4.7 Atomic and molecular packing in solids: the origin of density

Introduction to Guided Learning Unit 1: Simple ideas of crystallography

The properties of materials depend on the way the atoms or molecules within them are packed. In *glasses*, the arrangement is a disordered one with no regularity or alignment. *Polymers* are largely made up of tangled long-chain molecules. *Metals* and *ceramics*, by contrast, are crystalline, with a regularly repeating pattern of atomic packing in structural units. Crystals are described using the language of *crystallography*, which provides a framework for understanding their three-dimensional geometry. The key ideas of crystallography are introduced briefly in the following pages. Later in the book, you will find *Guided Learning Unit 1: Simple ideas of crystallography*, which develops the ideas in greater depth. The rest of this chapter will be intelligible without reference to the unit, but working through it and its exercises will give more complete understanding and confidence.

Atom packing in metals and the unit cell Atoms often behave as if they were hard, spherical balls. The balls on a pool table, when set, are arranged as a close-packed layer, as shown in Figure 4.27(a). The atoms of many metals form extensive layers packed in this way. There is no way to pack the atoms more closely than this, so this arrangement is called 'close-packed'. These two-dimensional layers of atoms can then be close-packed in three dimensions. Surprisingly, there are two ways to do this. Where three atoms meet in the first layer, layer A, there are natural depressions for atoms of a second close-packed layer B. A third layer can be added such that its atoms are exactly above those in the first layer, so that it, too, is in the A orientation, and the sequence is repeated to give a crystal with ABABAB … stacking, as in Figure 4.27(b); it is called *close-packed hexagonal*, or *CPH* (sometimes *HCP*) for short, for reasons explained in a moment. But there is an alternative stacking sequence. In placing the third layer, there are two choices of position – one aligned with A (as before), and one offset from layer A, giving a third layer, C, that is nested onto B in this alternative position. This stacking becomes (on repeating) ABCABCABC … as shown in Figure 4.27(c); it is called *face-centred cubic* (*FCC* for short). Many metals, such as copper, silver, aluminium and nickel, have the FCC structure; many others, such as magnesium, zinc, and titanium, have the CPH structure. The two alternative structures have the same packing fraction, 0.74, meaning that the spheres occupy 74% of the available space. But the small difference in layout influences properties, particularly those having to do with plastic deformation (Chapter 6).

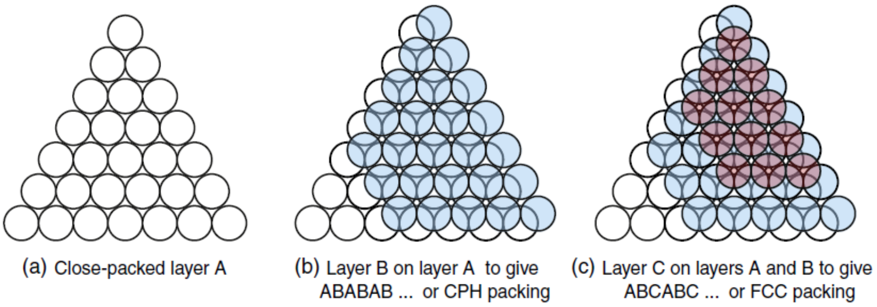


Figure 4.27 Close packing of spheres.

Not all structures are close-packed. Figure 4.28 shows one of these, made by stacking square-packed layers. It has a lower packing density than the hexagonal layers of the FCC and CPH structures. An ABABAB … stacking of these layers builds the *body-centred cubic* structure, *BCC* for short, with a packing fraction of 0.68. Iron and most steels have this structure. There are many other crystal structures, but for now these three are enough, covering most important metals.

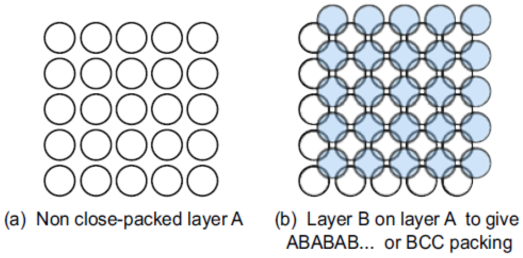


Figure 4.28 Square packing of spheres.

A regular packing of atoms that repeats itself is called a *crystal*. It is possible to pack atoms in a non-crystallographic way to give what is called an *amorphous* structure, sketched in Figure 4.29. This is not such an efficient way to fill space with spheres; the packing fraction is 0.64 at best.

