



UNIVERSITY COLLEGE LONDON

MENG MECHANICAL ENGINEERING

MECH0074 ENGINEERING IN EXTREME ENVIRONMENTS

TOPIC NOTES

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November 1, 2022

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Chapter 1

Materials, Molecules and Chemistry

1.1 Introduction

- Macorscopic response of material depends on their microscopic structure
- We need to be able to understand physics from molecular to continuum scales

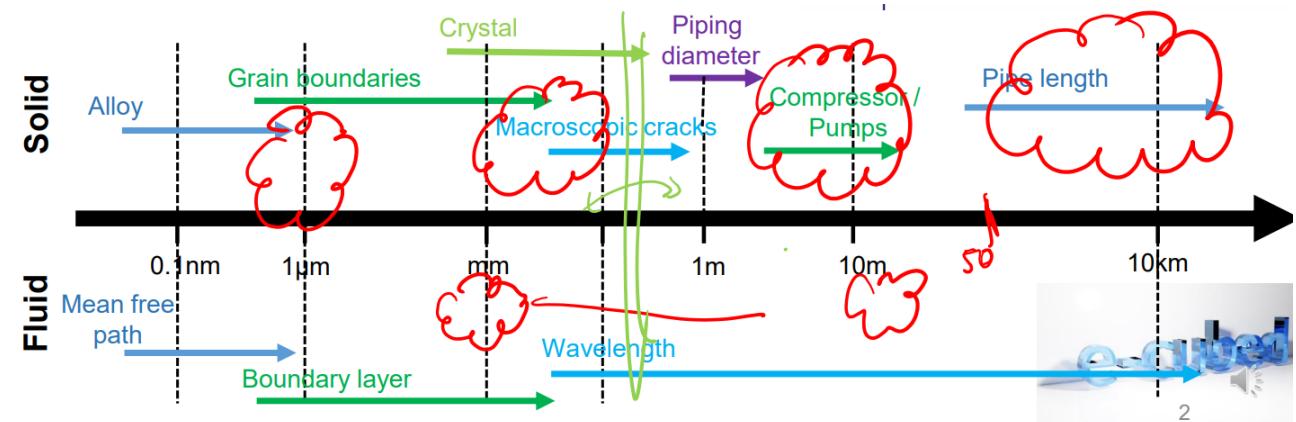


Figure 1.1: Pressure pulsation in a piping system

Cascade of length scales

1.1.1 Compelxity of the problem at different length scales

Complexity of representation changes with the scale.

Molecular	Continuum	Structural
Material is made on this level	Cracks operate on this level	Structures considered at this level
$< 10\mu\text{m}$	$10\mu\text{m} < x < 10\text{ m}$	$> 10\text{ m}$
Short range interactions	Long range interactions	Whole scale interactions
Failure / corrosion / chemistry	Tune model - variables change continuously / smoothly (can account for discontinuous behaviour, e.g. crack)	Long distance interaction - vibration (waves transporting energy)

Table 1.1: Cascade of length scales

Domain	Process
Bulk	Plasticity
Internal boundary	Hydrogen embrittlement - plastic deformation / slip
External boundary	Corrosion - chemistry

