

Part IA Paper 2: Structures and Materials

MATERIALS

Examples Paper 1 – TEACH YOURSELF PROPERTIES AND MICROSTRUCTURE

This *Teach Yourself* Examples Paper is based on extracts from Ashby MF, Shercliff HR and Cebon D, *Materials: Engineering, Science, Processing and Design*, 3rd/4th editions, Butterworth-Heinemann (2014/2019), Chapters 4-6, and Guided Learning Unit 1.

Introduction

Part I Materials is principally about materials in relation to design and manufacture. The performance of components and products may be limited by deformation, failure, weight, wear, and corrosion, or by the transport of heat or electric current – usually several of these simultaneously. And in almost all design, we need to consider both cost, and the impact on the environment. Hence to design products, we need to understand the intrinsic physical responses of materials to load, temperature, and other service conditions – that is, the *properties of materials*. And to understand (and control) these properties, we need to know how they depend on the underlying *microstructure*.

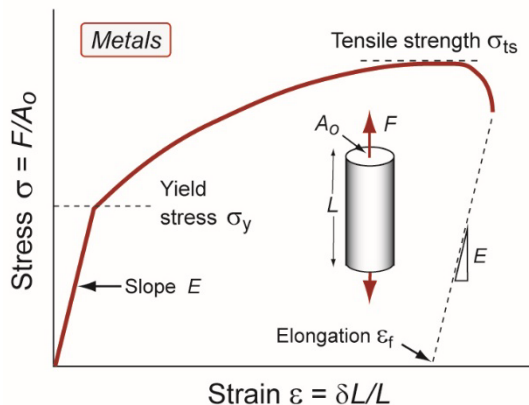
School Physics and Chemistry courses vary widely in their coverage of materials – this Examples Paper aims to bring everyone up to the same starting point on mechanical properties and microstructure. Some sections may be familiar to you – read and work through it all anyway.

This Examples Paper contains short sections to read through, followed by questions. Complete solutions will be posted on Moodle (1P2 Materials) – don't look at these until you have properly attempted a question.

Part A should be completed before the 2nd Materials lecture in the Lent Term. It is also directly relevant to Materials (Long) Experiment 4: Plasticity and Fracture.

Part B should be completed before the 3rd Materials lecture in the Lent Term.

PART A: Mechanical Properties



- A1. Definitions: Uniaxial Stress and Strain**
 - A2. Definition and Measurement: Young's Modulus**
 - A3. Definition and Measurement: Yield Stress and Ductility**
 - A4. Stiffness and Strength in Elastic Design**
- Solutions to Questions (on Moodle)**

Part A of this *Teach Yourself* Examples Paper covers: (i) tensile stress and strain, and stress-strain curves; (ii) an introduction to the material properties governing elastic and plastic deformation: Young's modulus and yield stress; (iii) elastic design, and the meaning of stiffness and strength.

A1. Definitions: Uniaxial Stress and Strain

Stress

The simplest loading state is *uniaxial loading* – the transmission of a force F along the axis of a component of uniform cross-sectional area A (Figure A1). Examples are the tie-rods in a truss, cables, and bicycle spokes – all loaded in *tension*. If the load is reversed, as in a vertical column supporting a downwards load, this is referred to as *compression*.

The intensity of the loading is called the *stress*: $\sigma = \frac{F}{A}$

The units are N/m² or Pascals (Pa) – but more usually expressed in N/mm² or MPa (10⁶ Pa).

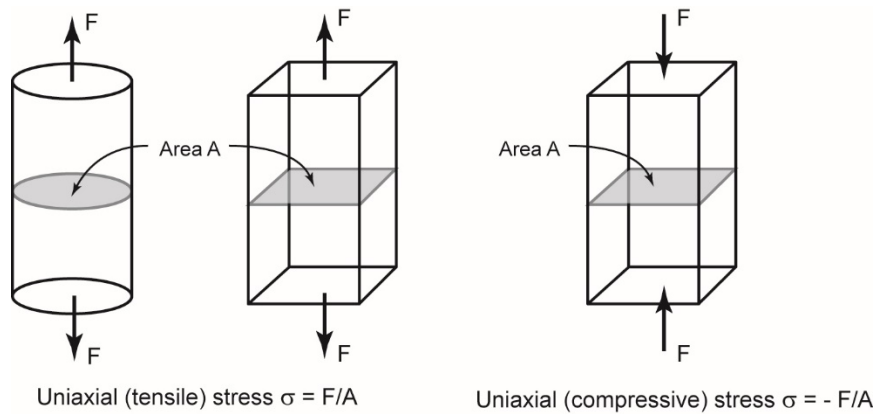


Figure A1: Uniaxial stress.

In uniaxial loading, the load is perpendicular to the cross-sectional area, referred to as a *normal* or *direct stress*. The usual convention is to treat tension as positive, and compression as negative.

Strain

The response of a material to applied stress is to deform. Under uniaxial loading (Figure A2), the length increases in tension (and decreases in compression).

The extension, $\delta = (L - L_0)$, divided by the original length L_0 is called the *strain*, ε :

$$\varepsilon = \frac{\delta}{L_0} = \frac{(L - L_0)}{L_0}$$

As this is a ratio of lengths, it is dimensionless, with no units. This is also referred to as a *normal* or *direct strain*, positive for tension (and negative for compression).

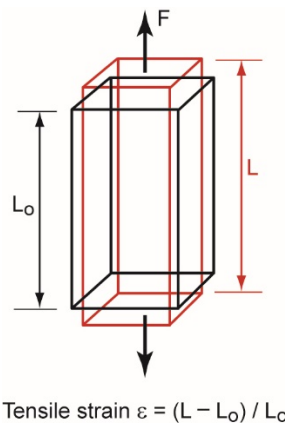


Figure A2: Strain under uniaxial load.

Note that uniaxial *loading* produces *triaxial* strain – the dimensions perpendicular to the tensile stress reduce, giving a negative lateral strain. This lateral strain is proportional to the tensile strain in the loading direction – this will be discussed further in lectures.

Question

A1. A brick chimney is 50m tall. The bricks have a density of $\rho = 1800 \text{ kg/m}^3$. What is the axial compressive stress at its base? Does the shape of the cross-section matter?

A2. Definition and Measurement: Young's Modulus

Consider the load-extension characteristic of a sample of material of length L_0 and initial cross-sectional area A_0 , loaded in uniaxial tension. It is a familiar observation that, for most engineering materials, the response is *linear-elastic*:

- the load is proportional to the extension;
- the extension is fully recovered on unloading.

The slope of the load-extension response (that is, the *stiffness*, F/δ) is proportional to the length, and inversely proportional to the area – Figure A3(a). If we convert the axes to tensile stress σ and tensile strain ϵ (defined above), the response becomes a unique material characteristic, independent of the sample dimensions – Figure A3(b). Note that any material property must satisfy this condition, and give the same value regardless of the sample geometry.

