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

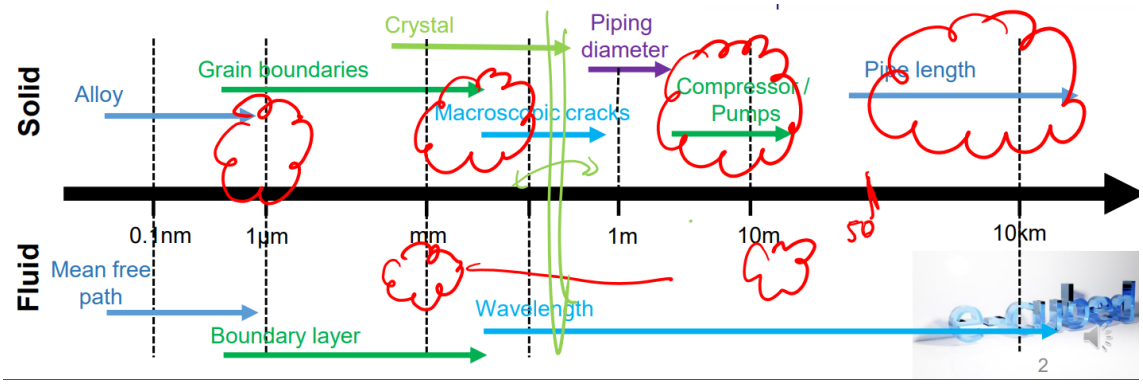

Figure 1.1: Pressure pulsation in a piping system

Cascade of length scales

Molecular	Continuum	Structural
Material is made on this level	Cracks operate on this level	Structures considered at this level
$< 10\,\mu m$	$10\,\mu m < x < 10\,m$	$> 10\,m$
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

1.1.1 Compelxity of the problem at different length scales

Complexity of representation changes with the scale.

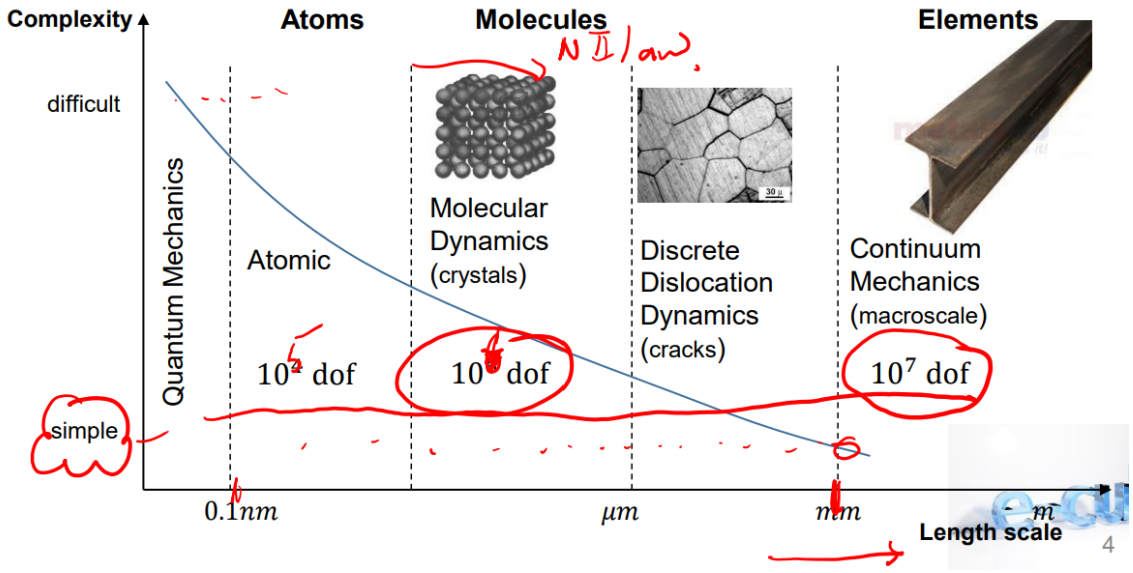

Figure 1.2: Graph to show complexity against scale.

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 controllbed by small vortices.

Micrograph

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

Table 1.2: Micrograph

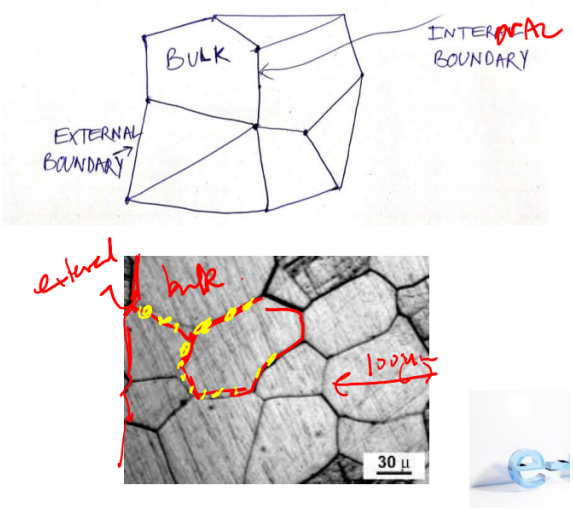

Figure 1.3: Graph to show complexity against scale.

Internal grain processes

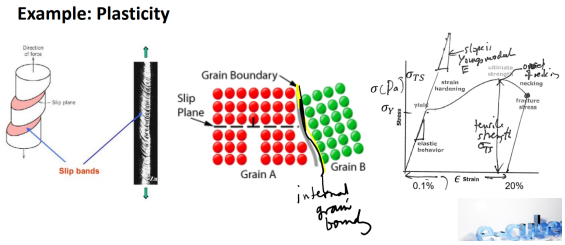

Figure 1.4: Example of plasticity from internal grain process level.

Internal boundary (hydrogen embrittlement - plastic deformation / slip)

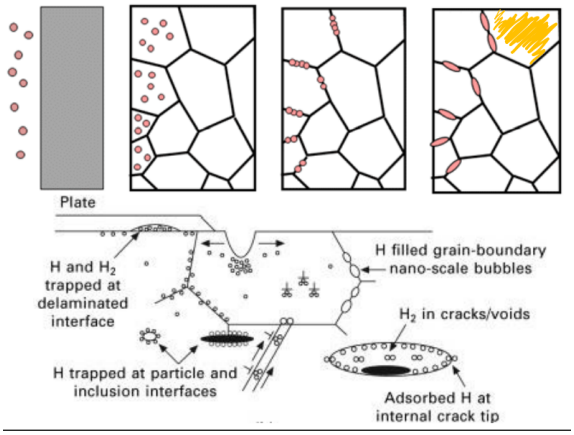

Figure 1.5: Hydrogen embrittlement - plastic deformation / slip

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.

$$\mathrm{Fe_2} + (\mathrm{ag}) + 2\,\mathrm{OH}(\mathrm{ag}) \longrightarrow \mathrm{Fe(OH)}_{2(s)} \tag{1.1}$$

$$4\,\mathrm{Fe(OH)}_{2(s)} + \mathrm{O}_{2(g)} + 2\,\mathrm{H_2O}_{(l)} \longrightarrow \mathrm{Fe(OH)}_{3(s)} \tag{1.2}$$

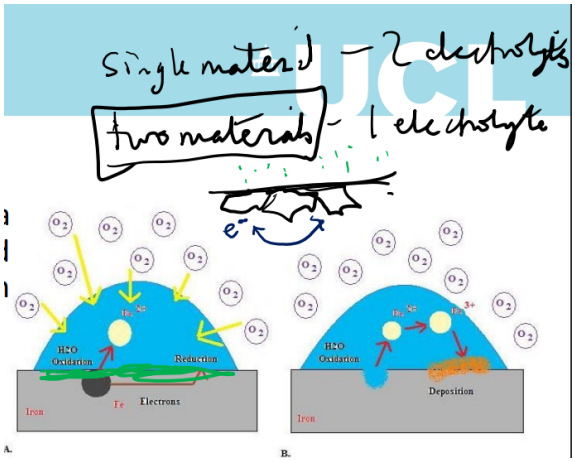

Figure 1.6: Rust corrosion from grain boundary level.

1.2 Categorisation of matter

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

Table 1.3: 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 $0.1\,\mathrm{nm} = 1 \times 10^{-10}\,\mathrm{m} = 1\,\mathrm{angstrom}$
- Nucleus diameter is $1 \times 10^{-15}\,\mathrm{m}$ (hydrogen) to $15 \times 10^{-15}\,\mathrm{m}$ (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 $E = \left.\frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon}\right|_{\varepsilon \to 0}$
- Tensile stress: σ_{TS}
- Yields stress: σ_Y
- Ductility: ϵ_T

It is important to understand the following:

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 ($\mathrm{J\,m^{-3}}$)	Resistance to crack propagation.
Ductility	ϵ_T	Material's ability to undergo plastic deformation.

Table 1.4: Key points on material properties

How are they related to the microstrucure?

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:

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

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

$$m_i \frac{\mathrm{d}\underline{v}_i}{\mathrm{d}t} = \underline{F}_i \tag{1.4}$$

$$\underline{v}_i = \frac{\mathrm{d}\underline{x}_i}{\mathrm{d}t} \tag{1.5}$$

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

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

The difficultuy 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

$$U = U_{stretch} + U_{bend} + U_{torsion} + U_{vanderWaal} + U_{electro} + U_{cross} \tag{1.7}$$

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 exteremes with most (electron distribution) bonds lying between (polar covalent)

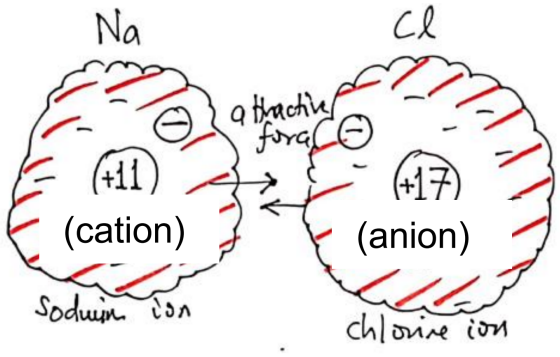

Figure 1.7: Ionic bond (electrovalence)

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

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

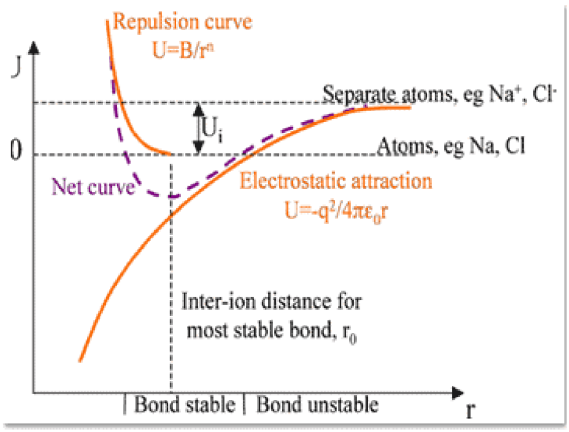

Figure 1.8: Bond stability.

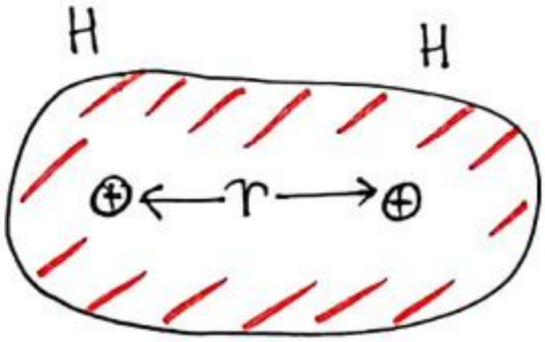

Figure 1.9: Covalent bond (covalence). Note the overlap of electron orbit.

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

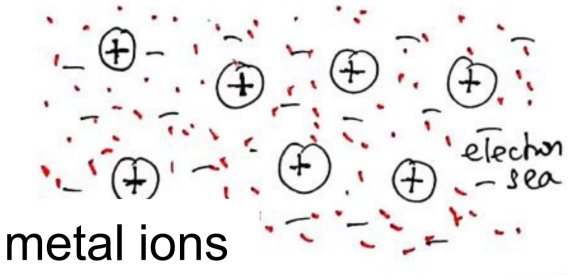

Figure 1.10: Metallic bond (electron cloud).

$$e = 1.6 \times 10^{-19}\,\mathrm{C} \tag{1.11}$$

$$\epsilon_0 = 8.8 \times 10^{-12}\,\mathrm{Nm^2C^{-2}} \tag{1.12}$$

$$1\,\mathrm{eV} = 1.6 \times 10^{-19}\,\mathrm{J} \tag{1.13}$$