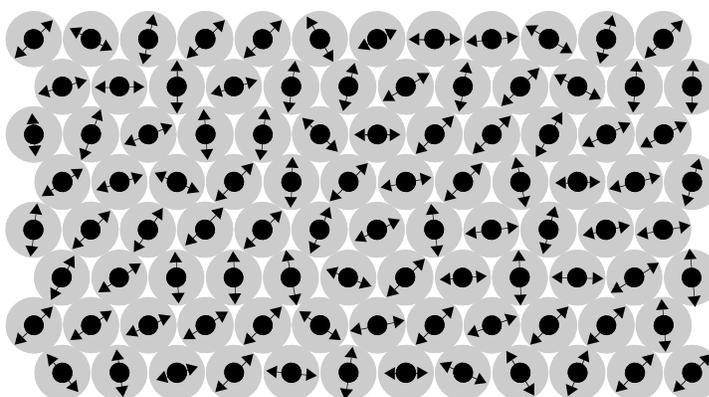


Solids: background theory

6.1 Introduction

We envisage a solid as a collection of atoms whose *average* positions are fixed with respect to one another. When we studied the properties of gases we essentially ignored the potential energy of interaction of the atoms, but in solids we cannot do this: solids exist *because* of the potential energy of interaction between atoms. The atoms of a solid can vibrate about their average position, but can only exceptionally change their position with respect to their neighbours. This picture will probably be familiar to you, but just in case it is not, Figure 6.1 illustrates how we imagine the motion of the atoms in a solid.

Figure 6.1 An illustration of the motion of atoms in a solid. The arrows indicate the direction of atomic motion. Notice the small separation between the atoms and the random orientation of their vibrations. The atoms themselves are shown as a central darkly-shaded region, where the electron charge density is high, and a peripheral lightly-shaded region. The electric field in this peripheral region significantly affects the motion of neighbouring atoms, and disturbs the electronic charge density of neighbouring atoms.



When we discussed the properties of gases we were able to arrive at the theory of a ‘ideal gas’, which for many purposes was a good approximation to the properties of real gases. Solids, however have many fewer properties that can be explained in terms of a theory of an ‘ideal solid’. The diversity of properties exhibited by solids calls for us to make *several* simple models to serve as starting points for attempts to understand the behaviour of real solids. Despite the diversity in the properties of solids, it is important to realise that in all the materials, the only force acting between atoms is the electrostatic coulomb force. The coulomb force, coupled with the different configurations of electrons in the outer parts of the 100 or so different types of atoms, is sufficient to produce solids with the diversity that you find around you. In this chapter, we will discuss four simplified models solids which represent idealised categories. However, most real solids do not fall neatly into one category or another. Our hope is that by looking at a few (rather rare) ‘simple solids’ which do fit this categorisation scheme, we will be able to shed light on what is happening in more common, but more complex, solids.

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In addition to copies of the figures and tables you will find: animations of some of the important equations in this chapter; a computer program which realistically simulates the dynamics of simple molecules in solids, liquids and gases; and Chapter W1 on the *band theory of solids*, which extends some of the topics dealt with in this chapter.

The four simple models of solids which we discuss in §6.2 to §6.5 are illustrated in Figure 6.2. As this figure indicates, it is the arrangement of the outer (valence) electrons on atoms in a solid that is the basis of our categorisation. The interaction of valence electrons with neighbouring atoms is responsible for *bonding* atoms together into a solid, and the four models correspond to four, relatively distinct, bonding mechanisms between atoms.

6.2 Molecular solids

6.2.1 General description

In molecular solids, the electronic structure of the atoms or molecules that make up the solid is the same (or similar to) the electronic structure of the atoms or molecules which move around independently in the gas. The solid is held together by the weak interactions that take place between all molecules, exactly the same interactions which we ignored when we considered such molecules in the gaseous state. This kind of solid is formed when the molecules that make up the gas are chemically stable enough that the outer electrons of each molecule stay with their ‘parent’ molecule when they form a solid.

The types of substance in which molecular bonding plays a key role are:

- the noble ‘gases’, i.e. the same gases which are such fine exemplars of the ideal gas law also make fine molecular solids
- the halogen molecules, i.e. F_2 , Cl_2 , Br_2 and I_2
- many long chain polymer molecules, such as polyethylene or polyvinyl chloride.

Two important factors affect the properties of solids made from these molecules: the *shape* of the molecules, and the *strength* of the interaction between the molecules. In this section, we will look quantitatively at the effect of the strength of the interaction on the properties of simply shaped molecules. The effects of molecular shape are discussed further in §6.6.1 on organic solids, §7.2 on the thermal expansivity of plastics and §8.4.4 on the properties of organic liquids.

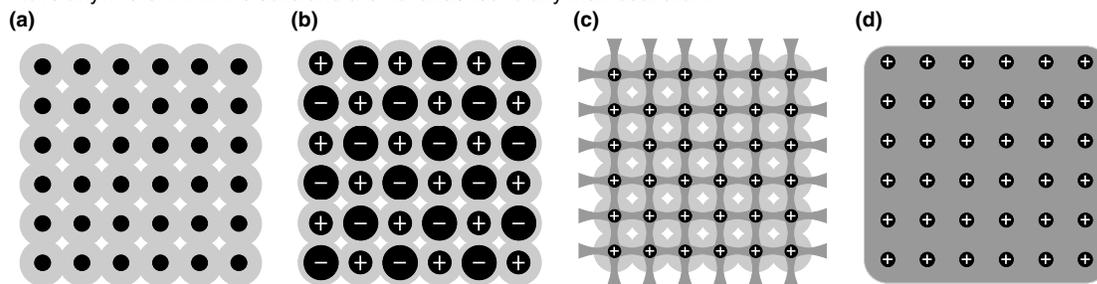
6.2.2 Attractive and repulsive forces between neutral molecules

The attractive force between neutral molecules

The origin of the attraction

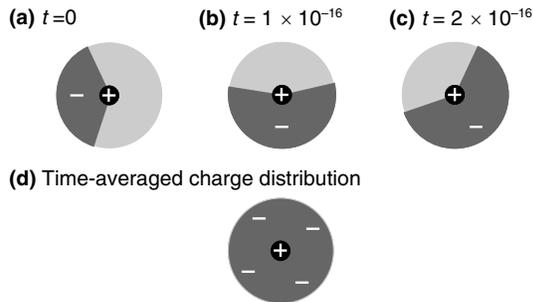
The distribution of electric charge around molecules in a molecular solid is broadly unchanged from the distribution when the molecules are in the gaseous state. In particular each molecule is

Figure 6.2 The four types of simple solid discussed in this chapter. (a) Molecular solids in which the entities which make up the solid (atoms or molecules) are essentially the same as the entities which made up the gas. (b) Ionic solids in which the entities that make up the solid are ions rather than atoms or molecules. Electrons from the outer part of one atom have moved *wholly* to another atom. (c) Covalent solids in which the entities that make up the solid (atoms or molecules) are greatly altered from their state in the gas. Electrons from the outer part of one atom have changed their ‘orbits’ so that they now move round more than one atom. This leads to a high electronic charge density in regions *in between* the mean positions of the atoms. (d) Metallic solids in which the electrons from the outer parts of the atoms can move anywhere within the solid and are not attached to any individual atom.



electrically neutral. So what holds the molecules together? The force which holds the molecules together is the Coulomb force, but the action of the force is subtle. The attraction between molecules arises not because each molecule has a net charge, but because the distribution of electrons around each molecule *fluctuates*. Consider a series of imagined snapshots of the electronic distribution around a single atom. (Figure 6.3)

Figure 6.3 A representation of the fluctuations of charge density around a neutral atom. The figure shows the charge distribution at three times separated by $\approx 10^{-16}$ second.



Averaged over a time greater than a *few* $\times 10^{-16}$ s, the charge distribution is symmetrical (Figure 6.3(d)). However, on a shorter time scale, the charge distribution fluctuates and is in general slightly ‘imbalanced’. This means that the atom behaves as a tiny *electric dipole*, the direction of which is constantly changing. An electric dipole has a weak electric field around it that can affect other atoms nearby (§2.3.2), and it is through the action of this field that bonding, sometimes known as *Van der Waals bonding*, takes place.

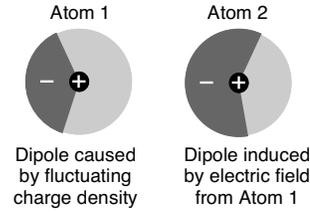
Rough calculation

Suppose that at a particular instant the charge distribution is asymmetrical such that an atom has an electric dipole p . As we mentioned in §2.3.2, the electric field due to p is given approximately by:

$$E(r) \approx \frac{p}{4\pi\epsilon_0 r^3} \quad (6.1)$$

A second atom placed in this field becomes electrically polarised by an amount that is proportional to the magnitude of the electric field. (See §5.7.2 on gases.) The electric dipole moment *induced* on the second atom, p_2 , will be given by:

Figure 6.4 Fluctuations of the charge-density distribution on atom 1 lead to a temporary electric dipole moment. The electric field from the electric dipole moment *induces* a dipole moment on neighbouring atoms, causing the two atoms to be attracted to one another.



$$p_2 = \alpha E(r) \quad (6.2)$$

where α is the *molecular polarisability* of atom 2 (Figure 6.4). The second atom will have an energy of interaction u with the first atom given by:

$$u = -p_2 E(r) \quad (6.3)$$

We now substitute for p_2 using Equation 6.2 and $E(r)$ using Equation 6.1 to yield:

$$\begin{aligned} u &\approx -\alpha E(r) E(r) \\ &\approx -\left[\alpha \frac{1}{r^3}\right] \frac{1}{r^3} \\ &\approx -\frac{\alpha}{r^6} \end{aligned} \quad (6.4)$$

which predicts that the energy of interaction between the two atoms therefore varies as $1/r^6$, and is proportional to the molecular polarisability α of the atoms involved. The attractive energy varies with distance more rapidly than the $1/r$ variation that occurs between uncompensated charges, which means that the interactions of this type are relatively short-range. As we saw in §5.7.2, the polarisability of atoms and molecules is generally rather small, and so the energy of interactions is also rather low.

The repulsive force between neutral molecules

The attractive force described above cannot be the only term involved in the interaction between two neutral atoms. If this were so the energy would become more negative without limit as the atoms came closer. There must be another term in the

energy which increases as the separation between the atoms gets smaller.

The origin of the repulsion

The repulsion arises because as the atoms get closer, the outer electrons on each atom come close together. The processes that take place as atoms approach each other closely are complex, but we can identify two separate ways in which bringing atoms closer together costs energy.

- First, the outer electrons of one atom have to attempt to occupy orbitals around the other atom. The lowest-energy orbitals are all occupied and so the Pauli exclusion principle forces electrons to occupy higher-energy orbitals.
- Second, when the electrons on the outer part of each atom get very close they begin to repel each other directly through their coulomb interaction.

There is no simple direct way to derive the variation of the repulsion with distance, but two approximate forms are commonly used that capture some of the behaviour of real solids. It is sometimes assumed that the repulsive energy varies as either:

$$u \approx + \frac{\text{constant}}{r^{12}} \tag{6.5}$$

or as:

$$u \approx +\text{constant} \times e^{-r/\rho}$$

where ρ is a ‘range parameter’. We will choose the first of these alternative forms because it is mathematically easier to manipulate.

6.2.3 Pair potential: the Lennard-Jones potential

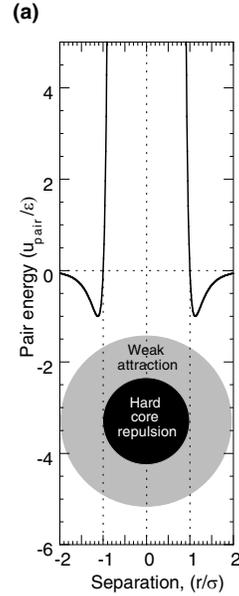
We can combine the attractive and repulsive terms (Equations 6.4 and 6.5) into an expression for the potential energy of a pair of interacting neutral atoms:

$$u_{\text{pair}}(r) = -\frac{A}{r^6} + \frac{B}{r^{12}} \tag{6.6}$$

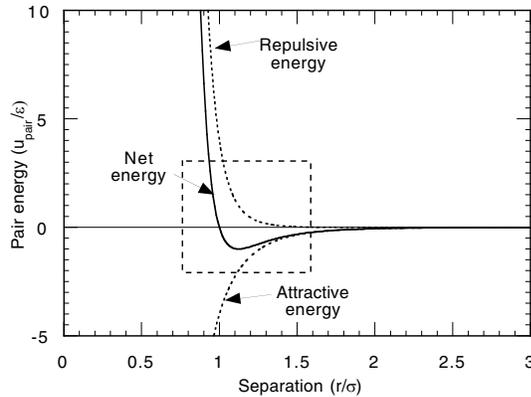
where A and B are constants that determine the relative size of the attractive and repulsive terms. Because it describes the interaction of just two

Figure 6.5 The potential energy versus separation of two atoms interacting via a Lennard-Jones potential. The energy scale is drawn in units of ϵ and the separation scale is drawn in units of σ where ϵ and σ are defined according to Equation 6.8.

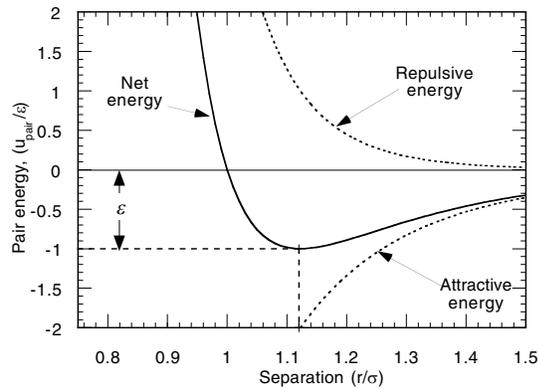
(a) The relationship between σ and the representation of a molecule shown in Figure 6.1. The steeply rising potential makes the atom behave as if it has a hard core. The shallow minimum gives rise to a region which is weakly attractive to other atoms.