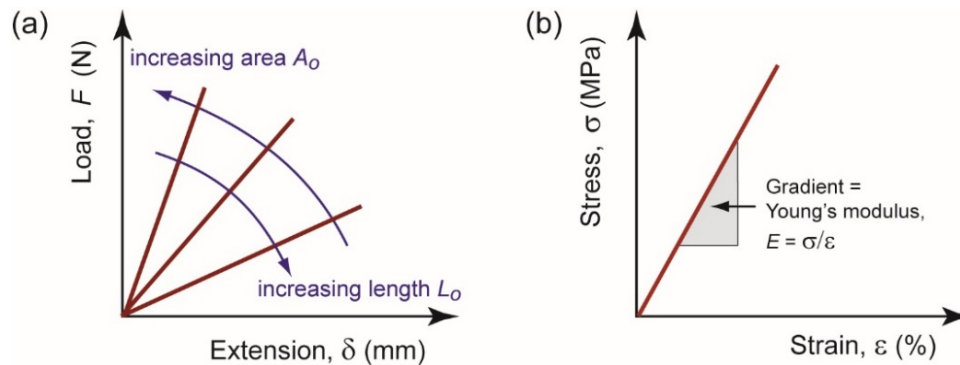


Figure A3: Linear-elastic material responses for uniaxial loading: (a) force-extension responses; (b) stress-strain response, defining Young's modulus, E .

On stress-strain axes, the slope of the linear-elastic response for uniaxial loading characterizes the intrinsic stiffness of the material – the property known as *Young's modulus*, E :

$$\text{Young's modulus, } E = \frac{\text{Tensile stress}}{\text{Tensile strain}} = \frac{\sigma}{\epsilon}$$

As strain is dimensionless, the units of E are the same as for stress: N/m^2 or Pascals (Pa). In practice, data are usually given in GPa (10^9 Pa).

There are practical limitations to the accuracy of using tensile testing to measure E , particularly in measuring the tensile strain (which is of the order of 0.1% or less). IA Experiment 4 explores the difficulties of measuring the extension δ in a tensile test, and compares this with an alternative device known as a *strain gauge*. Other techniques are used in practice, giving greater accuracy: loading in bending rather than tension, various vibration methods, and measuring the speed of sound in the material (a simple function of E and density).

Question

A2. The cable of a hoist has a cross section of 80 mm^2 . The hoist is used to lift a crate weighing 250 kg. What is the stress in the cable? The free length of the cable is 3 m. How much will it extend if it is made of steel (Young's modulus $E = 200 \text{ GPa}$)? How much if it is made of polypropylene, PP (Young's modulus $E = 1.2 \text{ GPa}$)?

A3. Definitions and Measurement: Yield Stress and Ductility

If we increase the tensile load in the elastic regime, then eventually the material will fail in some way. Figure A4 shows typical tensile stress-strain responses for brittle ceramics, ductile polymers and ductile metals. In all cases, there is an identifiable *elastic limit* – a stress σ_{el} at which the extension is no longer fully recoverable – either because of *brittle fracture* (the sample breaks in two), or because of *ductile yielding* (giving permanent deformation, while the sample remains intact). Figures A4(b,c) show that the post-yield behaviour varies significantly between polymers and metals – and there are many variants within these material classes too.

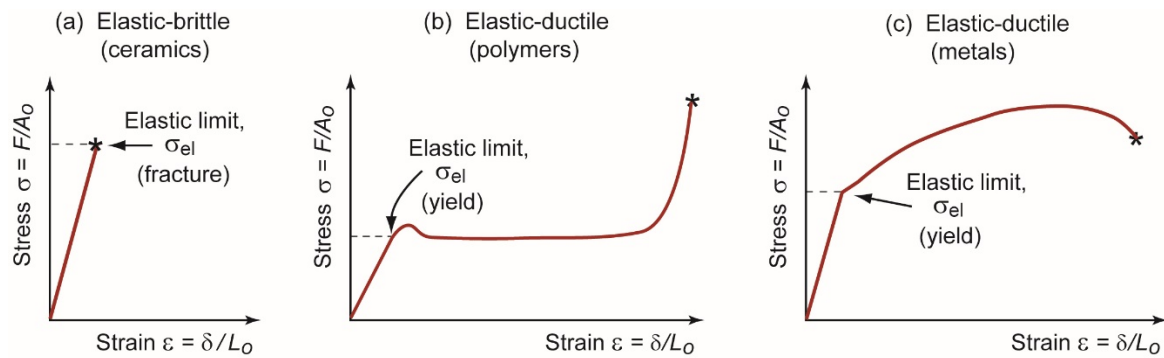


Figure A4: Typical stress-strain responses for: (a) ceramics; (b) polymers; (c) metals.

In all cases, the elastic limit σ_{el} defines a material property: the *strength* – the maximum uniaxial stress that can be applied to the material while remaining in the elastic regime.

Strength and Ductility for Metals

Stress-strain responses for metals are investigated in IA Experiment 4 – Figure A5 shows a typical stress-strain curve for a metal, annotated with a number of further properties.

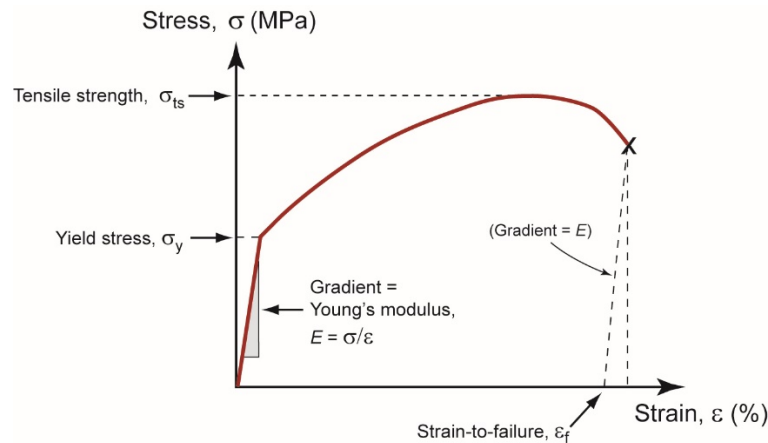


Figure A5: Stress-strain response for a metal, and associated mechanical properties.

First, the elastic limit for a ductile material is called the *yield stress*, σ_y . After yielding, part of the strain is permanent – the material is now referred to as *plastic*. The load required to maintain plastic deformation increases – a process known as *work hardening*. During this stage, the cross-sectional area reduces uniformly (conserving volume, for reasons discussed in lectures). The rate of increase in stress steadily falls to zero, leading to a maximum value, known as the ultimate *tensile strength*, σ_{ts} . Beyond this point, the test is unstable – deformation localises into one part of the sample (a process called *necking*), leading to internal voiding and a ductile fracture.

Note that after yielding, part of the strain remains elastic (given by σ/E). So after final failure, the broken sample unloads elastically – shown in Figure A5 as a gradient of slope E at failure, leading to the permanent *strain-to-failure*, also known as the *ductility*. This is an important quantity in materials design and in manufacturing – high ductility is useful for safe elastic design, in plastic collapse, and in metal forming processes. However, by the strict definition of a material property, ductility breaks the rule of being independent of the sample geometry – the strain during necking will vary with cross-sectional area for instance. So data for ductility needs to be used with caution – it is only really meaningful to compare the strain-to-failure between materials using a standard test geometry.

Questions

A3. Figure 2.1 in the Materials Databook (p.15) shows a selection of stress-strain curves for metals. Estimate the *yield stress*, *tensile strength* and *ductility* for annealed copper, drawn 70/30 brass [i.e. 70% Cu, 30% Zn, by weight], and mild steel. What general trend do you observe between tensile strength and ductility, within each class of alloys (copper alloys, steels)?

A4. For the cables loaded as in Question A2, find the factor of safety between normal operation and yield of the cable: (a) for steel ($\sigma_y = 300$ MPa); (b) for PP ($\sigma_y = 32$ MPa). Comment on the results.

A4. Stiffness and Strength in Elastic Design

Elastic design means that all deformation is fully recovered when the load is removed. There are two distinct types of consideration in elastic design:

- *stiffness*-limited: a maximum allowable *deflection* under the design load;
- *strength*-limited: a maximum allowable *load* can be applied while remaining in the elastic regime.

