Engineering Tripos   **FIRST YEAR**

<div align="center">

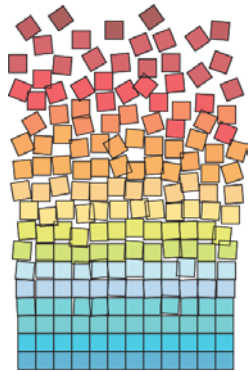**Part IA Paper 2: Structures and Materials**

MATERIALS

Examples Paper 1 – TEACH YOURSELF MICROSTRUCTURE

Mike Ashby and Hugh Shercliff

</div>

1. **Introduction**
2. **Atomic structure**
3. **Atomic and molecular bonding**
4. **Metal crystals structures**
5. **Theoretical density of metals**
6. **Interstitial space**
7. **Ceramic crystals**
8. **Glasses**
9. **Polymer microstructure**
10. **Solutions to Questions**

<div align="center">

Straightforward questions are marked with a †
Tripos standard questions are marked with a *

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

</div>

1. Introduction

Part I Materials is principally about materials and their properties in relation to design and manufacture. The *properties* of materials – strength, stiffness, toughness, conductivity and so on – are strongly influenced by the underlying *microstructure*. So it is important to be able to describe the relevant microstructural features.

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 polycrystal 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 (1nm = 10^{-9}m); grains are typically 1-100μm across (1μm = 10^{-6}m), and contain billions of atoms. The course will also introduce several other 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.

This "Teach Yourself" Examples Paper covers: (i) the methods for describing the 3-dimensional arrangement of atoms or molecules in crystals; (ii) how atomic packing leads directly to estimates of material density; and (iii) a brief summary of the types of bonding between atoms. Some of the content is background reading, while some sections contain questions (with complete solutions at the end – don't look at these until you have properly attempted a question). Physics and Chemistry courses at school vary widely in their coverage of materials – this Examples Paper aims to bring everyone up to the same initial level on microstructure. Some sections may be familiar to you – read and work through it all anyway.

2. 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: $_{82}Pb^{207}$.

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

So lead has 207 times more mass than hydrogen $_1H^1$.

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).
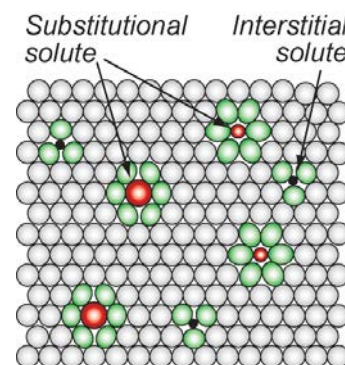
3. Atomic and molecular bonding

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_o, governed by the balance between attractive and repulsive forces. At the *dissociation separation* the atoms (or ions) can be separated completely.
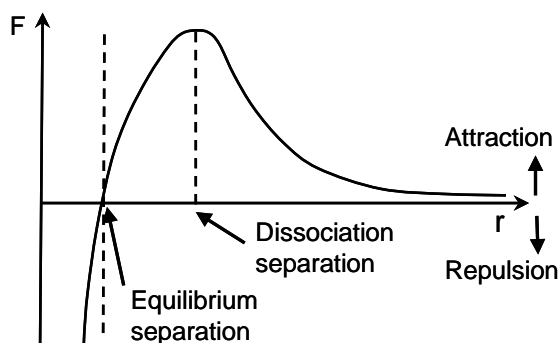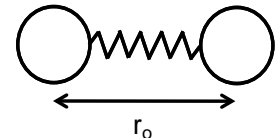
Atoms vibrate about the equilibrium separation, with kinetic energy $\approx k_B T$, where T is the absolute temperature (in K) and k_B is Boltzmann's constant (1.38×10^{-23} J per atom K^{-1}). All bonds effectively break down when $k_B T$ exceeds the bond energy – at this point the material melts. 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_BT) than primary, giving low melting points.

4. 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-centered cubic (FCC)
- close-packed hexagonal (CPH)
- body-centered 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).
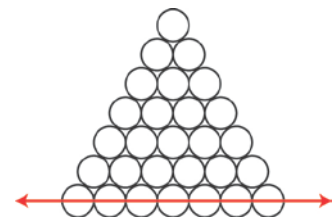

A 3D lattice can be built by stacking these close-packed planes – but there are 2 ways of doing it.