(b) The Lennard-Jones pair potential. Notice the shallowness of minimum in the potential energy,



(c) Detail from the rectangle in (b) showing that the minimum occurs at $r = 1.12\sigma$ and $U = -\epsilon$



atoms, expressions such as Equation 6.6 are known as *pair potentials*. This particular form of pair potential (with powers of '12' and '6') was discovered by Professor Lennard-Jones to be particularly appropriate to molecular solids and so is called a *Lennard-Jones* pair potential.

The Lennard-Jones potential is often rearranged into the form:

$$u_{\text{pair}}(r) = -4\varepsilon \left\{ \left[\frac{\sigma}{r} \right]^6 - \left[\frac{\sigma}{r} \right]^{12} \right\} \quad (6.7)$$

where:

$$\sigma = \left[\frac{B}{A} \right]^{1/6} \quad \text{and} \quad \varepsilon = \left[\frac{A^2}{4B} \right] \quad (6.8)$$

Although Equation 6.7 looks more complicated than Equation 6.6, it has the advantage that the parameters σ and ε have a clear physical interpretation in terms of the form of the $u_{\text{pair}}(r)$ (see Figure 6.5)

σ is a *range* parameter and indicates the approximate 'size' of an atom. At $r = \sigma$ the value of u_{pair} is zero.

ε is an *energy* parameter and indicates the *strength* of the interaction between atoms. At the minimum of the $u_{\text{pair}}(r)$ curve u_{pair} has the value $-\varepsilon$.

It is important to note that the interactions between molecules described above take place in the solid state *and in the gaseous state*. In the gaseous state, the most important feature is the strong repulsion that makes atoms which collide with one another behave as if they are hard spheres with radius of around 0.8σ (Figure 6.5). After extensive analysis we were just able to detect the effect of the attractive part of intermolecular interactions in §5.5.2 on the thermal conductivity of gases. In the solid state, the key feature of the pair potential is the shallow minimum. Molecules try to achieve positions relative to other molecules that allow them to sit as close to this minimum as possible.

6.2.4 Calculation of cohesive energy

In this section we will calculate the electrostatic energy of one mole of molecules which interact

with each other through the Lennard-Jones pair potential. This quantity is known as the *cohesive energy* U of a substance and is generally measured of kJ mol^{-1} or eV per molecule.

We will assume that the molecules are arranged in a regular crystal structure, and in §6.1.4 we shall work out which crystal structure the molecules would choose if they were to maximise their cohesive energy.

Calculation: Stage 1

To begin, we consider a particular molecule i surrounded by all the other molecules j in the crystal. We write its energy u_i as:

$$\begin{aligned} u_i &= u_{\text{pair}}(r_{i1}) + u_{\text{pair}}(r_{i2}) + \dots + [\text{not } u_{\text{pair}}(r_{ii})] \\ &\quad \dots + u_{\text{pair}}(r_{ij}) + \dots + u_{\text{pair}}(r_{iN_A}) \\ u_i &= \sum_{j \neq i}^{N_A} u_{\text{pair}}(r_{ij}) \end{aligned} \quad (6.9)$$

where r_{ij} is the distance between the i th molecule and each other molecule j in the crystal. The energy for N_A molecules in one mole of the solid is then given by:

$$U = \frac{N_A u_i}{2} \quad (6.10)$$

Notice the factor $\frac{1}{2}$ which arises because the energy u_i is the sum of the electrostatic energy of *pairs* of molecules, and we wish to calculate the energy per *individual* molecule. Remembering the form of the Lennard-Jones potential, (Equation 6.7) we can then write:

$$U = -\frac{N_A}{2} \sum_{j \neq i} 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^6 - \left(\frac{\sigma}{r_{ij}} \right)^{12} \right] \quad (6.11)$$

Calculation: Stage 2: A trick

Now we use a mathematical trick. We write the distance between the i th and j th atoms as a multiple of the nearest neighbour distance r_0 (as yet unknown):

$$r_{ij} = \alpha_{ij} r_0 \quad (6.12)$$

Note α_{ij} is just a number, not a distance. So, for example, for one pair of atoms, say $i = 1$ and $j = 4$, α_{ij} might take the value 2.314. This means that the distance from atom 1 to atom 4 is 2.314 times the distance r_0 . We can now rewrite our expression for U using this substitution:

$$U = -2\epsilon N_A \sum_{j \neq i} \left[\left(\frac{1}{\alpha_{ij}} \right)^6 \left(\frac{\sigma}{r_0} \right)^6 - \left(\frac{1}{\alpha_{ij}} \right)^{12} \left(\frac{\sigma}{r_0} \right)^{12} \right] \quad (6.13)$$

We can then separate the summation into two terms:

$$U = -2\epsilon N_A \sum_{j \neq i} \left[\left(\frac{1}{\alpha_{ij}} \right)^6 \left(\frac{\sigma}{r_0} \right)^6 \right] + 2\epsilon N_A \sum_{j \neq i} \left[\left(\frac{1}{\alpha_{ij}} \right)^{12} \left(\frac{\sigma}{r_0} \right)^{12} \right] \quad (6.14)$$

Notice that the fraction σ/r_0 does not depend on the index j in either summation. Hence, it may be brought outside the summation sign since it is a common factor to each term in the sum:

$$U = -2\epsilon N_A \left(\frac{\sigma}{r_0} \right)^6 \sum_{j \neq i} \left[\left(\frac{1}{\alpha_{ij}} \right)^6 \right] + 2\epsilon N_A \left(\frac{\sigma}{r_0} \right)^{12} \sum_{j \neq i} \left[\left(\frac{1}{\alpha_{ij}} \right)^{12} \right] \quad (6.15)$$

Each of the two terms in Equation 6.15 now has two parts, a term in σ/r_0 and a quantity in square brackets known as a *lattice sum*. The lattice sums are referred to as A_6 and A_{12} respectively.

$$A_6 = \sum_{j \neq i} \left[\left(\frac{1}{\alpha_{ij}} \right)^6 \right] \quad A_{12} = \sum_{j \neq i} \left[\left(\frac{1}{\alpha_{ij}} \right)^{12} \right] \quad (6.16)$$

On substituting for A_6 and A_{12} , the expression for the cohesive energy begins to look a little more tractable:

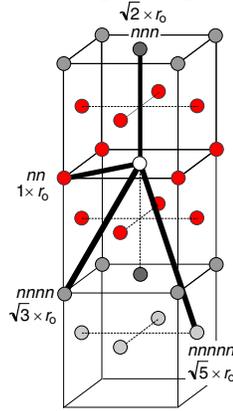
Example 6.1

Calculate the lattice sum A_{12} for the face-centred cubic lattice.

The lattice sum A_{12} is defined according to Equation 6.16 as:

$$A_{12} = \sum_{j \neq i} \frac{1}{\alpha_{ij}^{12}}$$

where α is the ‘multiplier’ of the nearest-neighbour distance required to reach a particular atom j from a chosen atom i . The figure shows a central atom i and the distance to several neighbouring atoms.



- Each nearest neighbour has a multiplier distance of 1 ($\times r_0$) and there are 12 such atoms (labelled *nn* in the figure).
- Each next-nearest neighbour has a multiplier distance of $\sqrt{2}$ ($\times r_0$) and there are 6 such atoms (labelled *nnn* in the figure).
- Each next next-nearest neighbour has a multiplier distance of $\sqrt{3}$ ($\times r_0$) and there are 24 such atoms (labelled *nnnn* in the figure).

Proceeding to successively more distant atoms we see that the expression for the lattice sum is given by:

$$A_{12} = 12 \times \frac{1}{1^{12}} + 6 \times \frac{1}{(\sqrt{2})^{12}} + 24 \times \frac{1}{(\sqrt{3})^{12}} + 24 \times \frac{1}{(\sqrt{5})^{12}} + \dots$$

Evaluating the terms we find:

$$\begin{aligned} A_{12} &= \frac{12}{1} + \frac{6}{64} + \frac{24}{729} + \frac{24}{15625} + \dots \\ &= 12 + 0.09375 + 0.03292 + 0.00154 + \dots \\ &= 12.128 \dots \end{aligned}$$

This sum converges rapidly and only a few terms are required to estimate A_{12} with good precision. The A_6 summation converges more slowly and to attain equivalent precision to A_{12} one must consider more distant neighbours than those in the figure above.

$$U = -2\varepsilon N_A \left(\frac{\sigma}{r_0}\right)^6 A_6 + 2\varepsilon N_A \left(\frac{\sigma}{r_0}\right)^{12} A_{12} \quad (6.17)$$

Calculation: Stage 3: Lattice sums

Evaluating lattice sums is a straightforward mathematical exercise (Example 6.1). The lattice sums A_6 and A_{12} depend only on the *form* of the lattice, i.e. on the *type* of crystal structure (e.g. face-centred cubic, body-centred cubic, etc.) and not on the particular separation between the molecules in the crystal of σ or r_0 . In other words A_6 and A_{12} are just numbers and each different crystal structure has uniquely characteristic values of A_6 and A_{12} .

The cohesive energy of an assembly of N_A atoms is now conveniently expressed in terms of the lattice sums as:

$$U = -2\varepsilon N_A \left[\left(\frac{\sigma}{r_0}\right)^6 A_6 - \left(\frac{\sigma}{r_0}\right)^{12} A_{12} \right] \quad (6.18)$$

Calculation: Stage 4: Minimising the cohesive energy

Equation 6.18 tells us the cohesive energy of a solid with particular values of σ/r_0 , ε , A_6 and A_{12} . What we need to do now is to find the particular set of values that yields the minimum value of the cohesive energy. We will do this in two steps. First we will find the value of σ/r_0 that minimises U . In the section we will consider the effect of the lattice sums.

To find the optimum value of σ/r_0 we differentiate Equation 6.18 for U with respect to σ/r_0 and set the result equal to zero. Differentiating we find:

$$\frac{dU}{d(\sigma/r_0)} = -2\varepsilon N_A \left[6\left(\frac{\sigma}{r_0}\right)^5 A_6 - 12\left(\frac{\sigma}{r_0}\right)^{11} A_{12} \right] \quad (6.19)$$

Setting this equal to zero requires that:

$$12\left(\frac{\sigma}{r_0}\right)^{11} A_{12} = 6\left(\frac{\sigma}{r_0}\right)^5 A_6 \quad (6.20)$$

Simplifying and rearranging we find:

Example 6.2

Calculate the cohesive energy per mole for a substance whose atoms interact via a Lennard-Jones potential.

According to Equation 6.18 the cohesive energy per mole is given by:

$$U = 2N_A \varepsilon \left[A_{12} \left(\frac{\sigma}{r_0}\right)^{12} - A_6 \left(\frac{\sigma}{r_0}\right)^6 \right]$$

and in equilibrium r_0 is given by Equation 6.23 as

$$r_0 = \sigma \left[\frac{2A_{12}}{A_6} \right]^{1/6}$$

Substituting the equilibrium value of r_0 into the expression for U should therefore yield the equilibrium value of cohesive energy per mole. The expression for U has two brackets in it: $(\sigma/r_0)^{12}$ and $(\sigma/r_0)^6$. These brackets simplify to:

$$\left[\frac{\sigma}{r_0} \right]^{12} = \left[\frac{\sigma}{\sigma(2A_{12}/A_6)^{1/6}} \right]^{12} = \left[\frac{A_6}{2A_{12}} \right]^2$$

and

$$\left[\frac{\sigma}{r_0} \right]^6 = \left[\frac{\sigma}{\sigma(2A_{12}/A_6)^{1/6}} \right]^6 = \left[\frac{A_6}{2A_{12}} \right]$$

Substituting into the expression for U we find:

$$\begin{aligned} U &= 2N_A \varepsilon \left[A_{12} \left(\frac{A_6}{2A_{12}} \right)^2 - A_6 \left(\frac{A_6}{2A_{12}} \right) \right] \\ &= 2N_A \varepsilon \left[\frac{A_6^2}{4A_{12}} - \frac{A_6^2}{2A_{12}} \right] \\ &= -N_A \varepsilon \left[\frac{A_6^2}{2A_{12}} \right] \end{aligned}$$

$$\left(\frac{\sigma}{r_0}\right)^6 = \frac{A_6}{2A_{12}} \quad (6.21)$$

$$\frac{\sigma}{r_0} = \left(\frac{A_6}{2A_{12}}\right)^{1/6} \quad (6.22)$$

$$r_0 = \sigma \left(\frac{2A_{12}}{A_6}\right)^{1/6} \quad (6.23)$$

This is the value of the nearest-neighbour distance that minimises the potential energy of the lattice. Notice that r_0 is a multiple of σ , the ‘range’ parameter in the Lennard-Jones potential. In order to evaluate the cohesive energy of the lattice, we can substitute the value for σ/r_0 from Equation 6.23 into Equation 6.18. This calculation is performed in Example 6.2.

According to Example 6.2 the cohesive energy per mole is given by:

$$U = -\left(\frac{A_6^2}{2A_{12}}\right)N_A \epsilon \quad (6.24)$$

and so the cohesive energy per molecule $u = U/N_A$ is:

$$u = -\left(\frac{A_6^2}{2A_{12}}\right)\epsilon \quad (6.25)$$

Summary of cohesive energy calculation

The calculation culminating in expressions 6.24 and 6.25 has involved the use of technical tricks such as the use of lattice sums. Because of this it is worth recalling that these tricks have been used in order to perform the (simple in principle) task of adding up the electrostatic interactions of a large number of molecules. The final question we need to answer is what values of A_6 and A_{12} minimise the cohesive energy. We will find the answer to this question in the next section.

