

CHAPTER 8

Figures

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Understanding the properties of matter

by Michael de Podesta.

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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.

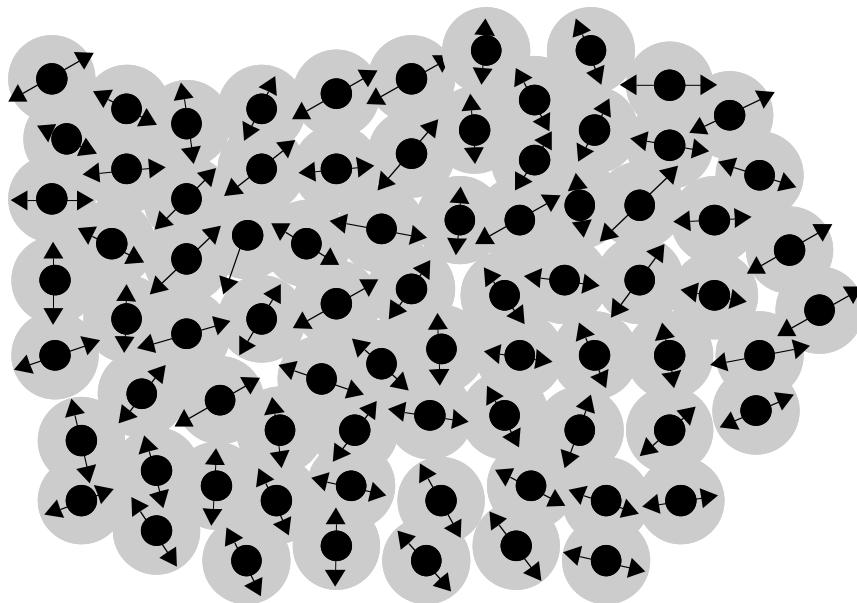
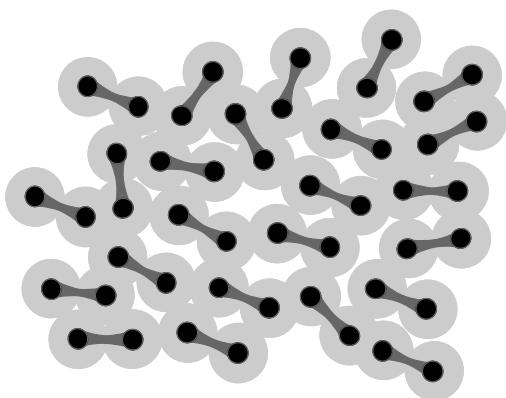
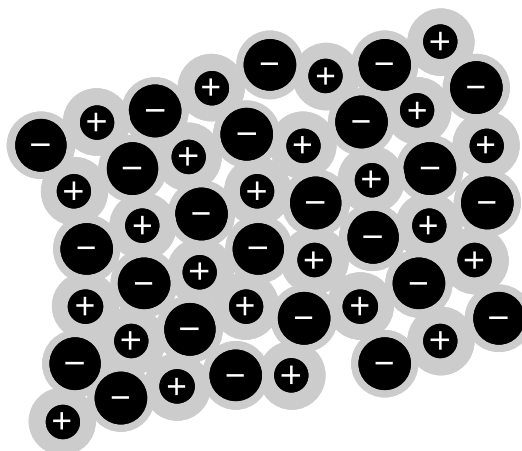


Figure 8.2 Types of bonding in liquids. (a) In molecular liquids the entities which make up the liquid (atoms or molecules) are essentially the same as the entities which made up the gas. Internally the atoms that comprise the molecules are bound within each molecule by primarily covalent bonding. Externally 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.