Examples:

“Structural” applications: bridges, buildings, vehicles, bicycles, furniture, machines

“Functional” applications: precision instruments, hard disk drives, mobile phone cases

Stiffness

The stiffness of a component or structure is defined as:

$$\text{Stiffness, } S = \frac{\text{Force}}{\text{Displacement}} = \frac{F}{\delta}$$

In general, the stiffness will depend on:

- *material* (e.g. steel, aluminium, wood, carbon fibre...)
- *mode of loading* (e.g. tension, bending....)
- *cross-section size*, and (for bending) its *shape* (e.g. solid cylinder, tube, I-beam ...)

Figure A6 shows schematically the stiffness in tension and bending, for a given material of constant cross-sectional size and shape.

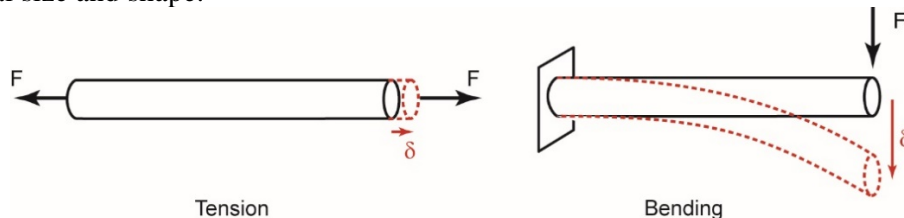


Figure A6: Stiffness in tension and bending.

Strength

The *strength* of a component or structure is defined when the maximum stress produced under the applied load reaches a limiting value. The maximum stress again depends on the mode of loading (tension or bending) and the cross-section size and (for bending) the shape; the limiting value depends on the material – for strength-limited design, we ensure that $\sigma_{\max} < \sigma_{\text{el}}$.

The IA Structures course covers the analysis of bending, and the effect of cross-section shape on the stiffness and strength of a component. Figure A7 shows the distribution of stress across a section in tension and in bending. In tension the stress is uniform – the whole section reaches the limiting value for the material simultaneously. Bending stresses are due to *bending moments*, giving a linear variation from tension on one side to compression on the other. The maximum stresses occur at the surface – so the limiting value for the material is reached here first.

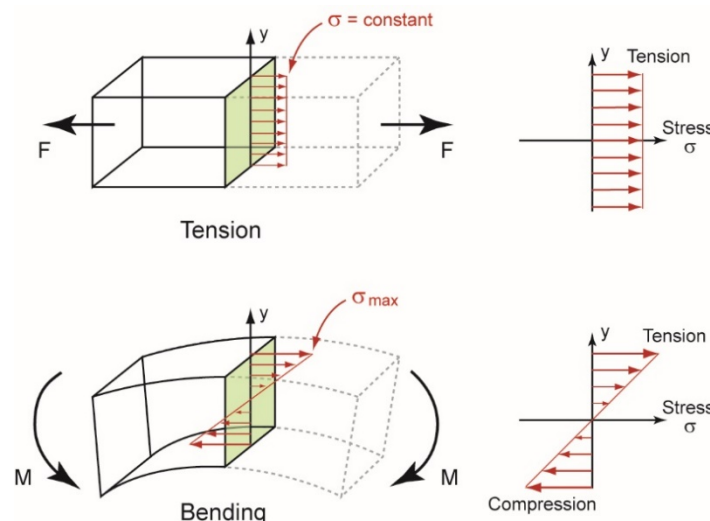


Figure A7: Stress distributions in tension and bending.

Uniaxial tension and simple bending occur frequently in engineering components. And, as noted earlier, they are commonly used to measure the key material properties that control stiffness and strength.

Questions

A5. If you wish to snap something like a stick, it is second nature to bend it, rather than to pull it in tension – let's see why.

- A metal ruler has a rectangular cross-section $2 \times 25\text{mm}$. The central 25cm of the ruler is loaded in tension until it starts to yield. What is the load required, and what is then the extension? (The yield stress of the metal σ_y is 300 MPa, and the Young's modulus E is 210 GPa).
- Now the ruler is clamped firmly to a bench, with 25cm protruding as a "cantilever" which is loaded transversely at its tip with a force F (as in Figure A6). In this bending configuration, the maximum stress (at the surface of the ruler, next to the clamp) is given by:

$$\sigma_{\max} = \frac{6 F L}{b d^2}$$

where L is the length of the cantilever, b is the width and d is the thickness of the cross-section.

The deflection of the tip is given by:

$$\delta = \frac{4 F L^3}{E b d^3}$$

(These formulae are derived in the IA Structures course).

What load F now causes failure (i.e. $\sigma_{\max} = \sigma_y$) ? And how much is the tip deflection at this load? Comment on the relative stiffness and failure load in tension and in bending.

A6. Your task is to design a light-weight tensile tie of length L , with a circular cross-section of radius R . It has to carry an axial force F , without stretching by more than δ . You will need to choose the material (with Young's modulus E and density ρ) and the corresponding cross section radius to suit your choice of material, i.e. R is a 'free variable'.

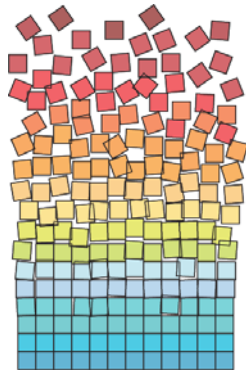
- Show that the extension of the tie is given by $\delta = FL/AE$, where $A = \pi R^2$.
- Rearrange this equation to find an expression for the radius R of the tie that will carry the load with the allowed deflection.
- If the length of the tie is $L = 0.3\text{m}$ and the extension is not to exceed 0.1mm for a load of $F = 1000\text{N}$, what value of R is needed if the tie is made of: (i) PEEK (a polymer commonly reinforced with carbon fibre); (ii) butyl rubber; (iii) titanium alloy; (iv) copper alloy? Use the material properties in the table below.
- Write an expression for the mass m of the tie and determine the mass of each of the ties in (c). Which one would you choose?
- Substitute the expression for radius R from (b) into the expression for mass m from (d) to show that the combination of material properties to be *minimised* is ρ/E – this is referred to as a *material performance index*. Determine the value of the index for each of the four ties.
- Comment on the relationship between the mass of each beam and its material index ρ/E .

	Young's Modulus E (GPa)	Density ρ (kg/m ³)	Radius R (mm)	Mass m (kg)	Material index ρ/E
PEEK	3.8	1300			
Butyl rubber	0.0015	2400			
Titanium alloy	110	4600			
Copper alloy	120	8900			

Part IA Paper 2: Structures and Materials
MATERIALS

Examples Paper 1 – TEACH YOURSELF PROPERTIES AND MICROSTRUCTURE

PART B: Microstructure



- B1. Introduction to Part B**
- B2. Atomic structure**
- B3. Atomic and molecular bonding**
- B4. Metal crystals structures**
- B5. Theoretical density of metals**
- B6. Interstitial space**
- B7. Ceramic crystals**
- B8. Glasses**
- B9. Polymer microstructure**
- Solutions to Questions (on Moodle)**

You will need to look up data in the Materials Databook.

B1. Introduction to Part B

Though they lacked the means to prove it, the ancient Greeks suspected that solids were made of discrete *atoms* that packed in a regular, orderly way to give *crystals*. With modern techniques of X-ray and electron diffraction and high-resolution microscopy, we know that all solids are indeed made up of atoms or molecules, and that most (but not all) are crystalline. Most engineering metals and ceramics are made up of many small crystals, or *grains*, stuck together at *grain boundaries* to make polycrystalline microstructures. Polymers are built up from long-chain molecules, but can also have ordered microstructures in some cases.