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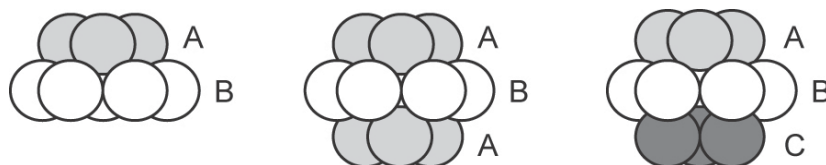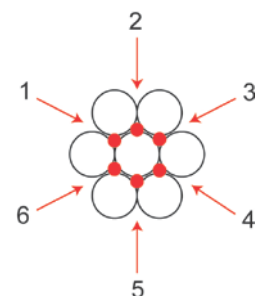
Continuing these patterns builds up the 3D lattices: ABAB…. or ABCABC….

Question

E1. Figure E1 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.
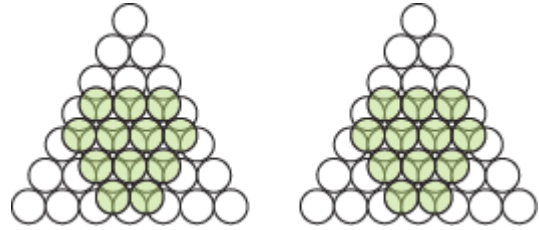

Figure E1.   Two layers of close-packed planes.

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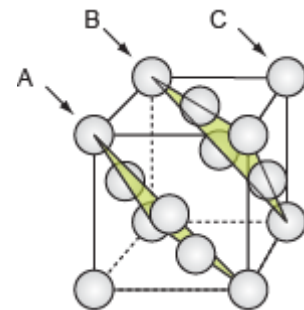
Unit cells are drawn with the atoms reduced in size, for clarity – remember that they touch in close-packed directions.

Face-centered 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).

FCC structure of packed spheres showing the ABC stacking.

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 E2).

Question

E2. 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
Sliver, 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_{1c} – 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).
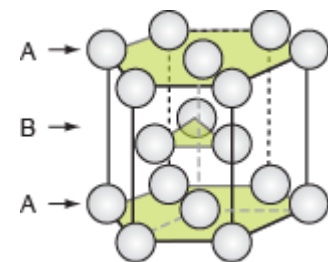
CPH structure of packed spheres showing the ABA stacking.

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 E3).

Question

E3. (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.

6

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

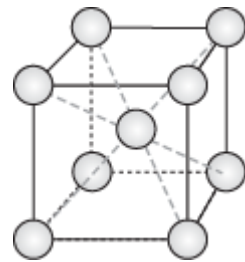| Material	Typical uses
Zinc	Die-castings, plating
Magnesium	Light-weight structures
Titanium and its alloys	Light, strong components for airframes and engines, biomedical and chemical engineering
Cobalt	High temperature superalloys, bone-replacement implants.
Beryllium	The lightest of the metals. Its 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-centered 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 E4).

BCC structure of non-close-packed spheres.

Question

E4. 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_{1c}) 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.

5. 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 E2, $a = 2\sqrt{2}\,R$

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: $8 \times 1/8 \;+\; 6 \times 1/2 \;=\; 4$

$$\qquad\qquad\qquad\qquad\qquad\text{(corners)}\qquad\text{(faces)}$$

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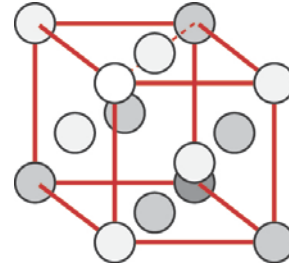
Question

E5. 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: $\rho = \dfrac{n\,A}{V_c\,N_A}$

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

**E6.** (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 E5).

    (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?