Table 1.2: Micrograph

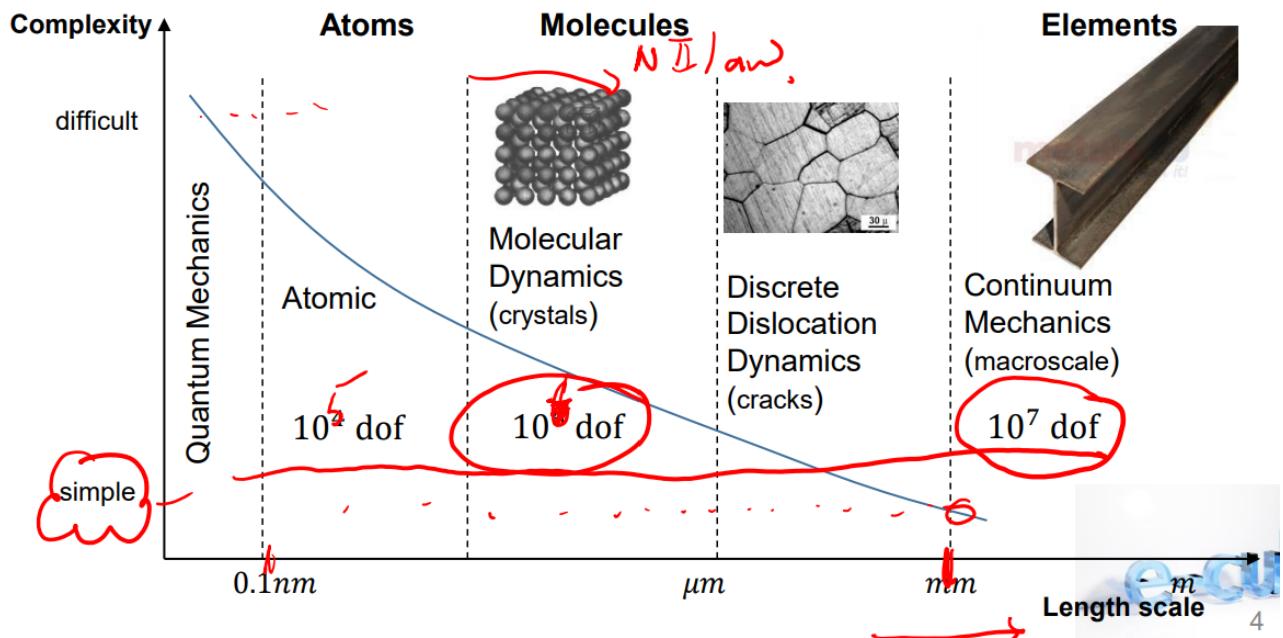


Figure 1.2: Graph to show complexity against scale.

1.1.2 Why focus on small scales?

- Small scale defects lead to crack initiation and propagation under external loading
- Failure can be corrected by changing material properties, for example, toughness
- Source of defects: complex chemical process (chemistry / corrosion) leads to corrosion at the surface
- Macroscale process is linked to microscale action
- Hypersonic flow - ionisation is non-continuum effect
- Analogy between defective liquids / solids

Note: turbulence is controlled by small vortices.

Micrograph

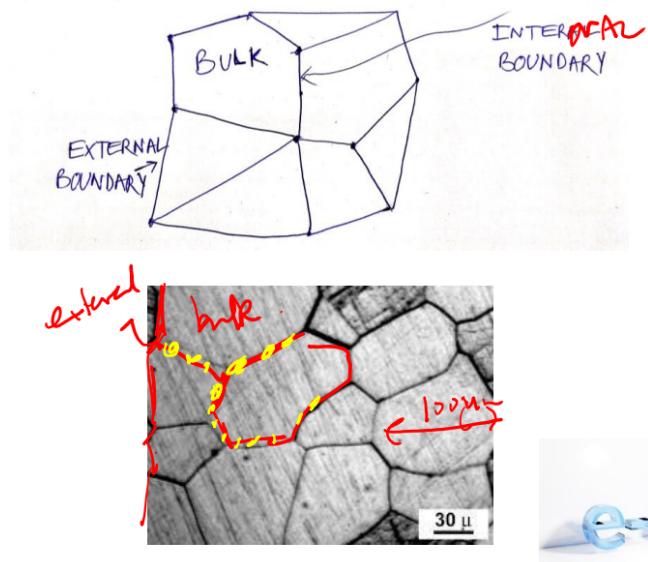


Figure 1.3: Graph to show complexity against scale.

Internal grain processes

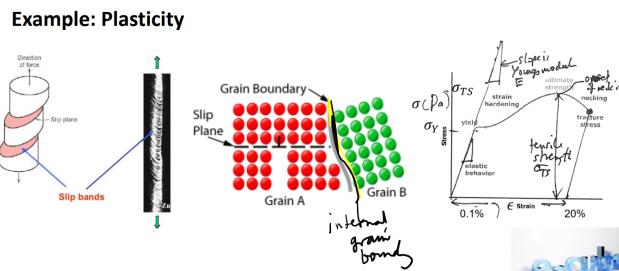


Figure 1.4: Example of plasticity from internal grain process level.

Internal boundary (hydrogen embrittlement - plastic deformation / slip)

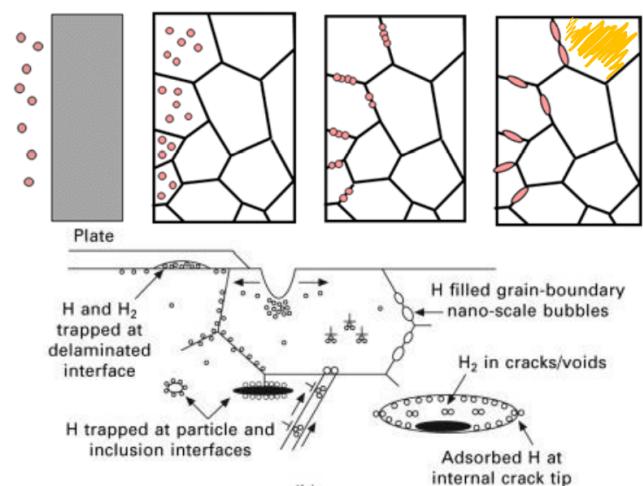


Figure 1.5: Hydrogen embrittlement - plastic deformation / slip

Matter	Modelling approach	
Solid	Atomistic	Continuum
Gas	Kinetic theory	Continuum
Liquid	Molecular	Continuum

Table 1.3: Categorisation of matter

External boundary (corrosion)

Corrosion happens over a long time and a range of scales. We need to understand how ions move around and interact with materials.