Atoms are typically around 0.1-0.2nm in diameter ($1\text{nm} = 10^{-9}\text{m}$); grains are typically 1-100 μm across ($1\mu\text{m} = 10^{-6}\text{m}$), and contain billions of atoms. The course will also introduce many microstructural features, at length scales from the atomic to the grain level. All play a role in determining the properties of materials, and thus the performance and manufacture of engineering components and structures, ranging in size from the millimetre to kilometre scale. This can be something of a surprise on first encounter: successful selection of materials in design at this macroscopic engineering scale is underpinned by material behaviour from the atomic scale upwards.

Part B of this *Teach Yourself* Examples Paper covers: (i) a brief summary of the types of bonding between atoms; (ii) the methods for describing the 3-dimensional arrangement of atoms or molecules in crystals; and (iii) how atomic packing leads directly to estimates of material density.

B2. Atomic structure

Atoms consist of a nucleus of protons (+ve charge) and neutrons, with different elements defined by the number of protons in the nucleus. Electrons (–ve charge) orbit the nucleus to balance the proton charge, in discrete “shells” of fixed energy levels (i.e. quantised).

The two most important quantities are the atomic *number*, Z , and the atomic *weight* (strictly *mass*), A .

e.g. for lead (Pb), $Z = 82$ and $A = 207$, sometimes written: ${}_{82}\text{Pb}^{207}$.

Z is the number of electrons (or protons) in atom; A is the mass of the nucleus (proton or neutron mass $\approx 1000 \times$ electron mass);

So lead has 207 times more mass than hydrogen ${}_1\text{H}^1$.

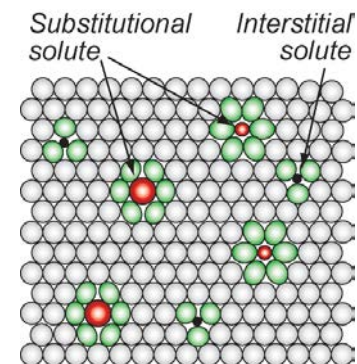
Atomic Size

A surprising and important feature is that all atoms are a similar size, i.e. atomic radii are all of order 0.1–0.2 nm, while the atomic weight spans a factor of over 200. In simple terms, this is because as the number of protons and electrons increase, the electron shells are drawn in to smaller radii.

Element	Atomic number, Z	Atomic weight, A	Atomic radius (nm)
Hydrogen, H	1	1	0.06
Aluminium, Al	13	27	0.14
Copper, Cu	29	64	0.13
Zinc, Zn	30	65	0.13
Tungsten, W	74	184	0.14
Lead, Pb	82	207	0.18

Consequences:

- mixtures of atoms of different elements (*alloys*) can pack together efficiently into crystal lattice structures, forming *solid solutions* or *compounds*;
- most solid solutions will be *substitutional*: atoms of similar size replace one another in the lattice (e.g. Cu-Zn: in *brass*);
- only small atoms (e.g. H, C) form *interstitial* solid solutions: these atoms can fit into the gaps between metal atoms (e.g. C in Fe: in *carbon steels*);
- *compounds* can form readily, with lattices that satisfy the required atomic fractions of the elements, or *stoichiometry* (e.g. Fe_3C , Al_2O_3).



B3. Atomic and molecular bonding

Atomic bonding is determined by the interaction between the outermost electrons in atoms. There are 2 types of bonds:

- Primary: metals, ceramics, and along long-chain polymer molecules
- Secondary: between polymer chains, and in materials such as ice.

Primary bonds are 100 times stronger than secondary, and hence more difficult to stretch and break.

Primary bonding

(1) Metallic bonding

In metallic bonding, the atoms form positively charged ions by releasing a few electrons, which form a “sea” of free electrons. Bonding is by electrostatic interaction between the ions and the free electrons.

- The bonds are equally strong in all directions – the metallic bond is non-directional.
- Metallically bonded compounds form regular crystal lattices.
- The free electrons are not bound to specific atoms, so metallically bonded materials are electrical conductors.

(2) Ionic bonding

Electrons are transferred permanently between atoms to produce stable, oppositely charged ions, which attract electrostatically.

- Electrostatic forces equal in all directions: ionic bond is non-directional.
- Positive and negative ions pack into regular crystal lattice structures.
- Electrons are bound to specific ions, so ionically bonded materials are electrical insulators.

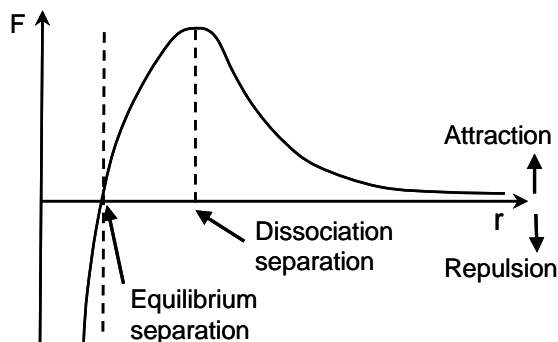
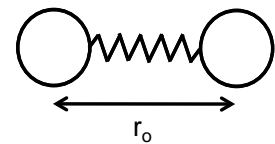
(3) Covalent bonding

Electrons shared between atoms to achieve an energetically stable number.

- The shared electrons are associated with particular electron shells of the bonding atoms, so the covalent bond is directional.
- Covalently bonded materials form regular crystal lattices (e.g. diamond), networks (glasses), or long-chain molecules (e.g. polymers).
- Electrons are bound to specific atoms, so covalently bonded materials are electrical insulators.

Modelling primary bonds

Primary bonds may be modelled as *stiff springs* between atoms (or ions), with a non-linear force-separation characteristic (below). The atoms (or ions) have an *equilibrium separation* r_0 , governed by the balance between attractive and repulsive forces. At the *dissociation separation* the atoms (or ions) can be separated completely.



Atoms vibrate about the equilibrium separation, with kinetic energy $\approx k_B T$, where T is the absolute temperature (in K) and k_B is Boltzmann's constant (1.38×10^{-23} J per atom K^{-1}). All bonds effectively break down when $k_B T$ exceeds the bond energy – at this point the material melts. Due to the strength of their primary bonds, metals and ceramics have a characteristically high melting temperature.

Secondary bonding

Secondary (or “van der Waals”) bonds operate at much larger atomic separation than primary bonds, and are much weaker. They are associated with *dipoles* – molecules in which the centres of positive and negative charge do not coincide.

- *Hydrogen bonds* form the strongest dipoles, and are the commonest secondary bond between polymer chains.
- In secondary bonded materials (polymers), the bonds become ineffective at much lower thermal energy ($k_B T$) than primary, giving low melting points.

B4. Metal crystal structures

Primary bonding gives a well-characterised equilibrium spacing, with stiff restoring forces. For the purposes of packing, the atoms may be treated as hard spheres, forming a solid crystal lattice.

The great majority of the 92 stable elements are *metallic*, and of these, the majority (68 in all) have one of just three simple structures:

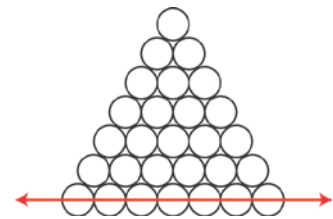
- face-centred cubic (FCC)
- close-packed hexagonal (CPH)
- body-centred cubic (BCC).

There are in fact 14 distinguishable three-dimensional crystal lattices, but these three simple structures are all that is needed for most engineering purposes.