6. 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) FCC tetrahedral hole

(b) FCC octahedral hole

(c) BCC tetrahedral hole

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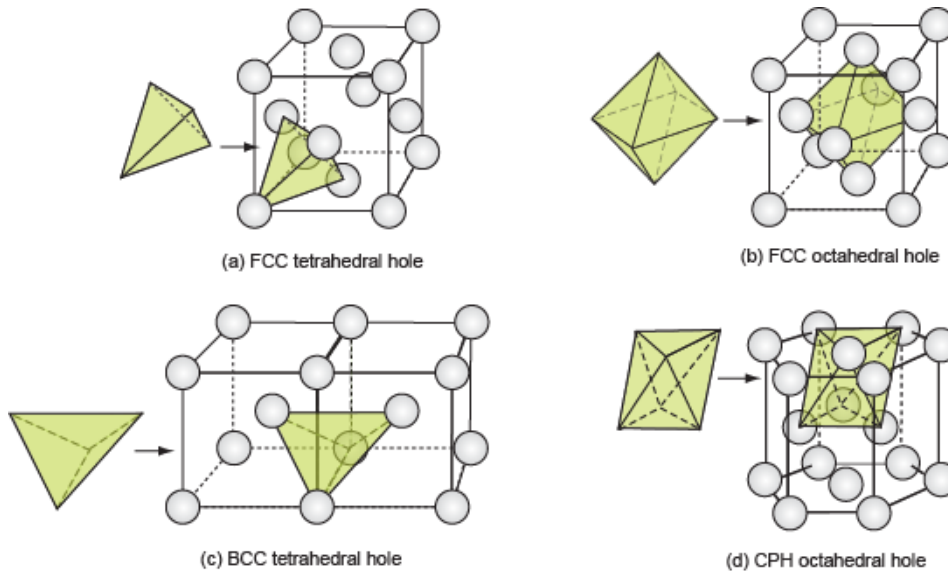
(a,b) The two types of interstitial hole in the FCC structure;
(c) the tetrahedral hole of the BCC structure; (d) the octahedral hole in the CPH structure.

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 E7. 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

E7. 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.

E8. The CPH structure contains tetrahedral interstitial holes as well as octahedral ones. Identify a tetrahedral hole on the CPH lattice of Figure E8.
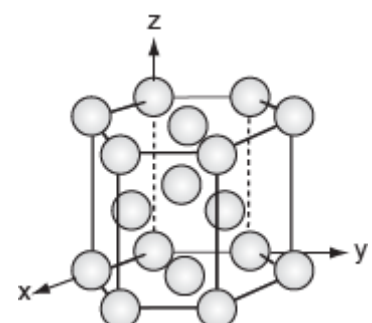

9

Figure E8. CPH structure

7. 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.
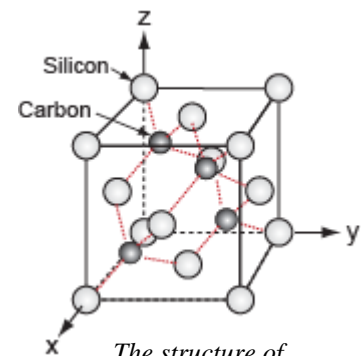
Diamond cubic (DC) structure

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.

The diamond-cubic (DC) structure.

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).
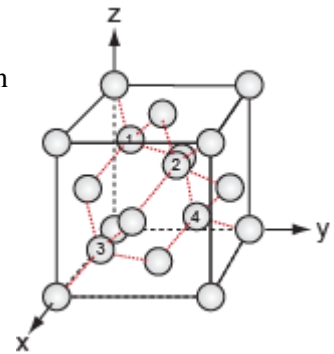
The structure of silicon carbide.

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).

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

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.

Questions

**E9.** 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.

E10. 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?

8. 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.