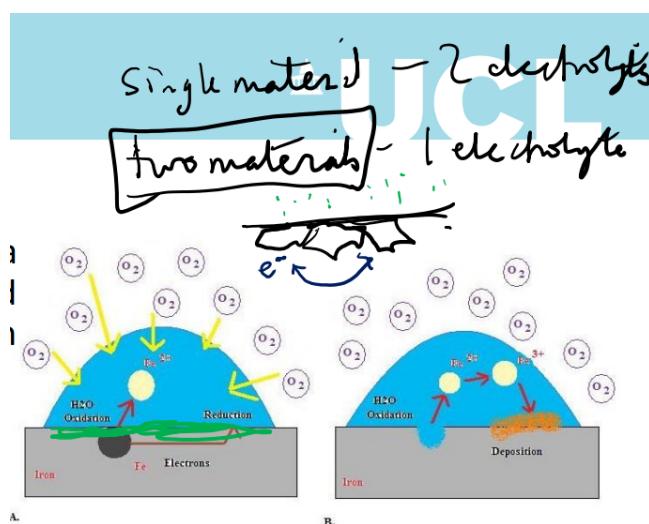
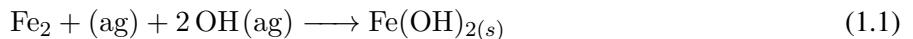


Figure 1.6: Rust corrosion from grain boundary level.

1.2 Categorisation of matter

Switch between states are due to p , V and T and is represented by phase diagram. States of matter have been part of most religious and scientific texts for the last two thousand years, with water (aqua), fire (ignis), air (aer) and earth (terra) with the fifth being the void.

1.3 Atomistic view of matter

Typical length scale:

- Diameter of atom is $0.1 \text{ nm} = 1 \times 10^{-10} \text{ m} = 1 \text{ angstrom}$
- Nucleus diameter is $1 \times 10^{-15} \text{ m}$ (hydrogen) to $15 \times 10^{-15} \text{ m}$ (uranium-238)

1.3.1 Bulk characteristic of materials

The aim is to understand the relationship between the macrostructure and the microstructure. Key measures are:

- Young's modulus $E = \frac{d\sigma}{d\varepsilon} \Big|_{\varepsilon \rightarrow 0}$

Properties		Definition
Elastic modulus	E (Pa)	Measure of material resistance to deformation.
Yield stress	σ_Y (Pa)	Measure of stress at which the elastic behaviour disappears and plastic behaviour initiates.
Hardness	HBW	Measure of material resistance to indentation
Creep		Time-dependant deformation at high temperature and constant stress.
Toughness	K (J m^{-3})	Resistance to crack propagation.
Ductility	ϵ_T	Material's ability to undergo plastic deformation.

Table 1.4: Key points on material properties

- Tensile stress: σ_{TS}
- Yields stress: σ_Y
- Ductility: ϵ_T

It is important to understand the following: How are they related to the microstructure?

1.3.2 Newtonian model of matter

Useful for biological, physical problems, solids, liquids and gases. This is based on a description of matter as a collection of point particles, an approach that is useful for gases, liquid and solids. The dynamics of the i-th molecule is:

$$\underline{F}_i = \sum_{j,j} \neq \nabla U(x_i, x_j) \quad (1.3)$$

Located at point \underline{x}_i whose dynamics are:

$$m_i \frac{d\underline{v}_i}{dt} = \underline{F}_i \quad (1.4)$$

$$\underline{v}_i = \frac{d\underline{x}_i}{dt} \quad (1.5)$$

The formulation requires the form of the interaction stated using the Lennard-Jones 6-12 potential:

$$U = 4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right) + \dots \quad (1.6)$$

The difficulty is that neighbourhood lists are kept and only sum over local interaction of molecules.

- Not hard collision
- Time stepping fixed
- Potentials can be empirical or chosen to now slow down calculations

$$U = U_{stretch} + U_{bend} + U_{torsion} + U_{vanderWaals} + U_{electro} + U_{cross} \quad (1.7)$$

Research gaps:

- Link between continuum and molecular
- Quantim - mechanical models

1.3.3 Vibrational modes and energy

Mechanical representation of matter. Molecules interact with their neighbours and fields. Interaction may be quite far, particularly when charges are important. We are familiar with how degrees of freedom influence properties of a gas, especially through the isentropic index. Energy is stored in various modes of vibration e.g. gas. This is called classical molecular dynamics.

1.3.4 Molecular description of material properties

Primary bonds

Ionic and covalent bonds are extremes with most (electron distribution) bonds lying between (polar covalent)

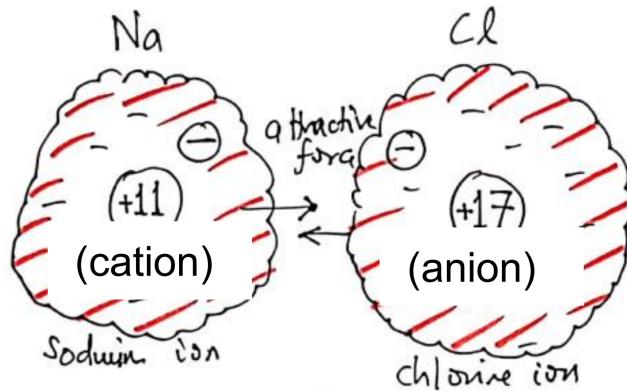


Figure 1.7: Ionic bond (electrovalence)