Close-packed crystal structures

The basic building block for the first two of these structures is the *close-packed plane* (i.e. the highest density of atoms arranged in a plane is a hexagonal packing).

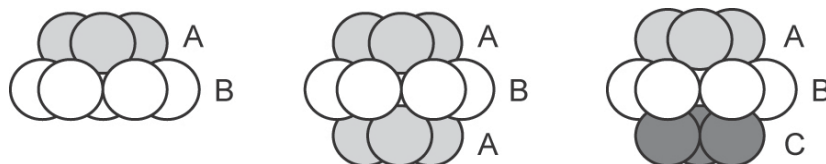
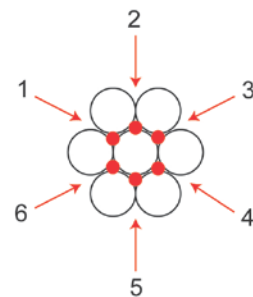
The *close-packed directions* are the straight lines through the centres of touching atoms (there are 3 in a close-packed plane).



A 3D lattice can be built by stacking these close-packed planes – but there are 2 ways of doing it.

Around each atom there are 6 locations in which atoms can sit. But only 3 of these can be occupied at once (“odd” or “even”).

Imagine placing a first layer above the reference layer (in either odd or even locations). There are then two options for placing a layer below: one using the same locations with respect to the initial layer (giving ABA stacking), the other using the alternative locations (giving ABC stacking), i.e. in side view:



Continuing these patterns builds up the 3D lattices: ABAB.... or ABCABC....

Question

B1. Figure B1 shows two stacked close-packed layers in plan view. Draw the two possible positions of the third layer on the Figure, and label them ABA, ABC.

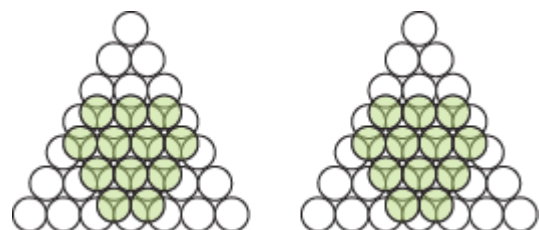


Figure B1. Two layers of close-packed planes.

These two structures are face-centred cubic, FCC (the ABC stacking) and close-packed hexagonal, CPH (the ABA stacking). The difference is seen more clearly from their *unit cells*, defined below. Both are *close-packed*, i.e. the spheres occupy as large a fraction of the volume as possible (this fraction is calculated later).

The apparently minor packing difference is of little consequence for *elastic properties*, but has a big influence on *plastic deformation*.

Unit cells

A *unit cell* is the smallest unit which can be replicated by translation in all directions to build up the 3D crystal structure. The unit cell dimensions are called the *lattice constants* – values for common elements are in the Materials Databook.

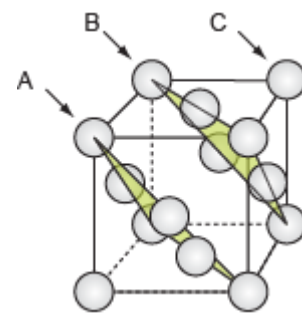
Unit cells are drawn with the atoms reduced in size, for clarity – remember that they touch in close-packed directions.

Face-centred cubic (FCC) structure

The FCC structure is described by a cubic unit cell with one atom at each corner and one at the centre of each face. The close-packed planes (ABC....) are perpendicular to the cube diagonals (see Figure).

Close-packed directions within a close-packed plane were previously identified in the ABC planes. But the FCC stacking has a high degree of symmetry, and generates close-packing in multiple orientations – *any* of the four diagonals of the cube lies normal to sets of ABC-stacked planes. Similarly any diagonal of any face is a close-packed direction.

Simple geometry gives relationships between the atomic radius and the lattice constant (Question B2).



FCC structure of packed spheres showing the ABC stacking.

Question

B2. For the FCC structure, show that the ratio of the lattice constant (the size of the cube) to the atomic radius is equal to $2\sqrt{2}$.

Among the metallic elements, 17 have the FCC structure. Engineering materials with this structure include the following (further applications in the Materials Databook).

Material	Typical uses
Aluminum and its alloys	Airframes, space frames and bodies of trains, trucks, cars, drink cans
Nickel and its alloys	Turbine blades and disks
Copper and α - brass	Conductors, bearings
Lead	Batteries, roofing, cladding of buildings
Austenitic stainless steels	Stainless cook-ware, chemical and nuclear engineering, cryogenic engineering
Silver, gold, platinum	Jewellery, coinage, electrical contacts

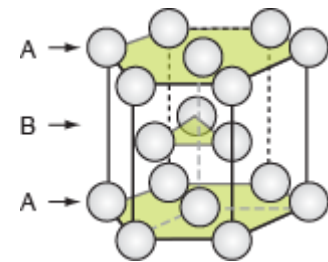
FCC metals have the following characteristics.

- They are very ductile when pure, work hardening rapidly but softening again when annealed, allowing them to be rolled, forged, drawn or otherwise shaped by deformation processing.
- They are generally tough, i.e. resistant to crack propagation (as measured by their fracture toughness, K_{Ic} – covered in the Easter Term lectures).
- They retain their ductility and toughness to absolute zero, something very few other materials allow.

Close-packed hexagonal (CPH) structure

The CPH structure is described by a prismatic hexagonal unit cell with an atom at each corner, one at the centre of the hexagonal faces and three in the middle. The close-packed planes stacked in an ABAB.... sequence are easily identified: the close-packed planes are perpendicular to the axis of the prism (see Figure).

There are three close-packed directions in the close-packed planes, as before, but this ABAB... stacking does *not* generate close-packed planes or directions in other orientations (in contrast to FCC).



CPH structure of packed spheres showing the ABA stacking.

There are two lattice constants in CPH – the side-length of the hexagonal base, a , and the height of the prism, c . The first is clearly equal to the atomic diameter, as the atoms are touching; geometry gives the relationship between this and the second lattice constant (Question B3).

Question

- B3.** (a) For the CPH structure, show that the ratio of the lattice constants, $c:a$ is equal to 1.633.
- (b) The atomic radius of CPH magnesium is 0.1605nm. Find the lattice constants for Mg.

Of the metallic elements, 30 have the CPH structure. They include the following.

Material	Typical uses
Zinc	Die-castings, plating
Magnesium	Light-weight structures
Titanium and its alloys	Light, strong components for airframes and engines, biomedical and chemical engineering
Cobalt	High temperature superalloys, bone-replacement implants.
Beryllium	The lightest of the metals. Its use is limited by expense and potential toxicity.

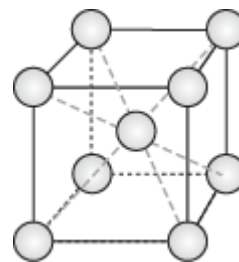
CPH metals have the following characteristics.

- They are reasonably ductile (at least when hot), allowing them to be forged, rolled, and drawn, but in a more limited way than FCC metals,
- Their structure makes them more anisotropic than FCC metals (i.e. crystal properties vary with direction).

Body-centred cubic (BCC) structure

The BCC structure is described by a cubic unit cell with one atom at each corner and one in the middle of the cube (see Figure).

This structure is *not close-packed* – it is made by stacking planes of atoms in a square array (not hexagonal). Atoms touch along the cube diagonals, so these are the close-packed directions. The geometric relationship between atomic diameter and the lattice constant is again straightforward to evaluate (Question B4).



BCC structure of non-close-packed spheres.