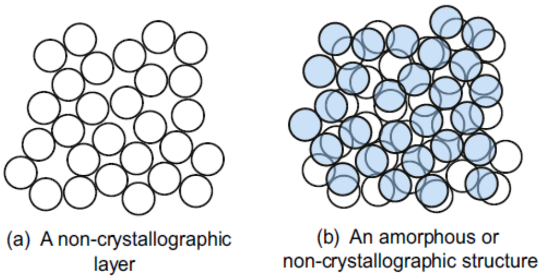


Figure 4.29 Amorphous structures.

The characterising unit of a crystal structure is its *unit cell*. Figure 4.30 shows three; the red lines define the cell. The atoms have been shrunk to reveal the cell more clearly; in reality, they touch in close-packed directions. In the first, shown at (a), the cell is a hexagonal prism. The atoms in the top, bottom and central planes form close-packed layers like that of Figure 4.27(b), with ABAB … stacking – that's why this structure is called CPH. The second, shown at (b), is also made up of close-packed layers, though this is harder to see; the shaded triangular plane is one of them. If we think of this as an A plane, atoms in the plane above it nest in the B position, and those in the plane below it, in the C position, giving ABCABC … stacking, as in Figure 4.27(c). The unit cell itself is a cube with an atom at each corner and one at the centre of each face – for this reason, it's called FCC. The final cell, shown at (c), is the characterising unit of the square-layer structure of Figure 4.28; it is a cube with an atom at each corner and one in the middle, called, appropriately, BCC.

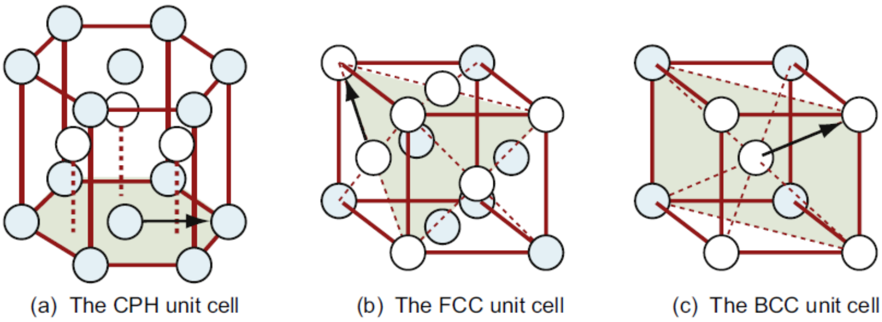

(a) The CPH unit cell (b) The FCC unit cell (c) The BCC unit cell

Figure 4.30 The close-packed hexagonal (CPH), face-centred cubic (FCC), and body-centred cubic (BCC) unit cells. All atoms are the same but are shaded differently to emphasise their positions.

Unit cells pack to fill space as in Figure 4.31. The resulting array is called the *crystal lattice*; the points at which cell edges meet are called *lattice points*. The crystal itself is generated by attaching one or a group of atoms to each lattice point so that they form a regular, three-dimensional, repeating pattern. The cubic and hexagonal cells are among the simplest; there are many others with edges of differing lengths meeting at differing angles. The one thing they have in common is their ability to stack with identical cells to completely fill space.

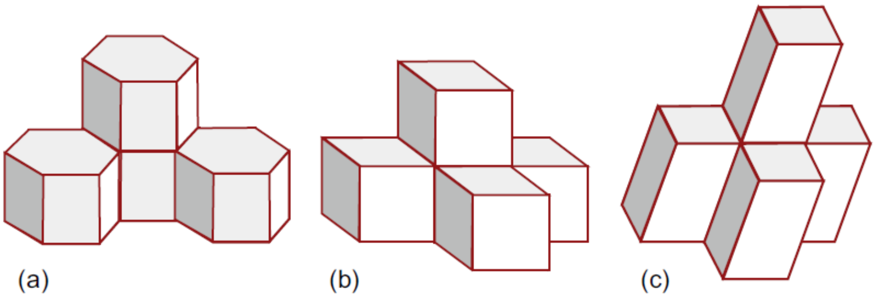
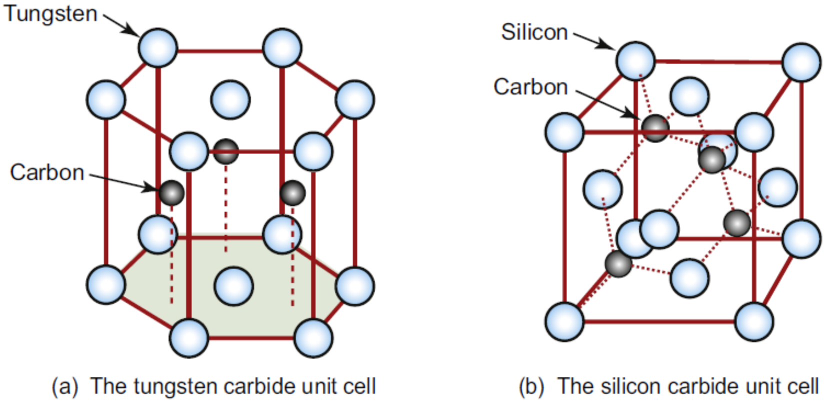


Figure 4.31 Unit cells stacked to fill space. (a) The hexagonal cell. (b) The cubic cell. (c) A cell with edges of differing length that do not meet at right angles.