$$F = \frac{q_1 q_2}{4\pi\epsilon_0 r^2} \quad (1.8)$$

$$U = U_i - \frac{q^2}{4\pi\epsilon_0 r} + \frac{B}{r^n} \quad (1.9)$$

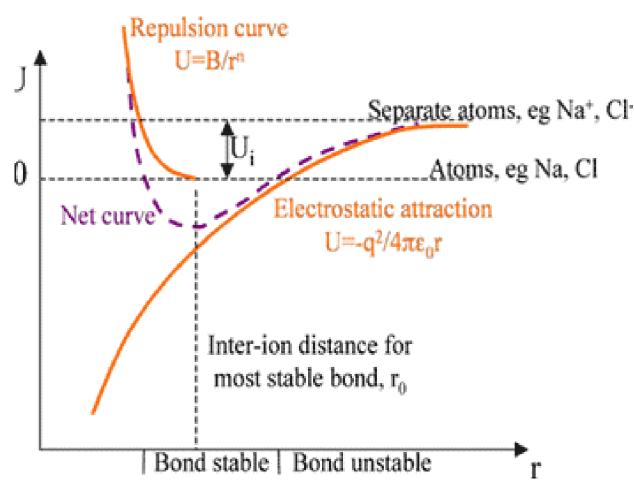


Figure 1.8: Bond stability.

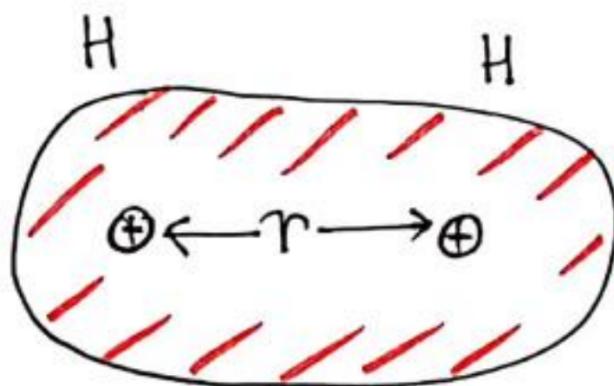


Figure 1.9: Covalent bond (covalence). Note the overlap of electron orbit.

$$U = -\frac{A}{r^m} + \frac{B}{r^n}, \quad m < n \quad (1.10)$$

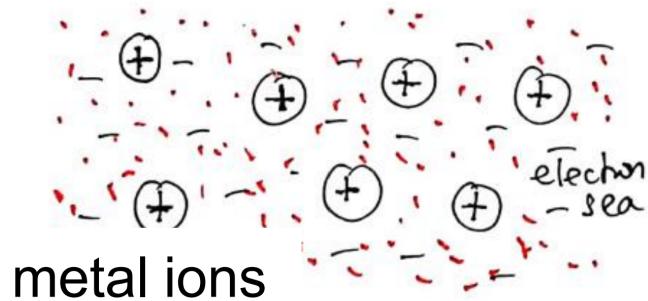


Figure 1.10: Metallic bond (electron cloud).

$$e = 1.6 \times 10^{-19} \text{ C} \quad (1.11)$$

$$\epsilon_0 = 8.8 \times 10^{-12} \text{ Nm}^2 \text{C}^{-2} \quad (1.12)$$

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J} \quad (1.13)$$

Secondary bonds

The secondary bonds are important - without them many gases would not condense. The relative displacement of the positive and negative charge gives rise to a dipolar force. This gives rise to an attractive force. Most usual form is the Lenard Jones 6-12 potential.

$$U = -\frac{A}{r^6} + \frac{B}{r^n} \quad (1.14)$$

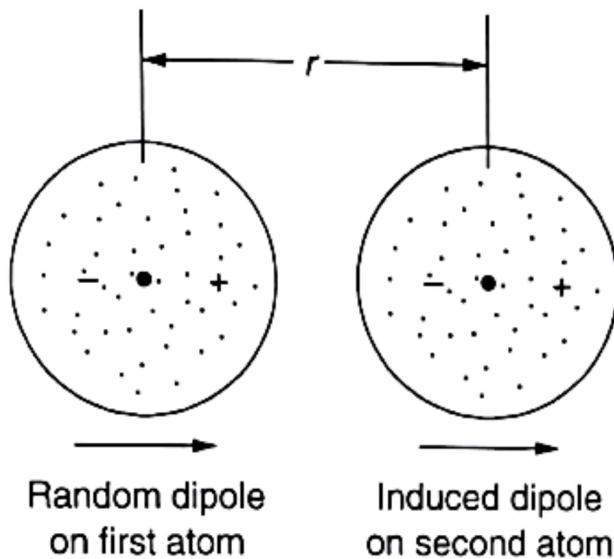


Figure 1.11: Secondary bonds. Note: long range attractive force - dipole-dipole interactions. Overlapping electron orbits - repulsive.

