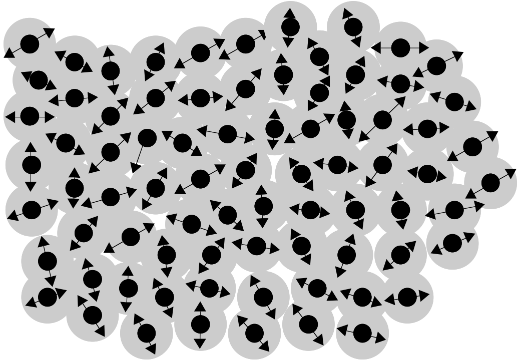
CHAPTER 8

Liquids: background theory

8.1 Introduction

If we raise the temperature of a solid it will, commonly, become liquid, and then on further heating it will evaporate to become a gas. In this sequence of states (solid ⇒ liquid ⇒ gas) the liquid state is intermediate between the solid and gaseous states. This intermediate position is a reflection of the fact that the arrangement of atoms or molecules in a liquid is, in general, intermediate between the crystalline order of the solid state and the random molecular motions of the gaseous state. In what follows we will discuss liquids as being *structurally* intermediate between solids and gases.

Figure 8.1 Illustration of the motion of atoms in a liquid. Notice the small separation between the atoms, and the random orientation of the vibrations of the molecules. 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, and disturbs the electronic charge density, of neighbouring atoms.



In general, we will find that most properties of liquids can be understood by explanations that begin in one of two ways. Either we will begin by saying that liquids are similar to solids, but more disordered and slightly less dense, *or* we will begin by saying that liquids are similar to gases, but more ordered and much more dense. Both approaches are useful for understanding the behaviour of liquids.

When we discussed the properties of gases we were able to arrive at the theory of an ‘ideal gas’ which was, for many purposes, a good approximation to the properties of real gases. However, there was no single model of an ‘ideal solid’ that could explain the diverse properties of solids. Liquids fall into an intermediate category and we will discuss their properties in terms of two simplified models. One model describes the *structure* of a liquid (§8.3): we will use this model to understand properties such as the density. The other model describes the *dynamics* of the liquid molecules (§8.4): we will use this model to understand properties such as the viscosity. We will find that we are able to understand many of the properties of real liquids in terms of these models. However, the models are so simplified that we will not really be able to ‘believe’ them in the way that we ‘believe’ the model of an ideal gas. The models capture just one or two key features of liquid behaviour and ignore many properties of the molecules that make up the liquid. The predictions of the models tend to be rather qualitative, allowing to us to examine trends among groups of substances, or variations with temperature, rather than predicting that the viscosity of, say, water at temperature T will be X.

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In addition to copies of the figures and tables, you will find a computer program which realistically simulates the dynamics of molecules in liquids, solids and gases.

8.2 Bonding in liquids

8.2.1 Bonding in liquids

Liquids consist of a ‘condensed’ collection of atoms or molecules with less average kinetic energy than a gas of the molecules, but too much kinetic energy to allow them to form a solid. We can divide the electrostatic bonding mechanisms into the same four categories as for solids (molecular, ionic, covalent and metallic) plus one exceptional category, *hydrogen bonding*, which is discussed below.

8.2.2 Hydrogen bonding

Hydrogen bonding is of special importance in discussing organic liquids, and also our most precious liquid, water. It occurs in substances composed of molecules which contain the chemical group OH: a combination of a hydrogen atom and an oxygen atom. This combination occurs in water (H_2O or HOH), in alcohols such as methanol (CH_3OH) or ethanol (C_2H_5OH), and numerous other organic molecules. Hydrogen bonding also occurs to a lesser extent in bonds between H and N, and H and a halogen F, Cl, or Br.

In liquids made from organic molecules, the *atoms within the molecules* are held together by primarily covalent bonding. However, the molecules are attracted to each other by the relatively weak *Van der Waals* force. The hydrogen bond is an attractive mechanism that acts between different molecules in addition to the Van der Waals force. It is much stronger and more directional than the Van der Waals force and is similar in effect to the covalent bonding that occurs within molecules.

The OH covalent bond within a water molecule is highly asymmetric, with the centre of charge symmetry being much closer to the oxygen rather than hydrogen atom. This leaves the hydrogen atom slightly positively charged, and the oxygen atom negatively charged. The extra electron charge density around the oxygen atom distributes itself so as to minimise its coulomb repulsion from the other electrons on the oxygen atom. The electron density in the region of an oxygen atom in a water molecule is shown in Figure 8.2 (a). Notice that the charge density forms two lobes on the

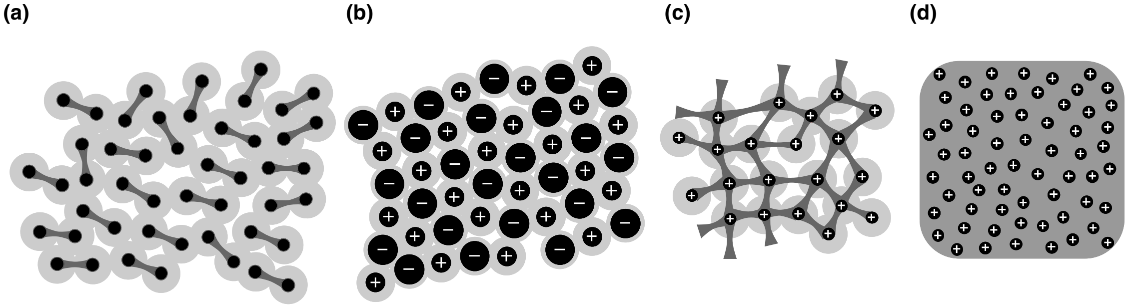


Figure 8.2 Types of bonding in liquids. (a) In molecular liquids the entities which make up the liquid (atoms or molecules) are essentially the same as the entities which made up the gas. Internally the atoms that comprise the molecules are bound within each molecule by primarily covalent bonding. Externally the molecules are bound together by the Van der Waals force discussed in §6.2. (b) In ionic liquids the entities which make up the liquid are ions rather than atoms or molecules. Locally most ions experience a situation similar to that experienced within a solid, but the regular periodicity of the solid lattice is absent. (c) In covalent liquids the entities which make up the liquid (atoms or molecules) are greatly altered from their state in the gas. In particular there is a high electronic charge density on some regions in between the mean positions of the atoms. Locally most ions experience a situation similar to that experienced within a solid, but the regular periodicity of the solid lattice is absent. (d) In metallic liquids the electrons from the outer parts of the atoms can move anywhere within the liquid and are not attached to any individual atom. Notice that the electrons are still free to move from ion to ion in any direction even though the regular periodicity of the lattice has been destroyed.

other side of the oxygen atom from the covalent bond regions.

A second water molecule may orient itself with respect to the first so that one of its hydrogen atoms is close to electron orbitals around the oxygen atom. This structure is known as a hydrogen bond and has many of the features of a covalent bond. For example, although it has only about one-tenth the strength of the OH covalent bond, it is rigid like a covalent bond. By 'rigid' I mean that the O–H–O link in Figure 8.3 (b) has a minimum energy when the three atoms are in line. Hydrogen bonding will be discussed further in §9.2.2.

8.2.3 Organic liquids

In this context, the term 'organic' historically referred to substances which originated from a once-living organism. In modern parlance the term has a technical sense in which it refers to substances the molecules of which contain *both* carbon and hydrogen atoms. Thus carbon tetrachloride CCl_4 and ammonia NH_3 are *inorganic* but methane CH_4 is organic. The distinction into organic and inorganic is important in this context, as data books frequently separate substances along these lines, and we shall follow suit in discussions of the experimental data in Chapter 9. Understanding the bonding in organic substances is particularly important, since much of the experimental data on liquids refers to organic liquids. The key features of this bonding may be fairly easily stated.

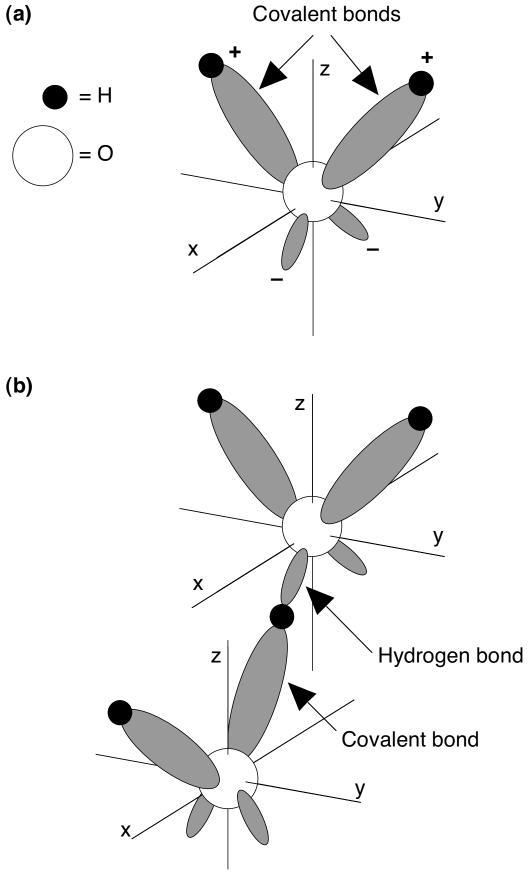
***Intra*molecular bonding**

The atoms within each molecule are held together by primarily covalent bonds that are extremely strong and highly directional. This gives the molecules of organic substances characteristic *shapes*.

***Inter*molecular bonding**

The molecules of the substance are (in general) attracted to each other by much weaker forces, primarily the non-directional Van der Waals force, and sometimes augmented by directional hydrogen bonds.

Figure 8.3 Qualitative indication of the structure of a hydrogen bond between water molecules. (a) The distribution of electric charge within an isolated water molecule. The hydrogen atoms are slightly positively charged and the oxygen atoms slightly negatively charged. The excess charge on the oxygen atom resides in two orbitals oriented so as to minimise their coulomb repulsion from the covalent bonds. (b) A second molecule may orient itself so as to place its hydrogen atoms close to the negatively charged electron orbitals around the oxygen atom. The two oxygen atoms shown are linked by a hydrogen atom and two bond regions: one bond is covalent and the other is known as a *hydrogen bond*.



The combination of strong intramolecular bonding and relatively weak intermolecular bonding results, as we shall see, in a complex array of properties.

8.3 The structure of liquids

8.3.1 Structural description

Having reviewed what actually holds liquids together, we will now develop a general model of the structure of a liquid. The structural description concentrates on a single atom or molecule, and then describes the *average* positions of its neighbours within the liquid.

Figure 8.1 shows our imagined picture of the situation of atoms or molecules in the liquid state. It might represent the result of taking a 'snapshot' of a microscopic amount of liquid. The atoms are vibrating about their average positions rather like the equivalent picture for a solid, Figure 6.1. The atoms are highly constrained by the closeness of neighbouring atoms and so their vibrational frequencies are similar to those in solids: around 10^{13} Hz. The equivalent picture taken, say, one vibrational period (i.e. roughly 10^{-13} second) later would look in detail almost exactly the same. However the equivalent picture taken say 10^{-10} second later (i.e. after around a thousand or so atomic oscillations) would typically look qualitatively similar, but in detail the picture would be completely different. All the positions of the atoms would have changed. This changing structure is the origin of difficulties in adopting a universally appropriate model of liquids.

I have said previously that the structure of a liquid is similar to that of a disordered solid, but that the structure of a liquid changes on a time-scale of a fraction of a nanosecond. Given this, it might at first seem that it would be impossible to say anything *quantitative* about the structure of liquids. In fact we can make rather precise statements about liquid structure as long as we are content with descriptions of the *average* structure. Obviously this will not describe the many individual and unique situations in which each molecule is placed. However, we have seen in previous chapters that many properties of materials depend on average properties of a substance (e.g. average speed, average separation, and average energy). So if we can calculate these averages, we may well be able make progress in understanding the relationship of liquid structure to the properties of liquids. So with the aim of quantitatively describing the average arrangement of molecules in a liquid, we use two related mathematical functions, called the *radial distribution function* $N(r)$ and the *radial density function* $n(r)$

8.3.2 The radial distribution function for spherical molecules

The radial distribution function is a mathematical function which describes the *average* distribution of molecules around a particular molecule. It specifies the average number of molecules that are found at a certain distance from a particular molecule. For spherical molecules the function answers the question:

On average*, how many molecules have centres which lie within a spherical shell of inner radius r and thickness* dr *centred on a particular molecule?*

The idea is complicated to depict in three dimensions, but is illustrated in Figure 8.4 for a two-dimensional liquid-like arrangement of molecules. In two dimensions we ask the question:

On average*, how many molecules have centres which lie within an* annular area *of inner radius r and thickness* dr *centred on a particular molecule?*

The number of molecules with centres in the annular area of inner radius r and thickness dr will increase as r increases. This is because annular areas of larger radius have a larger area and so tend to have the centres of more molecules within them. In two dimensions, an annulus has area $2\pi r\mathrm{d}r$ and so its area increases linearly with its radius r. In three dimensions, a spherical shell has volume $4\pi r^2\mathrm{d}r$ and its volume increases quadratically with r. However, in addition to the smooth increase we can discern shorter-range variations in the functions in either two or three dimensions. It is these variations that reflect the structure present within a liquid.

The significance of the radial distribution may become clearer if we work out the radial distribution function for the two-dimensional liquid-like arrangement of circles pictured in Figure 8.4. Within the annular area shown, lie the centres of 15 circles. If we count the numbers within similar rings of different radii then we obtain results similar to those shown in Figure 8.5. The procedure for constructing a radial distribution function for a two-dimensional liquid similar to that in Figure 8.4 is outlined in Example 8.1.

8.3.3 The radial density function

Of more fundamental significance in the study of liquids is a function closely related to the radial distribution function known as the *radial density* function $n(r)$ This function charts local variations in the *average* density of the substance as a function of distance from the centre of a molecule. At large distances from a particular molecule this function tends to the value of the bulk density of the substance. However, on an atomic scale we see peaks and troughs corresponding to the average separations of nearest and next-nearest neighbour molecules. In Example 8.1 we work out both the radial density and radial distribution functions for a two-dimensional solid, liquid and gas.

Having worked out the radial density function $n(r)$, the question arises of how to interpret it. The first point apparent from Figure 8.6 is that $n(r)$ for a liquid is rather similar to $n(r)$ for a solid. This indicates that around each molecule there remains some degree of order that was typical of the solid state. However that observable periodicity is reduced as we move further from the molecule under consideration. This is quite unlike a crystalline solid where the positions of the molecules remain correlated over long distances. Positional order of this type is called *short-range order*.

The question remains of precisely over what range the $n(r)$ of a liquid loses its correlations? The rate at which this occurs depends on the temperature of the liquid. Just above the melting temperature, $n(r)$ for the liquid is similar to that for a solid. But as the temperature is increased $n(r)$ becomes increasingly smoothed out, with the correlations between the positions of the molecules becoming

Figure 8.4 The radial distribution function describes the *average* distribution of molecules around any particular molecule. My count of the number of molecules reveals that there are 15 molecules in the ring shown.

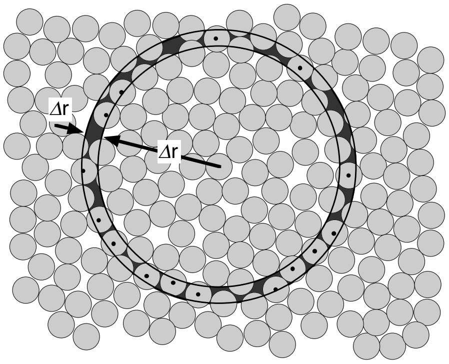
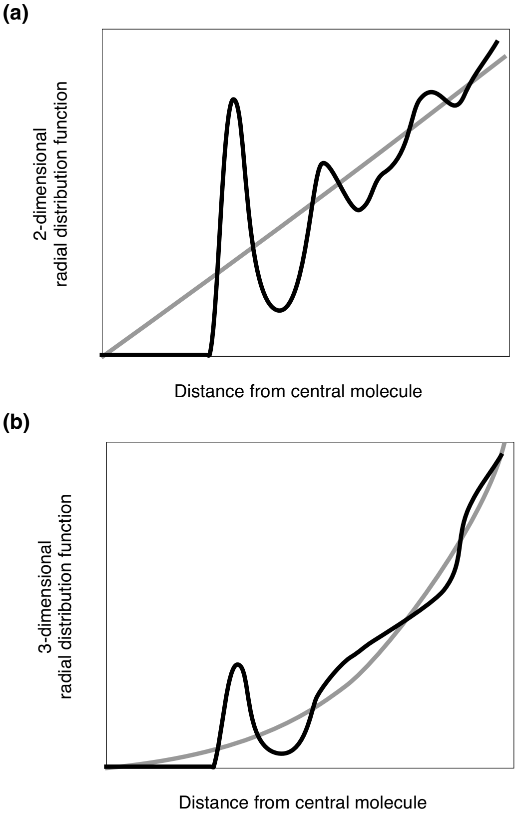
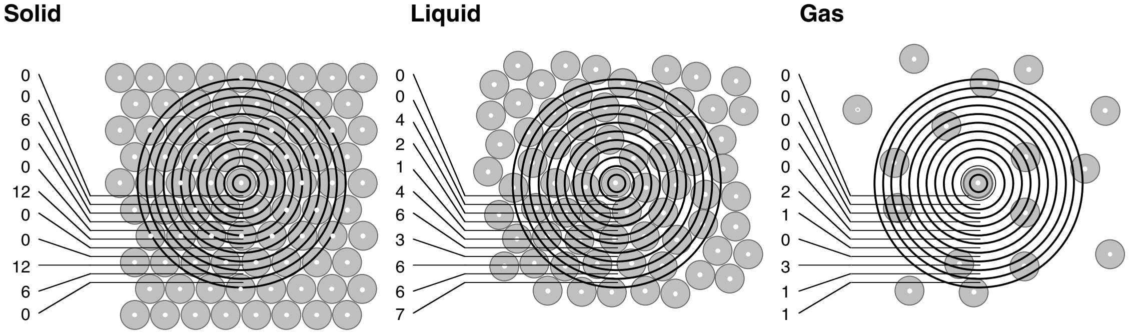


Figure 8.5 Qualitative illustration of the radial distribution function for simple liquid-like structures in (a) two-dimensions, and (b) three-dimensions. Notice the linear trend of the two-dimensional function, and the quadratic trend of the three-dimensional function. Constructing a radial distribution function for a two-dimensional liquid-like structure is described in Example 8.1.



Example 8.1

The *radial distribution function* for a two-dimensional solid, liquid and gas. The figures below represent two-dimensional solids, liquids and gases. Superimposed on these drawings is a ring structure that allows us to determine how many circles (atoms) have centres that lie within any particular annular area. The sums from each annular area are shown totalled in each figure and then transferred to Table 8.1.


Solid **Liquid** **Gas**

less pronounced. Just below the transition to the gaseous state the correlations may be considerably weakened. This is illustrated in Figure 9.22.

The exercise of constructing the two-dimensional radial density function $n(r)$ in Example 8.1 is clearly somewhat artificial, but the conclusion drawn is in fact rather general: liquids retain some degree of short-range order in the positioning of their molecules.

8.3.4 Non-spherical molecules

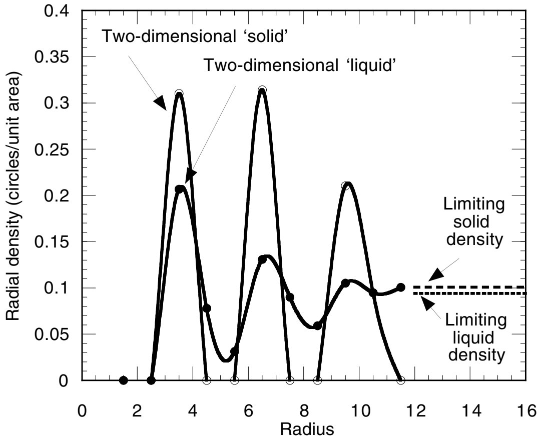
Many substances that form liquids around room temperature are organic in nature and have molecules that are not in the least spherical. Such molecules may have rings of atoms that make them essentially planar in shape, or they may have chains of atoms that make them essentially linear in shape. There are also many complicated combinations of rings and chains that are not well described by the idea of a simple spherical molecule that we have used in the previous section.

Thus for organic molecules, $n(r)$ can describe the positional correlations of the centres of molecules, but does not include information about the relative *orientations* of neighbouring molecules. Consider a molecule such as that illustrated schematically in Figure 8.7. The picture is intended to illustrate a molecule which is not symmetric, and which has covalent bonds within the molecule that give it a relatively fixed shape. Figure 8.8 illustrates two

Table 8.1 Data from Example 8.1. The table shows the mean radius of each ring in Example 8.1, and summarises the data for the solid, liquid and gas examples. For each ring, it divides the number of circles (atoms) found in each ring by the approximate area of that ring, $2\pi r\Delta r$. The units are such that the width of each ring $\Delta r = 1$. This is an approximation to the radial density function for the substance. The results for the solid and liquid case are plotted in Figure 8.6.

		Solid		**Liquid**		**Gas**	
Ring	**Radius**	N	$n = \frac{N}{2\pi r\Delta r}$	N	$n = \frac{N}{2\pi r\Delta r}$	N	$n = \frac{N}{2\pi r\Delta r}$
1	1.5	0	0	0	0	0	0
2	2.5	0	0	0	0	0	0
3	3.5	6	0.273	4	0.182	0	0
4	4.5	0	0	2	0.071	0	0
5	5.5	0	0	1	0.029	0	0
6	6.5	12	0.294	4	0.098	2	0.049
7	7.5	0	0	6	0.127	1	0.021
8	8.5	0	0	3	0.056	0	0
9	9.5	12	0.201	6	0.101	3	0.050
10	10.5	6	0.091	6	0.091	1	0.015
11	11.5	0	0	7	0.097	1	0.014

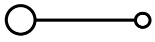
Figure 8.6 The radial density function of the two-dimensional 'liquid' and 'solid' shown in Example 8.1 and calculated in Table 8.1. The peaks in the solid data correspond to nearest neighbours, next-nearest neighbours, etc. Notice that these peaks are maintained in the liquid state, but that they are smoothed by the increased disorder of the liquid state. The figure also shows the limiting values of the macroscopic liquid and solid density.



such molecules in several different relative orientations but separated by the same distance between centres. It is not difficult to imagine that the interaction energy of one molecule with another depends not only on the separation of the two molecules, but also on their relative orientation. This orientation dependence of the interaction energy would be particularly significant if the molecules were *polar* (§5.7.2), i.e. if they had some regions that were electrically positive and others that were electrically negative. The hydrogen bond in Figure 8.3 is a special example of interactions between polar molecules.

The importance of the molecular shape will be seen in §9.9 when we compare data on organic liquids with data derived from molten metals which are better described by the spherical molecules model we have considered in §8.2.2.

Figure 8.7 A representation of an asymmetric molecule with relatively fixed shape.



8.3.5 Liquid crystals

Many molecules which have some of the properties of the molecule in Figure 8.7 exhibit a strong tendency to align themselves with their neighbours. For example, they may prefer to orient themselves so that their long axis is parallel with that of their neighbours. If we consider the centres of the molecules, defined as the position of the centre of mass of each molecule, we find that the radial density function is highly anisotropic. In some directions it may show essentially crystalline order, while in other directions it indicates order more typical of a liquid. States with this mixed order are known as *liquid crystals* or *meso-phase* states. The prefix *meso* is from the Greek for *middle* or *intermediate* and indicates that such states are structurally mid-way between the solid and liquid state.

Solid and liquid structures

We can look at the generic types of structures that arise in liquid crystal mesophases by considering the interactions between the molecules such as those illustrated in Figure 8.7. The molecules will have some relative orientation in which they can minimise their energy of interaction. Five possible orientations are shown in Figure 8.8. In this example, let us suppose that they have a low energy when they are aligned parallel, as indicated in Figure 8.9

Figure 8.9 We suppose that the molecules illustrated in Figure 8.7 have their lowest energy when they are oriented as shown

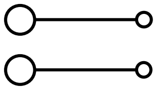
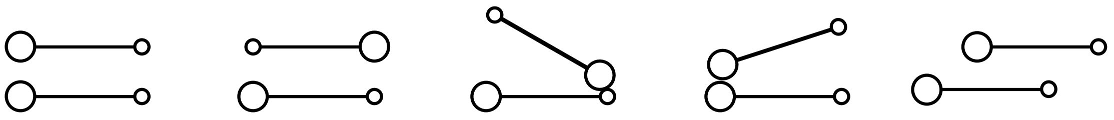


Figure 8.8 Five possible arrangements of pairs of the molecules from Figure 8.7.



The *solid* formed from such molecules might look something like either of the options in Figure 8.10.

In the liquid state, the positions of the molecules are disordered in a similar way to a 'normal liquid' and the orientations of the molecules are also highly randomised.

Liquid crystal structures

There are a number of possible states, known as *mesostates*, or more commonly as *liquid crystal states*, that are intermediate between the order of the solid and the disorder of the liquid. Perhaps the simplest state to describe is the *nematic state*. The word drives from the Greek *nema*, meaning 'thread', and the state describes thread-like molecules which remain roughly parallel to one another, but the positions of their centres are disordered. The orientation of the molecules within the liquid is indicated by a vector **n** known as the *director*. In general the director will change from one region to another, producing the equivalent of crystalline defects in a solid that are known as *disinclinations*. Figure 8.12 illustrates a nematic liquid crystal state of molecules which have a minimum energy configuration like that illustrated in Figure 8.7.

One special type of variation of **n** has important applications in the use of liquid crystals in digital displays, and is known as a *cholesteric* liquid crystal. The term cholesteric derives from two words: *chole* which is the Greek prefix for the bile or gall duct from which these chemicals were originally derived; and *stereo* which in this context refers to the three-dimensional waxy nature of the substance. Within any layer of the structure, the substance looks like a nematic liquid crystal structure, but its key feature is that the director *rotates* from one region of the crystal to another. As illustrated in Figure 8.13, the rotation of the director is perpendicular to the plane containing the nematic director. Molecules such as those illustrated in Figure 8.7 would be unlikely to form a cholesteric phase liquid crystal.

Figure 8.10 Two plausible solid structures that might be formed from molecules such as those illustrated in Figure 8.7 above.

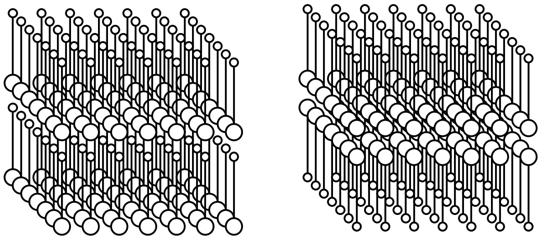
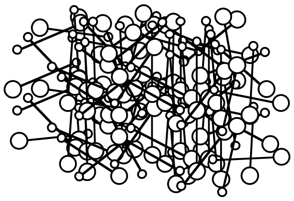


Figure 8.11 A plausible liquid structure that might be formed from molecules such as those illustrated in Figure 8.7 above.



The final type of liquid crystal state is known as a *smectic* state, in which molecules form layers similar to the layers indicated in the solid state (Figure 8.10). The word *smectic* derives from the Greek *smektikos* meaning *to wash*, because of the soap-like consistency of substances in this state. Different varieties of smectic liquid crystal are distinguished by the different relative orientations of the director **n** with respect to the layers of the structure, and by the degree of order within each layer. Molecules such as those illustrated in Figure 8.7 could quite feasibly form smectic structures.

Table 8.2 The transition temperatures of some substances which form liquid crystal mesophases.

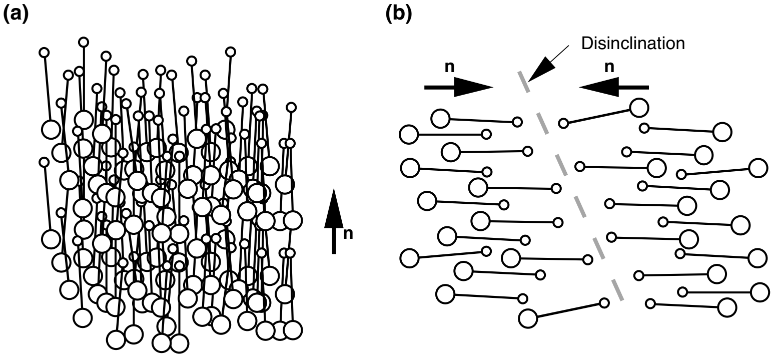
Ethyl-anisal-p-aminocinnamate:

$$\text{Crystal} \xleftrightarrow{83\ ^\circ\text{C}} \text{Smectic } B \xleftrightarrow{91\ ^\circ\text{C}} \text{Smectic } A \xleftrightarrow{118\ ^\circ\text{C}} \text{Nematic} \xleftrightarrow{139\ ^\circ\text{C}} \text{Liquid}$$

Cholesterol benzoate $C_{34}H_{50}O_2$: relative molecular mass 491

$$\text{Crystal} \xleftrightarrow{146\ ^\circ\text{C}} \text{Cholesteric} \xleftrightarrow{178.5\ ^\circ\text{C}} \text{Liquid}$$

Figure 8.12 Conceivable nematic liquid crystal structure of molecules which have a minimum energy configuration like that illustrated in Figure 8.9. In (a) the vector **n** is the *director* which describes the direction of the texture of the structure, while (b) illustrates a region in which two directors meet at a disinclination.



With a little imagination, you might be able to envisage other combinations of positional and orientational disorder that constitute what are known to be a multitude of different liquid crystal states. The liquid crystal phases discussed above generally exist over limited temperature ranges, commonly only a few degrees celsius, in between the solid and liquid states (Table 8.2).

Summary

At the level of this book it has been impossible to survey all the types of liquid crystal state. However it is important to notice that liquid crystal phases are a natural and common phenomenon in liquids whose molecules have anisotropic properties. Since many living organisms are constructed from large anisotropic molecules in a near-fluid state, liquid crystals have profound, but still poorly understood, effect on the functioning of biological systems, including our own bodies.

Figure 8.13 Cholesteric liquid crystal. Within any layer of the structure, the substance appears to be nematic. To appreciate the structure, consider for example the top layer on the diagram, which has a director pointed to the right. If we consider a neighbouring layer its nematic director is rotated with respect to the top layer. Similarly, the layer below is rotated with respect to the second layer. In this way the substance has a director which rotates in a plane whose normal is perpendicular to all the directors.

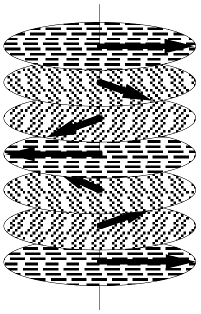
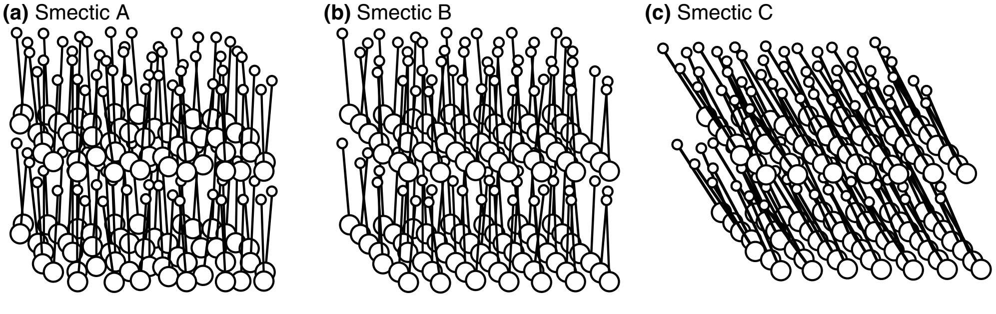


Figure 8.14 Some smectic liquid crystal structures. Smectic B is the most solid-like of the liquid crystal states, having positional order within each layer of the smectic structure. Smectic A is a structure in which this positional order *within* the layer is lost, but the orientational order within the layer is retained along with the layer structure itself. In Smectic C the layer structure remains, but the molecules orient themselves at an angle with respect to the layers.



8.4 The dynamics of a liquid: the cell model

8.4.1 The need for a dynamical description

In the previous section we considered how we could describe the structure of the liquids. We introduced the radial density function $n(r)$ as a method of describing the structure of a liquid of spherical molecules. We then considered some of the factors relevant to non-spherical molecules, and saw that ultimately these factors could give rise to liquid crystal structures.

However, in order to understand many phenomena that are characteristic of the liquid state, we need to describe the way the structure *changes*. For example the *viscosity* of liquid, which describes the ease with which a liquid changes shape, is essentially a measure of the ease with which the structure of a liquid can *change*. We will try to understand the dynamics of a liquid by first considering how the structure of a liquid of spherical molecules might change. The we will see how our conclusions would be affected if the molecules of the liquid were non-spherical.

8.4.2 Spherical molecules: a cell model

The following model of liquids, known generally as the *cell model*, is an attempt to develop a near universal model of liquids. It assumes that each molecule is constrained by its neighbours into a 'cell' of roughly atomic dimensions: this is certainly the case in real liquids. Each molecule vibrates within a 'cage' created by its neighbours.

However, as consideration of Figure 8.15 (b) shows, molecules such as *B* take part in the formation of several cells. In the figure *B* is part of the 'cell wall' constraining molecules *A* and *C* amongst others. In addition *B* is itself constrained within another cell not shown in Figure 8.15, in which *A* and *C* form part of the 'cell wall'. In order to break through this kind of complex analysis we need to make a dramatic simplification.

The simplification of the cell model is that it considers only the properties of an *average molecule* in an *average cell*. The cell model has four parameters:

- The average size of the cell *a* illustrated in Figure 8.15 (b).
- The size of the energy barrier which must be overcome in order to move a molecule from one cell to another ΔE_h. The subscript 'h' on ΔE_h is intended to indicate the 'hopping' process by which molecules move through the liquid.
- The energy cost to entirely remove a molecule from the liquid ΔE_e. The subscript 'e' on ΔE_e is intended to indicate 'escape' or 'evaporation' processes through which molecules leave the liquid.
- The energy cost to move a molecule from the body of the liquid to the surface of the liquid ΔE_s. The subscript 's' on the ΔE_s stands for 'surface'.

As Figure 8.16 illustrates, it is important to realise that the actual process by which a molecule moves through a liquid is not a single-particle process. It will in general involve the chance motions of several molecules conspiring to allow a molecule to

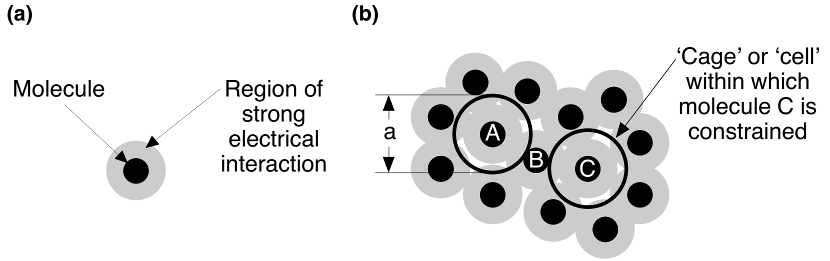


Figure 8.15 The cell model of a liquid. (a) A simple representation of a molecule. (b) The way closely-packed molecules form a cell or cage around other molecules.

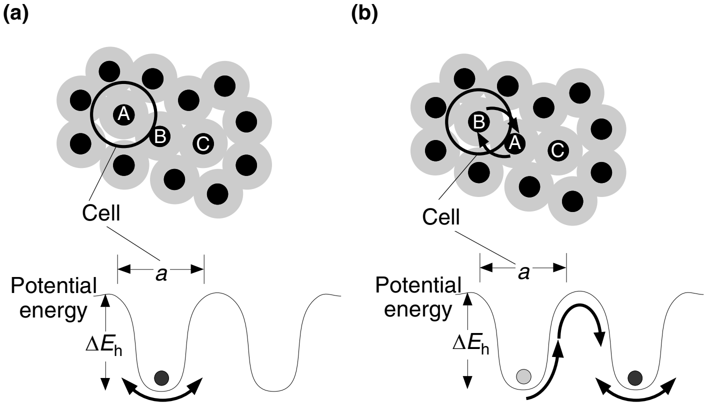


Figure 8.16 Illustration of the significance of the potential energy in the cell model of a liquid. In (a) a typical molecule *A* is shown trapped by its neighbours. This is represented on the potential energy diagram by a single *average* molecule vibrating inside a fixed *average* potential well. Occasionally, as illustrated in (b), the vibrations of neighbouring molecules conspire to allow a molecule to change its cell. Notice that, although this process of moving from cell to cell will normally involve two or more molecules, it is represented on the potential energy diagram as the motion of the single representative particle.

move. However, the simplification of the cell model is that it considers only the motion of a single *average* particle moving through an *average* potential which is empty of other molecules. The cell model thus represents a considerable simplification of the real situation. However it does capture the essence of the situation, in that molecules tend to vibrate about a position for a certain time but are still able move away from their neighbours, although with a relatively low probability. The chance of escape from a cell is determined by the strength of the interactions between molecules, by the shape of the molecules, and by temperature.

If the molecules were completely trapped in their cells then the model would describe a solid, i.e. a set of molecules vibrating about fixed positions. The solid would lack the crystalline order we normally assumed in Chapter 7 and would be known as an *amorphous* solid.

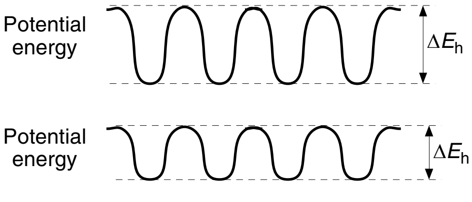
8.4.3 The potential energy in the liquid state

Let us consider how the (electrical) potential energy of an average molecule in the liquid state will vary with position throughout the liquid. As illustrated in Figure 8.17, we expect a potential which repeats through out the liquid, since the *average* experience of each molecule will be similar, independent of where it is the liquid.

Figure 8.17 indicates two different potentials, one with a barrier to hopping from cell to cell, ΔE_h, much greater than the other. Since a substance in which atoms remain in their original potential cells is a solid, we expect the liquid with the larger ΔE_h will be more solid-like, i.e. able change its shape less easily than one with the smaller ΔE_h. The ease of changing shape is related to the *viscosity* of a substance (§9.6), so we expect that a small ΔE_h will give rise to a low viscosity.

As the temperature increases the probability per unit time that a molecule will escape from its cell also increases, since the average kinetic energy of the molecule is roughly $\approx k_B T$. We thus expect that the viscosity of a liquid will be reduced at higher temperatures, a prediction which is compared with experimental data in §9.6.

Figure 8.17 The variation of the potential energy of an average molecule with position according to the cell model of a liquid. The upper curve represents a liquid in which the ‘hopping’ process described in Figure 8.16 is more difficult than for the liquid represented by the lower curve.



The energy required to activate ‘hopping’ from cell to cell within a liquid may be compared to the energy required to remove a molecule from the liquid altogether, ΔE_e. In general a molecule in the liquid will be interacting with a number of other adjacent molecules, typically between 8 and 11. The bonds with all these molecules must be broken if the molecule is to escape from the body of the liquid. The energy ΔE_e required to do this will thus in general be rather greater than ΔE_h.

The ease with which a molecule can leave the body of the liquid is related to the vapour pressure that a liquid creates above its surface. This matter is discussed more fully §9.8. However, we can say already that we expect that substances with a high ΔE_h will tend to have a high ΔE_e. Hence we can expect to find that the more viscous a substance, the lower its vapour pressure at a given temperature, i.e. the less volatile the substance will be.

Finally, we consider the situation of a molecule at the surface of a liquid. This molecule will only be bonded to perhaps 5 or 6 others, as opposed to between 8 and 11 others for a molecule in the body of the liquid. Its binding energy might therefore only be only around 50% of that a molecule in the body of the liquid. Thus we might expect that it will cost ΔE_s (roughly 50% of ΔE_e) to take a molecule from the body of the liquid and place it at the surface. This energy cost is the origin of the surface energy (or surface tension) of a liquid and is discussed more fully in the comparison with experimental surface energy data (§9.7)

Figure 8.18 The variation of the potential energy of an average molecule with position according to the cell model of a liquid, showing the relative values of ΔE_h and ΔE_e.

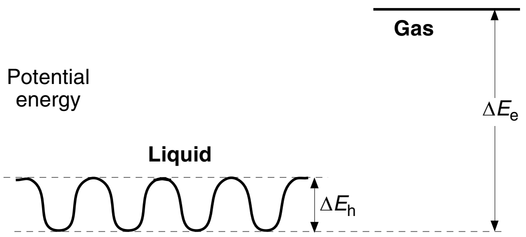


Figure 8.19 encapsulates the essence of the cell model of liquid dynamics. The three activation energies will have very different values for say molten sodium and molten aluminium, but we might expect that for each substance, the *ratio* of the activation energies $\Delta E_h : \Delta E_s : \Delta E_e$ should be similar. Furthermore, we might hope to find some similarities between the behaviour of molten metals and very different liquids, such as water or organic liquids. The extent to which the cell model achieves this is reviewed in §9.9

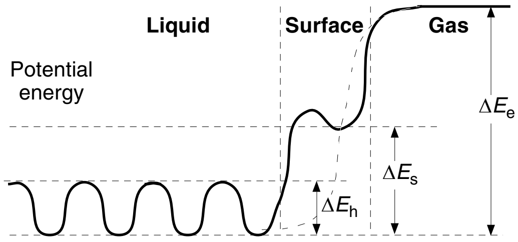
8.4.4 Non-spherical molecules

The dynamics of liquids formed from non-spherical molecules is likely to be more complex than for the simple liquids discussed above. However, within the framework of the cell model, we expect to find just two significant differences between non-spherical and spherical molecules.

First we expect that the ‘hopping’ or ‘swapping places’ process discussed for spherical molecules will be considerably more difficult. Long molecules will become ‘tangled’ and ‘hooked’ in a way which has no analogy for the simple liquids. We thus expect that for a given binding energy ΔE_e, substances with non-spherical molecules will have relatively large values of ΔE_h.

Second, we expect that it will be considerably easier to place a molecule on the surface. We expect this because it will be possible to orient the

Figure 8.19 The variation of the potential energy of an average molecule with position according to the cell model of a liquid, showing the relative values of ΔE_h, ΔE_s, and ΔE_e. The curve is likely to be most appropriate to spherical molecules which can ‘hop’ past one another relatively easily. The curve should be contrasted with the one shown in Figure 8.20, which is likely to be appropriate for non-spherical molecules.



molecule so that most of it stays ‘under’ the surface, i.e. still within the body of the liquid. Since this *can* happen relatively easily, we can expect that it *will* happen. So we expect that for a given binding energy ΔE_e, substances with non-spherical molecules will have relatively small values of ΔE_s, and appropriately low values of surface tension.

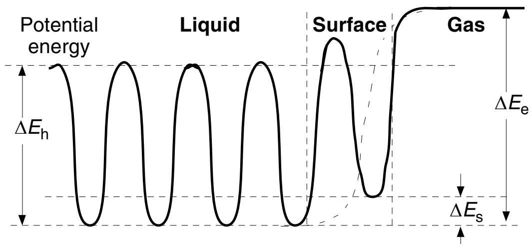
Thus, a cell model picture for non-spherical molecules might now look something like Figure 8.20. Notice the changes in the relative magnitudes of ΔE_h and ΔE_s compared with those for spherical molecules in Figure 8.19. Figure 8.20 describes a liquid that forms surfaces relatively easily, but which is more viscous than we would expect on the basis of its binding energy. The extent to which this change in the relative magnitudes of ΔE_h and ΔE_s actually occurs in real liquids is discussed in §9.9.

Finally, before leaving this description of the cell model of liquids, we stress again that the parameters of the cell model are not single-particle parameters. They are merely parameters allowing complex many-molecule correlations to be described in rather simple terms.

8.4.5 Non-Newtonian liquids

The two options outlined in Figures 8.19 and 8.20 for spherical and non-spherical molecules shows some of the flexibility of cell model. It can describe liquids that result from a wide variety of different molecular constituents. However, it is common to find liquids that are not well described by *any* variant of the cell model. These liquids are frequently:

Figure 8.20 The variation of the potential energy of an average molecule with position according to the cell model of a liquid, showing the relative values of ΔE_h, ΔE_s, and ΔE_e. This curve is likely to be appropriate for non-spherical molecules which cannot ‘hop’ past one another easily. The curve should be contrasted with the curve appropriate for spherical molecules shown in Figure 8.19.



- formed from very long molecules, often polymers, that may be hundreds of times longer than they are wide. Clearly such a molecule will not ‘hop’ from cell to cell. Its motion is dominated by the nature of its entanglements with its neighbours
- dissolved in a solvent, a more ‘normal’ liquid made of smaller molecules.

It is not possible to discuss the dynamics of these complex liquids here, but I can point out some interesting properties of such liquids and invite the you to experiment with the following:

> **Soup**: When stirring a smooth, thick soup in a bowl, if you stop stirring you find that the soup may ‘spring back’ and briefly rotate in the opposite direction. This is quite contrary to the expected behaviour for a simple fluid, which would continue to rotate. This phenomenon is known as *visco-elasticity*
>
> **Non-drip paint**: Paints are composed of pigments in specially formulated ‘carrier liquids’. Some carrier liquids are manufactured such that in the low-stress situation of a can, or on a paintbrush, they behave as a solid and retain their shape, i.e. they do not drip. Indeed, they may wobble like a jelly indicating elastic behaviour and some sense of a ‘shape’. However under the stress of brush stroke they behave as a liquid and leave the brush. Substances behaving in this way are known as *thixotropic*.
>
> **Cornflour and water**: Pour a small amount of cornflour (containing a natural medium-length polymer) onto a flat surface. Add water a drop at a time and stir thoroughly. Eventually a state is reached in which the substance may be ‘torn’ in two or ‘broken’ if pulled sharply, but which heals and flows like a liquid over the time scale of a few seconds.

Controlling the properties of substances with many molecules in solution is a problem of great complexity, one which still presents many challenges for scientists in both academic and industrial concerns.

8.5 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 that the P and C exercises. Answers to all the exercises are downloadable from www.physicsofmatter.com

Molecular dynamics

To answer questions 1 to 3 you need to download the molecular dynamics simulation from the web site www.physicsofmatter.com

C1. Set the simulation 'phase' control to 'liquid' and make some notes about the key features of the dynamics of molecules in a simple two-dimensional liquid. Contrast these with the dynamics of molecules in (a) a simple two-dimensional solid and (b) a simple two-dimensional gas.

C2. Run the simulation for the liquid phase with at least 25 molecules and allow it to run until the molecules form 'a blob'. Stop the simulation and examine the instantaneous positions of the molecules. To what extent do the figures in Example 8.1 and Figure 8.4 reflect the patterns seen in the simulation?

C3. Run the simulation for the liquid phase with at least 25 molecules and allow it to run until the molecules form 'a blob'. Look for the occurrence of processes in which molecules swap places in a manner similar to that described in Figure 8.16. One of the molecules is coloured red to allow you to keep track of it more easily. Notice that it requires the motion of many molecules to allow an individual molecules to change 'cells'.

Radial density functions

P4. Construct (a) the radial density function and (b) the radial distribution function for the data of Table 8.1.

P5. Construct two-dimensional liquid and solid structures (like those in Example 8.1) by positioning coins on a surface. Draw evenly-spaced, concentric circles (like those in Example 8.1) onto tracing paper or an overhead transparency, and use this to count the number of molecules within a certain distance of a central molecule. From this data you can construct an analogue to Table 8.1 and hence determine the radial density function and the radial distribution function. This is a fairly standard (if time-consuming) exercise and as long as you average your results sufficiently and make realistic liquids your results should be similar to those shown in Figures 8.4 (a) and 8.6

If you have more time on your hands you may make a liquid with two components, e.g. from penny pieces (component P) and two-penny pieces (component Q). To describe this liquid you need four radial distribution functions. You need one to describe the distribution of P molecules around a P molecule; one to describe the distribution of P molecules around a Q molecule; one to describe the distribution of Q molecules around a Q molecule; and finally, one to describe the distribution of Q molecules around an P molecule. You should find relationships amongst the functions, but what you find will depend on the relative sizes of the coins you use. Amazingly, it is possible to actually measure such distribution functions for real three-dimensional liquids!