Atom packing in ceramics Most ceramics are compounds, made up of two or more atom types, ionically or covalently bonded. They, too, have characteristic unit cells. Figure 4.32 shows those of two materials that appear on the property charts: tungsten carbide (WC) and silicon carbide (SiC). The cell of the first is hexagonal; that of the second is cubic, but now a pair of different atoms is associated with each lattice point: a W–C pair in the first structure and a Si–C pair in the second. More examples are investigated in *Guided Learning Unit 1*.

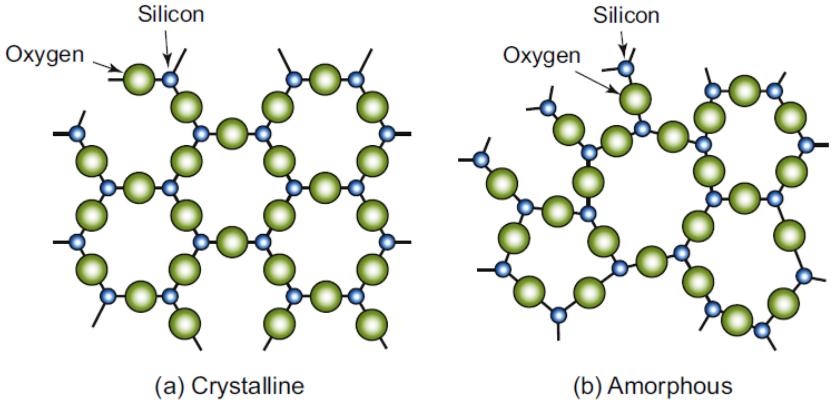


(a) The tungsten carbide unit cell

(b) The silicon carbide unit cell

Figure 4.32 Unit cells of compounds.

Atom packing in glasses The crystalline state is the lowest energy state for elements and compounds. Melting disrupts the crystallinity, scrambling the atoms and destroying the regular order. The atoms in a molten metal look very like the amorphous structure of Figure 4.29. On cooling through the melting point, most metals crystallise easily, though by cooling them exceedingly quickly, it is sometimes possible to trap the molten structure to give an amorphous metallic 'glass'. With compounds, it is easier to do this, and with one in particular, silica (SiO_2), crystallisation is so sluggish that its usual state is the amorphous one. Figure 4.33 shows, on the left, the atom arrangement in crystalline silica: identical hexagonal Si–O rings, regularly arranged. On the right is the more usual amorphous state. Now some rings have seven sides, some have six, some five, and there is no order – the next ring could be any one of these. Amorphous silica is the basis of almost all glasses; it is mixed with Na_2O to make soda glass (windows, bottles) and with B_2O_5 to make borosilicate glasses (Pyrex), but it is the silica that gives the structure. It is for this reason than the structure itself is called 'glassy', a term used interchangeably with 'amorphous'.



(a) Crystalline (b) Amorphous

Figure 4.33 Two alternative structures for silica, the basis of most glasses. (a) Crystalline silica. (b) Glassy or amorphous silica.

Atom and molecular packing in polymers Polymer structures are quite different. The backbone of a 'high' polymer ('high' means high molecular weight) is a long chain of sp^3-hybridised carbon atoms to which side groups are attached. Figure 4.34 shows a segment of the simplest: polyethylene, PE $(-CH_2-)_n$. The chains have ends; the ends of this one are capped with a CH_3 group. PE is made by the polymerisation (snapping together) of ethylene molecules, $CH_2{=}CH_2$, where the $=$ sign is a double bond, broken by polymerisation to give covalent sp^3 links to more carbon neighbours to the left and right. Figure 4.35 shows the chain structure of four more of the most widely used linear polymers.

Polymer molecules bond together to form solids. The carbon–carbon chains that form the backbone of a linear polymer are covalently bonded and strong. The molecules attract each other, but only weakly (Figure 4.36(a)); the weak dipole 'hydrogen' bonds that make them stick are easily broken or rearranged. The resulting structure is sketched in Figure 4.37(a): a dense spaghetti-like tangle of molecules with no order or crystallinity. This is the structure of polymers like those of Figure 4.35; the weak bonds melt easily, allowing the polymer to be moulded when hot – in other words, they are *thermoplastic*.