Physical basis of Young's Modulus

Classical mechanics:

$$m \frac{dv}{dt} = \frac{dU}{dr} \quad (1.15)$$

where U is the potential energy. At equilibrium:

$$\frac{dU}{dr} = 0 \quad (1.16)$$

so that close to this point, the energy potential can be expanded to give:

$$m \frac{d^2 r}{dt^2} = \left(\frac{d^2 U}{dr^2} \right) (r - r_0) \quad (1.17)$$

Around equilibrium point:

$$F = S_0 (r - r_0) \quad (1.18)$$

$$S_0 = - \frac{d^2 U}{dr^2} \quad (1.19)$$

The stress is:

$$\sigma = NS_0 (r - r_0) = \frac{S_0 (r - r_0)}{r_0^2} \quad (1.20)$$

The Young's modulus is:

$$E = \frac{\sigma}{\epsilon} = \frac{S_0}{r_0} \quad (1.21)$$

Estimate:

$$S_0 = \frac{\alpha q^2}{4\pi\epsilon_0 r^2} \quad (1.22)$$

$$E = \frac{\sigma}{\epsilon} = - \frac{\frac{d^2 U}{dr^2}}{r_0} = \frac{\delta e^2}{4\pi\epsilon_0 r_0^4} \quad (1.23)$$

Atom spacing:

$$\bar{r}_0 \approx 8.54$$

(1.24)

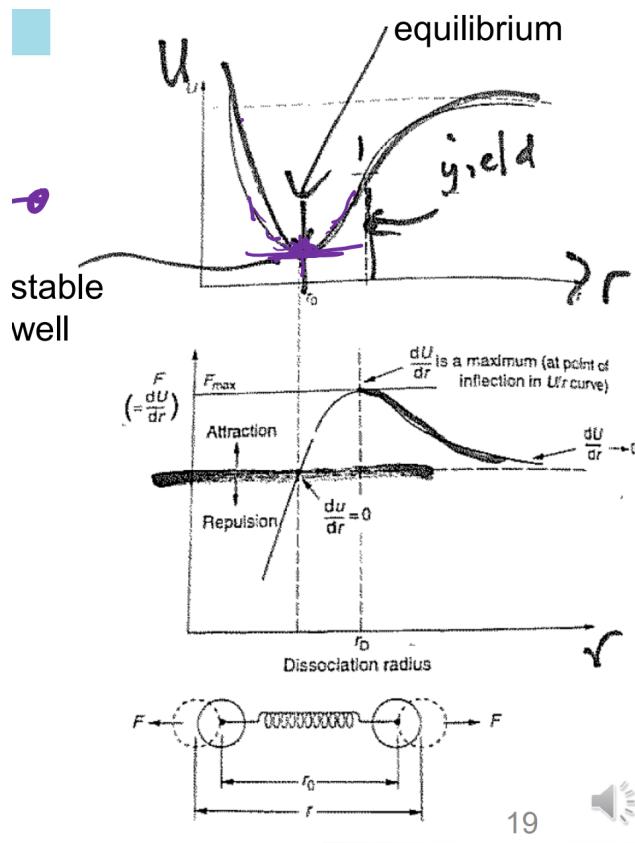


Figure 1.12: Young's modulus from atomic perspective.

Comparison between molecular and macroscopic measurements

Bond type	S_0 / Nm^{-1}	Young's modulus estimate E / GPa	Measurement
Covalent	50 - 180	200 - 1000	1000 (diamond)
Metallic	15 - 75	60 - 300	200 (nickel)
Ionic	8 - 24	32 - 96	15 - 91 (alkali halides)
H-Bond	2 - 3	8 - 12	9.1 (ice)
van der Waals	0.5 - 1	2 - 4	0.01 - 2 (rubber to nylon)

Table 1.5: Comparison between molecular and macroscopic measurements.

Estimation of yield stress

Returning to the molecular model since:

$$U = \epsilon \left(-\frac{A}{r^6} + \frac{B}{r^{12}} \right) \quad (1.25)$$

$$U'' = \epsilon \left(-\frac{6 \times 7A}{r^8} + \frac{12 \times 13B}{r^{14}} \right) \quad (1.26)$$

Then, maximum stress is:

$$\sigma_Y \approx \frac{E}{8} \quad (1.27)$$

Therefore:

$$\frac{\sigma_Y}{E} \frac{1}{8} \quad (1.28)$$

This estimated ratio is good for ceramics, but not good for metals. So what is missing from a molecular description?