Question

B4. For BCC, show that the ratio of lattice constant to atomic radius is $4R/\sqrt{3}$.

Of the metallic elements, 21 have this structure (most are rare earths). They include the following.

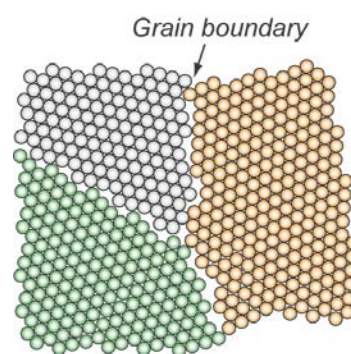
Material	Typical uses
Iron, mild steel	The most important metal of engineering: construction, cars, cans and more
Carbon steels, low alloy steels	Engine parts, tools, pipelines, power generation
Tungsten	Lamp filaments
Chromium	Electroplated coatings

BCC metals have the following characteristics.

- They are ductile, particularly when hot, allowing them to be rolled, forged, drawn or otherwise shaped by deformation processing.
- They are generally tough, and resistant to crack propagation (as measured by their fracture toughness, K_{Ic}) at and above room temperature.
- They become brittle at low temperatures. The change happens at the “ductile-brittle transition temperature”, limiting their use below this.

Footnote: Grain structure

Metal components are commonly manufactured by *casting* – solidification of a liquid poured into a shaped mould. The solidification mechanism involves the formation of many solid crystalline nuclei, which grow by attachment of atoms to the crystal at the interface between liquid and solid. This is explored further in the IB Materials course. For now, we note that solidification is completed when adjacent crystals impinge on one another. But because the orientation of the packing in each crystal is random, there is a misfit in the atomic packing at the interface between two crystals. The individual crystals are called *grains*, and the region of imperfect packing is called a *grain boundary* – see the Figure.



As grain diameters are typically of order 1-100 μm , they are 1000s of atoms across. Their boundaries are readily revealed under an optical microscope, by first etching a polished surface with a chemical that attacks the boundaries more severely than the bulk of the grains. Grain boundaries are an important microstructural feature, and will be encountered in relation to many different properties and material behaviours.

B5. Theoretical density of metals

Atomic packing fraction

First consider the *atomic packing fraction*: the fraction of space occupied by atoms (assuming a “hard sphere” model).

Example: Face-centred cubic, FCC

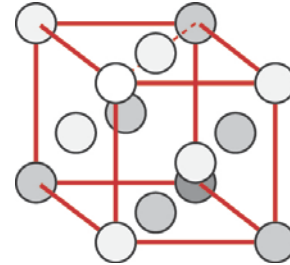
From Question B2, $a = 2\sqrt{2} R$

Volume of unit cell = $a^3 = 16\sqrt{2} R^3$

The number of atoms per unit cell needs to take account of atoms on the corners and faces being shared between adjacent unit cells (corner atoms shared between 8 cells, face atoms between 2).

Hence number of atoms per unit cell: $8 \times 1/8 + 6 \times 1/2 = 4$
(corners) (faces)

Hence atomic packing fraction = $\frac{4 \times \frac{4}{3} \pi R^3}{16\sqrt{2} R^3} = 0.74 \quad (74\%)$



Question

B5. Use the same method to find the atomic packing fractions for: (a) CPH; (b) BCC. Compare these with the value for FCC, and comment on the differences.

Evaluation of theoretical density

The *density* of crystalline materials depends directly on the number of atoms per unit volume, and the atomic mass of the atoms.

Atomic mass, A = mass (in grams) of 1 mole of that element

Atoms/mole = Avogadro's number, $N_A = 6.02 \times 10^{23}$

Hence *mass of 1 atom* = A/N_A

Let n = number of atoms per unit cell, and V_c = volume of unit cell

Mass of unit cell = $n \times$ mass of 1 atom

Hence the *theoretical density* = mass/volume for the unit cell: $\rho = \frac{n A}{V_c N_A}$

This agrees well with experimental density (see Questions below).

Key points to note: Since the atomic mass and the crystal packing are both physically well-defined:

- densities of metals and ceramics have *narrow ranges*
- there is *no scope to modify density* (e.g. by processing a metal differently).

Question

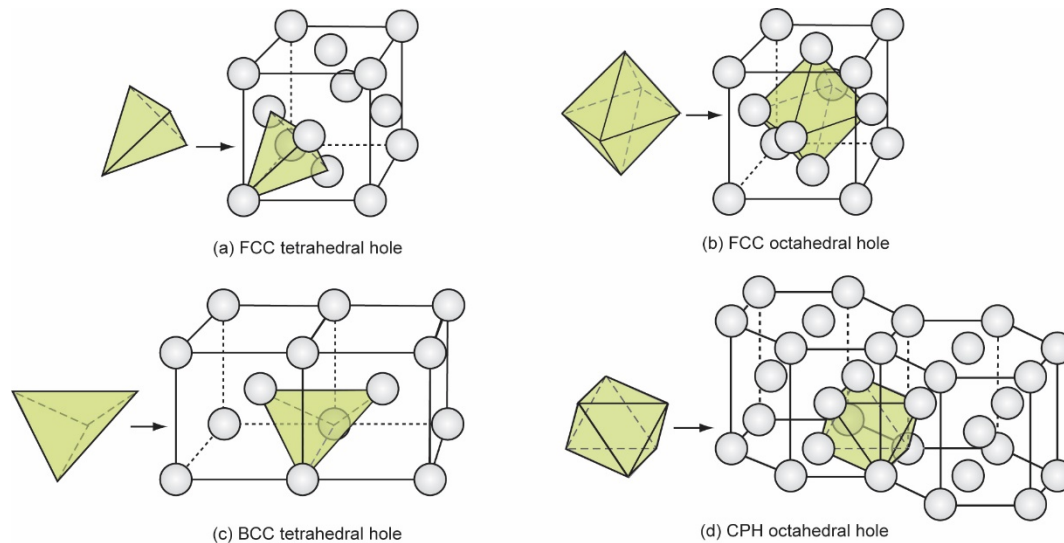
B6. (a) Determine the theoretical density for BCC iron, Fe, at room temperature (using atomic data from the Materials Databook). (Note: the volume of the unit cell was determined in Question B5).

(b) Use the same method to find the theoretical (room temperature) densities of gold, Au (FCC) and magnesium, Mg (CPH).

(c) How do the values compare with the measured densities (Mg/m^3): Fe: 7.87; Au: 19.3; Mg: 1.74?

B6. Interstitial space

An *interstitial space* (or hole) is the space between the atoms or molecules. The FCC, CPH and BCC structures contain interstitial space of two sorts: *tetrahedral* and *octahedral*. These are defined by the arrangement of the surrounding atoms, as shown in the Figure below. (Note that the space itself is *not* this shape, as part of the shaded volumes is occupied by the spherical atoms themselves).



(a,b) The two types of interstitial hole in the FCC structure;
(c) the tetrahedral hole of the BCC structure; (d) the octahedral hole in the CPH structure.

Interstitial holes are important because small foreign atoms can fit into them. For FCC and CPH structures, the tetrahedral hole can accommodate, without strain, a sphere with a radius of 0.22 of that of the host. The octahedral holes are almost twice as large: the size of sphere they can hold is found in Question B7. Atoms are in reality somewhat elastic, so that foreign atoms that are larger than the holes can be squeezed into the interstitial space.

Interstitial solute atoms are particularly important for carbon steel, which is iron with carbon in some of the interstitial holes. Iron is BCC (at room temperature), and only contains tetrahedral holes (shown in Figure (c) above). These can hold a sphere with a radius 0.29 times that of the host, without strain. Carbon will go into these holes, but because it is a bit too big, it distorts the crystal structure. It is this distortion that gives carbon steels much of their strength.

Another significant factor in carbon steels is the difference in maximum hole size between FCC and BCC. Iron transforms to FCC (at temperatures around 800°C, depending on the C content). This means that much more carbon will “dissolve” in FCC (at high temperature) than in BCC (at room temperature) – this is central to the heat treatment and strengthening of carbon steel (covered in Part IB).

Interstitial holes appear in another context below: they give a way of understanding the structures of many ceramic compounds: oxides, carbides and nitrides.

Questions

B7. Calculate the diameter of the largest sphere which will fit into the octahedral hole in the FCC structure. Take the diameter of the host-spheres to be unity.

B8. The CPH structure contains tetrahedral interstitial holes as well as octahedral ones. Identify a tetrahedral hole on the CPH lattice of Figure B8.

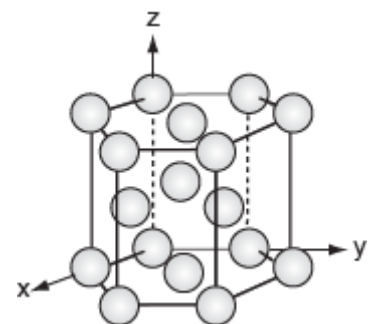


Figure B8. CPH structure

B7. Ceramic crystals

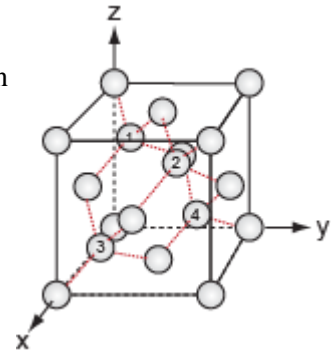
Technical ceramics are the hardest, most refractory structural materials – examples are given in the tables below. The ceramic family also includes many *functional materials* (semiconductors, piezo-electrics, ferromagnetic etc.). Their structures often look complicated, but can mostly be interpreted as atoms of one type, arranged on a simple FCC, CPH or BCC lattice, with the atoms of the second type (and sometimes a third) inserted into the interstitial holes of the first lattice. There are four main crystal structures for engineering ceramics: diamond cubic, halite, corundum and fluorite. Two of these are illustrated here, to demonstrate the underlying principles.

Diamond cubic (DC) structure

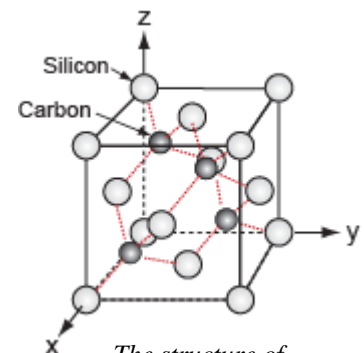
The hardest ceramic of all is diamond, of major importance for cutting tools, polishes and scratch-resistant coatings. Silicon and germanium, the foundation of semiconductor technology, have the same structure. Carbon, silicon and germanium atoms have a 4-valent nature – each atom prefers to have 4 nearest neighbours, symmetrically placed around them. The DC structure achieves this.

The Figure shows the DC unit cell. If you first ignore the numbered atoms, the remainder form an FCC lattice; the atoms numbered 1-4 are then additional atoms located in half of the tetrahedral interstitial spaces. As the tetrahedral hole is far too small to accommodate a full-sized atom, the others are pushed further apart, lowering the density.

Silicon carbide (like diamond) is very hard, and its structure is closely related. Carbon lies directly above silicon in the Periodic table, it has the same crystal structure and is chemically similar. So it is no surprise that silicon carbide, with the formula SiC, has the diamond structure with half the carbon atoms replaced by silicon. Think of it as FCC Si, with carbon in half the tetrahedral interstitial holes (i.e. those previously labeled 1-4).



The diamond-cubic (DC) structure.



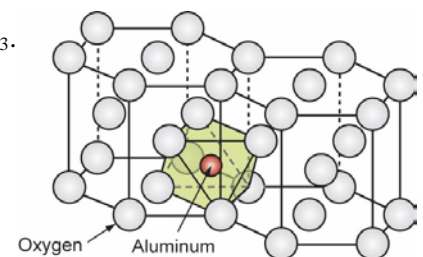
The structure of silicon carbide.

Materials with the Diamond Cubic structure	Typical uses
Silicon, Germanium	Semiconductors
Carbon as diamond	Cutting and grinding tools, jewellery
Silicon carbide	Abrasives, cutting tools

Oxides with the Corundum structure

A number of oxides have the formula M_2O_3 , among them alumina, Al_2O_3 . The oxygen, the larger of the two ions, is close-packed in a CPH stacking. The M atoms occupy two thirds of the octahedral holes in this lattice (one shown in the Figure).

Materials with the Corundum structure	Comment
Alumina, Al_2O_3	The most widely used technical ceramic
Iron oxide, Fe_2O_3	The oxide from which iron is extracted
Chromium oxide, Cr_2O_3	The oxide that gives chromium its protective coating.



The M atoms of the corundum structure lie in the octahedral holes of a CPH oxygen lattice.

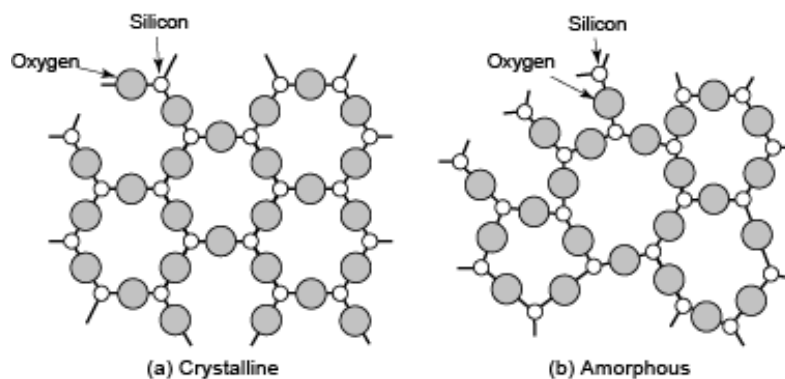
Questions

B9. How many atoms are there in the unit cell of the DC structure? Show that the lattice constant for DC is equal to $2.309 D$, where D is the atomic diameter. Hence find the atomic packing fraction for the DC structure, and comment on the result compared to a close-packed structure.

B10. The lattice constant of DC silicon carbide is $a = 0.436$ nm. The atomic mass of silicon is 28.09 kg/kmol, and that of carbon is 12.01 kg/kmol. What is the theoretical density of silicon carbide?

B8. Glasses

When crystalline materials melt, the atoms lose their regular packing but are still loosely held together; on solidification, crystals usually form readily. *Glasses* are all based on *silica*, SiO_2 , for which crystallisation is difficult. In the solid state silica usually has an *amorphous* (or glassy) structure, and only crystallises if cooled very slowly. The difference is shown schematically in 2D below.



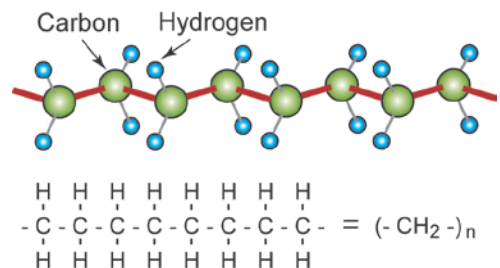
Amorphous structures give transparency, with the colour and refractive index of the glass readily being customised by alloying.

B9. Polymer microstructure

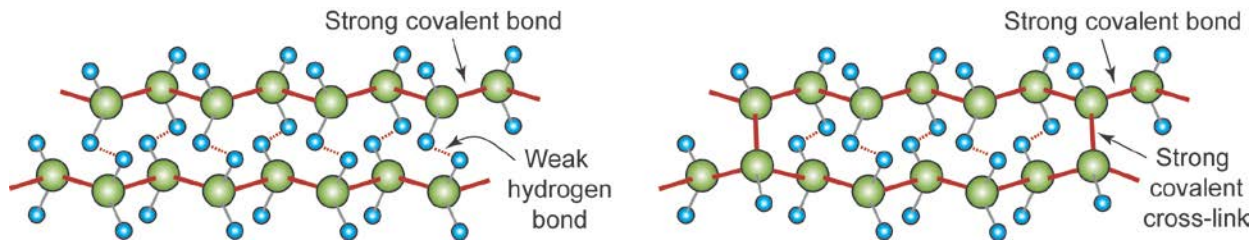
Bonding in polymers

Polymers are *long-chain molecules* of carbon (typically $10^4 - 10^6$ atoms). Along the chains are side-bonds to atoms of H, Cl, F, or groups of atoms such as a methyl group, CH_3 .

The simplest polymer (polyethylene, PE), is formed by polymerisation of a basic CH_2 “mer” into a chain molecule:



Primary bonding between the C atoms is by strong *covalent* bonds – both *along* the chains, and at *cross-links* (where two chains are bonded together). *Secondary bonding* acts *between* the chains (via the side-groups) by weak *van der Waals* bonds.



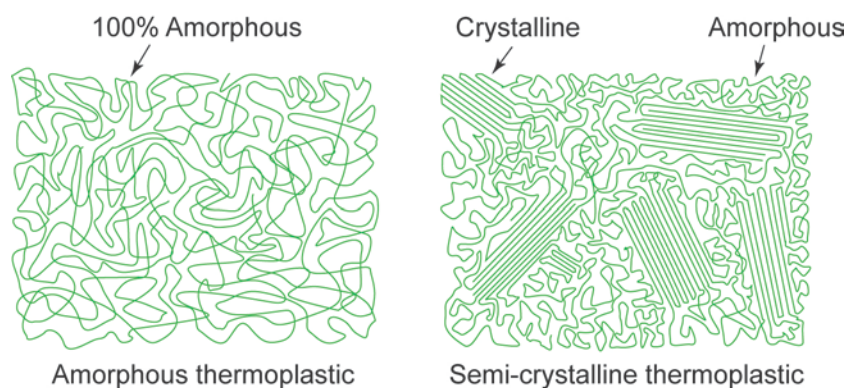
Polymers are inherently low in density (similar to that of water): they are made of light elements (carbon, hydrogen), and the low packing density of the molecules leaves more “free space” in the structure.

Microstructure in polymers

There are three main classes of polymer: *thermoplastics*, *thermosets* and *elastomers*. In all cases the long-chain molecules pack together randomly, giving an amorphous “spaghetti-like” microstructure. The classes are then distinguished by the detail in the molecular architecture, in particular, whether the extent of covalent cross-linking between chains.

(1) Thermoplastics

Thermoplastics contain *no cross-links* (covalent bonds between the chain molecules), but are divided into two sub-groups: *amorphous* and *semi-crystalline*.

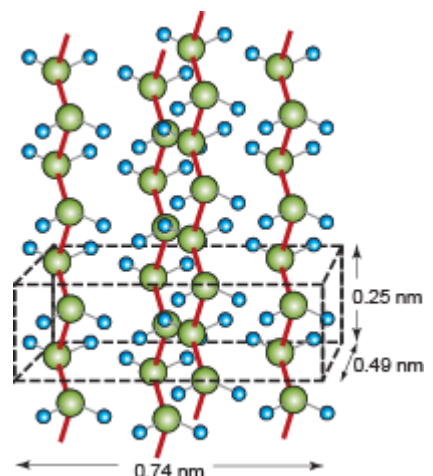


In *amorphous* thermoplastics, the long-chain molecules are arranged entirely at random, with occasional *entanglement points* between chains. At these points there is no additional bonding, but they do restrain the deformation and sliding of the molecules.

Semi-crystalline thermoplastics are partly amorphous, and partly ordered in *crystalline regions* (known as “spherulites”).

In crystalline regions, the long chains line up and pack to give an ordered, repeating structure, just like any other crystal. The low symmetry of the individual molecules means that the unit cell is usually defined by three dimensions, as illustrated in the Figure, showing crystalline polyethylene.

Few polymers are completely crystalline, but many have as much as 90% crystallinity. Since the crystalline regions are more tightly packed than amorphous regions (less “free space”), this can lead to significant shrinkage on crystallisation. This can lead to lower dimensional precision in manufactured polymer components.



The structure of a crystalline polyethylene.

The ease with which a thermoplastic crystallises is determined by the complexity of the side groups:

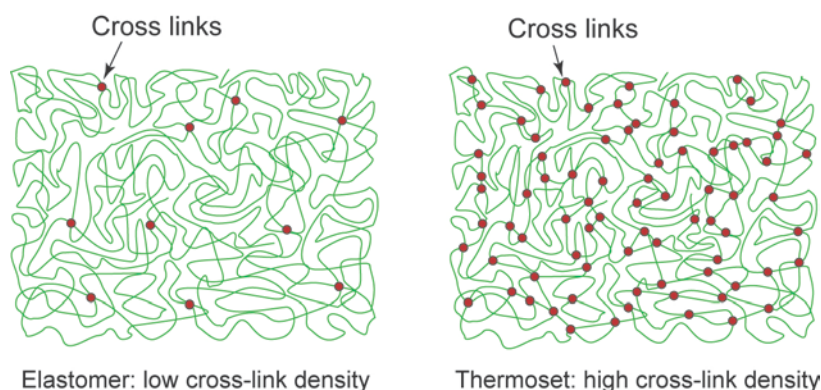
- simple thermoplastics: semi-crystalline – nylon (PA), polyethylene (PE)
- complex thermoplastics: fully amorphous – perspex (PMMA), polycarbonate (PC)

In pure form, amorphous thermoplastics are transparent, and semi-crystalline thermoplastics are translucent. Both are easily artificially coloured with fillers and dyes – this versatility in colour is one reason that polymers are so widely used for household products and packaging.

(2) Elastomers and (3) Thermosets

Elastomers contain a *small number of cross-links*, between simple chain molecules. Natural rubber is an example, in which the cross-links are provided by sulphur. Further cross-linking can be triggered in service (e.g. by UV light or ozone), leading to polymer degradation.

Thermosets, in contrast, have *extensive cross-links* between chains.



Typical polymers of engineering importance are:

Polymer Class	Material	Typical uses
Thermoplastic	Polyethylene, PE	Bags, tubes, bottles
	Polyvinylchloride, PVC	Pipes, gutters, window frames, packaging
	Polypropylene, PP	Mouldings, rope
	Polystyrene, PS	Toys, packaging, cutlery
	Nylon, PA	High quality parts, gears, catches
Thermoset	Epoxy	Adhesives, fibre composites
	Phenolics	Electrical plugs and sockets, cookware
Elastomer	Natural/synthetic rubber	Tyres, electrical insulation, tubing
	Isoprene, neoprene	Wetsuits, footwear

Suggested Tripos Questions

2012 Q11(b); 2013 Q9; 2014 Q9; 2015 Q7; 2017 Q8; 2018 Q8.

H.R.Shercliff
Lent Term 2019