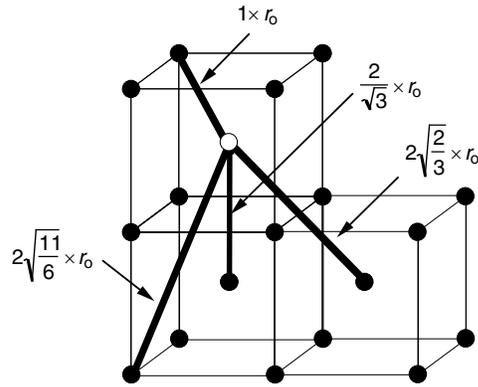
6.2.5 Equilibrium crystal structure

Equation 6.25 succinctly expresses the cohesive energy of a crystal in terms of the lattice sums A_6 and A_{12} . But notice that A_6 and A_{12} could refer to *any crystal structure*. When a crystal forms from a melt, the crystal structure adopted is generally the one with the lowest (i.e. most negative) cohesive energy. (This matter is discussed further in Chapter 10.)

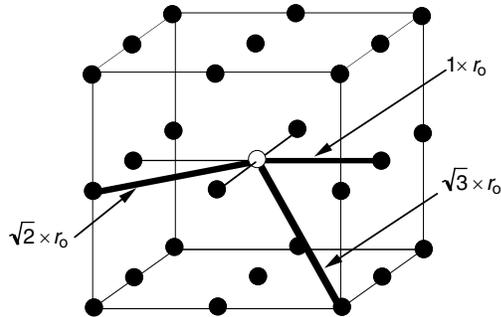
In order to predict which crystal structure actually forms, we need to calculate u according to Equation 6.25 for all likely crystal structures. We then work out which crystal structure has the largest

Figure 6.6 When a crystal forms it could conceivably form any one of several different structures. The actual structure formed depends strongly on the cohesive energy U of the structure. For atoms that interact via the Lennard-Jones potential Equation 6.7, the cohesive energy can be expressed in terms of the lattice sums A_6 and A_{12} described in the text. The figures illustrate two crystal structures showing (i) that the *number* of nearest-neighbour atoms differs from crystal structure to crystal structure and (ii) that the relative distances to next-nearest neighbours also differs from one structure to another. The calculation of the lattice sums for fcc is considered in Example 6.1.

(a) Body-centred cubic



(b) Simple cubic



value of $A_6^2/2A_{12}$. Table 6.1 shows the lattice sums and calculated cohesive energy for three different crystal structures in which a molecular solid might conceivably crystallise. The face-centred cubic structure is illustrated in Example 6.1 and the body-centred cubic and simple cubic structures are illustrated in Figure 6.6

Table 6.1 Values of the lattice sums A_6 and A_{12} for three crystal structures. The bottom line of the table shows the cohesive energy U for each crystal structure calculated in terms of A_6 and A_{12} according to Equation 6.25.

| | Simple cubic | Body-centred cubic | Face-centred cubic |
|----------------------|--------------------|--------------------|--------------------|
| A_6 | 8.4 | 12.25 | 14.45 |
| A_{12} | 6.2 | 9.11 | 12.13 |
| Cohesive energy, U | -5.69ε | -8.24ε | -8.61ε |

All the crystal structures in Table 6.1 have a negative cohesive energy, i.e. they all represent arrangements of molecules which are energetically favourable compared to molecules being separated from one another by large distances. The crystal structure naturally chosen however will be the one with the *largest* cohesive energy (i.e. the most negative value) which in this case is the face-centred cubic (*fcc*) structure. This expectation is indeed borne out and all the noble gases neon, argon, krypton and xenon form solids with an *fcc* structure at low temperature.

Comparison with experiment for noble gases

Once the crystal structure is known to be *fcc*, the appropriate values of A_6 and A_{12} can be substituted into Equation 6.23 for r_0 . For *fcc*, the predicted values of r_0 and u are $r_0 = 1.09\sigma$ and $u = -8.6\varepsilon$. Values of σ and r_0 can be deduced from analysis of the deviations of gases from perfect gas behav-

our (e.g. §5.5 on the thermal conductivity of gases), i.e. σ and ε are estimated from the behaviour of the substance *in the gaseous phase!* Using values of σ and ε derived from these experiments, allows us to predict values of r_0 and u which may be compared with experimental values deduced from analysis of data on X-ray scattering, and latent heat of vaporisation of the substances. Table 6.2 compares predicted and experimental values of the cohesive energy per molecule and the lattice spacing in the *fcc* crystal structure. We see that there is fair agreement between theory and experiment.

Table 6.2 Values of the lattice constant r_0 and the cohesive energy per atom u calculated according to Equations 6.23 and 6.25 are compared with experimental values for neon, argon, krypton, and xenon. The values of σ and ε for each substance have been deduced from measurements in the *gaseous* phase of each substance by observing the deviations from perfect gas behaviour.

| | Substance | | | |
|---|-----------|-------|-------|-------|
| | Ne | Ar | Kr | Xe |
| $\sigma \times 10^{-10}$ m | 2.74 | 3.44 | 3.65 | 3.98 |
| $r_0 (=1.09\sigma) \times 10^{-10}$ m | 2.99 | 3.71 | 3.98 | 4.34 |
| $r_0(\text{expt}) \times 10^{-10}$ m | 3.13 | 3.75 | 3.99 | 4.33 |
| Ratio(theory/expt) | 0.955 | 0.989 | 0.997 | 1.002 |
| $\varepsilon \times 10^{-3}$ eV | 3.1 | 10.3 | 14.0 | 20.0 |
| $u = -8.6\varepsilon \times 10^{-3}$ eV | -27 | -89 | -120 | -172 |
| $u(\text{expt}) \times 10^{-3}$ eV | -20 | -80 | -110 | -170 |
| Ratio(theory/expt) | 1.35 | 1.11 | 1.09 | 1.01 |

6.3 Ionic solids

6.3.1 General description

In ionic solids, the ‘entities’ that make up the solid are essentially *ions*, atoms stripped of one or more of their electrons, or with one or two more added.

As with molecular solids, it is the Coulomb force which holds the substance together, but in ionic solids not all the forces are attractive. There are equal numbers of positively and negatively charged ions, and although the positively and negatively charged ions attract one another, the negative ions repel the other negative ions and the positive ions repel the other positive ions. The fact that ionic solids actually exist tells us that the at-

tractive forces will eventually outweigh the repulsive forces, but we need to make a detailed calculation in order to see why.

6.3.2 Calculation of the cohesive energy

The calculation of the cohesive energy of an ionic solid is similar to the calculation in §6.2 for the cohesive energy of a molecular solid. We have to add up all the pair-interactions between ions in the solid. Before we do the calculation for a real three-dimensional crystal, we can get the flavour for what the calculation involves by looking at a two-dimensional problem.

A two-dimensional problem

What is the potential energy of a single ion in a large ‘net’ of charges, of which a section is illustrated in Figure 6.7?

In order to answer this question, consider one particular ion, a positive ion say, and add up the energy of interaction of all the other ions with the chosen ion. We must be careful to consider the ions systematically in order to make sure that all of them are counted (but only once!). We start by adding up the Coulomb terms as follows:

$$\begin{aligned} \text{Energy} = & \frac{-e^2}{4\pi\epsilon_0 r_0} + \frac{-e^2}{4\pi\epsilon_0 r_0} + \frac{-e^2}{4\pi\epsilon_0 r_0} + \\ & \frac{-e^2}{4\pi\epsilon_0 r_0} + \frac{-e^2}{4\pi\epsilon_0(\sqrt{2}r_0)} + \dots \end{aligned} \quad (6.26)$$

Notice that *energy* in Equation 6.26 is the sum of energies of ion *pairs*. The energy associated with the central ion is just $\frac{1}{2}$ this quantity. We therefore write the coulomb energy per ion, u as:

$$u = \frac{1}{2} \left[\frac{-e^2}{4\pi\epsilon_0 r_0} + \frac{-e^2}{4\pi\epsilon_0 r_0} + \frac{-e^2}{4\pi\epsilon_0 r_0} + \frac{-e^2}{4\pi\epsilon_0 r_0} + \frac{-e^2}{4\pi\epsilon_0(\sqrt{2}r_0)} + \dots \right] \quad (6.27)$$

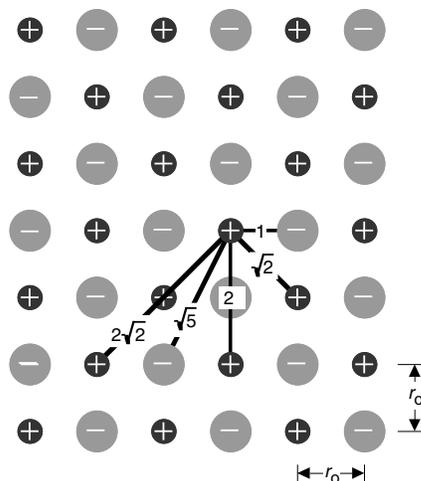
If we collect together the terms that correspond to ions at the same distance from the origin, and take out a common factor, we find a series, the first four terms of which are:

$$u = \frac{e^2}{8\pi\epsilon_0 r_0} \left[4 \times \frac{-1}{1} + 4 \times \frac{+1}{\sqrt{1^2+1^2}} + 4 \times \frac{+1}{2} + 8 \times \frac{-1}{\sqrt{1^2+2^2}} + \dots \right] \quad (6.28)$$

This series is similar to the lattice sums considered in the previous section on molecular bonding (Example 6.1), except that in this case the sign of each term oscillates. In each term within the brackets in Equation 6.28:

- the first number (4 or 8 for the terms shown) is the number of ions at that distance,
- the sign in the numerator of the fraction is

Figure 6.7 A section from an infinite two-dimensional ‘net’ of charges. The charge on each ion is either $+e$ or $-e$. The numbers on the lines indicate the number of times r_0 must be multiplied to reach between the lattice sites indicated.



determined by whether the charges are of the same or opposite sign, and

- the denominator of the fraction is the distance from the origin in units of r_0 .

Evaluating the terms we find the first eight terms are:

$$u = \frac{e^2}{8\pi\epsilon_0 r_0} \left[-4 + \frac{4}{\sqrt{2}} + 2 - \frac{8}{\sqrt{5}} + \frac{4}{2\sqrt{2}} - \frac{4}{3} + \frac{8}{\sqrt{10}} - \frac{8}{\sqrt{13}} + \dots \right] \quad (6.29)$$

| Term | Value | Running total |
|------|------------|---------------|
| 1 | -4.0000000 | -4.0000000 |
| 2 | +2.8284271 | -1.1715729 |
| 3 | +2.0000000 | +0.8284271 |
| 4 | -3.5777088 | -2.7492817 |
| 5 | +1.4142136 | -1.3350681 |
| 6 | -1.3333333 | -2.6684014 |
| 7 | +2.5298221 | -0.1385793 |
| 8 | -2.2188008 | -2.3573801 |

The problem with this summation may be becoming apparent to you. The terms are getting smaller, but only very slowly. Using a ‘brute force’ computer program to whip through the first few thousand terms in the sum yields an approximate answer of -1.57 . This is likely to be close,

but not quite right. However this problem of adding up a long series of slowly converging terms will come to haunt us with a vengeance when we come to the three-dimensional problem in just a moment.

The significance of the calculation we have just done is that an ion in a net such as the one described will be bound into the net with an energy equal to approximately 1.57 times the energy of interaction of the ion with just one other ion of the opposite charge.

The three-dimensional problem

Now we proceed to the three-dimensional problem (Figure 6.8) actually encountered in ionic crystals. We approach the calculation in a similar way to the two-dimensional calculation, but the geometry is now a little more taxing. The summation for the energy of an ion now looks like:

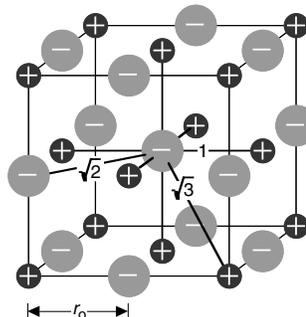
$$u = \frac{e^2}{4\pi\epsilon_0 r_0} \times \frac{1}{2} \left[6 \times \frac{-1}{1} + 12 \times \frac{+1}{\sqrt{1^2+1^2}} + 8 \times \frac{-1}{\sqrt{1^2+1^2+1^2}} + 6 \times \frac{+1}{2} + \dots \right] \quad (6.30)$$

$$u = \frac{e^2}{4\pi\epsilon_0 r_0} \times \frac{1}{2} \left[-6 + \frac{+12}{\sqrt{2}} - \frac{8}{\sqrt{3}} + \frac{6}{2} + \dots \right] \quad (6.31)$$

| Term | Value | Running total |
|------|-------------|---------------|
| 1 | -6.0000000 | -6.0000000 |
| 2 | +8.4852813 | +2.4852813 |
| 3 | -4.6188022 | -2.1335208 |
| 4 | +3.0000000 | +0.8664792 |
| 5 | -10.7331263 | -9.8666471 |
| 6 | +9.7979589 | -0.0685121 |
| 7 | -6.0000000 | -6.0685121 |
| 8 | +7.5894666 | +1.5209545 |

Again we have taken care to calculate the energy per ion and not per ion pair. Using a 'brute force' computer program to evaluate the sum (Eq. 6.31) yields a sum which does not clearly converge, but instead oscillates at a value of around -1.5 . Series of this type are called *Madelung Sums* after the person who solved the three-dimensional problem. The sum evaluates to -1.748 for the NaCl type

Figure 6.8 The arrangement of ions in a crystal with the same structure as NaCl. The numbers on the lines are the distance between the ions in units of r_0 . This diagram should be compared with its two-dimensional equivalent in Figure 6.7.



crystal structure and to similar values for other common ionic crystal structures, i.e. the energy of an ion in an ionic crystal of the NaCl type is:

$$u = \frac{e^2}{8\pi\epsilon_0 r_0} [-1.748] \quad (6.32)$$

However, this seems to indicate that if r_0 is reduced the energy of the ion will become very large and negative. Of course there must be some repulsive term between atoms which stops the crystal 'collapsing'. This repulsive term is due to the Pauli exclusion principle effect discussed in §6.2.2. It may be modelled once again as:

$$u = + \frac{c}{r_0^{12}} \quad (6.33)$$

Adding the repulsive effect between the ion and its six nearest neighbours we find its energy is:

$$u = \frac{-1.748e^2}{8\pi\epsilon_0 r_0} + \frac{6c}{r_0^{12}} \quad (6.34)$$

It is clear that reducing r_0 makes the attractive term more negative, but it also rapidly increases the Pauli repulsion between the outer orbitals of each ion.