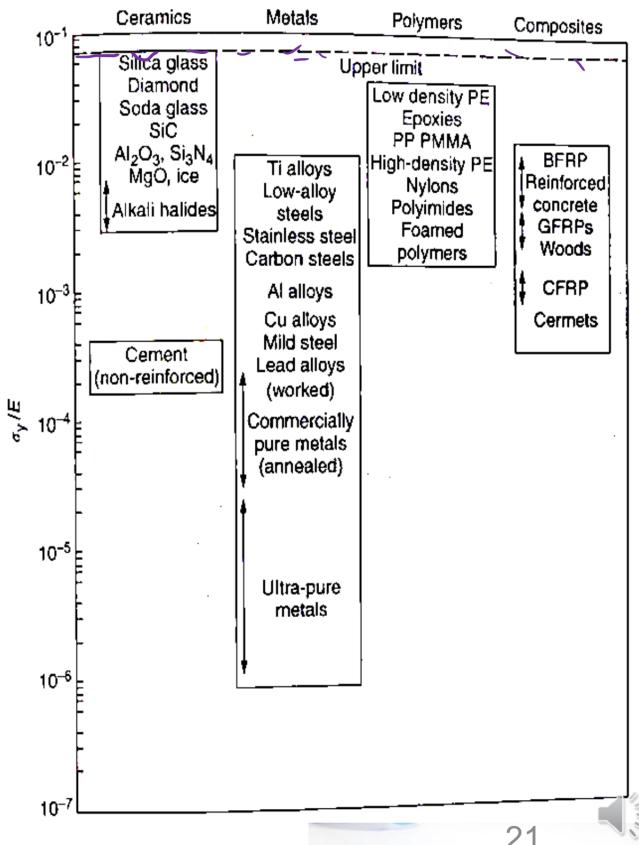


Figure 1.13: Graph to show yield stress ratio for different materials.

1.3.5 Material classification

- Metals
 - Ferrous metals and alloys
 - Non ferrous metals and alloys
 - (focus on here)
- Polymeric (non metallic, non crystalline)
 - Thermoplastic plastics
 - Thermoset plastics
 - Elastomers
- Ceramics
 - Glass
 - Diamond
 - Glass ceramics
- Composites (everything else)

- Metal-matrix composites
- Sandwich structures
- Concrete

Three common configurations

Type	Name	Description	Example
BCC	Body centred cube - 2 atoms	Harder and less malleable Packing factor 0.68	Lithium, Sodium, Potassium
FCC	Face centred cube	malleable, softer 0.74	Chromium, Barium, Alpha-iron Copper, Gold, Aluminium Iridium, Lead, Nickel, etc.
HCP	Hexagonal close packed	6 atoms Packing ratio 0.74	Cadmium, Magnesium, Titanium Zinc, Zirconium

Table 1.6: Configurations of atoms.

Solidification and crystal growth

Under normal circumstances, crystal growth starts at many nucleation points. Solidification leads to crystals growing and stop growing when they meet another crystal. A crystal is usually called a grain. The boundary between grains is the grain boundary where structure is disordered. This is controlled using nucleation points and directional solidification and liquid freezing-dendritic growth and shrinkage occurs during cooling.

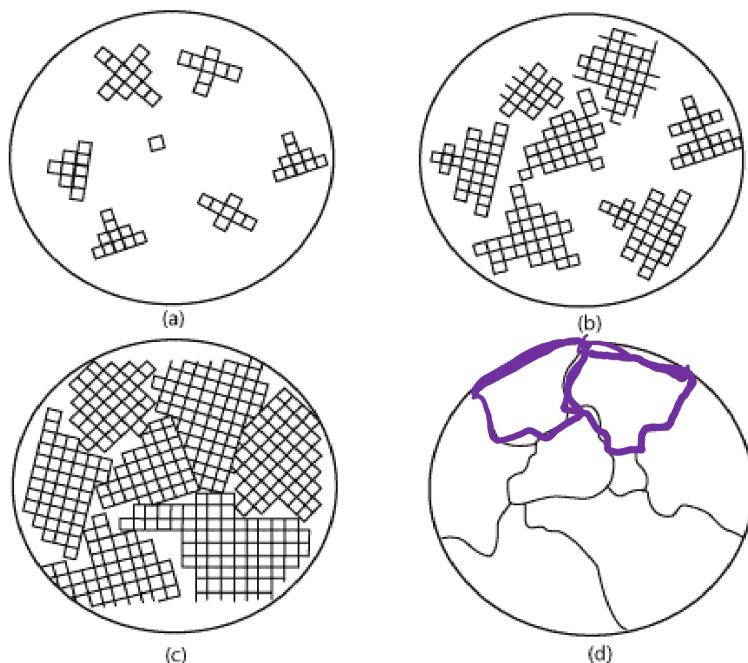


Figure 1.14: Nucleation of crystals.

Crystal defects

Three types of defects:

1. Point defects: which are places where an atom is missing or irregularly placed in the lattice structure.
Point defects include lattice vacancies, self interstitial atoms, substitution impurity atoms and interstitial impurity atoms

2. Linear defects: which are groups of atoms in irregular positions. Linear defects are commonly called dislocations
3. Planar defects: which are interfaces between homogeneous regions of the material. Planar defects include grain boundaries, stacking faults and external surfaces

Atomistic view of plastic deformation

Elastic deformation - stress is small, the metal can recover to initial state when the stress is removed. This involves stretching the bonds but atoms do not move over one another.

Plastic deformation - stress is large, plastic deformation involves the breaking of a limited number of atomic bonds by the movement of dislocations. Since the energy required to move is lowest along the densest planes of atoms, dislocations have a preferred direction of travel within a grain of the material. This results in slip that occurs along parallel planes within the grain. These parallel slip planes group together to form slip bands. A slip band appears as a single line under the microscope, but it is in fact made up of closely spaced parallel slip planes as shown in the image.