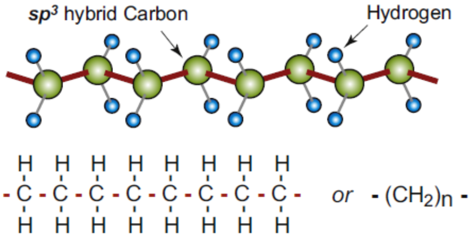


Figure 4.34 Polymer chains have a carbon—carbon backbone with hydrogen or other side groups. The figure shows three alternative representations of the polyethylene molecule.

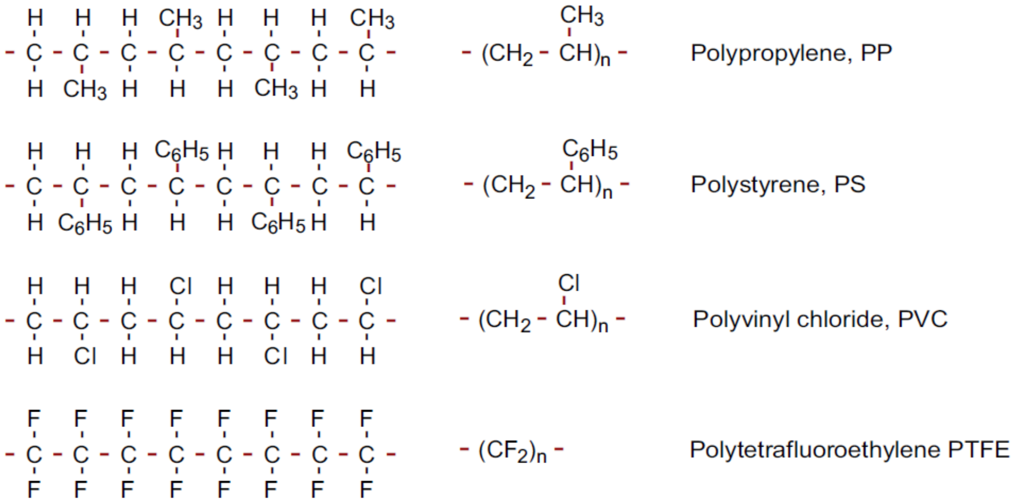


Figure 4.35 Four more common polymers, showing the chemical makeup. The strong carbon—carbon bonds are shown in red.

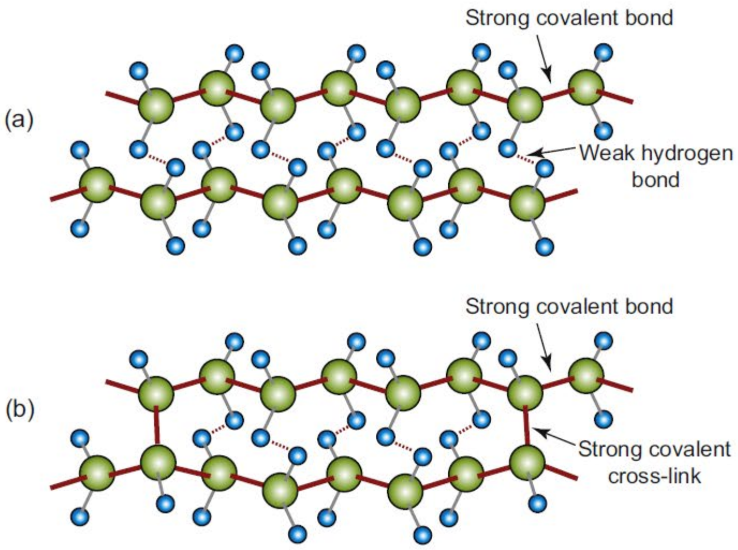


Figure 4.36 The bonding between polymer chains: dipolar hydrogen bonds and covalent cross-links.

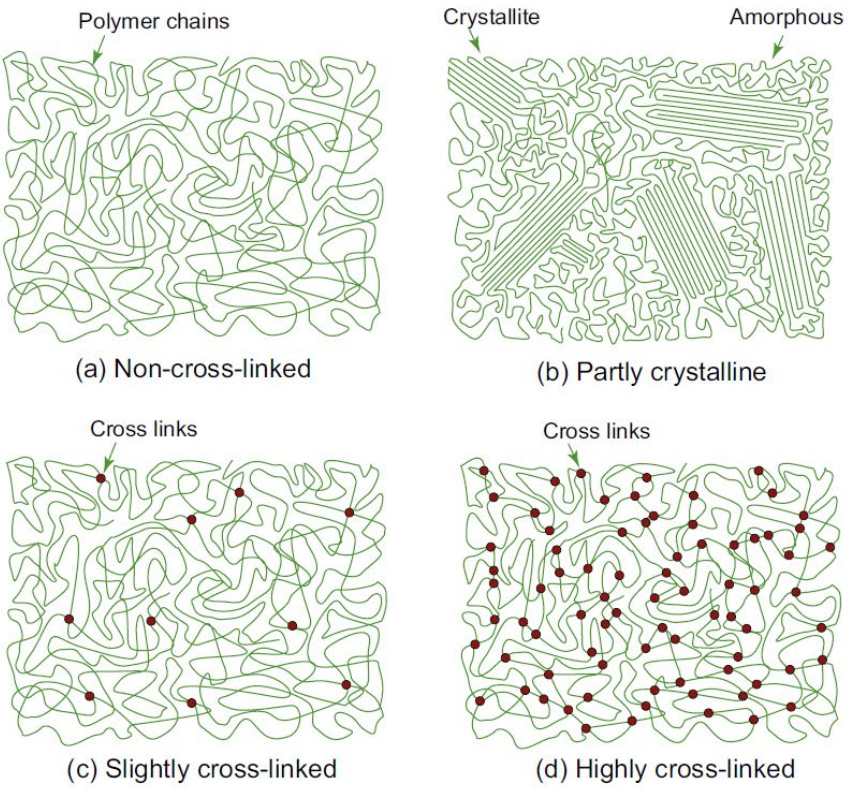


Figure 4.37 Polymer structures: (a) amorphous thermoplastic; (b) semi-crystalline thermoplastic; (c) elastomer; (d) thermoset.

The weak bonds of thermoplastics do, however, tend to line segments of the molecules up. Total alignment is not possible, but where segments of molecules manage it, there are small crystalline regions, as in Figure 4.37(b). These *crystallites* are small – often between 1 and 10 microns across, just the right size to scatter light. So amorphous polymers with no crystallites can be transparent; polycarbonate (PC), polymethyl-methacrylate (PMMA, Plexiglas) and polystyrene (PS) are examples. Those that are *semi-crystalline*, like PE and nylon (PA), scatter light and are translucent.

The real change comes when chains are *cross-linked* by replacing some of the weak hydrogen bonds by much more muscular covalent C–C bonds, as in Figure 4.36(b), making the whole array into one huge multiply connected network. *Elastomers* (rubbery polymers) have relatively few cross-links, as in Figure 4.37(c). *Thermosets* like epoxies and phenolics have many cross-links, as in Figure 4.37(d), making them stiffer and stronger than thermoplastics. The cross-links are not broken by heating, so once the links have formed, elastomers and thermosets cannot be thermally moulded or (for that reason) recycled.

Physical origin of density Atoms differ greatly in weight but little in size. Among solids, the heaviest stable atom, uranium (atomic weight 238), is about 35 times heavier than the lightest, lithium (atomic weight 6.9), yet when packed to form solids, their diameters are almost exactly the same (0.32 nm). The largest atom, caesium, is only 2.5 times larger than the smallest, beryllium. So density is mainly determined by the atomic weight and only to a lesser degree by the atom size and the way they are packed. Metals are dense because they are made of heavy atoms, packed densely together (iron, for instance, has an atomic weight of 56). Ceramics, for the most part, have lower densities than metals because they contain light Si, O, N or C atoms. Polymers have low densities because they are largely made of light carbon (atomic weight: 12) and hydrogen (atomic weight: 1) in low-density amorphous or semi-crystalline packings. The lightest atoms, packed in the most open way, give solids with a density of around 1000 kg/m^3 – the same as that of water (see Figure 4.8). Materials with lower densities than this are *foams* (and woods), made up of cells containing a large fraction of pore space.

Density of metallic alloys Most metallic alloys are not pure but contain two or more different elements. Often they dissolve in each other, like sugar in tea, but as the material is solid, we call it a *solid solution*; examples are brass (a solution of Zn in Cu) and stainless steel (a solution of Ni and Cr in Fe). As we shall see in later chapters, some material properties are changed a great deal by making solid solutions; density is not. As a rule, the density $\widetilde{\rho}$ of a solid solution lies between the densities ρ_A and ρ_B of the materials that make it up, following a *rule of mixtures* (an arithmetic mean, weighted by volume fraction) known, in this instance, as Vegard's law:

$$\widetilde{\rho} = f\rho_A + (1-f)\rho_B \tag{4.23}$$

where f is the fraction of A atoms.