(a) Crystalline   (b) Amorphous
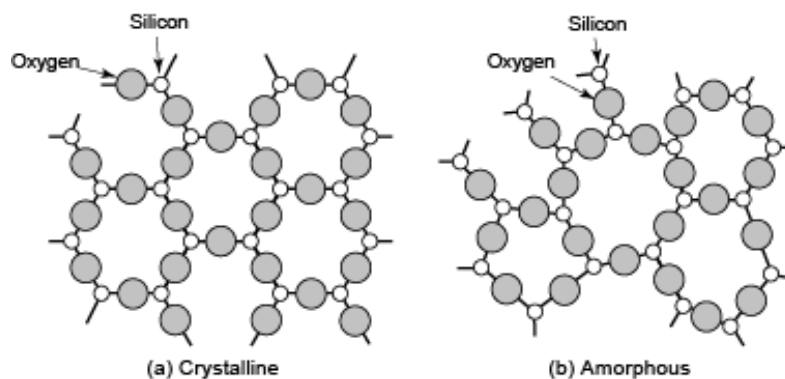
Amorphous structures give transparency, with the colour and refractive index of the glass readily being customised by alloying.

9. 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:
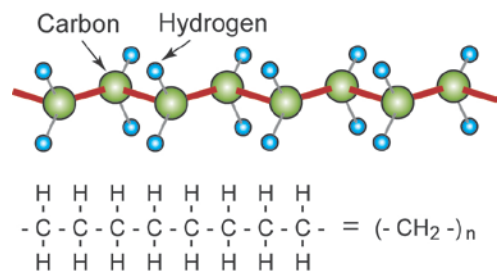
Changing 1 H in 4 to Cl gives polyvinyl chloride (PVC); changing 1 H in 4 to CH_3 gives polypropylene (PP), and so on

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.

11
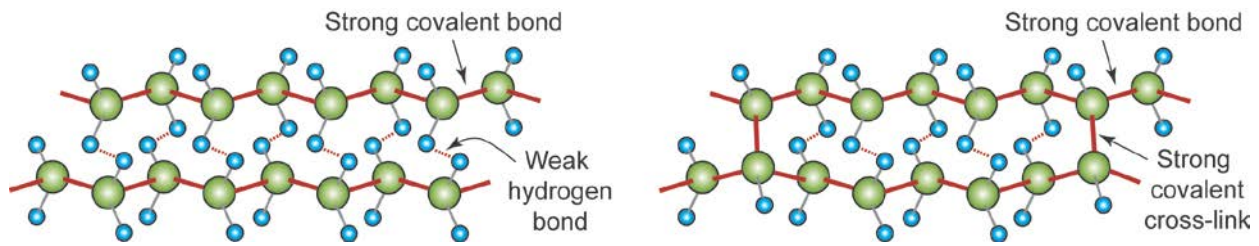
Polymers are inherently low in density (similar to that of water): they are made of light elements (carbon, hydrogen), and the low packing density of the molecules leaves more "free space" in the structure.

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.
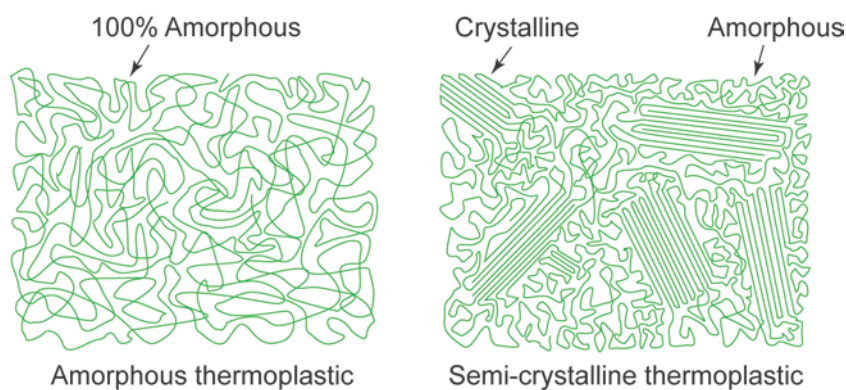
(1) Thermoplastics

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.
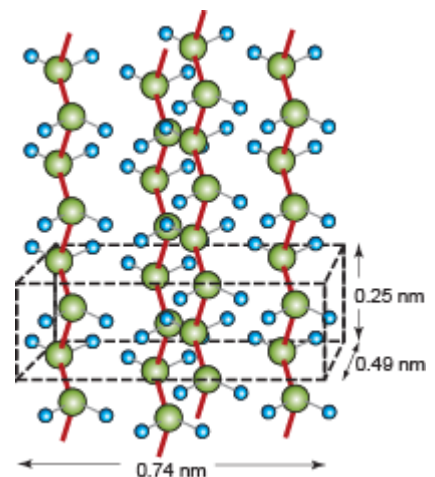
The structure of a crystalline polyethylene.