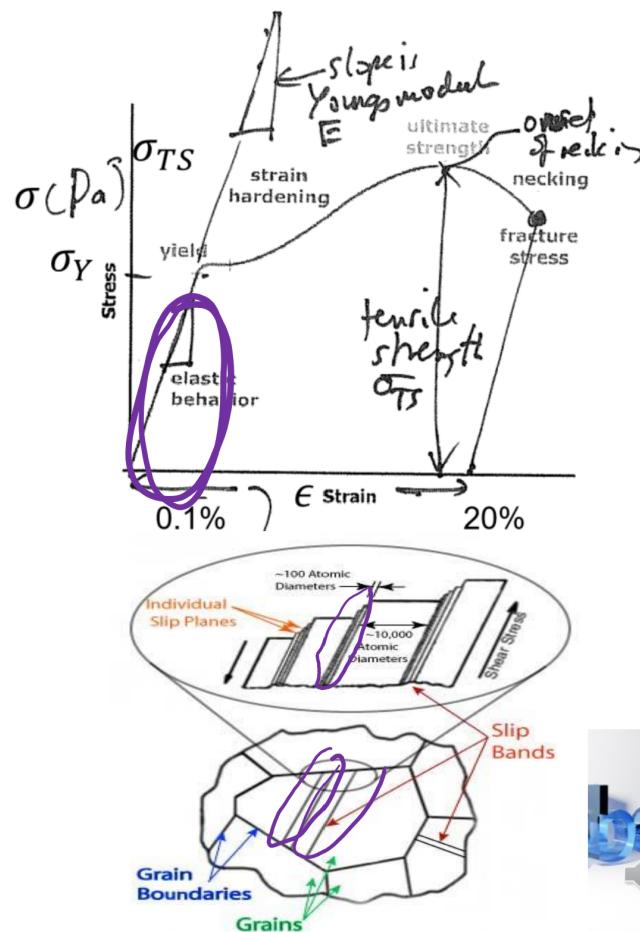


Figure 1.15: Stress-strain curve.

Fatigue crack initiation

The life of a fatigue crack has two parts, initiation and propagation. Dislocations play a major role in the fatigue crack initiation phase. It has been observed in laboratory testing that after a large number of loading cycles dislocation pile up and form structures called persistent slip bands. Initiation has a molecular origin.

Topological change in crystal structure

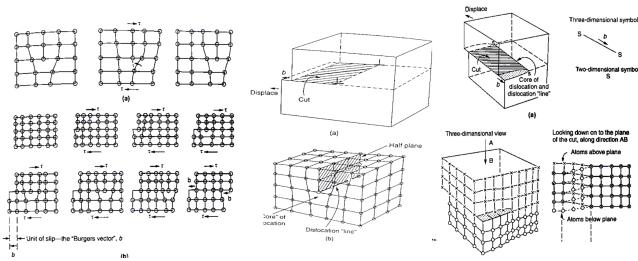


Figure 1.16: Topological changes in crystal structure.

1.4 Kinetic theory of gases

Statistical 19th century view of macroscopic properties of gas. Boltzmann and colleagues developed new techniques to describe matter. Heavily influenced the theory of turbulence ← based on kinetic theory of a gas.

$p = \rho RT$ origin with statistical theory.

This is an excellent macroscopic model of matter. The problem is that it does not work well for low pressure, high pressure or when density is low (and continuum concepts don't work).

1.4.1 Speed of molecules

Results tell us about average speed but not the distribution.

$$n_v(E) = n_0 e^{-\frac{E}{k_B T}} \quad (1.29)$$

where, $n_v(E)$ is the Boltzmann distribution which coups a lot. The speed of the molecules satisfies the Maxwell-Boltzmann distribution.

$$f(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} v^2 \exp \left(-\frac{mv^2}{2k_B T} \right) \quad (1.30)$$

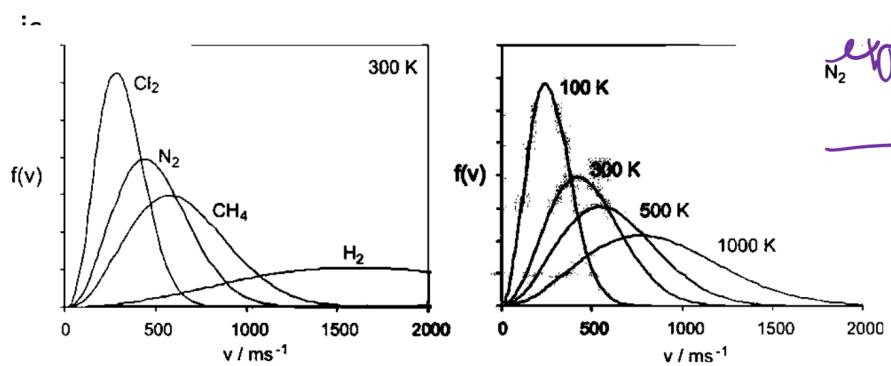


Figure 1.17: Speed of molecules.