Finding the equilibrium separation

If we differentiate Equation 6.34 for u with respect to r_0 we can find the value of r_0 which minimises the cohesive energy per ion:

$$\frac{du}{dr_0} = \frac{+1.748e^2}{8\pi\epsilon_0 r_0^2} - \frac{12 \times 6c}{r_0^{13}} \quad (6.35)$$

Equating this to zero yields:

$$\frac{+1.748e^2}{8\pi\epsilon_0 r_0^2} = \frac{72c}{r_0^{13}} \quad (6.36)$$

Solving for r_0 yields:

$$r_0^{11} = \frac{576c\pi\epsilon_0}{+1.748e^2} \quad (6.37)$$

$$r_0 = \left[\frac{576c\pi\epsilon_0}{+1.748e^2} \right]^{1/11} \quad (6.38)$$

This formula predicts the nearest-neighbour ionic separation in terms of the Madelung sum (-1.748) and the constant c that determines the magnitude of the repulsive forces between atoms.

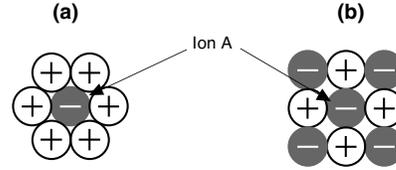
6.3.3 Crystal structure

Determining the crystal structure of an ionically-bonded substance from first principles is considerably more difficult than the equivalent task for molecularly-bonded substance (§ 6.2.3). This is because in the molecularly-bonded solid that we considered there, all the molecules were identical. For ionically-bonded substances there are always at least two different types of ions. This introduces a new consideration: the relative sizes of the ions.

We are however able to say some general things about the types of crystal structure we may expect ionically-bonded substances to form. The presence of both positive and negative ions rules out densely-packed crystal structures with large numbers of nearest neighbours. To see why, consider the two-dimensional situation illustrated in Figure 6.9. Suppose a single ion A surrounded itself with six nearest neighbours of opposite charge to itself (Figure 6.9(a)). This would lower A 's electrostatic energy considerably, however the six neighbours would all have the same sign of charge and thus *their* energy would be *increased* considerably. Further, the structure could not be extended throughout the crystal while keeping the crystal

electrically neutral overall. Similar arguments apply to the equivalent three-dimensional close-packed structures.

Figure 6.9 Two possible local arrangements of ions; see text for details.



For this reason ionically-bonded substances form crystal structures that are more ‘open’. Notice that in Figure 6.9(b) nearest neighbours always have opposite charges: only next-nearest neighbours have the same charge.

6.3.4 Cohesive energy

We have already gone a substantial way to calculating the cohesive energy of an ionic solid by calculating the separation between ions in equilibrium (Equation 6.38). In this section we will complete the calculation by substituting the expression for the equilibrium separation back into the expression for the cohesive energy.

The expression for the cohesive energy per ion (Equation 6.34) is:

$$u = \frac{-1.748e^2}{8\pi\epsilon_0 r_0} + \frac{6c}{r_0^{12}} \quad (6.34^*)$$

We can make the substitution for r_0 much simpler if we first take out a factor $1/r_0$ from each term, to yield:

$$u = \frac{1}{r_0} \left[\frac{-1.748e^2}{8\pi\epsilon_0} + \frac{6c}{r_0^{11}} \right] \quad (6.39)$$

Substituting for r_0 inside the bracket only yields:

$$u = \frac{1}{r_0} \left[\frac{-1.748e^2}{8\pi\epsilon_0} + \frac{6c}{\left[\frac{576c\pi\epsilon_0}{+1.748e^2} \right]^{11/11}} \right] \quad (6.40)$$

Simplifying, and cancelling terms we arrive at:

$$u = \frac{1}{r_0} \left[\frac{-1.748e^2}{8\pi\epsilon_0} + \frac{1.748e^2}{96\pi\epsilon_0} \right] \quad (6.41)$$

$$u = \frac{-1.748e^2}{8\pi\epsilon_0 r_0} \left[1 - \frac{1}{12} \right] \quad (6.42)$$

This evaluates to:

$$u = \frac{-1.602e^2}{8\pi\epsilon_0 r_0} \quad (6.43)$$

Notice that the repulsive component in Equation 6.42 is one twelfth of the attractive component. The expression yields the cohesive energy per ion in a simple-cubic ionic solid. In order to convert this into a cohesive energy per mole, we must multiply this figure by the number of formula units in a mole. Note that in the simple two-component ionic solids we have been considering, each chemical formula unit contains two ions (e.g. Na^+ and Cl^-). We therefore expect to find that the cohesive energy per mole for such a substance is:

$$U = 2N_A u \quad \text{mol}^{-1} \quad (6.44)$$

Following Example 6.3 we conclude that the molar cohesive energy of NaCl is given by:

$$U = 2 \times 6.02 \times 10^{23} \times 6.55 \times 10^{-19} = 789 \text{ kJ mol}^{-1}$$

This is the energy required to separate a mole of NaCl into one mole of Na^+ ions and one mole of Cl^- ions. The value of U inferred from experiments is given in C. Kittel: *Introduction to Solid State Physics (seventh edition)*: Table 7 as 774 kJ mol^{-1} . We may take this agreement at the level of a few per cent as validation of the theory we have developed so far.

Cohesive energy per atom

The cohesive energy determined in Equation 6.44 is the energy required to separate an ionic solid into its constituent *ions*. It is interesting to consider what would be the energy required to separate an ionic solid into its constituent *atoms*. In order to calculate this we need to know:

- the energy u_1 (known as the *ionisation energy*) required to remove an electron from a

Example 6.3

Evaluate the cohesive energy per ion (Equation 6.41) for NaCl (common salt).

We can evaluate r_0 from the density (Table 7.2); the atomic masses of Na and Cl (Table 7.2); and the crystal structure which is known from X-ray diffraction patterns to be of the simple type described in Figure 6.8. We have:

- 1 mole of Na has a mass of $22.99 \times 10^{-3} \text{ kg}$
 - 1 mole of Cl has a mass of $35.45 \times 10^{-3} \text{ kg}$
- So 1 mole of NaCl has a mass of $58.44 \times 10^{-3} \text{ kg}$ and one chemical formula unit of NaCl has a mass of:

$$m = \frac{58.44 \times 10^{-3}}{N_A} = 9.708 \times 10^{-26} \text{ kg}$$

Consideration of Figure 6.8 indicates that one chemical formula unit of NaCl occupies a volume of $2r_0^3$ and hence a density of $\rho = m/2r_0^3$.

The experimental determined density of NaCl is $\rho = 2165 \text{ kg m}^{-3}$ and so we deduce that:

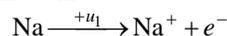
$$r_0 = \left[\frac{m}{2\rho} \right]^{1/3} = \left[\frac{9.708 \times 10^{-26}}{2 \times 2165} \right]^{1/3} \\ = 2.82 \times 10^{-10} \text{ m}$$

Using this value in Equation 6.46 for the cohesive energy per ion we have:

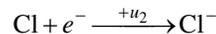
$$u = -\frac{1.602 \times (1.6 \times 10^{-19})^2}{8\pi \times 8.85 \times 10^{-12} \times 2.82 \times 10^{-10}} \\ = -6.55 \times 10^{-19} \text{ J/ion}$$

This can also be expressed as 4.09 eV per ion.

sodium atom



- The energy u_2 (known as the *electron affinity*) required to add an electron to a chlorine atom



For NaCl, $u_1 = +5.139 \text{ eV}$ per Na ion and $u_2 = -3.617 \text{ eV}$ per Cl ion (*Emsley*). Thus to take two neutral atoms of Na and Cl and form an Na^+ and a Cl^- ion requires $u_1 + u_2 = +5.139 - 3.617 = 1.522 \text{ eV}$ per NaCl formula unit. Equivalently this can be stated as $146.9 \text{ kJ mol}^{-1}$ of NaCl. Notice that it actually costs energy to transfer an electron from the sodium atom to the chlorine atom. However if

we take account of the cohesive electrostatic energy of the ions when they are arranged in a crystal, there is an additional energy gain u given by Equation 6.44 and which we evaluated as -789 kJ mol^{-1} . Thus the cohesive energy of NaCl relative to neutral atoms is $+146.9 - 789 \approx -642 \text{ kJ mol}^{-1}$ (or -6.65 eV per NaCl formula unit).

6.4 Covalent solids

6.4.1 General description

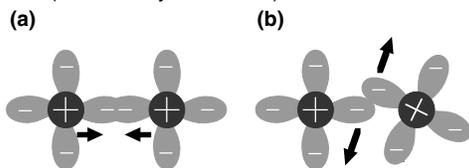
In covalent solids, electrons, which in isolated atoms occupied quantum states localised around a single atom, occupy orbitals that are distributed around at least one other atom in addition to their 'parent' atom: literally 'co-valence'. The materials which tend to form covalent solids are:

- elements from the centre of the periodic table e.g. C, Si and Ge
- compounds of elements from the centre of the periodic table
- many compounds of oxygen (oxides), sulphur (sulphides) and nitrogen (nitrides)

Covalency often occurs when the outer valence electrons have orbitals that are not spherical, but have 'lobes' that point in different directions. This gives rise to some directionality in the attraction between atoms. In other words, atoms will be attracted to one another if their orbitals point in a certain direction (perhaps towards each other), but if the orbitals point in a slightly different direction the atoms may well repel one another.

Notice that because of the directionality of the attraction/repulsion, we cannot simply write down

Figure 6.10 A simple model of a covalent bond between atoms illustrating the directional nature of the bond. In (a) two similar atoms are shown with overlapping electron orbits. The increased charge density in between the atoms pulls the atoms together, as shown by the black arrows. In (b) a misalignment of the atoms causes a repulsion (indicated by the arrows) between the atoms.



Summary

We have seen in this section that we can understand the magnitude of the cohesive energy of ionic solids in terms of the coulomb interaction of ions distributed on a crystal lattice.

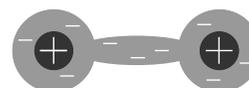
a law of attraction that depends only on the separation between atoms, such as the Lennard-Jones equation (Equation 6.7). Thus calculating the properties of covalent solids is considerably more complex than calculating the properties of molecular solids. However, we will attempt a simple calculation for one of the simplest (but rarest!) covalent solids: carbon in the form of diamond.

6.4.2 Calculation of covalent bond length or strength

A 'point charge' model of a covalent bond

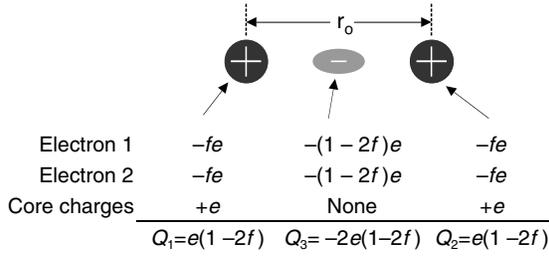
We can make a simple model of a covalent bond as follows. We consider a 'solid' consisting of just carbon atoms, and imagine the charge in the region between the atoms to be distributed as shown below:

Figure 6.11 A simple model of the charge distribution in a C–C bond



The C–C bond of Figure 6.11 is electrically neutral overall, but electrons 'originally' from each atom spend some time 'orbiting' both atoms, and some time in the bond region. We will assume that each electron spends some fraction f of its time orbiting the atoms at each end of the bond. It therefore spends a fraction $(1 - 2f)$ of its time in the region between the atoms. We see that if $f = 0.5$ then the electrons spend essentially no time in the bond region and if $f = 0$ the electron spends all its time in the bond region. If we recall that one electron from each atom will take part in the bond, then *on average* we can make a 'point charge' model of the charge distribution in the bond like that illustrated in Figure 6.12.

Figure 6.12 A point-charge model of a covalent bond. The term 'core charges' refers to the electrical charges in the core electrons and the nucleus.



Notice that when an electron leaves an atom, the atom is left positively charged due to the balance of nuclear and core electrons. If we imagine the charges Q_1 , Q_2 and Q_3 to be point charges, we can work out the approximate energy of this charge distribution using Coulomb's Law. We have:

$$u = \frac{Q_1 Q_2}{4\pi\epsilon_0 r_0} + \frac{Q_1 Q_3}{4\pi\epsilon_0 (r_0/2)} + \frac{Q_2 Q_3}{4\pi\epsilon_0 (r_0/2)} \quad (6.45)$$

Substituting for Q_1 , Q_2 and Q_3 from Figure 6.12

$$u = \frac{e^2(1-2f)^2}{4\pi\epsilon_0 r_0} + \frac{-2e^2(1-2f)^2}{4\pi\epsilon_0 (r_0/2)} + \frac{-2e^2(1-2f)^2}{4\pi\epsilon_0 (r_0/2)} \quad (6.46)$$

and taking out a common factor we have:

$$u = \frac{e^2(1-2f)^2}{4\pi\epsilon_0 r_0} \left[\frac{1}{1} + \frac{-2}{1/2} + \frac{-2}{1/2} \right] \quad (6.47)$$

which simplifies to:

$$u = \frac{e^2(1-2f)^2}{4\pi\epsilon_0 r_0} [-7] \quad (6.48)$$

Equation 6.48 indicates that if an electron spends no time in the bond region ($f = 0.5$) then the binding energy $u = 0$. This corresponds to two neutral atoms which do indeed have zero electrostatic attraction. The maximum binding energy occurs for $f = 0$ which corresponds to an electron spending all its time in the bond region. We find:

$$u_{\max} = [-7] \frac{e^2}{4\pi\epsilon_0 r_0} \quad (6.49)$$

Comparison with experiment: a plausibility test

In *Kaye and Laby*, we can find tabulated values of the C–C bond length and binding energy in different compounds and molecules. Taking the C–C bond length in a typical diatomic molecule, we have $r_0 = 0.1312$ nm and a cohesive energy per bond (actually tabulated as a *dissociation energy* D) of $D = 603$ kJ mol⁻¹. Converting this into a cohesive energy per bond $u = D/N_A$ evaluates to $603 \times 10^3 / 6.02 \times 10^{23} = 1.00 \times 10^{-18}$ J = 6.25 eV.

We can use these *experimental* values to deduce an estimate for f . Rearranging Equation 6.48 and solving for f we have:

$$(1-2f)^2 = -\frac{4\pi\epsilon_0 r_0 u}{7e^2} \quad (6.50)$$

$$f = 0.5 \left[1 - \sqrt{-\frac{4\pi\epsilon_0 r_0 u}{7e^2}} \right] \quad (6.51)$$

Substituting the values discussed above:

$$f = 0.5 \left[1 - \sqrt{\frac{4\pi \times 8.85 \times 10^{-12} \times 0.1312 \times 10^{-9} \times -1.00 \times 10^{-18}}{7(1.6 \times 10^{-19})^2}} \right]$$

$$f = 0.5 [1 - \sqrt{0.08146}] = 0.357 \quad (6.52)$$

Equation 6.52 indicates that an electron in a C–C covalent bond spends roughly 35% of its time orbiting the atoms at either end of the bond, and around 30% of its time in the central bond region. This estimate for f is unlikely to be accurate. However, it does show at least that our assumptions are self-consistent.

The above calculation is extremely crude: we have ignored, for example, the quantum mechanical rules that govern the distribution of charge around the atom and in the bond region. However, the purpose of the calculation has *not* been to calculate a realistic answer for the charge distribution in a covalent bond. If we wanted to do this we would have to quantum mechanically calculate (or experimentally determine) the charge density around, and in between, each atom. The purpose of this calculation is to show that, given the exis-

tence of the bond structure (i.e. its length and strength) we can understand the connection between the two using only Coulomb's Law.

We have also ignored the fact that in a solid, each carbon atom takes part in other covalent bonds with other atoms. There will therefore be other contributions to the binding energy of a solid because the neighbouring electrically-negative bond regions will repel one another. The consequences of this are discussed in the next section on crystal structure and illustrated in Figures 6.13, 6.14 and 6.15.

6.4.3 Crystal structure

The directionality of the covalent bond means that solids with covalent bonds tend to form crystals with quite different structures from those formed by molecular solids. In molecular solids, the maximum cohesive energy was achieved by atoms packing themselves in a way which achieved the largest possible number of nearest neighbours. In covalent solids, the structures are dictated by the geometry of the electron orbitals around atoms: adding extra nearest neighbours in general results in no extra bonding. For this reason, covalent solids often form rather 'open' structures with relatively low numbers of nearest neighbours.

For example, a carbon atom has four valence electrons and so can take part in, at most, four covalent bonds. It will therefore be of no benefit to form a crystal structure with more than four nearest neighbours. Each lobed orbital on the atom points in a different direction, and since each orbital has an excess of negative charge in it, it will repel the other orbitals in the same atom. The lobes therefore point away from one another, in the directions towards the corners of the regular tetrahedron (Figure 6.13)

In order to benefit from a covalent bond, other atoms must orient their orbitals with respect to the first atom so they can create overlapping orbital regions (Figure 6.13 (b)). The crystal structure formed is rather difficult to describe in words but is sketched in Figures 6.14 and 6.15.

Figure 6.13 (a) An illustration of the arrangement electric charge around a carbon atom. The four valence electrons orient their orbitals towards the points of a regular tetrahedron in order to minimise their repulsive Coulomb interaction. (b) An illustration of the arrangement of orbitals in two C atoms covalently bonded together.

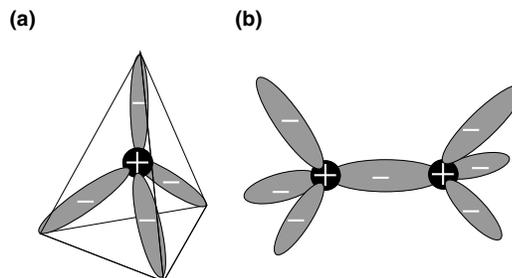


Figure 6.14 The crystal structure of diamond as deduced from X-ray scattering. The separation between atoms is 0.154 nm. The lines indicate the bonding regions and the spheres indicate the location of the atoms. The different shading is to aid the clarity of the picture, and allow identification of the four atoms entirely contained within the outer cube.

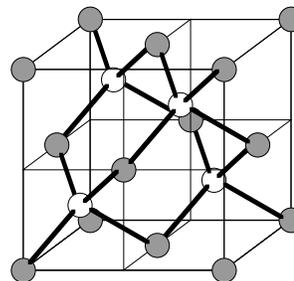
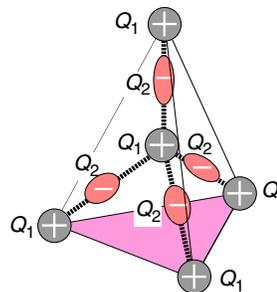


Figure 6.15 A simplified model of a small region of a diamond lattice. The model uses point charges to represent the continuous charge distribution that exists in the real lattice. It is a three-dimensional extension of the two-atom point charge model discussed in the text.



6.4.4 Cohesive energy calculations

The cohesive energy of a covalently-bonded solid is rather difficult to calculate, and we will not proceed to a full calculation here. However, we can indicate how such a calculation would be made. Consider the case of diamond which has the crystal structure illustrated in Figure 6.14 and 6.15. The complex three-dimensional nature of the charge distribution throughout the lattice makes a

systematic evaluation of the electrostatic energy of the structure more complicated than it was for ionic substances (§ 6.3). In particular the situation of the positively-charged ions and the negatively-charged bond regions are not equivalent. However, we may reasonably imagine how we could determine the cohesive energy of such a lattice in a way broadly similar to that discussed in §6.3.1.

6.5 Metals

6.5.1 General description

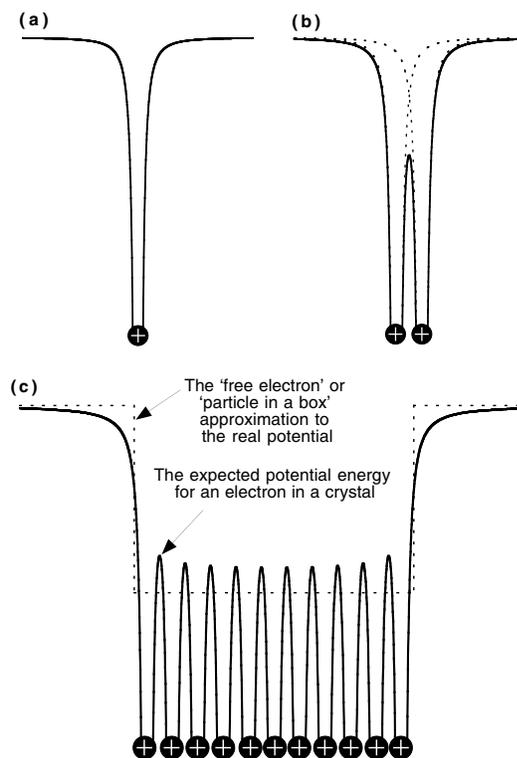
In metals, the entities that make up the solid are essentially positive ions (i.e. atoms stripped of one or more of their electrons) and electrons free to move in between the ions. One can think of this as a kind of delocalised covalent bond. However in order to understand even the simplest properties of metals we need to look at one factor which has been ignored in the previous three models of solids: *quantum mechanics*.

The 'particle in a box' problem

In this section, we will develop a strikingly simple model of a metal. We envisage that the electrons are unable to leave the metal, but that they are free to move around within it. This is a description of a metal as a 'box' and the determination of the quantum states of electrons in a metal is then reduced to the 'particle in a box' problem (§2.3). The way in which the Coulomb potentials around single ions can add up to form a box-like potential is illustrated in Figure 6.16.

The approximation that the potential energy experienced by an electron is box-like is known as the *free electron approximation*, and amounts to neglecting the corrugated details on the bottom of the expected potential in Figure 6.16 (c). The main justification of this approximation is that (as we shall see) the electrical properties of metals are generally rather similar to each other and very different from non-metals. This being so, their properties might be expected to arise from some general feature of their situation, and not on details particular to certain types of atoms.

Figure 6.16 The variation of the potential energy of a single electron in the vicinity of (a) a single ion, (b) two ions close together, and (c) a collection of ions close together. In (a) the potential will vary approximately like the Coulomb law $\approx 1/r$. In (b) the two potentials add together to make the region in between the ions a particularly attractive place to be for an electron. In (c) the ions have formed a box-like region capable of containing an electron with its walls, but allowing it to move within the box if its energy is not so low as to get trapped into the 'corrugations' at the bottom of the box. The dotted line shows the essence of the free electron approximation discussed in the text.



Quantum mechanics tells us (§2.3) that the energy of an electron in a cubic box of side L is given by:

$$E(n_x, n_y, n_z) = \frac{h^2}{8mL^2} [n_x^2 + n_y^2 + n_z^2] \quad (6.53)$$

where n_x, n_y, n_z are quantum numbers allowed to take only integer values 1, 2, 3, ... The quantum state with lowest energy is the state with $n_x = n_y = n_z = 1$, which we denote as $E(1,1,1)$. The quantum state with the next lowest energy is $E(1,1,2)$. There are three states with this same energy since from Equation 6.53, $E(1,1,2) = E(1,2,1) = E(2,1,1)$. The properties of a few of the low energy states are listed in Table 6.3.

The Pauli exclusion principle (§2.4) allows only one electron in each quantum state. In order to apply the exclusion principle correctly we need to recall that because an electron in a state (n_x, n_y, n_z) can have two possible spin states, there are *two* electron quantum states associated with each unique (n_x, n_y, n_z) combination. Importantly, because of the exclusion principle, if we place several electrons in the same box, then not all electrons will be able to occupy the lowest energy state. Some electrons are forced to occupy higher energy states.

An example: an eight-atom metal

In order to see how these quantum mechanical results affect our understanding of metals, we will consider a specific example of a cluster of eight atoms. We consider that each atom has one valence electron which could be relatively easily detached from its parent atom. We thus have eight electrons to be accommodated in one of two ways. Let us call them options *A* and *B*.

- In Option *A* we model each atom as a box of side a , with each box containing a single electron. The solid is then just a collection of these eight separate boxes
- In Option *B* we model the solid as a single large box of side $2a$ which contains all eight electrons.

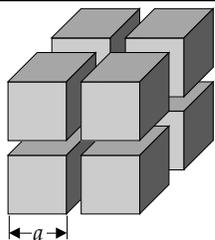
Notice that both options refer to electrons with the same overall electron density, $n = 1/a^3$. The energy of option *B* is dramatically lower than the energy of option *A*. This means that electrons prefer to be in ‘one big box’ rather than eight small boxes. Although this calculation is specific, the result is quite general: electrons ‘like to spread out if they can’. Of course, what we are really interested in is not the properties of an eight-atom piece of metal, but the limit of this problem for large numbers of atoms. In other words, we need to compare the

Table 6.3 The first few energy levels for particles trapped in a box. The columns show (i) the quantum numbers of the states, (ii) the energy of the states in units of $h^2/8mL^2$, for example $E(1,1,3) = A[1^2 + 1^2 + 3^2] = 11A$ where $A = h^2/8mL^2$, (iii) the number of quantum states with the same energy, (iv) the number of electrons that can be accommodated at that energy, and (v) the running total of the number of electrons able to be accommodated with energy equal to or less than the current energy, i.e. the running total of column (iv).

| Quantum numbers n_x, n_y, n_z | Energy in units of $h^2/8mL^2$ | Number of states | Number of electrons able to be accommodated with this energy (including spin) | Number of electrons able to be accommodated with energy less than or equal to the current energy |
|---|-----------------------------------|------------------|---|--|
| (1,1,1) | 3 | 1 | 2 | 2 |
| (1,1,2) (1,2,1) (2,1,1) | 6 | 3 | 6 | 2 + 6 = 8 |
| (1,2,2) (2,1,2) (2,2,1) | 9 | 3 | 6 | 2 + 6 + 6 = 14 |
| (1,1,3) (1,3,1) (3,1,1) | 11 | 3 | 6 | 2 + 6 + 6 + 6 = 20 |
| (2,2,2) | 12 | 1 | 2 | 2 + 6 + 6 + 6 + 2 = 22 |
| (1,2,3) (1,3,2) (2,1,3) (2,3,1) (3,2,1) (3,1,2) | 14 | 6 | 12 | 2 + 6 + 6 + 6 + 2 + 12 = 34 |

Figure 6.17 Options A and B for accommodating eight electrons within a solid.

Option A



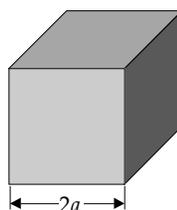
Each electron is confined to its own separate box (atom) with side $\approx a$. Each electron enters the ground state in its own box, and so the total energy will be:

$$E = 8 \times \frac{h^2}{8ma^2} \times [3]$$

And so the total energy of Option A is:

$$E_{\text{option A}} = 24 \times \frac{h^2}{8ma^2}$$

Option B



Each electron is contained in the same box with side $\approx 2a$. The electrons enter the lowest quantum states available. Two electrons can occupy the ground state and so the total energy of these two electrons will be:

$$2 \times \frac{1}{4} \times \frac{h^2}{8ma^2} \times [3]$$

The factor $1/4$ arises from Equation 6.59 because the box has side $L = 2a$ as opposed to $L = a$ in Option A. The next six electrons can occupy the states (1,1,2), (1,2,1), (2,1,1) so their total energy will be:

$$6 \times \frac{1}{4} \times \frac{h^2}{8ma^2} \times [6]$$

Adding up these terms we find that the total energy of Option B is:

$$\begin{aligned} E_{\text{option B}} &= \left[\frac{2 \times 3}{4} + \frac{6 \times 6}{4} \right] \frac{h^2}{8ma^2} \\ &= 10.5 \times \frac{h^2}{8ma^2} \end{aligned}$$

energy of N electrons trapped in boxes of side a with energy of N electrons trapped in a single box of side $\sqrt[3]{Na}$. We consider this problem in §6.5.4, but surprisingly, the result does not change much.

The importance of quantum mechanics

Considering again the 8-atom metal of the previous section, we see that it is not difficult to imagine how changes in electron density could result in different total energies. However in both options A and B, the electron density was the same, $n = 1/a^3$, so the change in energy has not arisen from a change in electron density. The lowered energy is a result of the change in the nature of the electron wave functions. Thus an arrangement of atoms can lower their energy by allowing their electrons to become *delocalised* i.e. to move freely through the crystal, while still being trapped within the crystal and not allowed to leave. This is nothing more than a gigantic version of option B, the big box. In other words, the cohesive energy of metals derives from this delocalisation energy.

The importance of Coulomb interactions

Notice that no mention has been made of the Coulomb interaction either: between *electrons and ions* or; between *electrons and the other electrons* with whom they share a 'box'. Since we have seen the importance of Coulomb interactions in the other three types of bonding, we can assume that Coulomb interactions are important and that a full theory must consider them. The theory we have outlined is known as the theory of a *free electron gas*. The neglect of Coulomb interactions is dignified by giving it two special names:

- The *Free Electron Approximation* assumes we can neglect the interactions between electrons and ions, *except that occasionally electrons are scattered by vibrations of the lattice.*
- The *Independent Electron Approximation* assumes we can neglect the interactions between electrons and other electrons, *except that electrons somehow(!) know about each other sufficiently to obey the exclusion principle.*

We take the first few steps in going beyond the free electron approximation in Web Chapter W1. Going beyond the independent electron approximation is beyond the scope of this book.

6.5.2 Counting quantum states

In a real metal, we have to deal with more than ‘just a few’ electrons in a box, and counting the occupied quantum states individually becomes impossible. If you think this is not so, please try Exercise 7 at the end of this chapter! In order to cope with the large number of electrons, several statistical mechanical techniques have been developed to allow calculations to be made about metals. They correspond to rather sophisticated ways of counting quantum states whose energies lie in particular energy ranges, as opposed to the rather laborious method of ‘just counting’ adopted for Table 6.3. The methods are discussed in some detail in Web Chapter W1, and here we just note the general approach.

The counting methods are based on the following rather simple idea. We plot points representing allowed states on a three-dimensional graph. The graph is generally called a k -space graph, or sometimes just ‘ k -space’. Importantly, the points, which represent the allowed states, are distributed in a fine *uniform* mesh on the graph. So by measuring ‘volumes’ on this three-dimensional k -space graph, we can also count states.

k -space

So far we have used the quantum numbers (n_x, n_y, n_z) to represent each allowed quantum state. In order to make the most of the k -space idea, we need to change our description of the quantum states and use three different quantum numbers (k_x, k_y, k_z) . The rationale for this is that (n_x, n_y, n_z) represent *standing wave* solutions of the Schrödinger equation, while (k_x, k_y, k_z) represent *travelling wave* solutions. As you may know, a standing wave can be considered as the sum of two travelling waves moving in opposite directions. The key advantage of this change from a physicist’s point of view is that it allows us to visualise electrons as *moving* within a metal.

The mathematical complexities of this change are

discussed in Web Chapter W1, but here I would like you to note three important points.

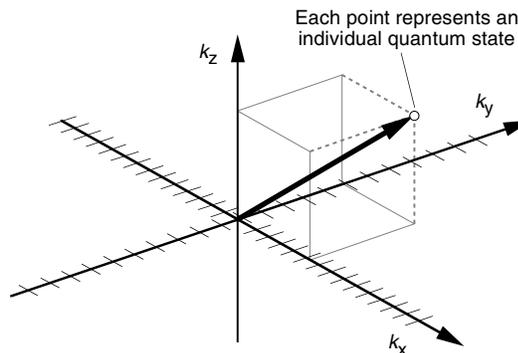
- First, not all values of (k_x, k_y, k_z) are valid solutions of the Schrödinger equation. This should not really surprise you since it just reflects the fact that only integer values (n_x, n_y, n_z) were allowed.
- The second point concerns the significance of (k_x, k_y, k_z) . In fact, (k_x, k_y, k_z) are no longer just numbers: they are directly related to the wavelength of the wave function, and hence to the energy and momentum of the quantum state that they represent.
- The final point is that the k -space scheme can seem very abstract, so it is important to remember why we have needed to introduce the concept. It allows us to count large numbers of quantum states, and in particular it allows us to calculate the *density of states* function that we discussed in §2.5.3.

Let us look at each of these three points in turn.

1. Allowed values of k_x , k_y and k_z

Whereas the quantum numbers n_i in Equation 6.59 had allowed values $n_i = 1, 2, 3, \dots$ where $i = x, y, z$, the quantum numbers k_i can have negative or positive values corresponding to mo-

Figure 6.18 k -space is a concept which enables for counting quantum states of the particle in a box problem when lots of particles are present. Each quantum state is represented by a point on a k_x, k_y, k_z graph. The energy of the state is proportional to the square of its distance from the origin on this graph. So in order to minimise their energy the occupied quantum states cluster in a sphere around the origin.



tion in either direction. The k_i 's are related to the wavelength of each quantum state as follows. If our waves were just one-dimensional, then we would simply write:

$$\lambda = \frac{2\pi}{k} \quad (6.54)$$

In three dimensions, things are a little more complicated. We imagine the k_i 's are components of a vector \mathbf{k} that points from the origin to the point $\mathbf{k} = (k_x, k_y, k_z)$. Now the wavelength of the wave represented by $\mathbf{k} = (k_x, k_y, k_z)$ is given by:

$$\lambda = \frac{2\pi}{|\mathbf{k}|} = \frac{2\pi}{\sqrt{k_x^2 + k_y^2 + k_z^2}} \quad (6.55)$$

In our particle in a box problem, we found that the allowed wavelengths of the wave functions formed the following series:

$$\lambda = 2L, L, L/3, L/4 \dots \quad (6.56)$$

There is a pattern here, but it might not be clear to you. You may be able to see the pattern more clearly if I write it out again in a different format:

$$\begin{aligned} \lambda &= \frac{2L}{1}, \frac{2L}{2}, \frac{2L}{3}, \frac{2L}{4} \dots \\ &= \frac{2L}{m} \end{aligned} \quad (6.57)$$

where $m = 1, 2, 3 \dots$ etc. We can express this series in λ as a series in k :

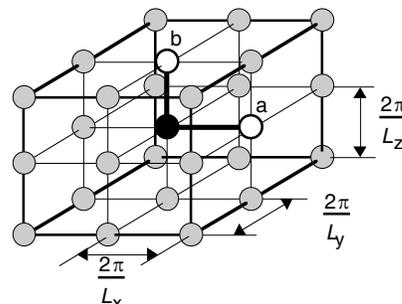
$$\begin{aligned} k &= \frac{2\pi}{\lambda} = \frac{2\pi}{2L/m} \\ &= \frac{\pi m}{L} \end{aligned} \quad (6.58)$$

In fact, because we separated each standing wave into *two* travelling waves, this expression needs to be altered. The analysis in Web Chapter W1 shows that the allowed values of (k_x, k_y, k_z) are in fact given by:

$$k_x = \frac{2m_x\pi}{L_x}, k_y = \frac{2m_y\pi}{L_y}, k_z = \frac{2m_z\pi}{L_z} \quad (6.59)$$

where $m_x = \pm 1, \pm 2, \pm 3 \dots$ and L_x is length of the piece of metal in the x -direction. There are similar

Figure 6.19 Close up view of 'k-space'. The circles represent allowed values of \mathbf{k} . If the central point represents a solution of the Schrödinger equation with a particular value of k_x, k_y, k_z , then point *a* represents a solution with k_x component increased by $2\pi/L_x$. Similarly point *b* represents a solution with k_z component increased by $2\pi/L_z$.



relationships for y and z . Thus the allowed states form a mesh in k -space (Figure 6.18) and the distance from one allowed value of k_x to the next is:

$$\begin{aligned} \Delta k_x &= \frac{2(m_x+1)\pi}{L_x} - \frac{2(m_x)\pi}{L_x} \\ &= \frac{2\pi}{L_x} \end{aligned} \quad (6.60)$$

So, as illustrated in Figure 6.19, each allowed \mathbf{k} -state occupies a small cuboid of 'volume':

$$\begin{aligned} \Delta k_x \Delta k_y \Delta k_z &= \frac{2\pi}{L_x} \times \frac{2\pi}{L_y} \times \frac{2\pi}{L_z} \\ &= \frac{8\pi^3}{V} \end{aligned} \quad (6.61)$$

where V is the total volume of the crystal. I have used the word 'volume' in quotation marks above Equation 6.61 because I am referring to 'volume' on a k -space graph. As you can see from Equation 6.61, the 'volume' on the k -space graph actually has the dimensions of inverse volume, i.e. m^{-3} rather than m^3 . The final point we need to make is that we need to take account of the internal spin of electrons. This allows two electrons with opposite spin to occupy each k -state. Thus, the 'volume' of k -space required for each electron is given by half the value in Equation 6.61:

$$\Delta \mathbf{k} = \frac{4\pi^3}{V} \quad (6.62)$$

2. Energy and momentum

Equation 6.55 allows us to use the de Broglie relation (Equation 2.42) to infer the momentum and energy of the wave represented by (k_x, k_y, k_z)

The momentum may be written as:

$$\begin{aligned} p &= \frac{h}{\lambda} = \frac{h}{\frac{2\pi}{|\mathbf{k}|}} \\ &= \hbar|\mathbf{k}| \\ p &= \hbar\sqrt{k_x^2 + k_y^2 + k_z^2} \end{aligned} \quad (6.63)$$

Notice that the quantum states with small amounts of momentum have small values of $|\mathbf{k}|$. Thus in k -space they will be represented by points near the origin. The energy, which is just the kinetic energy of a free particle, may be written as:

$$\begin{aligned} E &= \frac{1}{2}m_e v^2 = \frac{p^2}{2m_e} \\ E &= \frac{\hbar^2 |\mathbf{k}|^2}{2m_e} \\ E &= \frac{\hbar^2}{2m_e} [k_x^2 + k_y^2 + k_z^2] \end{aligned} \quad (6.64)$$

Notice again that the low-energy quantum states have small values of $|\mathbf{k}|$. Thus in k -space they will be represented by points near the origin. Importantly, Equation 6.64 is the equation of a sphere. Thus, all quantum states with energy E will be represented by points in k -space which lie on the surface of a sphere with radius:

$$|\mathbf{k}| = \sqrt{\frac{2m_e E}{\hbar^2}} \quad (6.65)$$

3. The density of states function

Using the concept of k -space allows to work out the *density of states* function $g(E)$ that we met §2.5.3. The density of states function answers the question: how many quantum states are there with energy between E and $E + dE$? The answer is $g(E)dE$. To find $g(E)$ in terms of our k -space graph, we can ask a related question: how many quantum states are there with k -vector of length

Example 6.4

An electron occupies a quantum state with:

$$k_x = 10^{-10} \text{ m}^{-1} \quad k_y = 10^{-10} \text{ m}^{-1} \quad k_z = 0 \text{ m}^{-1}$$

Work out the wavelength, energy, and speed of an electron occupying this state.

Wavelength

The total magnitude of the electrons k -vector is:

$$\begin{aligned} |\mathbf{k}| &= \sqrt{k_x^2 + k_y^2 + k_z^2} = 10^{10} \sqrt{1^2 + 1^2 + 0^2} \\ &= 1.41 \times 10^{10} \text{ m}^{-1} \end{aligned}$$

So the wavelength is given by Equation 6.55:

$$\lambda = \frac{2\pi}{|\mathbf{k}|} = \frac{2\pi}{1.41 \times 10^{10}} = 4.44 \times 10^{-10} \text{ m}$$

Energy

The energy is given by Equation 6.64:

$$\begin{aligned} E &= \frac{\hbar^2 |\mathbf{k}|^2}{2m_e} = \frac{(1.054 \times 10^{-34})^2 (1.41 \times 10^{10})^2}{2 \times 9.1 \times 10^{-31}} \\ &= 1.21 \times 10^{-18} \text{ J} \\ &= 7.58 \text{ eV} \end{aligned}$$

Speed

The speed can be calculated from the momentum $p = mv$ and $p = \hbar k$:

$$\begin{aligned} v &= \frac{\hbar |\mathbf{k}|}{m_e} = \frac{1.054 \times 10^{-34} \times 1.41 \times 10^{10}}{9.1 \times 10^{-31}} \\ &= 1.633 \times 10^6 \text{ m s}^{-1} \end{aligned}$$

between k and $k + dk$? We can work out the answer to this question by working out the ‘volume’ of a spherical shell with inner radius k and thickness dk . The answer is:

$$\text{‘volume’} = 4\pi k^2 dk \quad (6.66)$$

The number of states in this ‘volume’ is:

$$\begin{aligned} dN &= \frac{4\pi k^2 dk}{4\pi^3/V} \\ &= \frac{Vk^2 dk}{\pi^2} \end{aligned} \quad (6.67)$$

We can convert this to an expression for $g(E)$ by changing references to k to references to E . We note that $k^2 = 2m_e E / \hbar^2$ and that dk is given by:

$$\begin{aligned}
 k &= (2m_e / \hbar^2)^{1/2} E^{1/2} \\
 \frac{dk}{dE} &= (2m_e / \hbar^2)^{1/2} \frac{1}{2} E^{-1/2} \\
 dk &= \frac{1}{2} (2m_e / \hbar^2)^{1/2} E^{-1/2} dE
 \end{aligned} \tag{6.68}$$

Substituting for k^2 and dk in Equation 6.67 we find:

$$\begin{aligned}
 dN &= \frac{V}{\pi^2} k^2 dk \\
 &= \frac{V}{\pi^2} \times \frac{2m_e E}{\hbar^2} \times \frac{1}{2} \left(\frac{2m_e}{\hbar^2} \right)^{1/2} E^{-1/2} dE \\
 &= \underbrace{\left[\frac{V}{\pi^2} \frac{\sqrt{2m_e^3}}{\hbar^3} E^{1/2} \right]}_{g(E)} dE
 \end{aligned} \tag{6.69}$$

This is the sought-after density of states function:

$$\begin{aligned}
 g(E) &= \frac{V \sqrt{2m_e^3 E}}{\pi^2 \hbar^3} \\
 &= \left[\frac{V \sqrt{2m_e^3}}{\pi^2 \hbar^3} \right] \sqrt{E}
 \end{aligned} \tag{6.70}$$

Notice that $g(E)$ depends only a group of fundamental constants, and increases as the square root of the energy. It is illustrated in Figure 2.16 and is used in Examples 2.6 and 2.7 to calculate the average energy of an electron in a metal.

Occupying k -states

In the previous few paragraphs we have seen how the idea of k -space can be used to help develop a theoretical model of a metal. We have seen that the \mathbf{k} -vectors of the allowed quantum states are distributed on a uniform mesh throughout k -space. Now we need to consider which of these quantum states are occupied by electrons.

We could answer this question by following the formal approach described in §2.5.3. To do that we would combine the density of states function (Eq. 6.70) with the Fermi–Dirac occupation function (Eq. 2.61) to calculate the distribution function (Eq. 2.64), which we could use to calculate

the properties of metals. We used that approach in Example 2.7 where we calculated the average energy of an electron in a metal. However, here we will approach the question of the occupancy of quantum states in a slightly simpler way, by considering the case of a metal at absolute zero. At $T = 0$ the Fermi–Dirac function (Figure 2.17) tells us that the N electrons in the metal occupy the N lowest energy quantum states.

Consider the following analogy: k -space is like an ‘auditorium’ into which we allow an ‘audience’ (electrons) to enter. The first electrons to enter occupy the ‘cheapest seats’ (low-energy k -states), and those who enter later have to occupy ‘more expensive seats’ (higher-energy k -states). The density of states function tells us exactly how many seats (k -states) there are in each ‘price range’ (energy range). The Fermi–Dirac function tells us that at $T = 0$ the N electrons in the metal occupy the N ‘cheapest seats’ (lowest energy quantum states).

The low-energy quantum states are those clustered around the origin on a k -space graph. The mesh of allowed states is actually very fine indeed, so by the time the first few thousand electrons have been accommodated, the region of occupied states looks rather like a sphere centred on the origin (Figure 6.20). By the time a number of the order of 10^{23} electrons have been accommodated, the region of occupied states forms an essentially perfect sphere, known as the *Fermi sphere*, with Fermi radius k_F . Since each electron requires a ‘volume’ of k -space $4\pi^3/V$ we can write:

$$\frac{4}{3} \pi k_F^3 = N \tag{6.71}$$

where we have remembered that a sphere of radius r has a volume $\frac{4}{3}\pi r^3$. If we cancel some terms, and solve for k_F we find:

$$\begin{aligned}
 k_F^3 &= 3 \left[\frac{N}{V} \right] \pi^2 \\
 k_F &= (3n\pi^2)^{1/3}
 \end{aligned} \tag{6.72}$$

where $n = N/V$ is the electron density. We can

also work out an expression for the energy (called the *Fermi energy*) of electrons on the ‘surface’ of the Fermi sphere:

$$E_F = \frac{\hbar^2 k_F^2}{2m_e} \quad (6.73)$$

6.5.4 A real metal

The previous section has been rather theoretical and so in this section we will evaluate some of the key results from the last section for a real metal: copper.

A numerical example

To estimate the number density n of ‘free electrons’ in a metal we can proceed as follows. We first work out the number density n of atoms in a metal. Then we imagine that (say) 1, 2, or 3 electrons, the *valence electrons* from each atom, can leave the ‘parent’ atom to form the electron gas. Which integer value we choose will depend upon our prior knowledge of the metal under consideration. There are several ways to estimate n , but perhaps the simplest is to divide the *density* by the mass of an atom to get the *number density* of atoms. If we then multiply by the valence we arrive at n . From Table 7.2 we see that the density of copper is $8.933 \times 10^3 \text{ kg m}^{-3}$, and the mass of an atom is $63.55 \times 1.66 \times 10^{-27} \text{ kg}$. Assuming copper has a valence of one, then our estimate for n is:

$$\begin{aligned} n &= \frac{1 \times 8.933 \times 10^3}{63.55 \times 1.66 \times 10^{-27}} \\ &= 8.47 \times 10^{28} \text{ electrons m}^{-3} \end{aligned} \quad (6.74)$$

If we use this estimate for n in Equation 6.72 for the Fermi wave vector k_F we find:

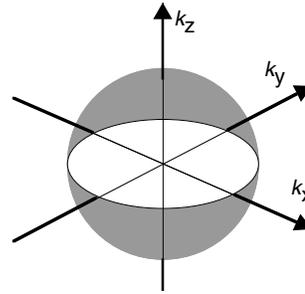
$$\begin{aligned} k_F &= (3 \times 8.47 \times 10^{28} \times \pi^2)^{1/3} \\ &= 1.36 \times 10^{10} \text{ m}^{-1} \end{aligned} \quad (6.75)$$

Substituting this in Equation 6.73 for the Fermi energy E_F we find:

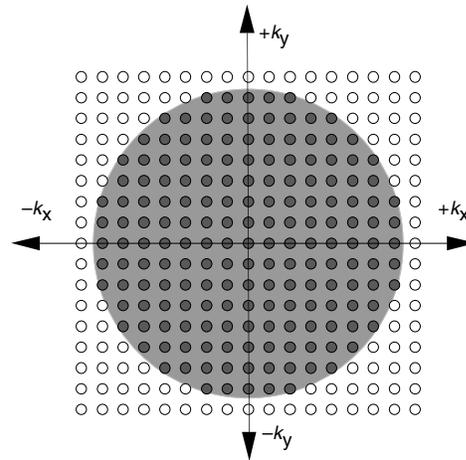
$$\begin{aligned} E_F &= \frac{(1.054 \times 10^{-34})^2 (1.36 \times 10^{10})^2}{2 \times 9.1 \times 10^{-31}} \\ &= 1.13 \times 10^{-18} \text{ J} \\ &= 7.06 \text{ eV} \end{aligned} \quad (6.76)$$

Figure 6.20 (a) In three-dimensions the occupied states form a sphere in k -space known as the *Fermi sphere* which is shown shaded in the figure. If we imagine slicing through the Fermi sphere in plane where $k_z = 0$ we would find a situation represented in (b). Each small circle represents an allowed travelling wave solution to the Schrödinger Equation. The filled circles represent occupied quantum states and the unfilled circles represent empty quantum states. At absolute zero, only the lowest energy states (low k = long wavelength = low energy) are occupied. For any macroscopic piece of metal the quantum states would be much more densely packed than in the figure.

(a)



(b)



We can evaluate $g(E)$ per unit volume from Equation 6.70:

$$\begin{aligned} \frac{g(E)}{V} &= \left[\frac{\sqrt{2 \times (9.1 \times 10^{-31})^3}}{\pi^2 (1.054 \times 10^{-34})^3} \right] \sqrt{E} \\ &= 1.062 \times 10^{56} \sqrt{E} \text{ states J}^{-1} \text{ m}^{-3} \end{aligned} \quad (6.77)$$

And we can evaluate this at the Fermi energy:

$$\begin{aligned}\frac{g(E_F)}{V} &= [1.062 \times 10^{56}] \sqrt{1.13 \times 10^{-18}} \\ &= 1.13 \times 10^{47} \text{ states J}^{-1} \text{m}^{-3}\end{aligned}\quad (6.78)$$

Let us look at the significance of k_F , E_F and $g(E)$ in turn.

The significance of k_F

The significance of k_F can be seen more easily if we look at the wavelength of electrons with wave vector k_F . Since k_F is the *maximum* k -vector, then electrons with this k -vector will have the *minimum wavelength* since $k = 2\pi/\lambda$. Substituting from Equation 6.75:

$$\begin{aligned}\lambda_{\min} &= \frac{2\pi}{1.36 \times 10^{10}} \\ &= 4.63 \times 10^{-10} \text{ m}\end{aligned}\quad (6.79)$$

We find a wavelength comparable to the spacing a between atoms. We can see the significance of this if we consider again Figure 6.16, which was the basis of the free-electron approximation. We have been able to ignore the ‘corrugations’ on the bottom of the potential well because the wavelengths of electron wave functions are not related to the spacing between ions a . Thus the peaks in the probability density $|\Psi|^2$ sometimes fall exactly on an ion, and sometimes in between ions. On average, each electron experiences a smoothly-averaged potential.

However, if the periodicity of the electron probability density has a periodicity which *exactly* matches the lattice periodicity, then the peaks in the probability density will either always fall on an ion, or always fall between ions. In either case, the electron–ion interaction becomes much significantly larger, and can no longer be ignored. This phenomenon is critical to understanding the detailed electronic properties of solids, and we consider it further in Chapter W1 on the band theory of solids.

The significance of E_F

The significance of E_F can be seen if we compare it with the typical amount of thermal energy an electron might expect to receive as it interacts with the ions in a metal crystal ($\approx \frac{3}{2}k_B T$). Evaluating this at room temperature $\approx 290\text{K}$:

$$\begin{aligned}\frac{3}{2}k_B T &= 6.0 \times 10^{-21} \text{ J} \\ &= 0.038 \text{ eV}\end{aligned}\quad (6.80)$$

This energy is smaller than E_F by a factor ≈ 200 .

The electrons with energies near E_F also travel very fast. Since E_F is the kinetic energy of the electron, $\frac{1}{2}mv_F^2$, we can work out the Fermi speed v_F as:

$$\begin{aligned}v_F &= \sqrt{\frac{2E_F}{m}} = \sqrt{\frac{2 \times 1.122 \times 10^{-18}}{9.1 \times 10^{-31}}} \\ &= 1.6 \times 10^6 \text{ ms}^{-1}\end{aligned}\quad (6.81)$$

which is $\approx 1\%$ of the speed of light. Also, notice that the electrons with energies near E_F travel with this speed independent of the temperature. This may be contrasted with the situation of molecules in a *molecular* gas whose distribution of speeds depends strongly on temperature (Figure 4.7).

The significance of $g(E_F)$

As we heat a metal above absolute zero, some quantum states above the Fermi energy will become occupied, and some states below the Fermi energy will become empty. However, the exclusion principle restricts this process very strongly. Only electrons occupying quantum states with energies within about $k_B T$ of the Fermi energy are able to change state. This is because only those electrons have access to the empty quantum states above the Fermi energy. As we saw above, $k_B T \ll E_F$, and so the number of electrons able to accept thermal energy is rather small, of the order of $\Delta N = g(E_F)k_B T$. Hence the *fraction* of electrons able to accept thermal energy is:

$$\begin{aligned}\frac{\Delta N}{N} &= \frac{g(E_F)k_B T}{N} \\ &= \frac{1.13 \times 10^{47} \times 1.38 \times 10^{-23}}{8.47 \times 10^{28}} T \\ &= 1.84 \times 10^{-5} T\end{aligned}\quad (6.82)$$

It is important to note how small this fraction is.

Even at a temperature of 2000 K, which is above the melting temperature of most metals, only around $1.84 \times 10^{-5} \times 2000 \approx 4\%$ of the ‘free’

electrons in the metal have changed their quantum state. We shall see the effect of this when we consider the heat capacity of metals in §7.6

6.5.4 Cohesive energy

The cohesive energy of a metal is rather difficult to calculate accurately. However, even at the level of this book, we can show that the cohesive energy is quite large, potentially of the order of several electron volts per atom (several hundred kJ mol⁻¹).

Cohesive energy of the eight-electron metal

Consider again the calculations illustrated in Figure 6.17. These showed the energy of eight electrons on eight isolated atoms of volume a^3 (Option A) was significantly greater than the energy of eight electrons able to move around a single box of volume $8a^3$ (Option B). Table 6.4 summarises the total energy of the eight electrons, the average energy per electron, and the difference between the average energy per electron in the two options.

Now for a metal, a has a typical value of ≈ 0.3 nm and so a typical energy benefit per electron in Table 6.4 is given by:

$$\begin{aligned} u &= -1.69 \times \frac{h^2}{8ma^2} \\ &= -1.69 \times \frac{(6.626 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} (0.3 \times 10^{-9})^2} \\ &= -3.4 \times 10^{-18} \text{ J per electron} \\ &= -21.2 \text{ eV per electron} \\ &= -2043 \text{ kJ per mole} \end{aligned} \quad (6.83)$$

The cohesive energy of a 'real' metal

In order to calculate the cohesive energy of real metal consisting of more than eight electrons, we need to calculate the average energy per electron. This is done in Example 2.8, where it is shown that the average energy per electron in the free electron approximation is $\frac{3}{5}E_F$

Table 6.5 summarises the calculation we need to make. Let us try to evaluate this energy difference. First of all we can express E_F in terms of k_F (see Equation 6.73)

Table 6.4 Evaluating the energy difference between options A and B in Figure 6.17 for eight electrons.

| | Option A (separate atoms) | Option B (metallic state) |
|--------------------------------|------------------------------|------------------------------|
| Energy of 8 electrons | $24 \times h^2/8ma^2$ | $10.5 \times h^2/8ma^2$ |
| Average energy per electron | $3 \times h^2/8ma^2$ | $1.31 \times h^2/8ma^2$ |
| Energy difference per electron | $-1.69 \times h^2/8ma^2$ | |

$$\begin{aligned} u &= \frac{3}{5}E_F - \frac{3h^2}{8ma^2} \\ &= \frac{3}{5} \times \frac{\hbar^2 k_F^2}{2m} - \frac{3h^2}{8ma^2} \end{aligned} \quad (6.84)$$

Now we write k_F in terms of n (Equation 6.72):

$$u = \frac{3}{5} \times \frac{\hbar^2 (3n\pi^2)^{2/3}}{2m} - \frac{3h^2}{8ma^2} \quad (6.85)$$

Finally, we recall that $\hbar = h/2\pi$ and that the number density of electrons is just $n = 1/a^3$:

$$u = \frac{3}{5} \times \frac{h^2 (3\pi^2)^{2/3}}{4\pi^2 \times 2ma^2} - \frac{3h^2}{8ma^2} \quad (6.86)$$

Taking out common factors we arrive at:

$$\begin{aligned} u &= \left[\frac{(3\pi^2)^{2/3}}{5\pi^2} - 1 \right] \times \frac{3h^2}{8ma^2} \\ &= -0.806 \times \frac{3h^2}{8ma^2} \end{aligned} \quad (6.87)$$

Table 6.5 Evaluating the energy difference between options A and B in Figure 6.17 for a free electron gas.

| | Option A (separate atoms) | Option B (metallic state) |
|--------------------------------|------------------------------|------------------------------|
| Energy of N electrons | $3N \times h^2/8ma^2$ | $N \times 3E_F/5$ |
| Average energy per electron | $3 \times h^2/8ma^2$ | $3E_F/5$ |
| Energy difference per electron | $3E_F/5 - 3h^2/8ma^2$ | |

which amounts to roughly 50% of the cohesive energy per electron of the eight electron metal we considered earlier. We therefore find for the cohesive energy of a typical metal a figure of:

$$\begin{aligned} u &\approx -1.6 \times 10^{-18} \text{ J per electron} \\ &\approx -10.11 \text{ eV per electron} \\ &\approx -974 \text{ kJ per mole} \end{aligned} \quad (6.88)$$

Clearly, this is a potentially strong form of bonding. Astonishingly, we arrived at this figure without any consideration of the Coulomb interaction between electrons! When we consider the Coulomb interactions between electrons and other electrons, and between electrons and ions, then the problem becomes considerably more complex. These matters are discussed in Chapter W1 on the band theory of solids.

6.6 Real solids

The four types of bonding we discussed in §6.2 to §6.5 represent ideal situations: only rarely can solids be understood by considering just one type of bonding. The solids which can be understood this way are sometimes called *simple* (although they are not!) and have been studied extensively in the first 70 years or so of modern solid-state physics. However most solids are not simple, in the sense of having only type of bonding: most materials have two or more types of bonding. Indeed, in general it is not always possible to clearly separate the types of bonding present: there are just interacting electrons following the Coulomb law and the rules of quantum mechanics. However, despite this reservation, we consider below some combinations of types of bonding found in real solids.

6.6.1 Organic solids

Many of the most common solids that we encounters in normal life are classed as organic in nature. Originally the term *organic* meant that the substance was derived from a living organism. In modern terms however it denotes a substance composed primarily of carbon and hydrogen atoms. If we consider plastics, just one class of organic substance, one can begin to appreciate the astonishingly diverse properties of organic solids. Clearly we cannot specify everything about bonding in organic substances, but we can make one or two generalisations.

Bonding between molecules

Organic substances are composed of molecules

which are bound to each other by Van der Waals bonding similar to that discussed in §6.1. The relatively weak Van der Waals force acts between all molecules, and is non-directional in nature.

However, some molecules have other types of bonds between them. In particular, hydrogen bonds are especially important for molecules which contain the OH chemical group. We discuss them further in Chapter 8.

Bonding within molecules

Organic molecules can consist of anything from just a few to many thousands of atoms. Within each organic molecule, the atoms are held together by relatively strong covalent bonding similar to that discussed in §6.3. Since the covalent bonding is directional in nature, this leads to organic molecules having relatively well-defined shapes. The broad picture is shown in Figure 6.21.

When we consider complex organic molecules we have to consider yet another effect we have glided over in this chapter, but which we will return to in Chapter 10: *entropy*. Consider, for example, a collection of organic molecules which are each, say, 100 carbon atoms long and studded with various hydrogen and other atoms. By considering the shape of the molecules and the interactions between them, we can predict the crystal structure for the substance with the lowest energy. However, in practice this crystal structure will never be attained because the molecules will become tangled in a way which is essentially irreversible.

For such materials, their equilibrium properties are dominated by this disorder and their minimum energy state is nearly irrelevant. This highlights an important feature that we discuss again in Chapter 10. The equilibrium structure for *any substance* is *not* the lowest energy structure, but the one which minimises a combination of entropy and internal energy known as the *Gibbs free energy*.

6.6.2 Hydrogen bonding

Hydrogen bonding is a specific combination of ionic and covalent bonding that occurs in substances which contain oxygen and hydrogen atoms bonded together, e.g. H_2O . It is given a specially category to itself because of its importance in organic substances where it acts between molecules and is much stronger than the Van der Waals force. The nature of the hydrogen bond is discussed in detail in §9.1 where we consider its effect on the density of liquid water.

6.6.3 The ionic–covalent continuum

In ‘pure’ ionic bonding, an electron is transferred completely from one atom to another. Of course, once this transfer is complete, the electric forces will act to try to pull this electron back to its parent ion. If these forces partially succeed then there will be some electron density in the region in be-

tween the ions, which is the situation in a covalent bond. Thus ‘pure’ ionic and ‘pure’ covalent bonds can be seen as two extremes of a continuum. Symmetry considerations dictate that a ‘pure’ covalent bond can only exist between two identical atoms. Any difference in the electron affinity of the atoms at either end of the bond will result in an asymmetric charge distribution which has both ionic and covalent character (Figure 6.22).

The figure illustrates four possible electronic charge distributions in between two atoms. In the lower picture, the atoms have identical electron affinity. The other three cases refer to situations where the right-most atom has increasing electron affinity compared to the left-most atom.

The differing electron affinities of atoms are caused by the different distributions of charge around the nucleus of the atoms. Atoms with complete shells of electrons have essentially zero electron affinity. Atoms with one electron missing from a shell have particularly high electron affinity the ‘gap’ in the shell allows other electrons to ‘see’ the nuclear charge and hence be attracted to the atom.

6.6.4 Transition metals

Most elements are metallic. However most ele-

Figure 6.21 Within an organic substances there are in general at least two types of bonding:

- **Within** an organic molecule the atoms are held together by relatively strong, directional covalent bonds
- **Between** organic molecules the bonding is due to relatively weak, non-directional, Van der Waals bonds.

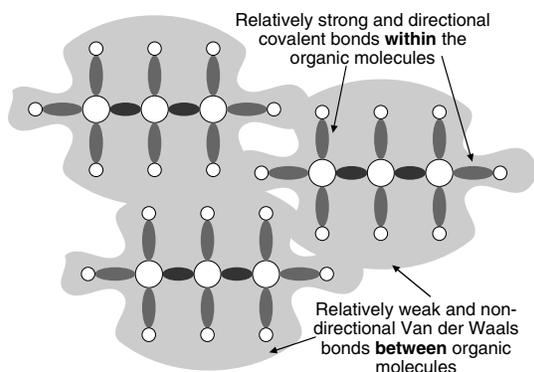
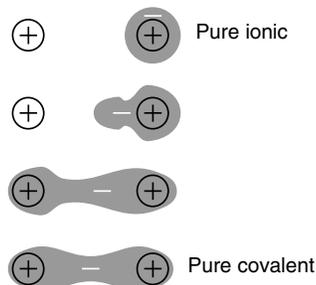


Figure 6.22 An illustration of the ionic-covalent continuum. In the text ionic and covalent bonding were presented as distinct categories. In practice, many substances have bonding which is intermediate between the two cases. The figure illustrates four possible electronic charge distributions in between two atoms. In the lower picture, the atoms have identical *electron affinity*. The other three cases refer to situations where the rightmost atom has increasing electron affinity compared to the leftmost atom.



ments are bonded in a way which is a mixture of metallic and covalent bonding. In the transition metals for example, electrons in d -orbitals form bonds which are partly covalent and partly metallic, while electrons occupying s -orbitals form almost purely metallic bonds. The situation is too complex for detailed consideration here.

6.6.5 What have we neglected?

In considering molecular, ionic and covalent bonding in §6.2 to §6.4 we concentrated entirely on the effect of Coulomb interactions, and neglected to take account of quantum mechanics.

Clearly this cannot be quite right, since we saw when considering metals in §6.5, that quantum mechanics played a critical role in determining, for example, the cohesive energy of metals. Also, in metallic bonding, when we did consider the effect of quantum mechanics, we then neglected to take account of the Coulomb interaction between electrons.

In reality, both Coulomb interactions and quantum mechanics are important considerations in all types of bonding. Table 6.6 summarises some of the effects we neglected in §6.2 to §6.5.

Table 6.6 Summary of what has been considered and neglected in Chapter 6.

| Bonding type | What we considered | What we neglected |
|--------------|--|--|
| Molecular | We calculated the cohesive energy of an array of neutral molecules interacting through fluctuations of their electric charge distribution. | We neglected to consider the origin of the charge distributions, and the origin of their fluctuations. These can only be properly calculated using quantum mechanics. |
| Ionic | We calculated the cohesive energy of an array of positive and negative ions interacting through the coulomb interaction. | We neglected to consider why electrons transfer themselves completely from one ion to another. This can only be understood by quantum mechanical calculations of the charge distribution around atoms and ions. |
| Covalent | We calculated the cohesive energy of a covalent bond in terms of a simple model of the charge distribution within the bond. | We neglected to consider <i>why</i> that particular charge distribution occurs. This can only be understood by quantum mechanical calculations of the electron wave functions near both atoms. Notice that in addition to the Coulomb energy which we calculated, there will be an additional 'delocalisation' term analogous to that which occurs on a larger scale in metals |
| Metallic | We calculated the cohesive energy of a metal by considering the change in energy of the wave functions as they were allowed to expand into a large volume. | We neglected to include the effects of the strong Coulomb interactions between electrons and other electrons, and between electrons and ions. |

6.7 Exercises

Exercises marked with a P prefix are 'normal' exercises. Those marked with a C prefix are best solved numerically by using a computer program or spreadsheet. Exercises marked with an E prefix are in general rather more challenging than the P and C exercises. Answers to all the exercises are downloadable from www.physicsofmatter.com

C1. Download the molecular dynamics simulation from the web site www.physicsofmatter.com and observe the

dynamics of molecules in a solid. Notice how the initial 'square' structure spontaneously 'collapses' into a 'hexagonal' structure. Can you explain why this happens?

C2. Use a spreadsheet program to draw the functional form of Equation 6.6 for a range of values of A and B .

P3. Given the entries in Table 6.2 for σ and ϵ for krypton, estimate (a) the molar cohesive energy and (b) the density. Check your answers in Table 11.5 and Table 7.2 respectively.

C4. Write a computer program to evaluate the Madelung

sum for an ion at the centre of a small ionic crystal with $12 \times 12 \times 12$ ions. Re-evaluate the Madelung sum for an ion displaced from its equilibrium position by an amount Δ and plot a graph of the Madelung sums versus Δ . You should find a roughly quadratic variation with Δ indicating that the ion will vibrate in a roughly simple harmonic potential.

P5. In §6.3 we considered calculations of the potential energy of electrons in a covalent bond, but did not consider their kinetic energy. The kinetic energy is difficult to calculate accurately, but one can estimate it roughly by considering the electrons in the bond region of length L to be confined to a three dimensional box of side L . The kinetic energy of an electron in such a box may be estimated using Equation 2.39 (or Equation 6.59). Calculate this energy.

The calculated kinetic energy for the C–C bond is large, but a more realistic calculation would compare the kinetic and potential energies of electrons on isolated at-

oms, with the kinetic and potential energies of electrons when bonded. Unfortunately, this is a much more difficult calculation than the simple estimates we have made.

P6. Work out the separation between neighbouring atoms in (a) silicon and (b) germanium given that their crystal structure is illustrated in Figure 6.14. The densities of silicon and germanium may be found from Table 7.1. (See also Example 7.3)

P7. Repeat the Option A/Option B (Figure 6.17) exercise for metals with $3^3 = 27$ and $4^3 = 64$ electrons. Compare the energy per electron with the value calculated for the 8-electron metal and the value for ‘real’ metal. (Tables 6.4 and 6.5)

C8. Download the molecular dynamics simulation from the web site www.physicsofmatter.com and run the simulation for the solid state. When the simulation is running turn off the radio button for molecular interactions and observe the destruction of the solid. Would the solid state be possible without molecular interactions?