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.

Elastomer: low cross-link density   Thermoset: high cross-link density
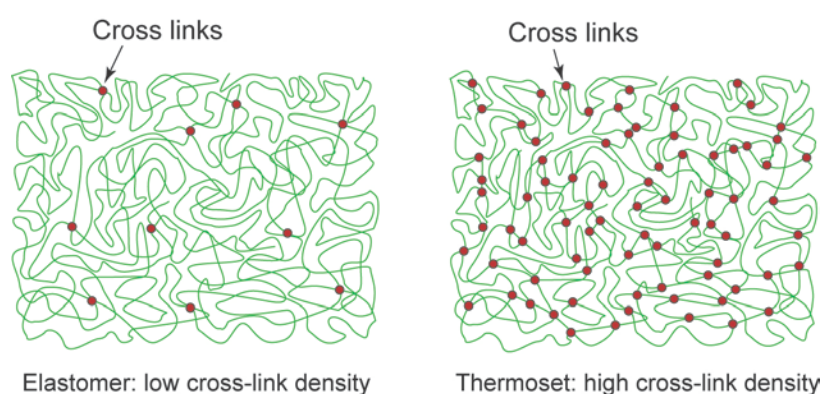
Typical polymers of engineering importance are:

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

Reference

This Teach Yourself Examples Paper is based on Ashby MF, Shercliff HR and Cebon C, *Materials: Engineering, Science, Processing and Design*, 3rd edition, Butterworth-Heinemann 2014, Chapter 4 and Guided Learning Unit 1.

Suggested Tripos Questions

2010 Q7; 2012 Q11(b); 2013 Q9.

10. Solutions to Questions

E1.
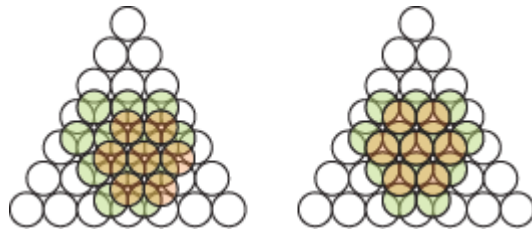
FCC (ABCABC) and CPH (ABAB) stacking of close-packed layers.

E2. FCC (one face – atoms shown full size)
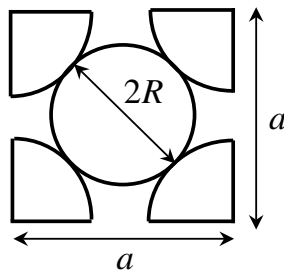
Let the lattice constant $= a$, and the atomic radius $= R$.

From the Figure: $a^2 + a^2 = (4R)^2$

Hence $a = 2\sqrt{2}\,R$.

E3. (a) CPH

The figure shows a regular tetrahedron between 4 atom centres: 3 atoms in the base-plane of the unit cell, and the atom from the middle layer that sits on top of them.

The height of the unit cell c is twice the height of the tetrahedron, and the side-length of the hexagonal base, $a = 2R$.
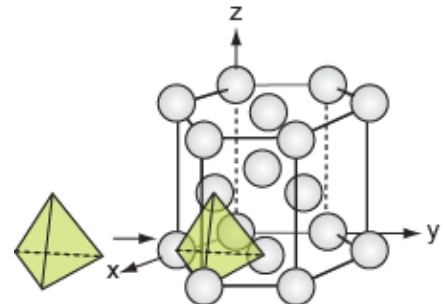
It is readily shown using Pythagoras' theorem that the height of a regular tetrahedron of side-length a is $a\sqrt{2}/\sqrt{3}$. Hence $c{:}a = 2\sqrt{2}/\sqrt{3} = 1.633$.

(b) For Mg, $R = 0.1605$nm, hence $a = 0.321$nm, $c = 0.524$nm.