1.4.2 Equations of state of real gases

The molecular continuum view of matter are linked. Virial equation:

$$pV = nRT \left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \right) \quad (1.31)$$

where B, C are the second and third virial coefficients. Van der Waals equation:

$$\left(p + a \frac{n^2}{V^2} \right) (V - nb) = nRT \text{ or} \quad (1.32)$$

$$P = \frac{nRT}{V - nb} - a \frac{n^2}{V^2} \quad (1.33)$$

n is the number of moles. nb is the volume excluded since molecules cannot overlap. $\frac{an^2}{V^2}$ pressure reduced due to attractions between pairs of molecules.

Critical constants for van der Waals equation

Solving these two equations in two unknowns (temperature and molar volume) gives the critical temperature and critical molar volume:

$$T_c = \frac{8a}{27Rb} \quad (1.34)$$

$$V_c = 3b \quad (1.35)$$

Van der Waals

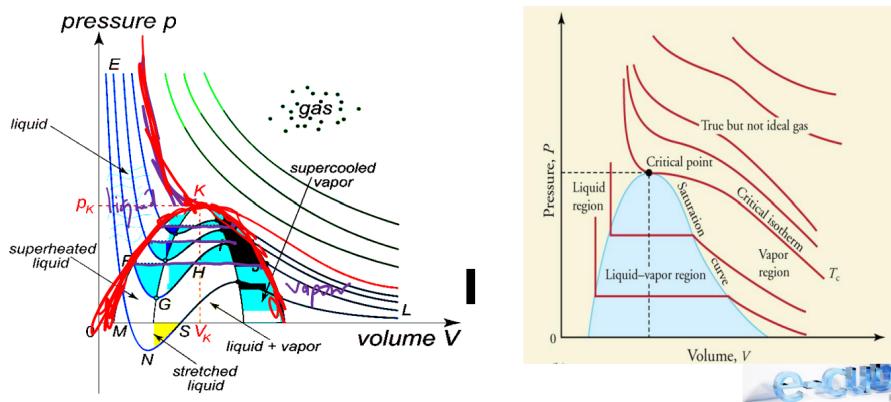


Figure 1.18: Van der Waals.

Link between molecular and microscopic

Most of the important 19th century breakthroughs were determining link between macroscopic (could be seen) and microscopic (could not be seen). For example, Brownian motion:

$$\frac{RT}{5\pi\mu dN_A} = D = \lim_{t \rightarrow \infty} \frac{(x^2)}{2t} \approx 10 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \quad (1.36)$$

This represented a link between Avogadro's constant and macroscopic movement of particles. Here $N_A = 6 \times 10^{23} \text{ mol}^{-1}$. Theory by Einstein (1905) and Sutherland (1905). Millikan's experiments: determination of the charge on an electron. The link between molecular and microscopic last areas of modern science to be worked out.

Einstein theory and Millikan's experiment

Based around kinetic theory of gases and momentum change due to collision. Pressure is a manifestation of a:

$$P = \frac{2}{3} \frac{N}{V} \frac{1}{2} m_0 \bar{v}^2 \quad (1.37)$$

$$\therefore PV = nRT = \frac{N}{N_a} RT = Nk_B T \quad (1.38)$$

$$\therefore KE = \frac{3}{2} N k_B T = \frac{3}{2} nRT = \frac{NDF}{2} nRT \quad (1.39)$$

where NDF is number of degrees of freedom.

Model assumptions

- No intermolecular forces between the gas particles
- The volume occupied by the particles is negligible compared to the volume of the container they occupy
- The only interactions between the particles and with the container walls are perfectly elastic collisions.
- Real gas, the atoms or molecules have a finite size, and at close range they interact with each other through a variety of intermolecular forces, including dipole-dipole interactions, dipole induced dipole interactions and van der Waal's (induced dipole - induced dipole) interactions
- When applied to real gases, the ideal gas model breaks down when molecular size effects or intermolecular forces become important. This occurs under conditions of high pressure , where the molecules are forced close together and therefore interact strongly, and at low temperatures, when the molecules are moving slowly and intermolecular forces have a long time to act during a collision

The pressure at which the ideal gas model starts to break down will depend on the nature and strength of the intermolecular forces between the gas particles, and therefore on their identity. The ideal gas model becomes more and more exact as the pressure is lowered, since at very low pressures the gas particles are widely spaced apart and interact very little with each other.

$$\text{number density} = \frac{N}{V} = \frac{nN_A}{V} \quad (1.40)$$

$$\Delta p_x = (2mv_x) \left(\frac{1}{2} \frac{nN_A}{V} Av_x \Delta t \right) = \frac{nMAv_x^2 \Delta t}{V} \quad (1.41)$$

$$p = \frac{F_x}{A} = \frac{nMv_x^2}{V} \quad (1.42)$$

1.5 Chemistry for engineers

Chemistry has a molecular origin. The engineering challenge is how to include chemistry into multiphysics problems. Chemistry might be simple:

