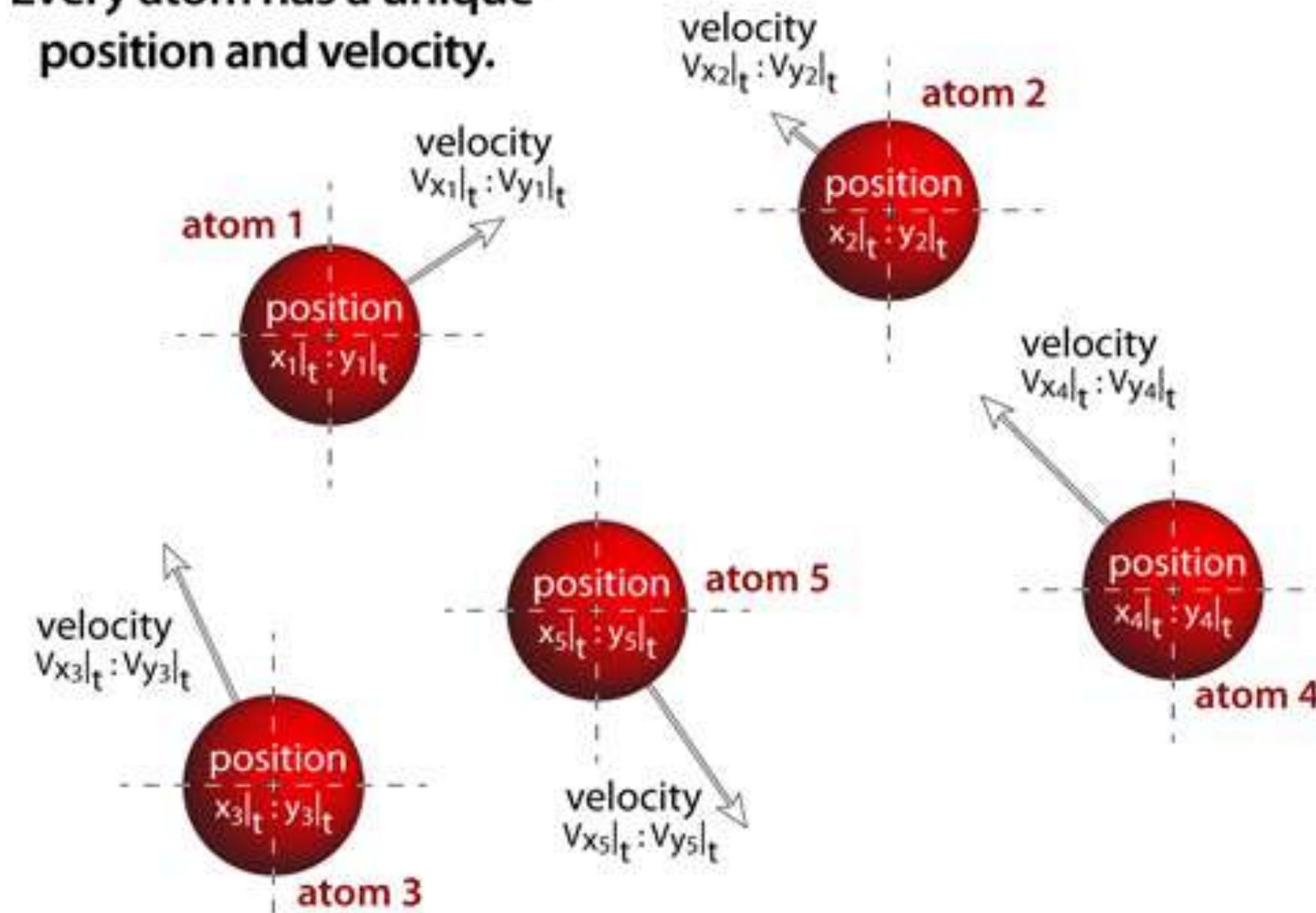
$$\vec{F} = m\vec{a}$$

$$\vec{F}_i = m_i \frac{d^2 \vec{r}_{ij}}{dt^2} = -\nabla U(\vec{r}_{ij})$$

6N-coupled second order  
differential equations

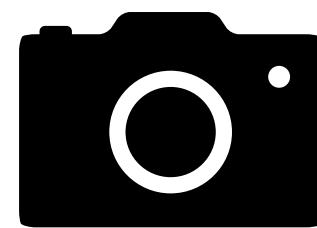
$$U(\mathbf{r}) = \frac{1}{2} \sum_i \sum_{j \neq i} u_{pair}(r_{ij})$$

Every atom has a unique  
position and velocity.

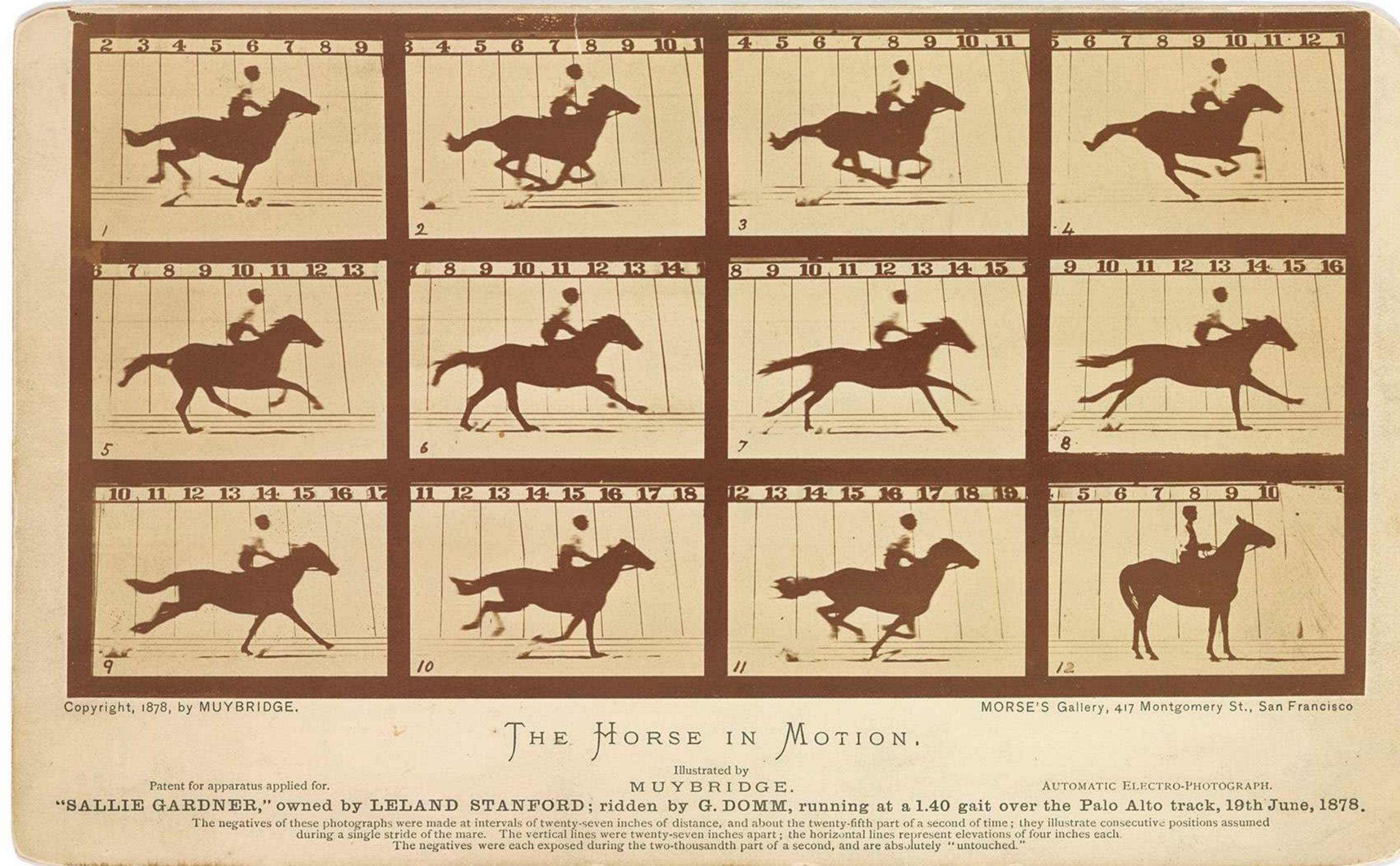


# Molecular dynamics simulations

In MD, the natural time evolution of a system is computed and the quantity of interest is averaged over a sufficiently long time.

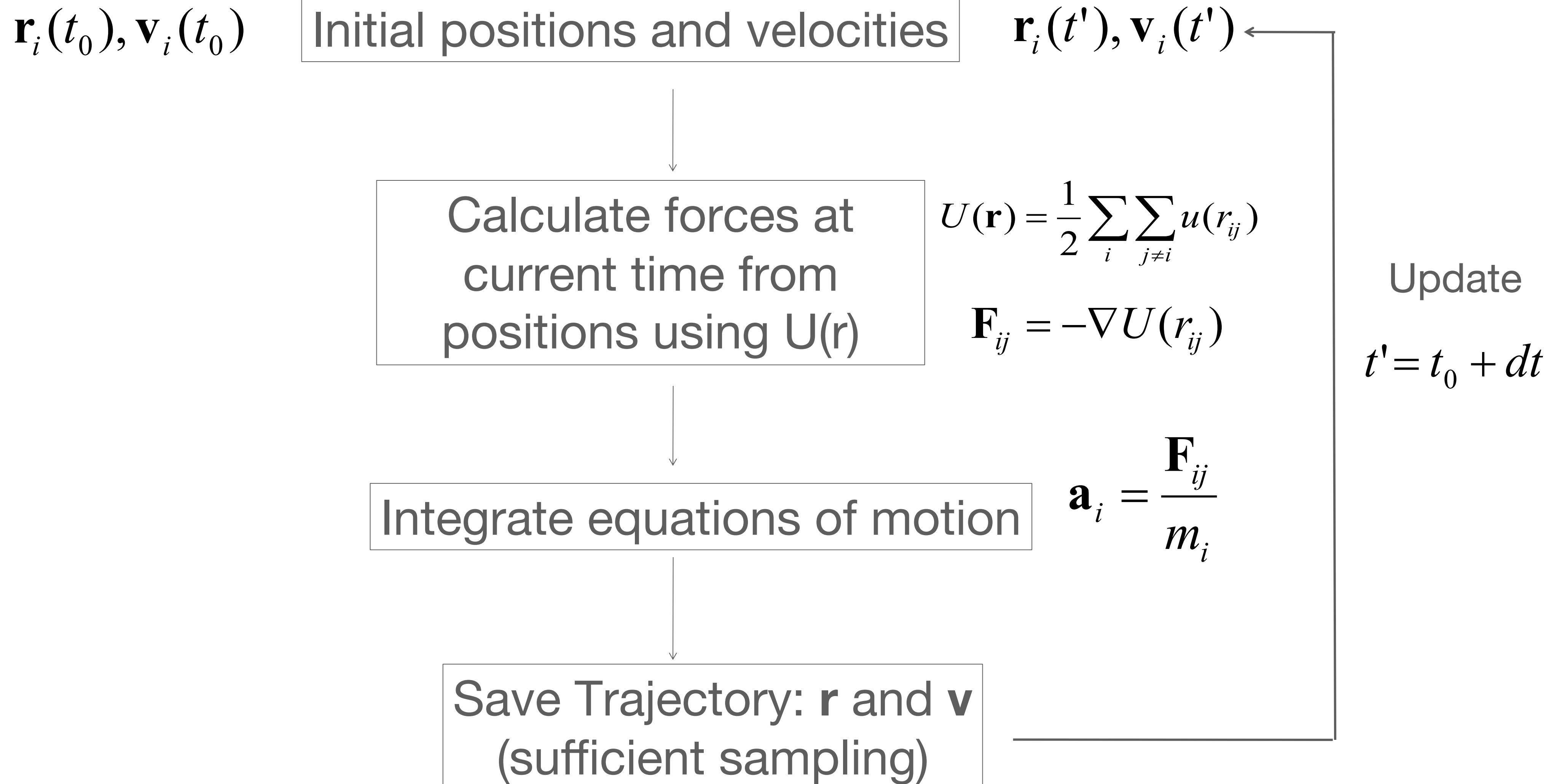


**t=0**

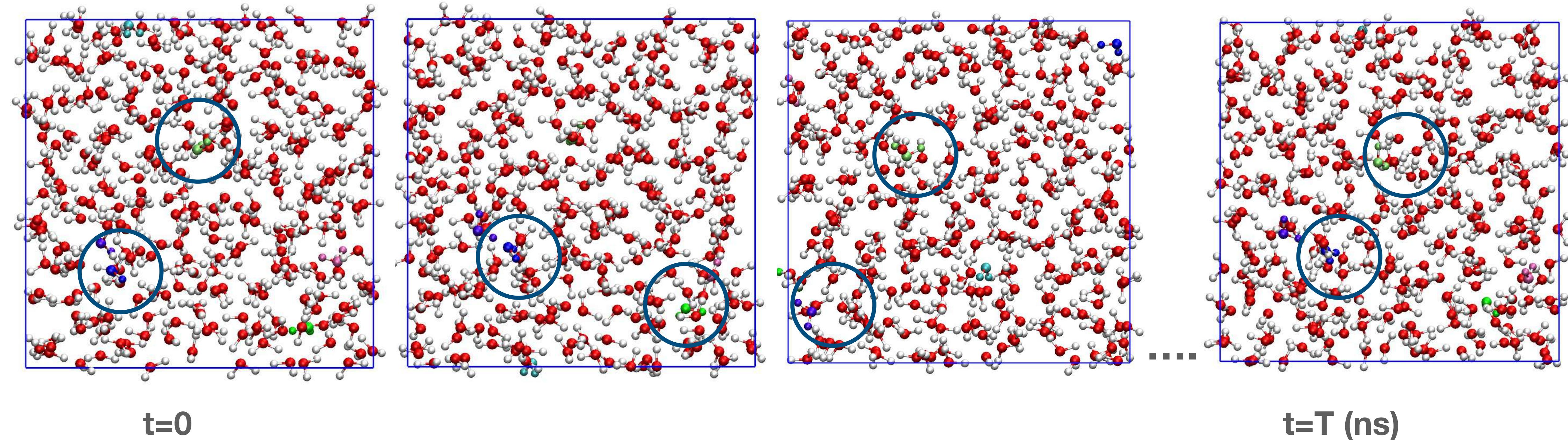


**t=10 mins**

# Structure of MD algorithm

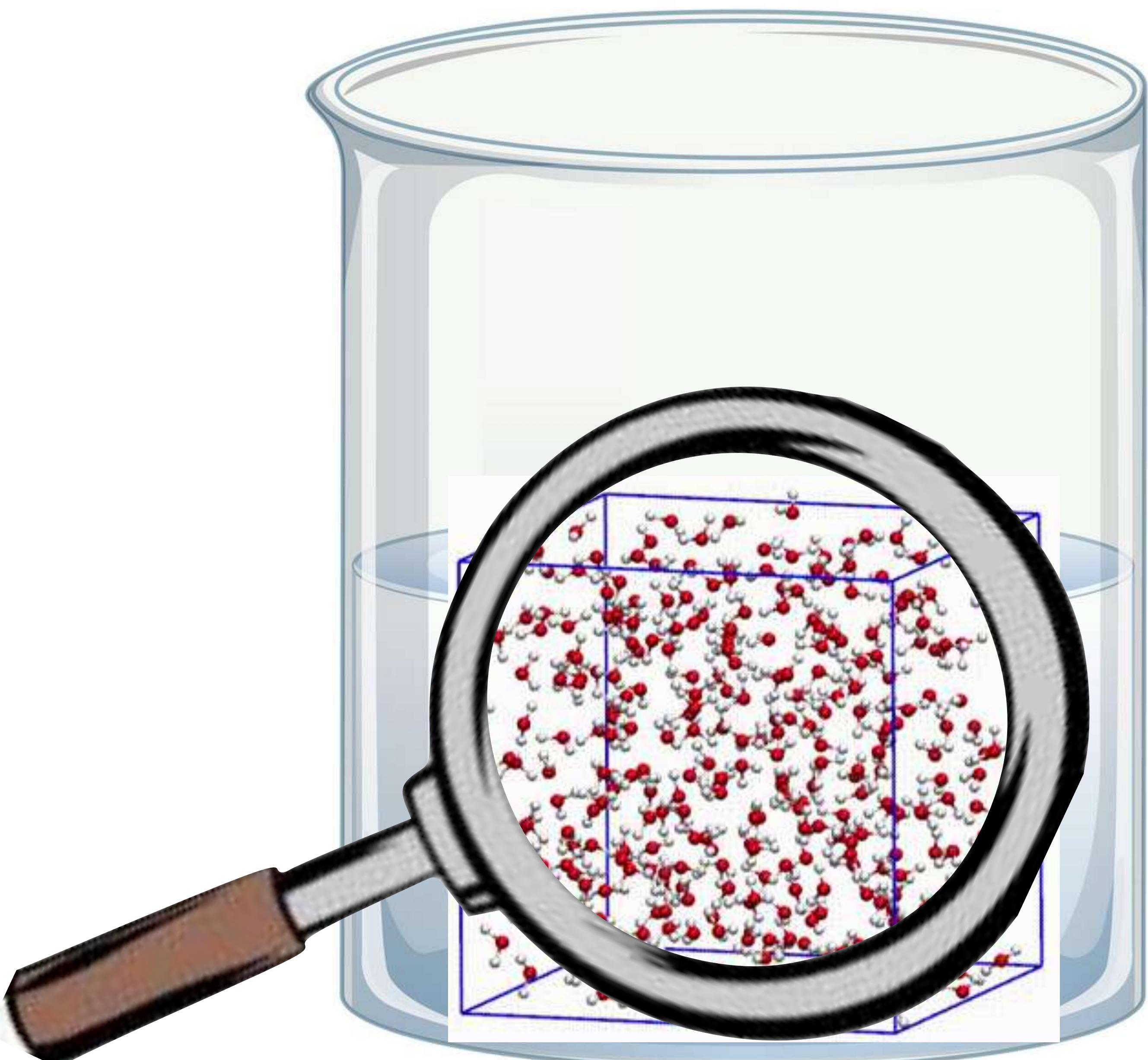


# Observing the behaviour of water over time



- Average density under certain temperature and pressure conditions
- Hydrogen bonding network
- Diffusion
- Viscosity ....and many more properties....

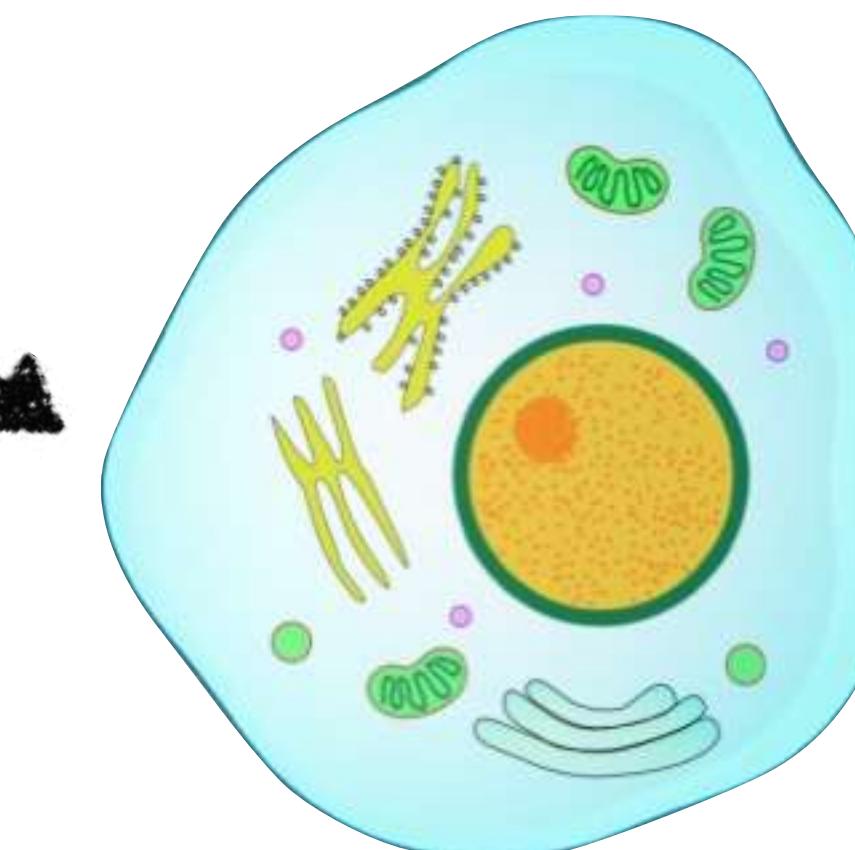
# Study water over certain time (nanoseconds)



Solution of  
salt/sugar  
(Solvent)

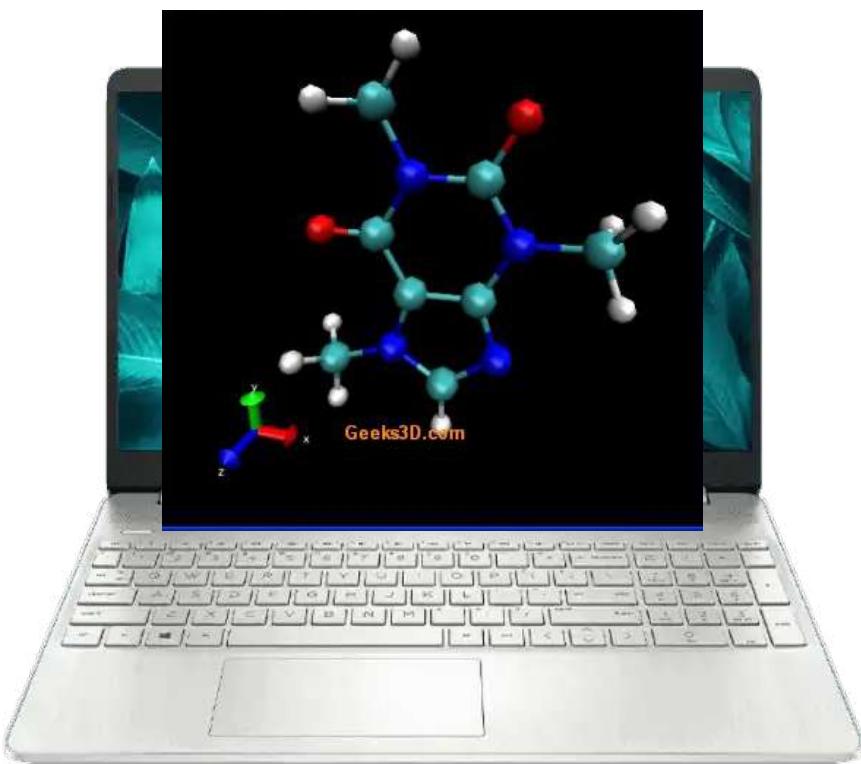


Melting of ice  
(Phase diagram)



Solvent for  
biomolecules  
(Protein folding,  
ion transport)

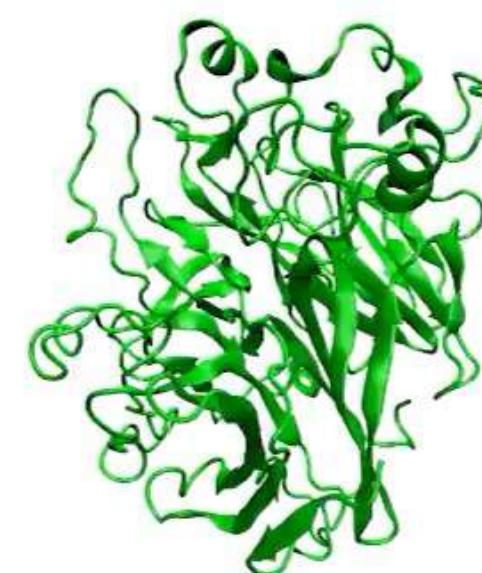
# The power of computing and technology



Laptop  
4-8 CPU cores  
10-100 atoms



Workstation (GPU)  
16-150 CPU cores



Approx. 0.1 million atoms



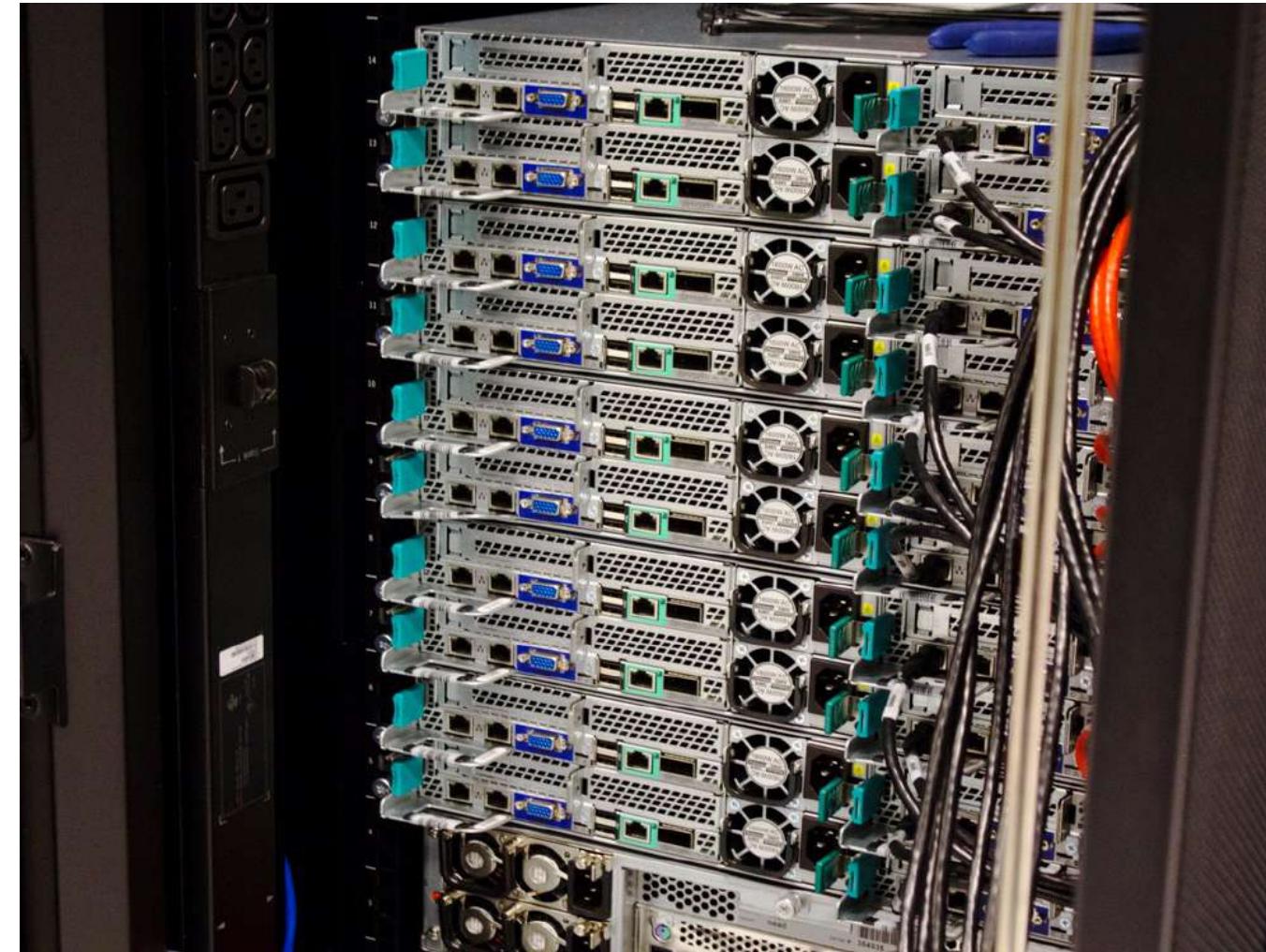
Supercomputer

10000-100000 CPU cores



Appox. 10 million atoms

# Supercomputer



Many efficient computers stacked in a rack and connected by high speed network



A cluster of computers in 2002...

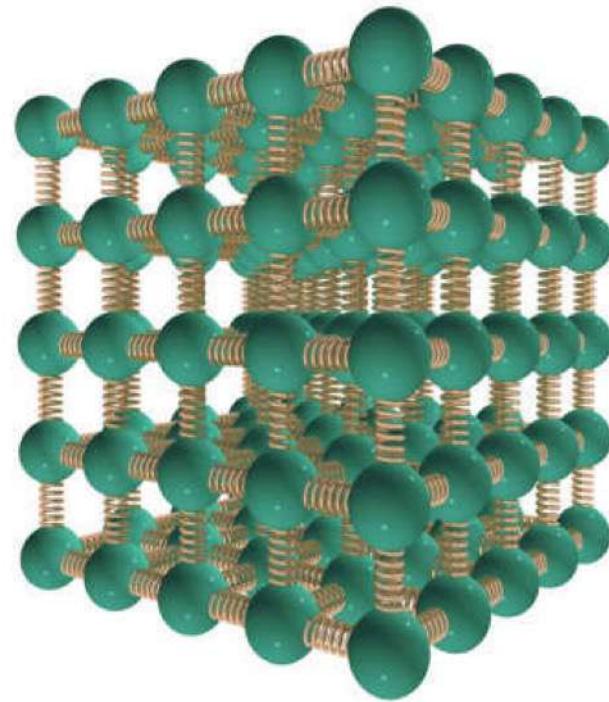
World's fastest supercomputer: *Fugaku*, Japan  
442 PetaFLOPs: can do  $442 \times 10^{15}$  operations per second



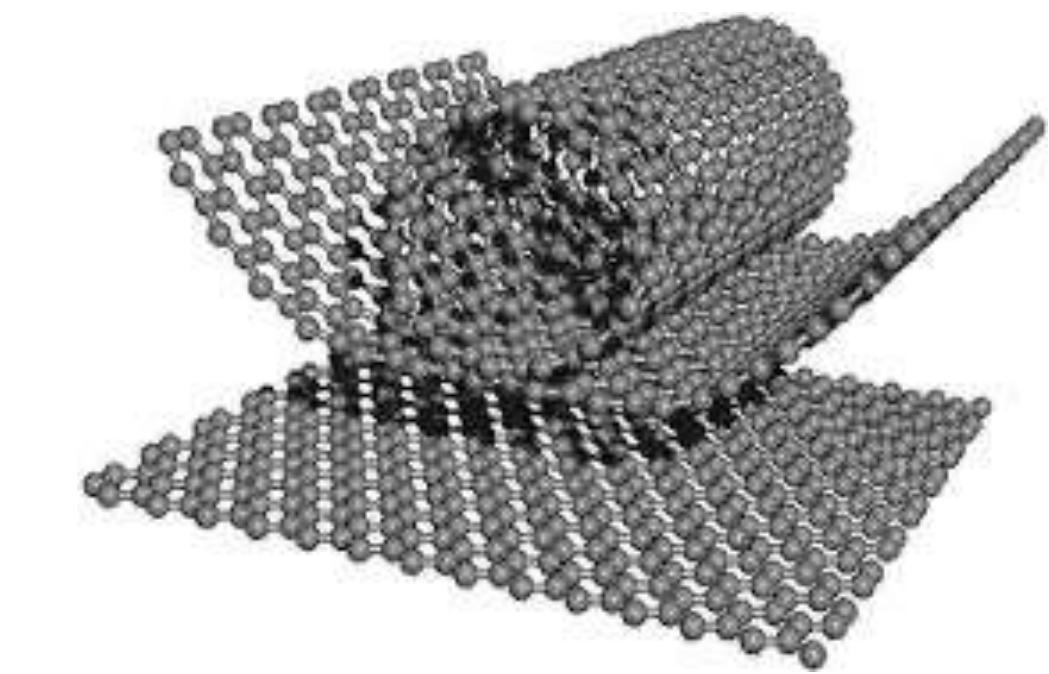
# What does computational experiments on Supercomputer enable?

# Desipher, Design, Discover, Develop...

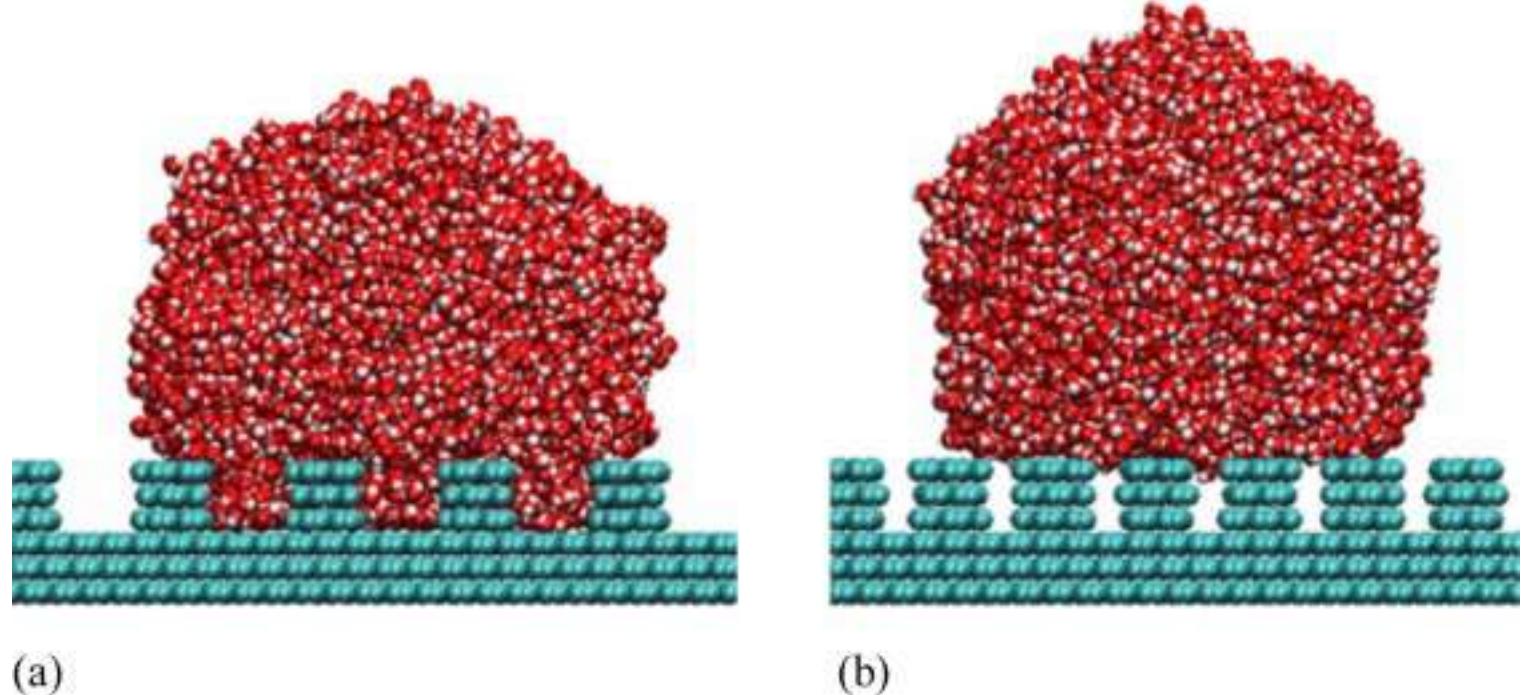
# Designing new (nano)materials



# Models of crystals

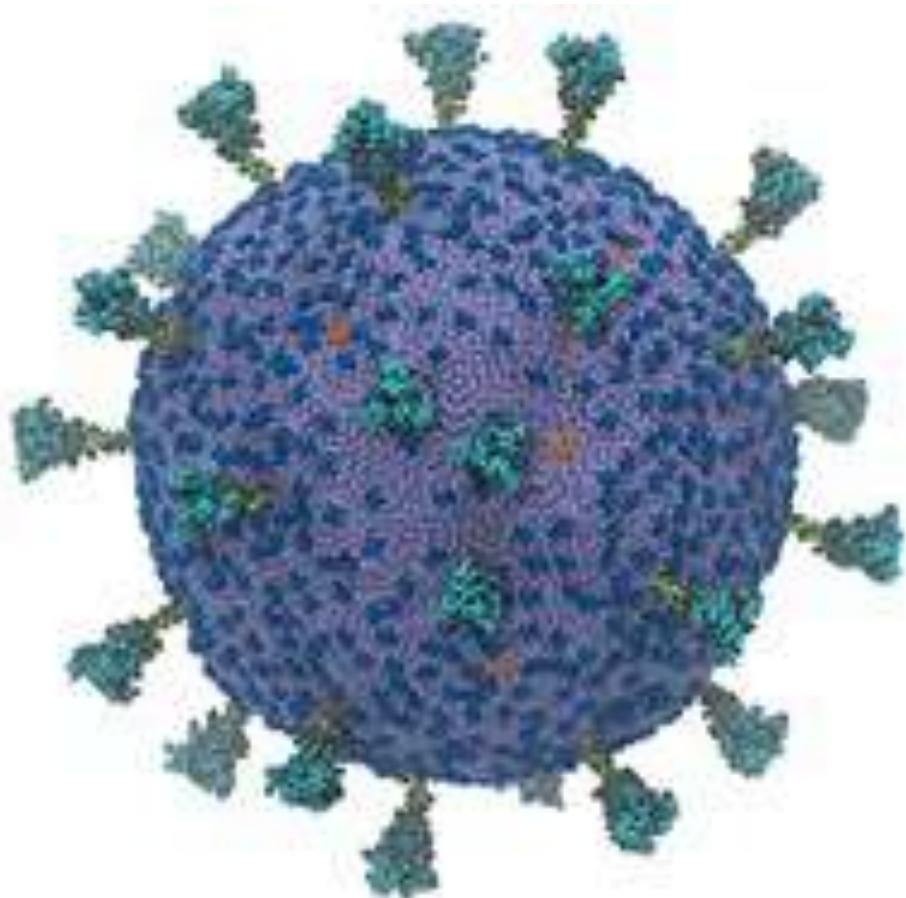


# Carbon nanotubes, nanorods, nanosheets



# Developing hydrophobic surfaces

# Drug design



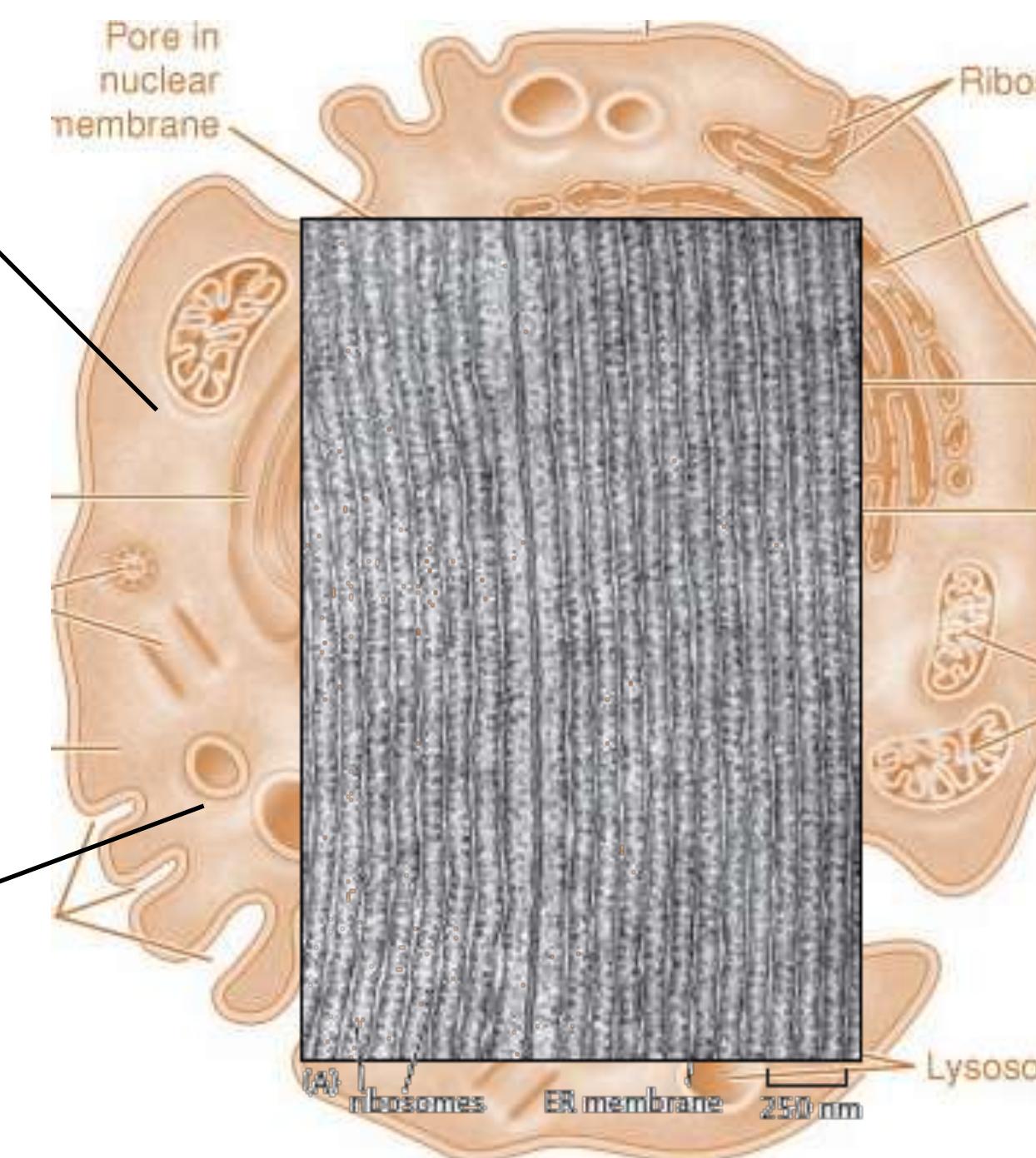
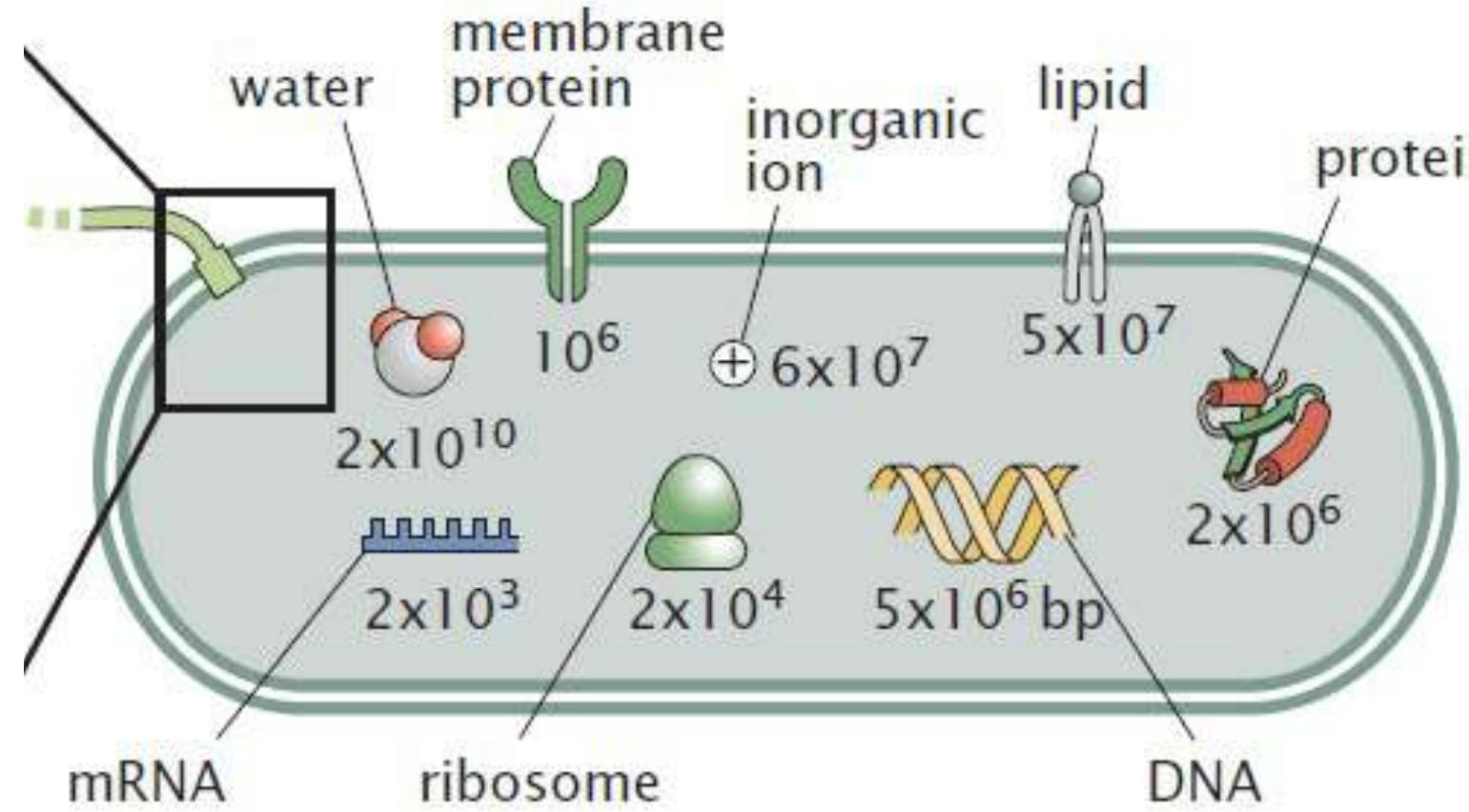
# Corona Virus COVID-19 (Complete virus simulation)



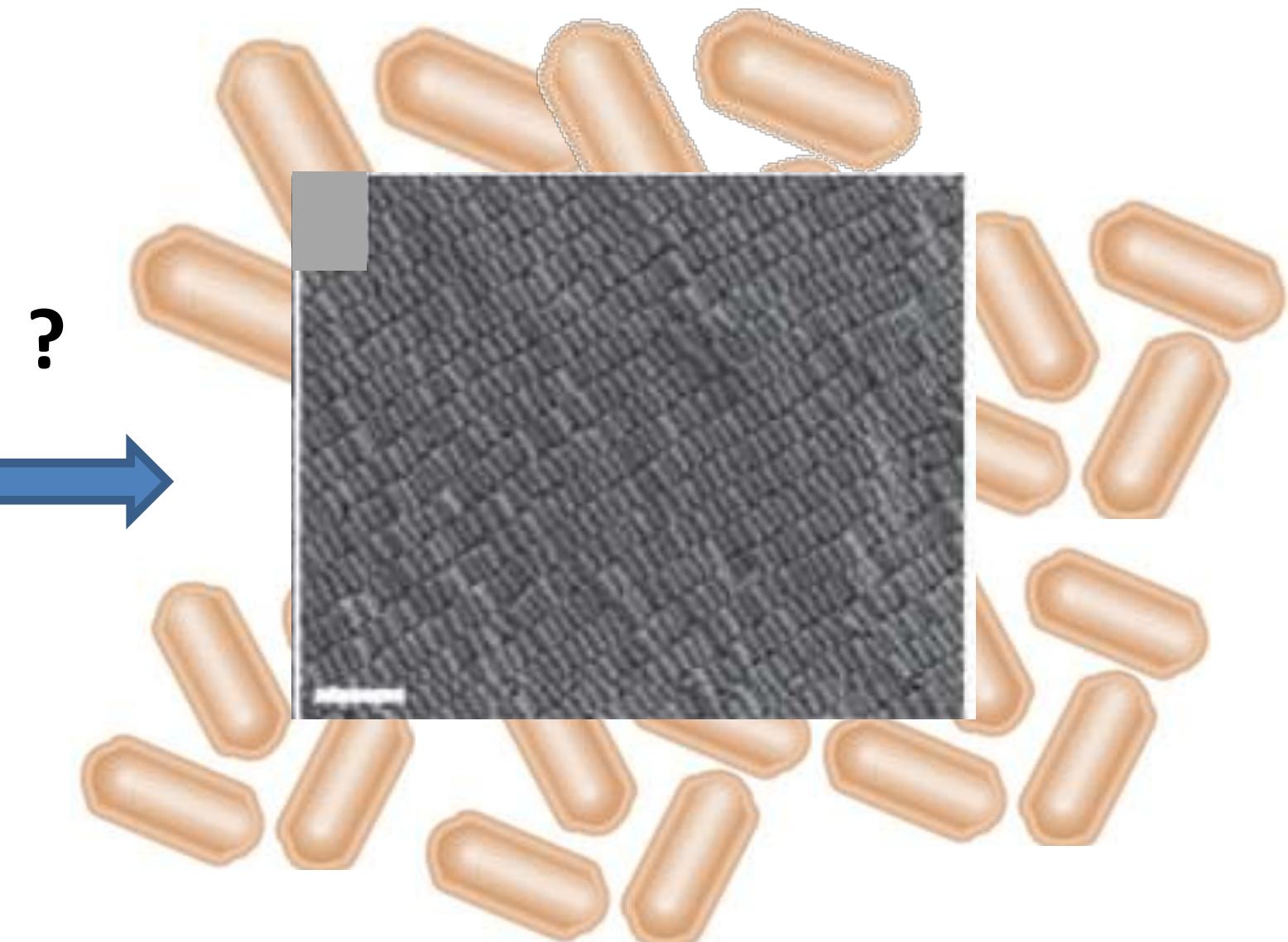
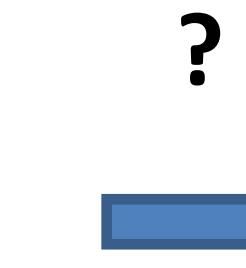
# Ultimate challenge: Simulating the whole living cell (Trillion atoms!)

# Self assembly: living cell to materials

Research glimpse: Applications of MD simulations in our group



Physical Biology of Cell, Rob Phillips et al.



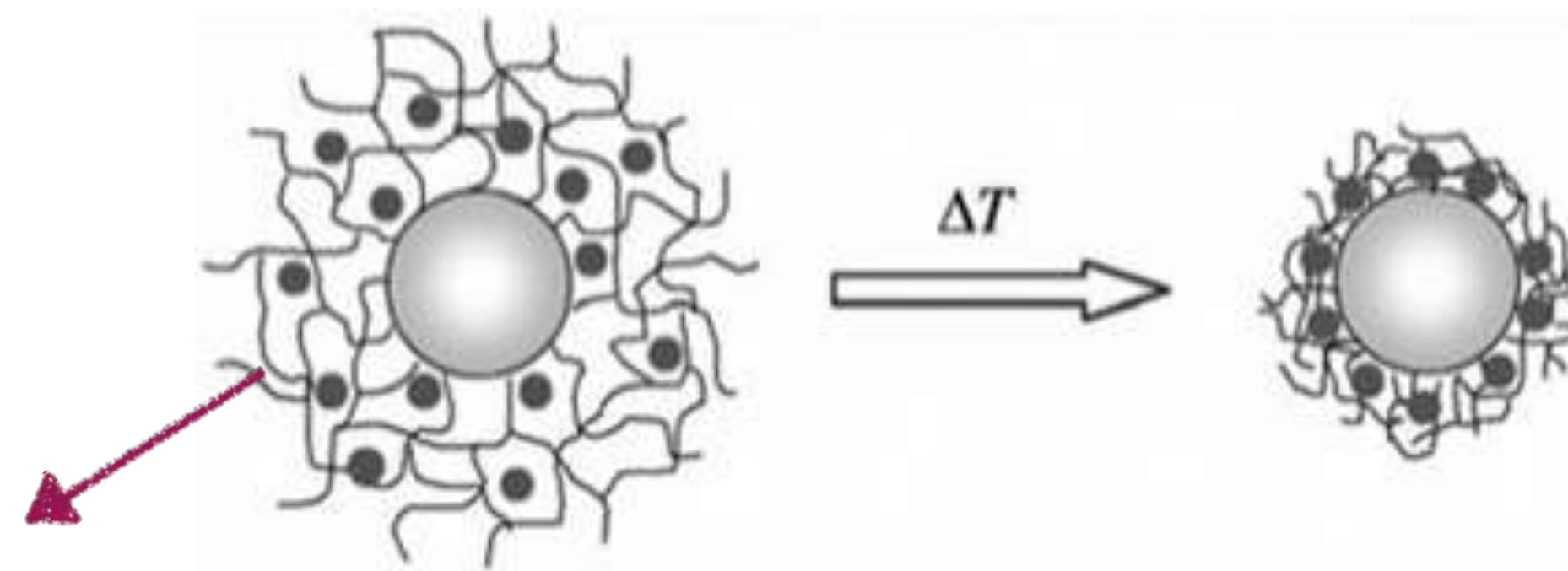
*Using Nature's design of biological self-assemblies in designing nanomaterials self-assembly!*

# *Smart polymers*

## Why they are smart and how can we design new smart materials?

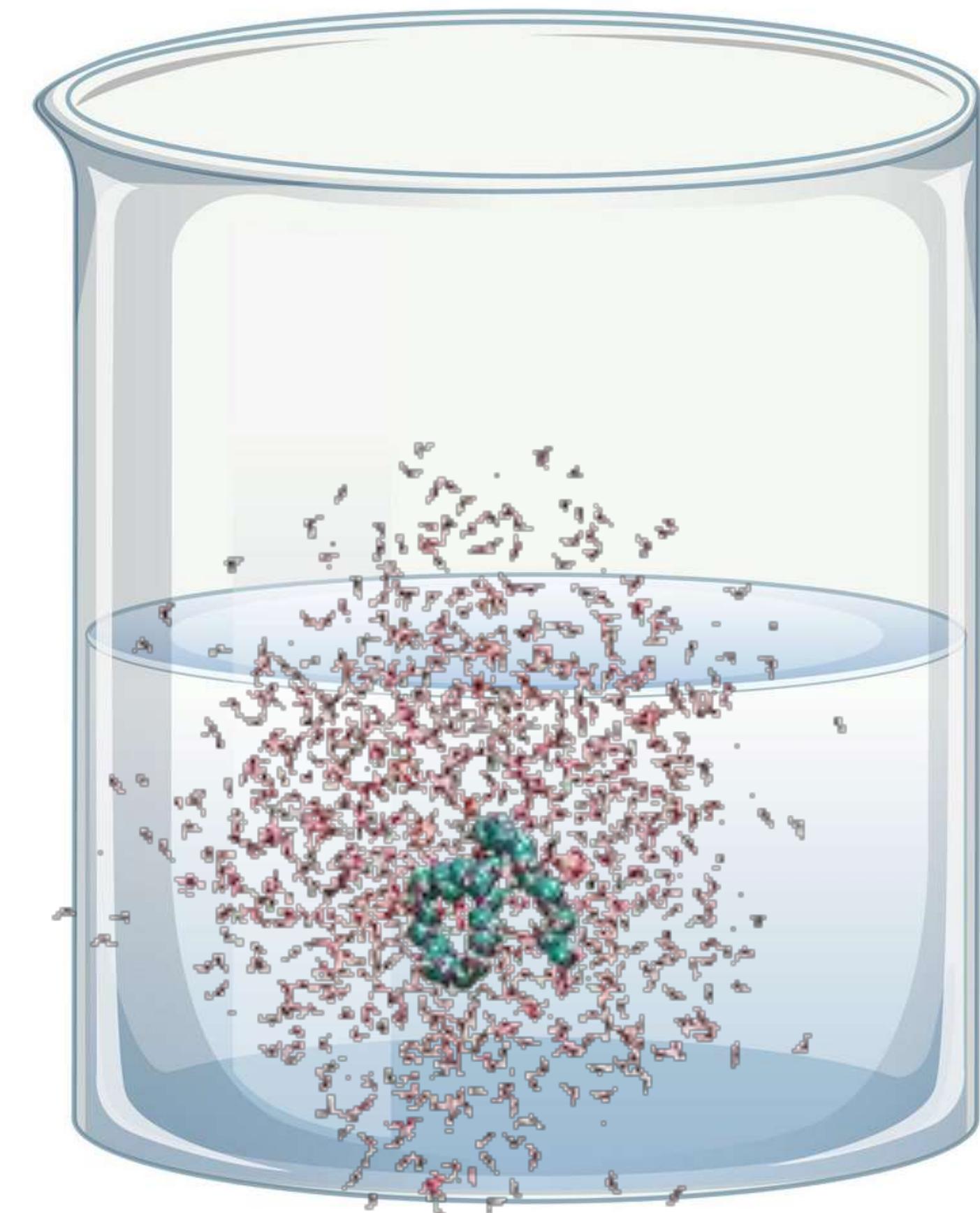


Heating  
→  
←  
Cooling  
Or chemicals  
called osmolytes

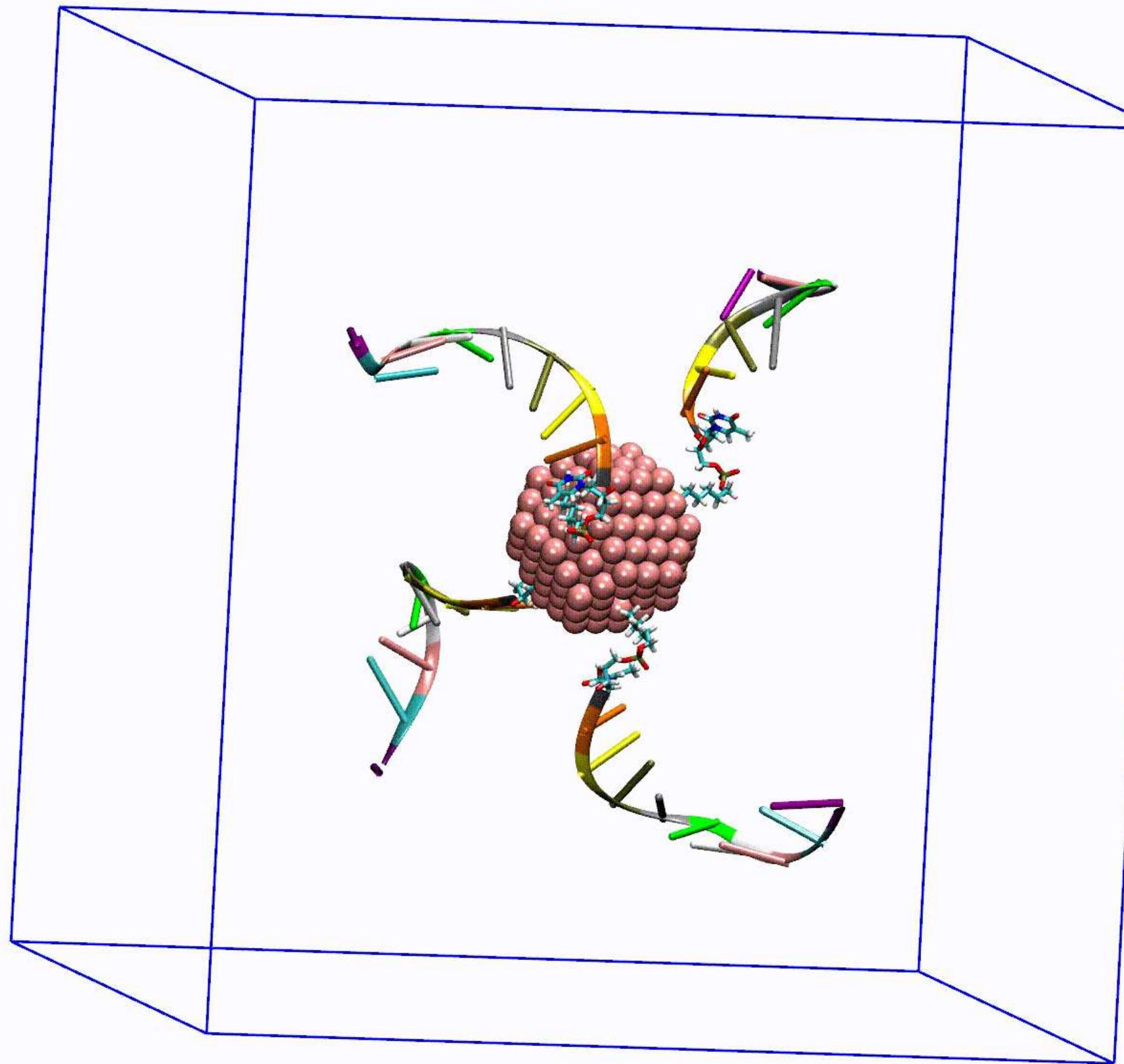


**Smart Polymers**

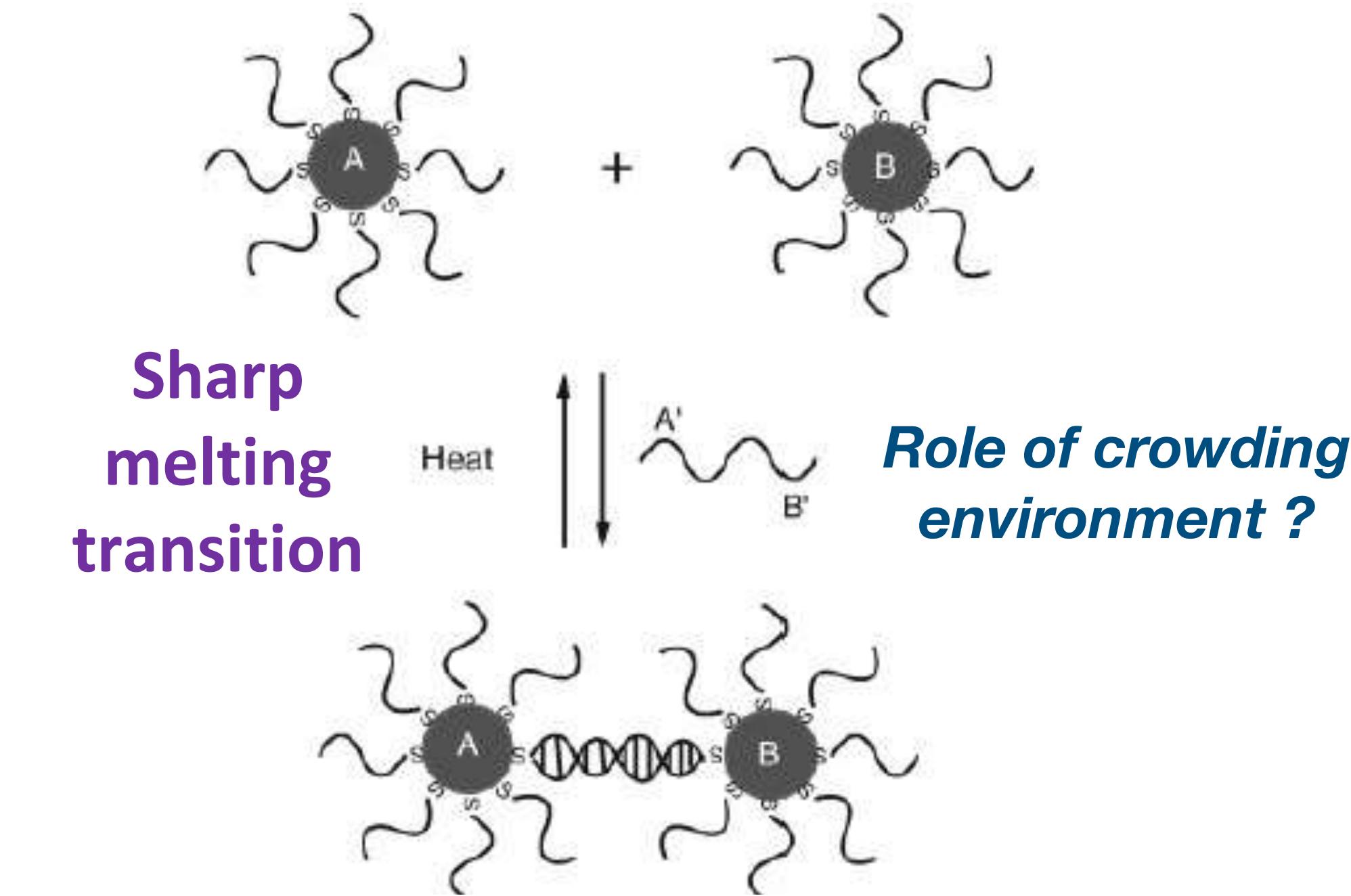
(Change their shape and size  
in response to external  
stimuli)



# Designing functionalized gold nanoparticle self-assemblies in crowded environment

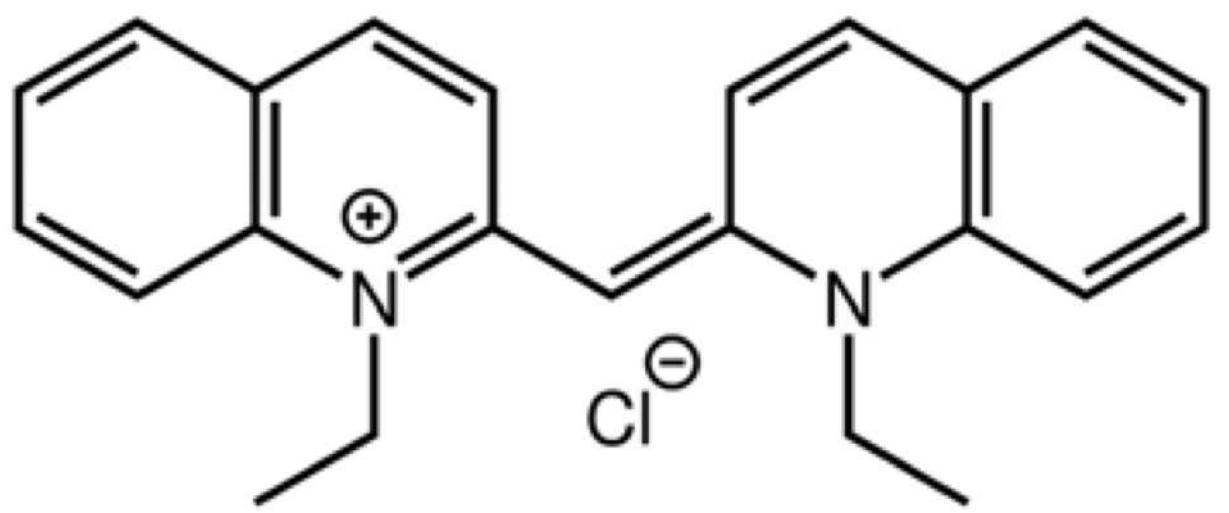


Self-assembled gold nanoparticles find applications in drug delivery and therapeutics

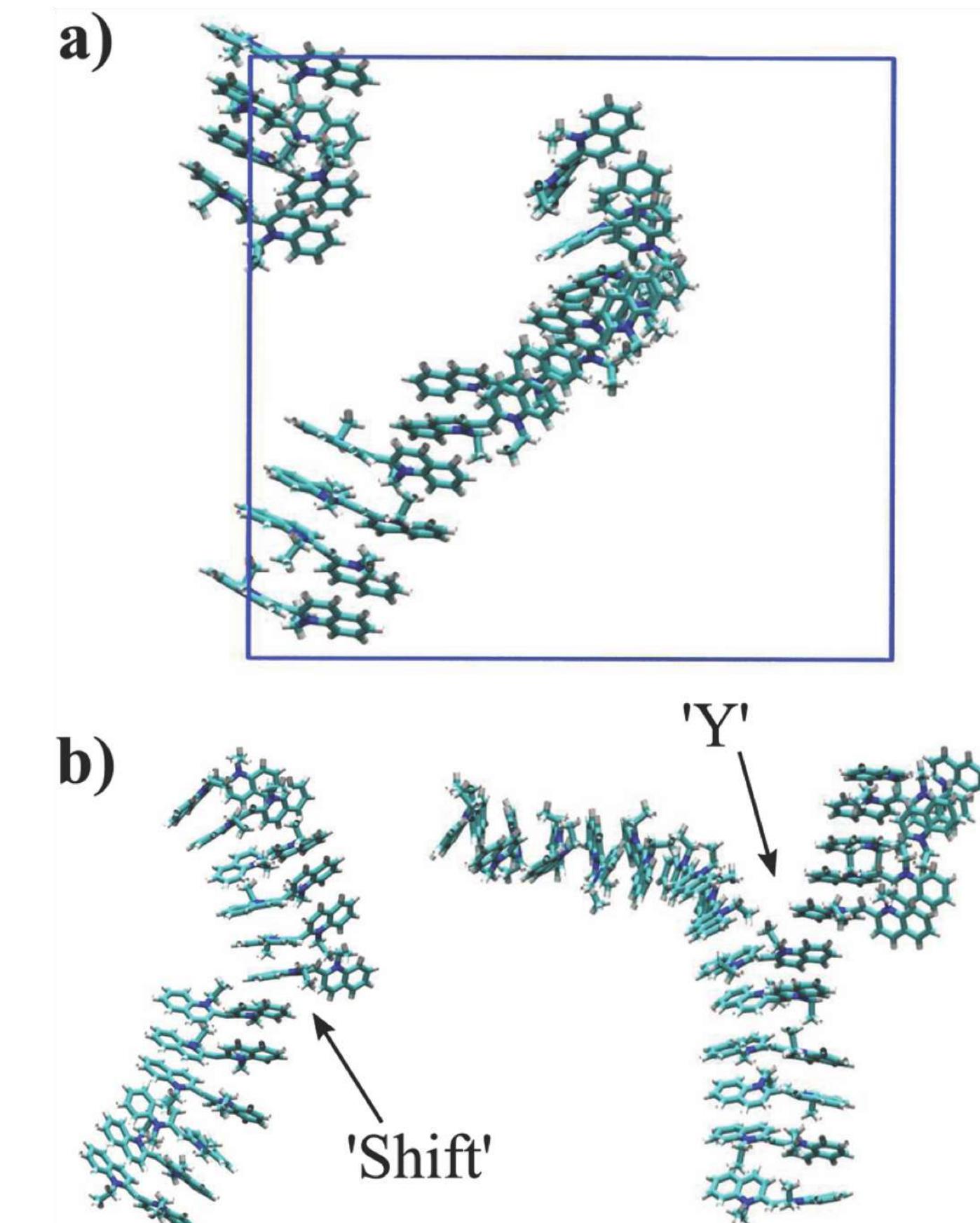
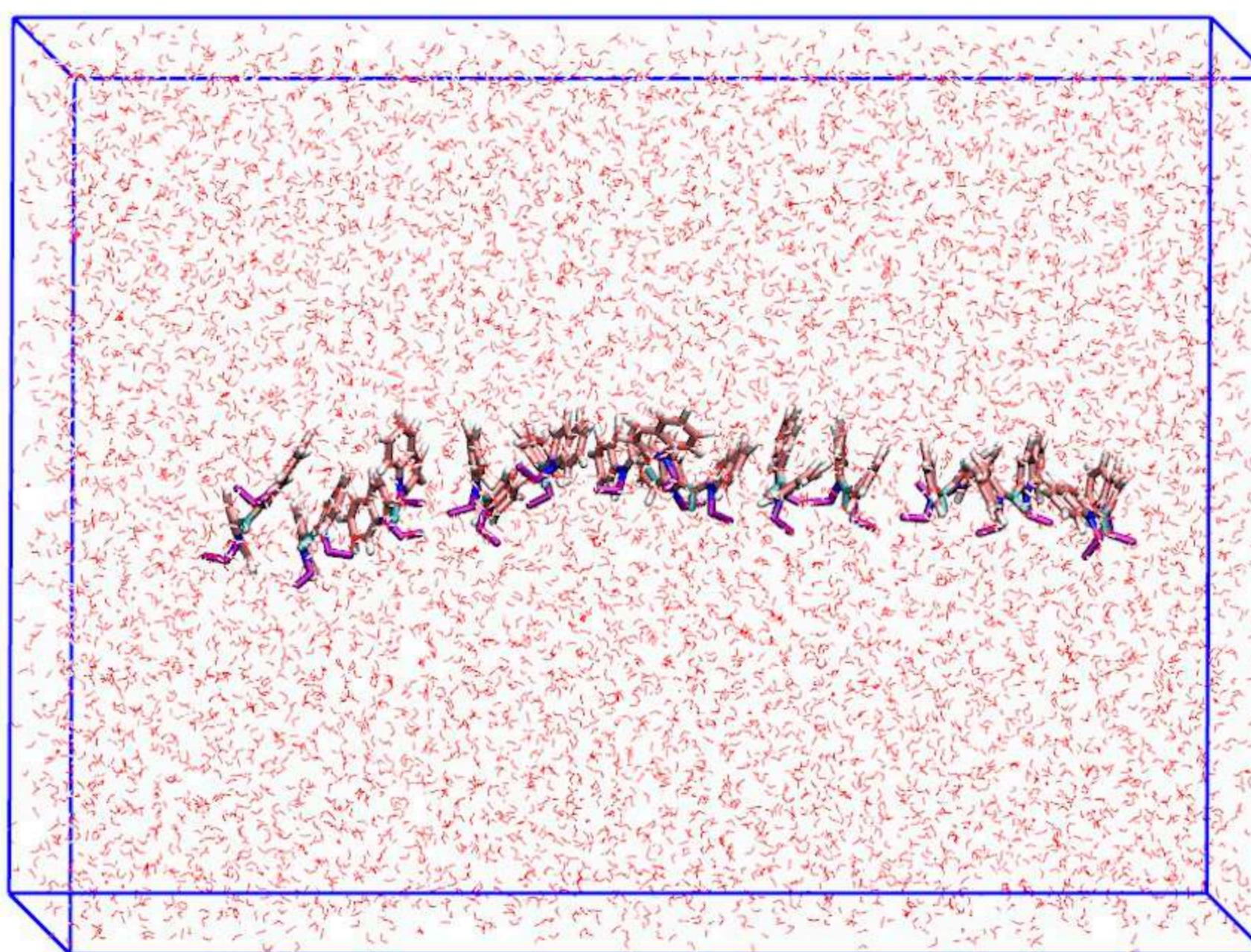


# Designing molecular sensors for living cells

## Self-assembly of fluorescent dyes

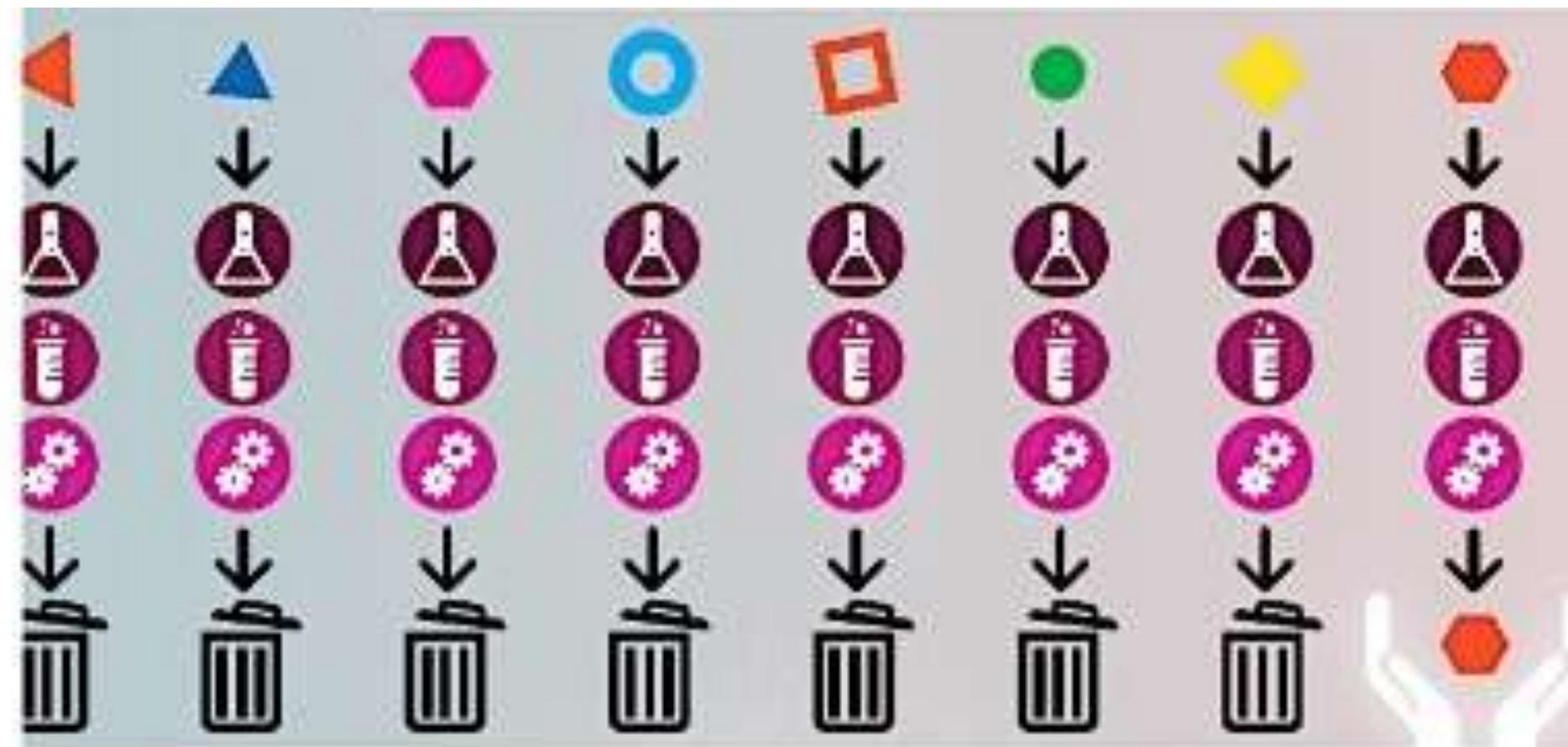


Pseudo isocyanine dye

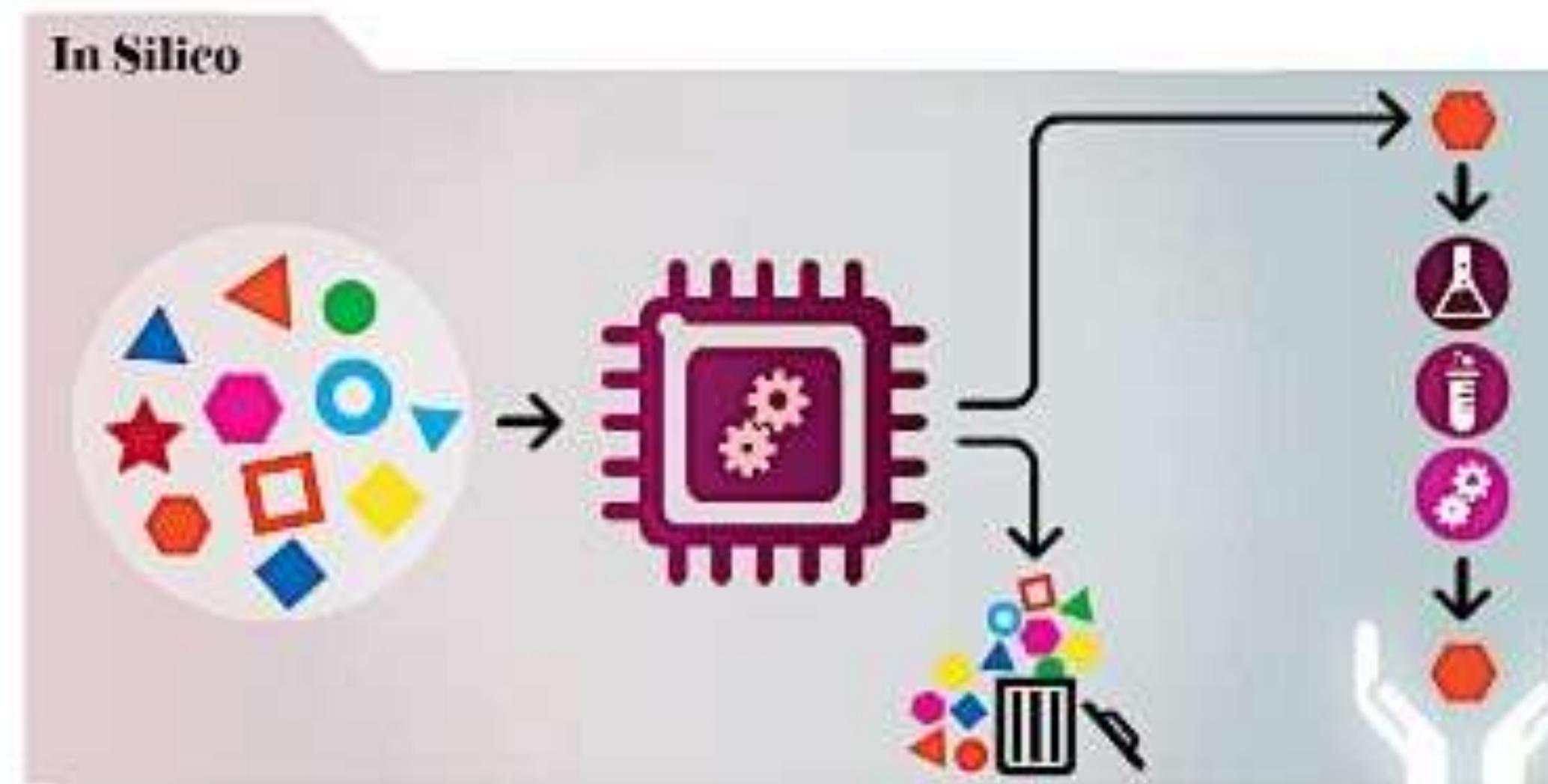


# Artificial Intelligence in Materials Science

## *Experiments*

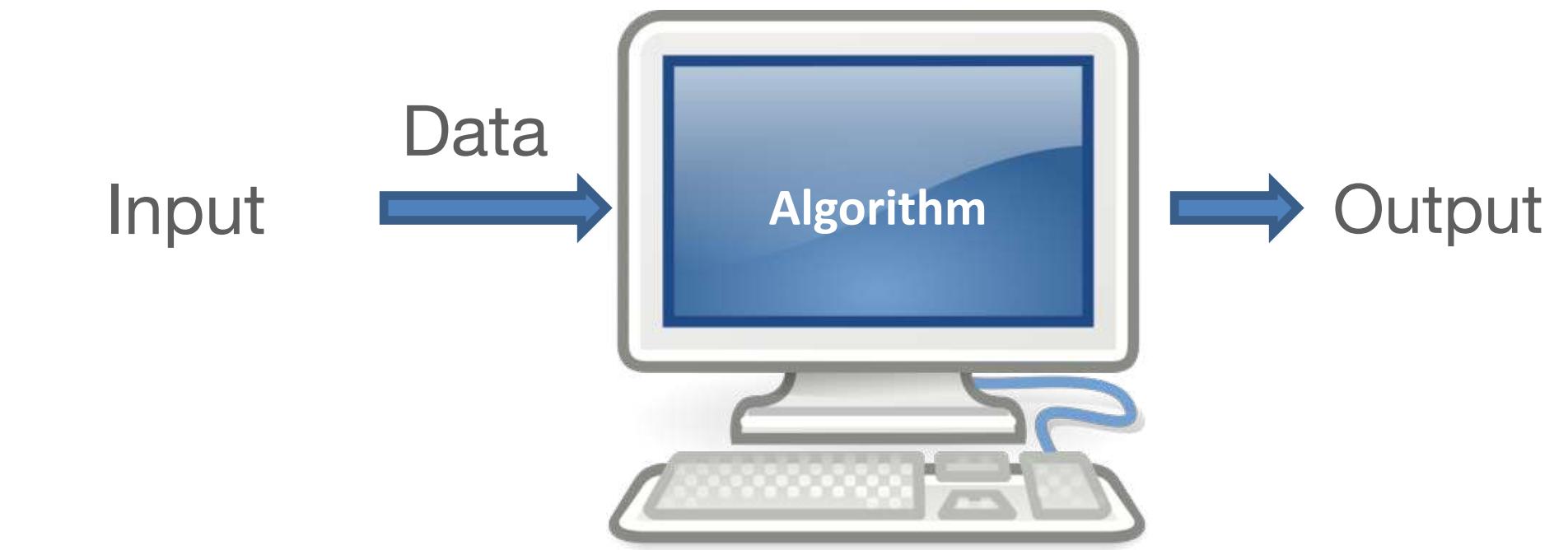


## *Machine learning*



[1] Jain, A., Shin, Y. & Persson, K. A. Computational predictions of energy materials using density functional theory. *Nature Reviews Materials* 1, 15004 (2016).

## General Computing



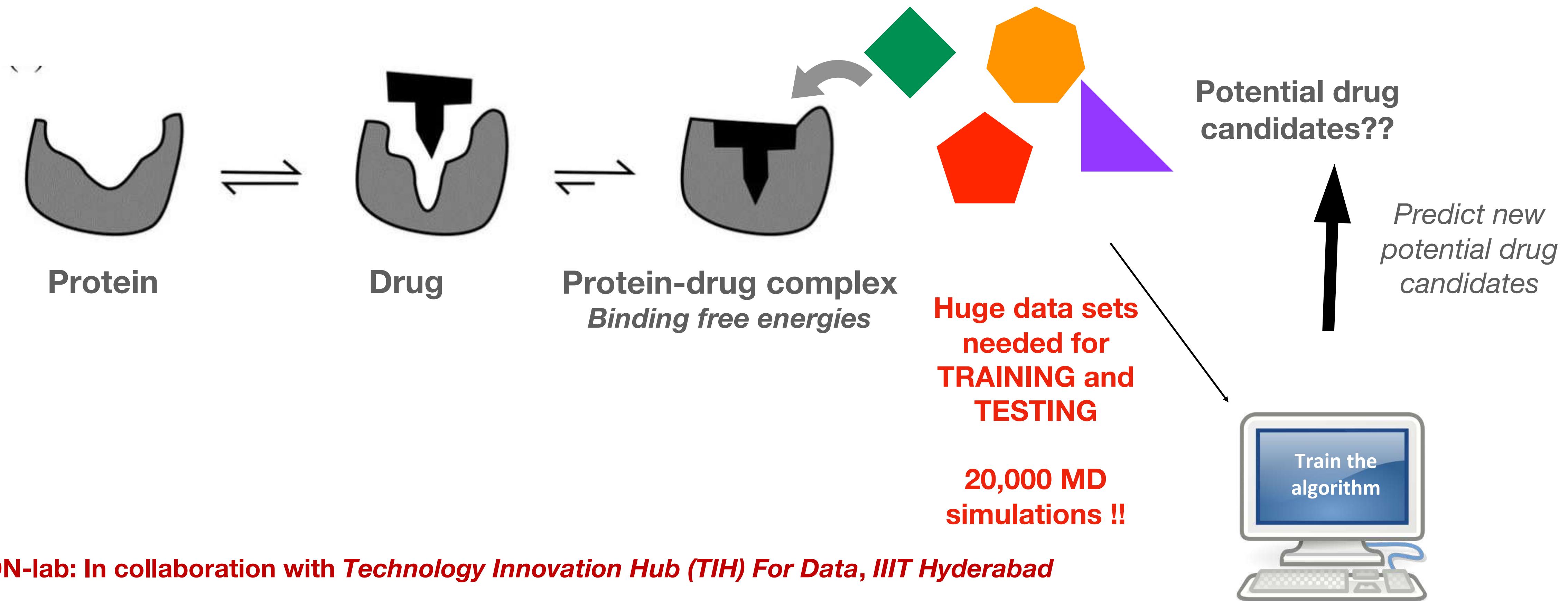
## Machine learning



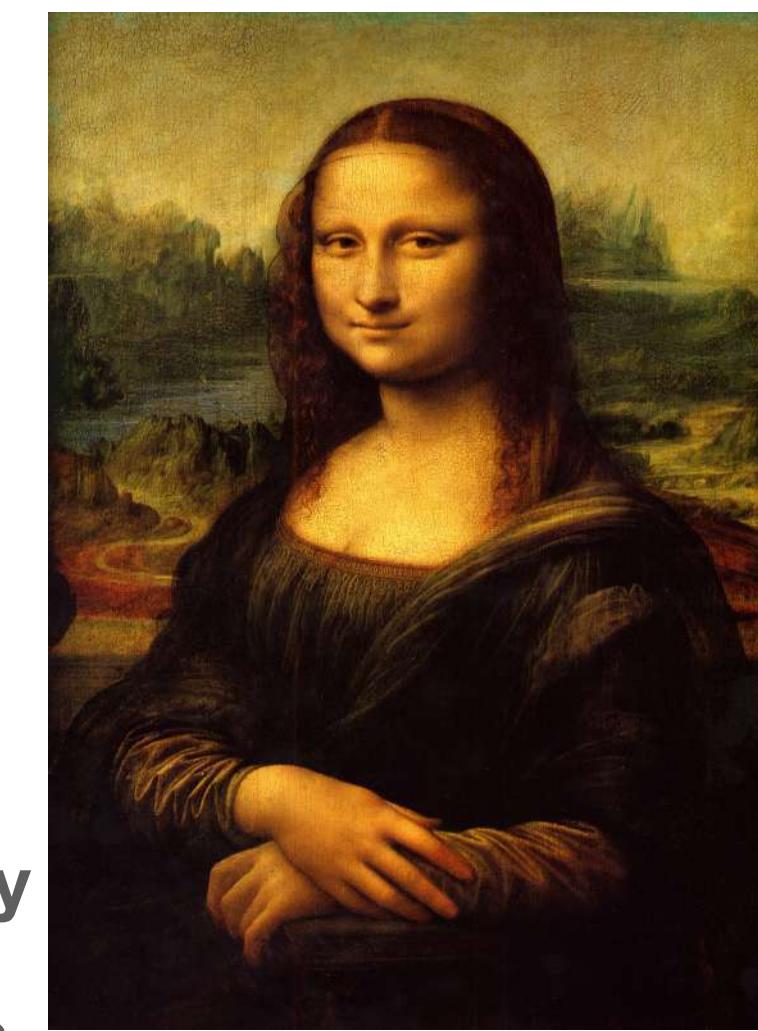
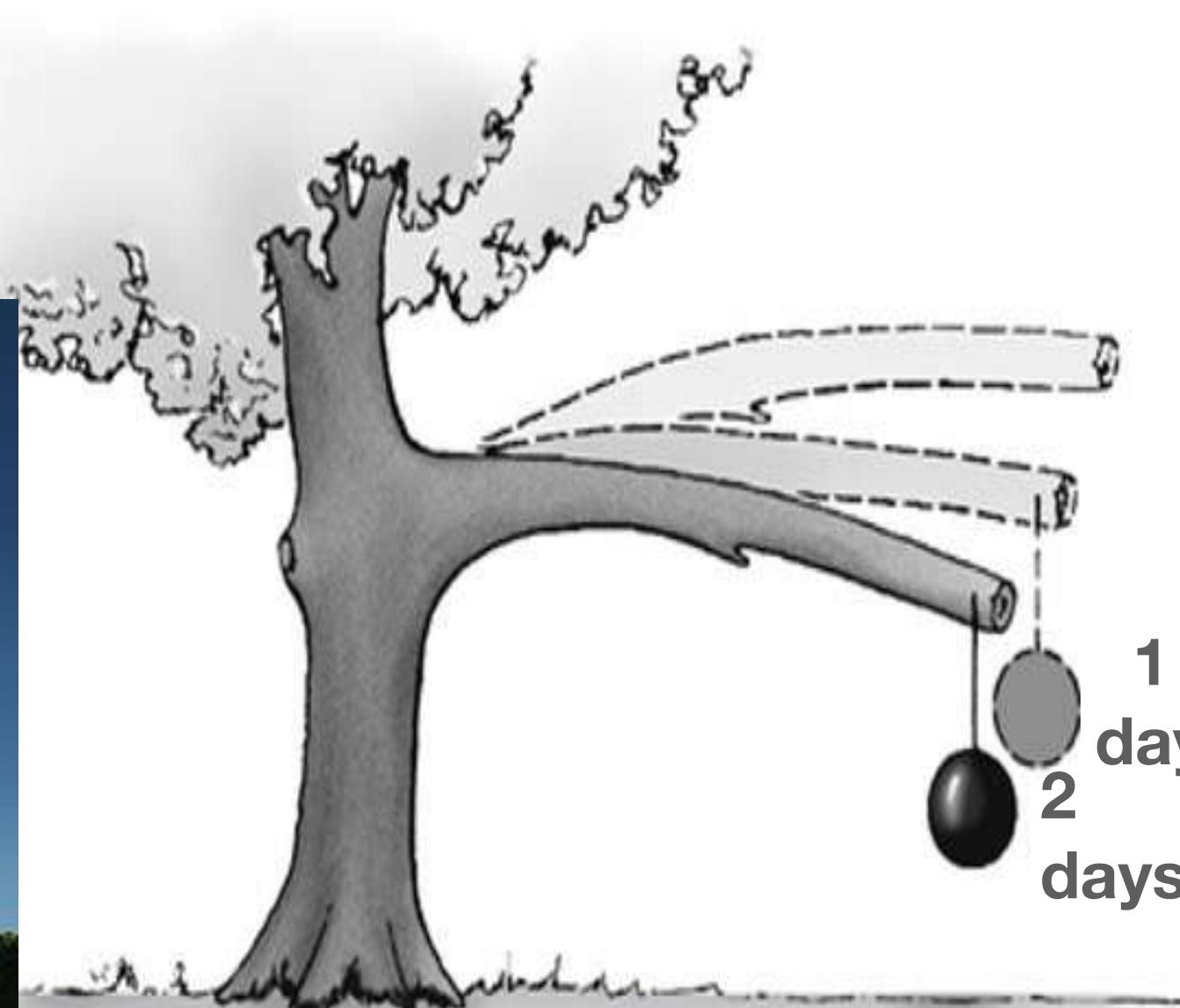
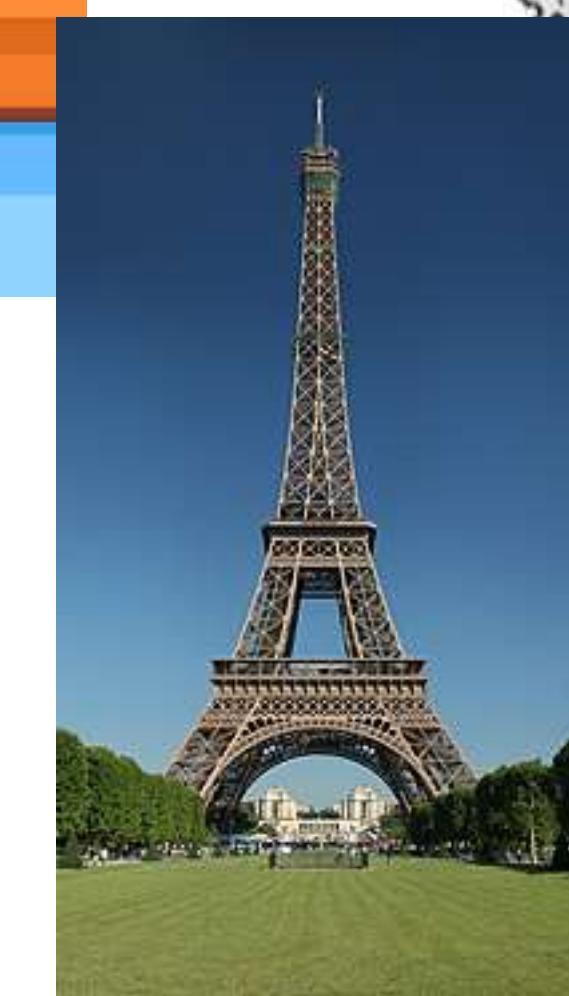
- Materials Discovery
- Materials Design
- Structure-property relationships

# Machine Learning for Drug Design: Generating Ultra-large Datasets for ML models using MD simulation

Which drug molecule can bind to protein to cure the disease?



# Our journey through the last few weeks...



# Some good books to read..

*Food for curious minds!*

- *Brain: The Story of You* (BBC Documentary also available) and *Icognito* by David Eagleman
- *The Double Helix* by James Watson
- *What is Life?* by Erwin Schrödinger
- *Phantoms in the Brain* by V. S. Ramachandran
- *Entropy Demystified* by A. Ben-Naim
- *Surely, You're Joking Mr. Feynman* by Richard P. Feynman
- *The Power of Habit* by Charles Duhigg
- *The New Science of Strong Materials* by J. E. Gordon
- *The Hope Circuit* by Martin Seligman
- *What You can Change and What You Can't* by Martin Seligman

**Thank you all for being an awesome and a wonderful class. You have survived the course topics courageously through the online lectures! ☺**

**Thanks for asking all the interesting questions that helped me in making the lectures more interesting (or were they really interesting!?)..).**

**It has been an amazing experience teaching and interacting with you all !**

***Keep up the creative spirit, inquisitive energy and the burning curiosity!***

***All the very best for your future!***

***Looking forward to working with some of you in near future!***