E4. BCC
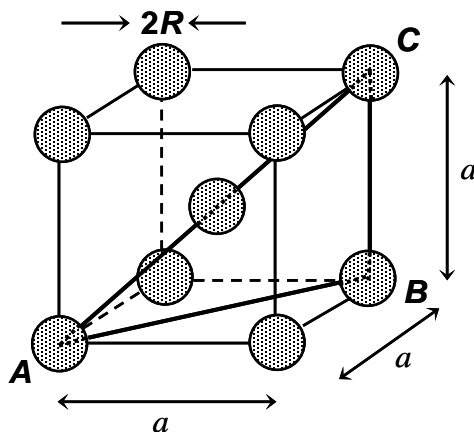
Atom radius $= R$ (shown reduced in size for clarity). Central atom and atoms at A and C are in contact, so unit cell diagonal has length $4R$.

$$(\mathrm{AB})^2 = 2\,a^2$$

$$(\mathrm{AC})^2 = (\mathrm{AB})^2 + (\mathrm{BC})^2 = 2\,a^2 + a^2 = (4R)^2$$

Hence $a = 4\,R/\sqrt{3}$

E5. (a) CPH, lattice constants a and c

Base area of hexagonal unit cell: $a^2 \, 3\sqrt{3}/2$; height $c = a \, 2\sqrt{2}/\sqrt{3}$ (from Question E3).

Volume of unit cell $=$ base $\times$ height $= a^2 \, 3\sqrt{3}/2 \, \times c = a^2 \, 3\sqrt{3}/2 \, \times a \, 2\sqrt{2}/\sqrt{3} = a^3 \, 3\sqrt{2} = R^3 \, 24\sqrt{2}$

Corner atoms shared between 6 cells, hexagonal face atoms between 2, plus 3 complete internal atoms.

Hence number of atoms per unit cell: $12 \times 1/6 \ + \ 2 \times 1/2 \ + \ 3 \times 1 \ = 6$

$\qquad\qquad\qquad\qquad\qquad\qquad$ (corners) $\qquad$ (faces) $\qquad$ (internal)

Atomic packing fraction $= \dfrac{6 \times \frac{4}{3} \pi R^3}{R^3 \, 24\sqrt{2}} = 0.74$ (74%), i.e. same as FCC (both close-packed).

(b) BCC, lattice constant a

From Question E4, $a = 4R/\sqrt{3}$

Volume of unit cell $= \left(\dfrac{4R}{\sqrt{3}}\right)^3 = \dfrac{64 R^3}{3\sqrt{3}}$

Number of atoms per unit cell $= \ 8 \times 1/8 \ + \ 1 \times 1 \ = 2$

$\qquad\qquad\qquad\qquad\qquad\qquad\quad$ (corners) $\qquad$ (internal)

Hence atomic packing fraction $= \dfrac{2 \times \frac{4}{3} \pi R^3}{64 R^3 / 3\sqrt{3}} = 0.68$ (74%)

BCC is not close-packed: compared with the packing fraction in close-packed FCC and CPH ($=0.74$), close packing is 8.8% more dense than BCC.

**E6.**   Theoretical density $\rho = \dfrac{n A}{V_c \, N_A}$; data for lattice constant a and relative atomic weight A from

Materials Databook.

(a) For BCC: $n = 2$, $V_c = a^3$.   For Fe, $a = 2.8663$ Å, $A = 55.847$.

$\rho = \dfrac{2 \times 55.847}{\left(2.8663 \times 10^{-10}\right)^3 \times 6.02 \times 10^{23}} = 7.878 \text{ Mg m}^{-3}$

(b) For FCC: $n = 4$, $V_c = a^3$.   For Au, $a = 4.0786$ Å, $A = 196.967$.

$\rho = \dfrac{4 \times 196.967}{\left(4.0786 \times 10^{-10}\right)^3 \times 6.02 \times 10^{23}} = 19.29 \text{ Mg m}^{-3}$

For CPH: $n = 6$, $V_c = a^3 \, 3\sqrt{2}$. For Mg, $a = 3.2094$ Å, $A = 24.312$.

$\rho = \dfrac{2 \times 24.312}{3\sqrt{2} \times \left(3.2094 \times 10^{-10}\right)^3 \times 6.02 \times 10^{23}} = 1.728 \text{ Mg m}^{-3}$

(c) In all three cases, the values agree very well with the measured densities (better than 1%). This supports the validity of the hard sphere approximation. Crystal defects such as grain boundaries make a very small difference, and the distortion of the outer electron shells is not taken into account in the hard sphere model.

E7. The Figure shows how to calculate the octahedral hole size in the FCC structure. The face diagonals are close-packed directions, so the atom spacing along the diagonal is 1 unit. The cell edge thus has length $\sqrt{2} = 1.414$ units. That is also the separation of the centers of the atoms at opposite corners of the octahedral hole. The atoms occupy 1 unit of this, leaving a hole that will just contain a sphere of diameter 0.414 units without distortion.
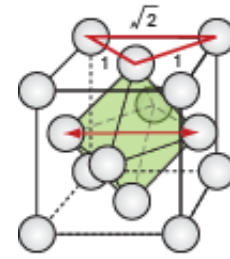
The calculation of the octahedral interstitial hole size in the FCC lattice

**E8.** The figure shows a tetrahedral hole of the CPH structure.

(The geometry of this tetrahedron was considered in evaluating the height of the unit cell).
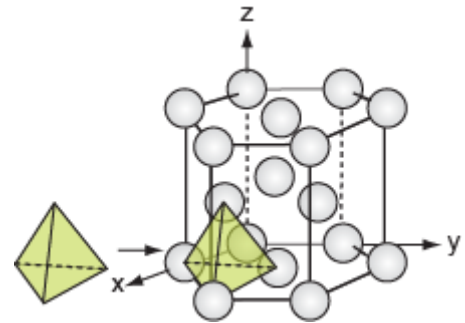
A tetrahedral hole of the CPH structure.

E9. In diamond cubic there are 8 atoms per unit cell: 8×1/8 (corners) + 6×1/2 (faces) + 4 (internal).

Referring to the DC unit cell in the figure, atom number 3 sits in the middle of a regular tetrahedron. The atom spacing along the horizontal edges of the tetrahedron is equal to half the length of the diagonal of one face of the cube, i.e. $a/\sqrt{2}$, where a is the lattice constant. The shaded triangles, height $a/4$, link the centre of the internal atom number 3 to the face/corner atoms that it touches.
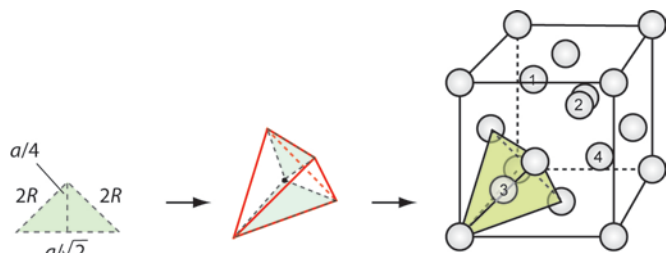
The geometry of the tetrahedral packing in DC.

From Pythagoras' theorem: $(2R)^2 = (a/4)^2 + (a/2\sqrt{2})^2$, from which $R = \sqrt{3}\,a/8$, or $a = 8R/\sqrt{3} = 4D/\sqrt{3} = 2.309D$. Hence the atomic packing fraction $= \dfrac{8 \times \frac{4}{3}\pi R^3}{8^3\,R^3\,/3\sqrt{3}} = 0.34$ (34%). This is remarkably low compared to close-packing (74%).

E10. For DC silicon carbide, there are 4 Si atoms and 4 C atoms in the unit cell. The mass of the unit cell is therefore $[(4 \times 28.09) + (4 \times 12.01)] / 6.022 \times 10^{26} = 26.636 \times 10^{-26}$ kg. The volume of the SiC unit cell $= (0.436 \times 10^{-9})^3 = 8.288 \times 10^{-29}$ m^3.
Hence the theoretical density $= 26.636 \times 10^{-26}$ kg $/ 8.288 \times 10^{-29}$ m$^3 \approx 3.21$ Mg/m^3.

H.R. Shercliff
Lent Term 2014