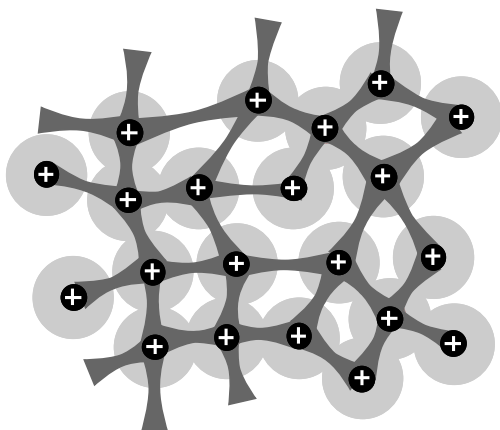
(a)



(b)



(c)



(d)

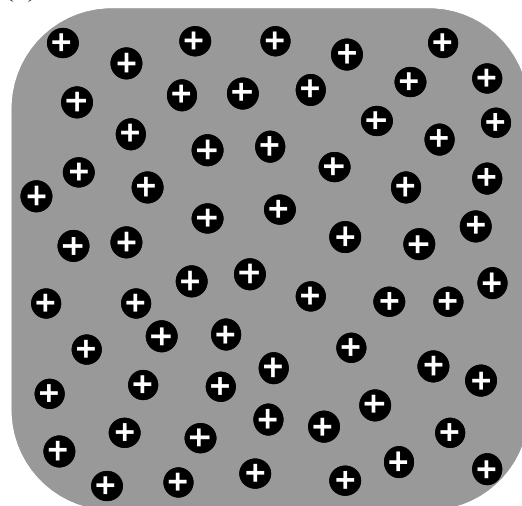


Figure 8.3 Qualitative indication of the structure of a hydrogen bond between water molecules. (a) The distribution of electric charge within an isolated water molecule. The hydrogen atoms are slightly positively charged and the oxygen atoms slightly negatively charged. The excess charge on the oxygen 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*.

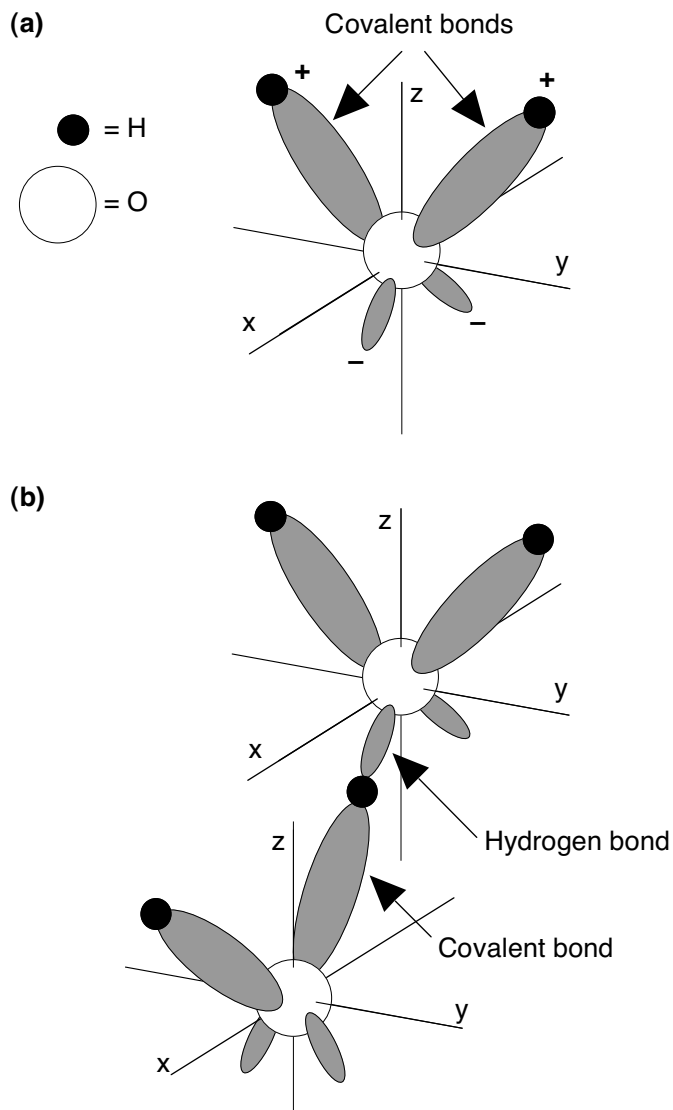
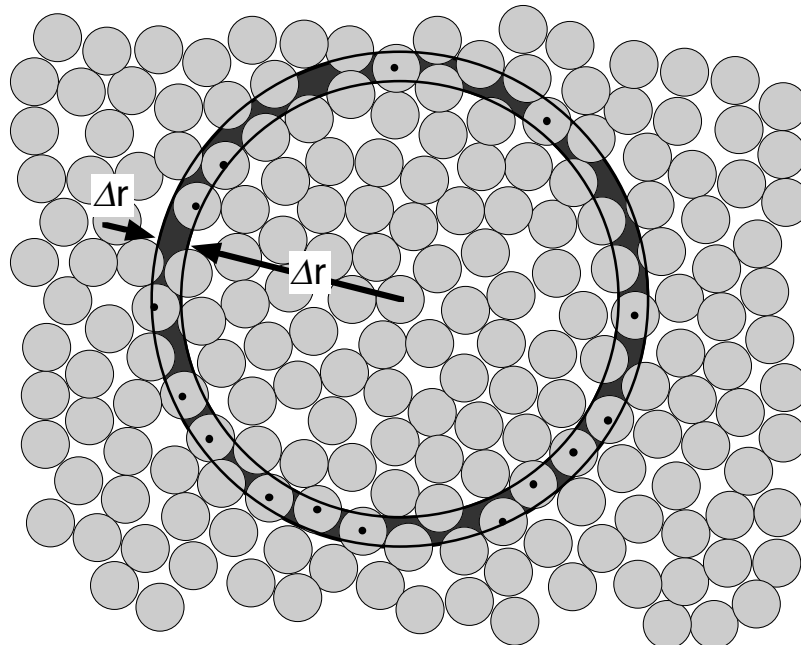
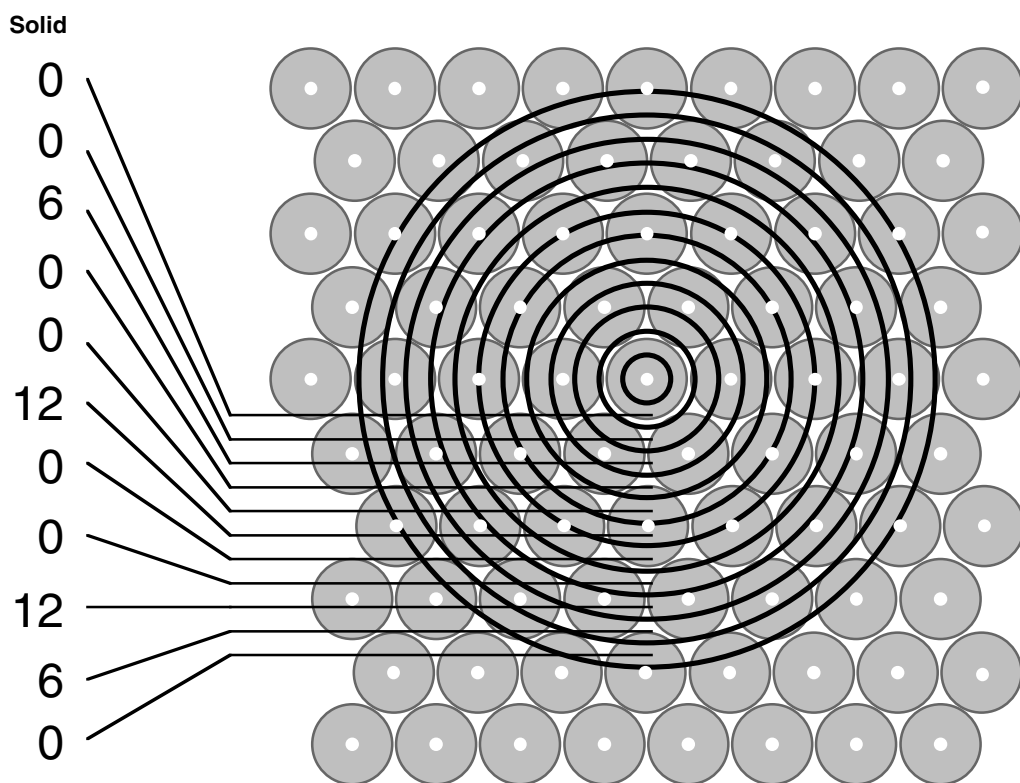


Figure 8.4 The radial distribution function describes the *average* distribution of molecules around any particular molecule. My count of the number of molecules reveals that there are 15 molecules in the ring shown.



Example 8.1

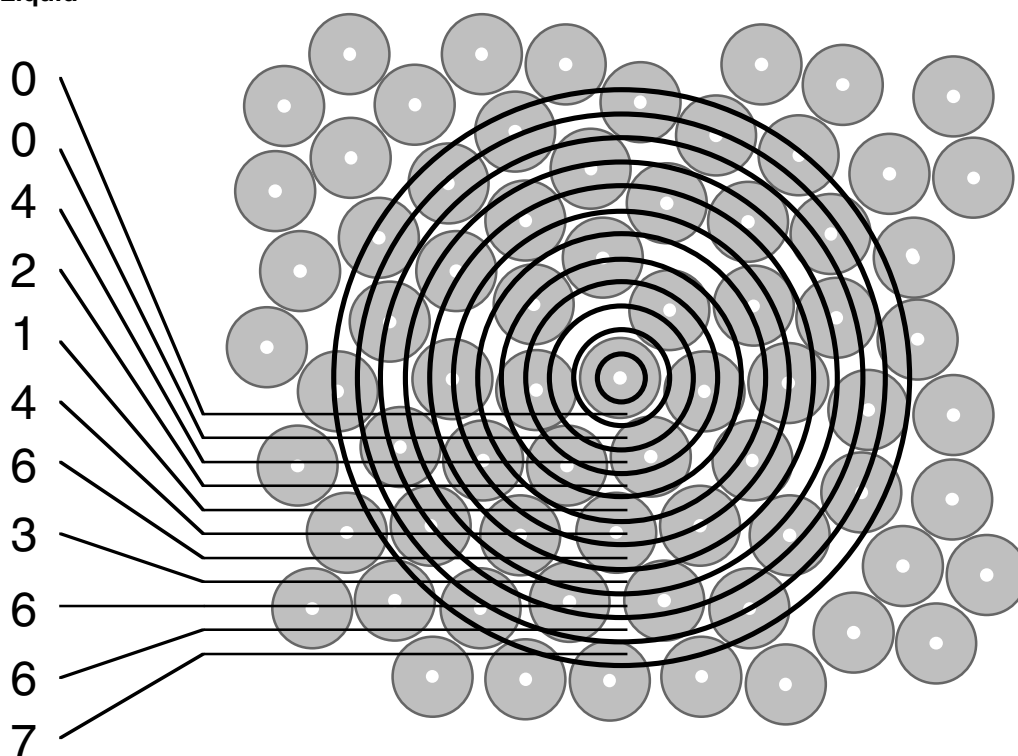
The *radial distribution function* for a two-dimensional solid, liquid and gas. The figures below represent two-dimensional solids, liquids and gases. Superimposed on these drawings is a ring structure that allows us to determine how many circles (atoms) have centres that lie within any particular annular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



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.

Liquid



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.

Gas

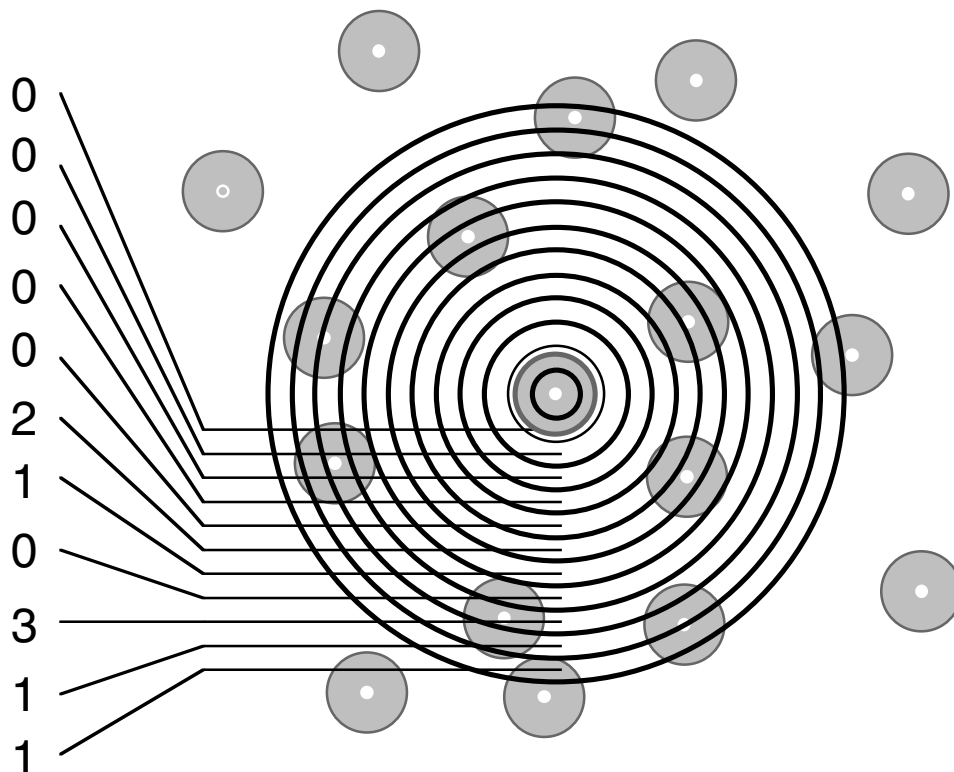
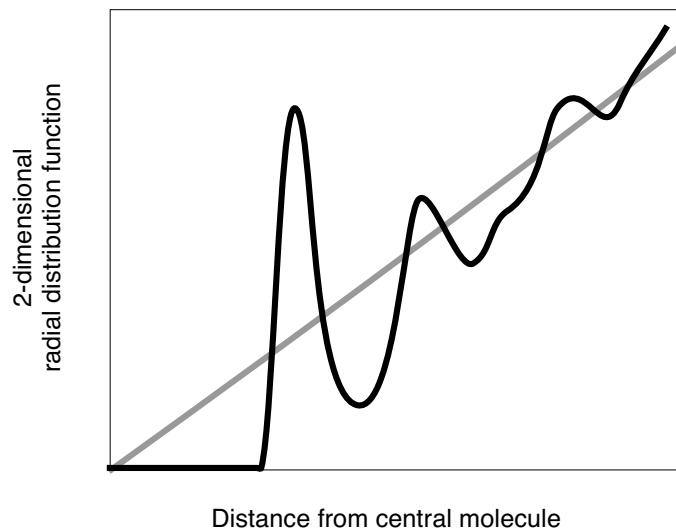
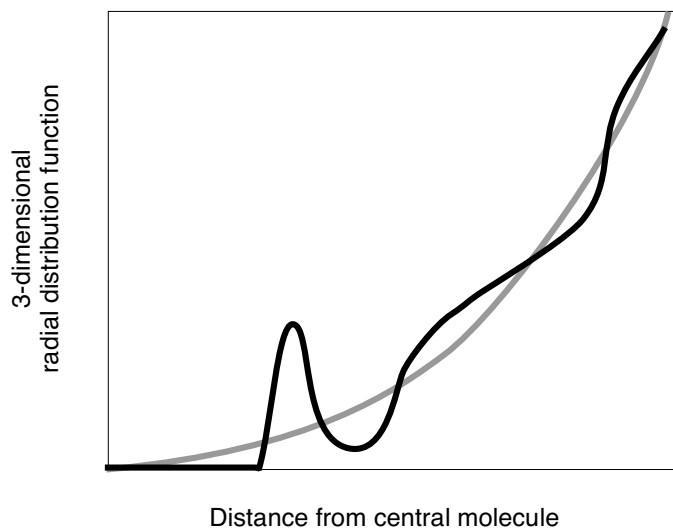


Figure 8.5 Qualitative illustration of the radial distribution function for simple liquid-like structures in (a) two-dimensions, and (b) three-dimensions. Notice the linear trend of the two-dimensional function, and the quadratic trend of the three-dimensional function. Constructing a radial distribution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

(a)



(b)



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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.

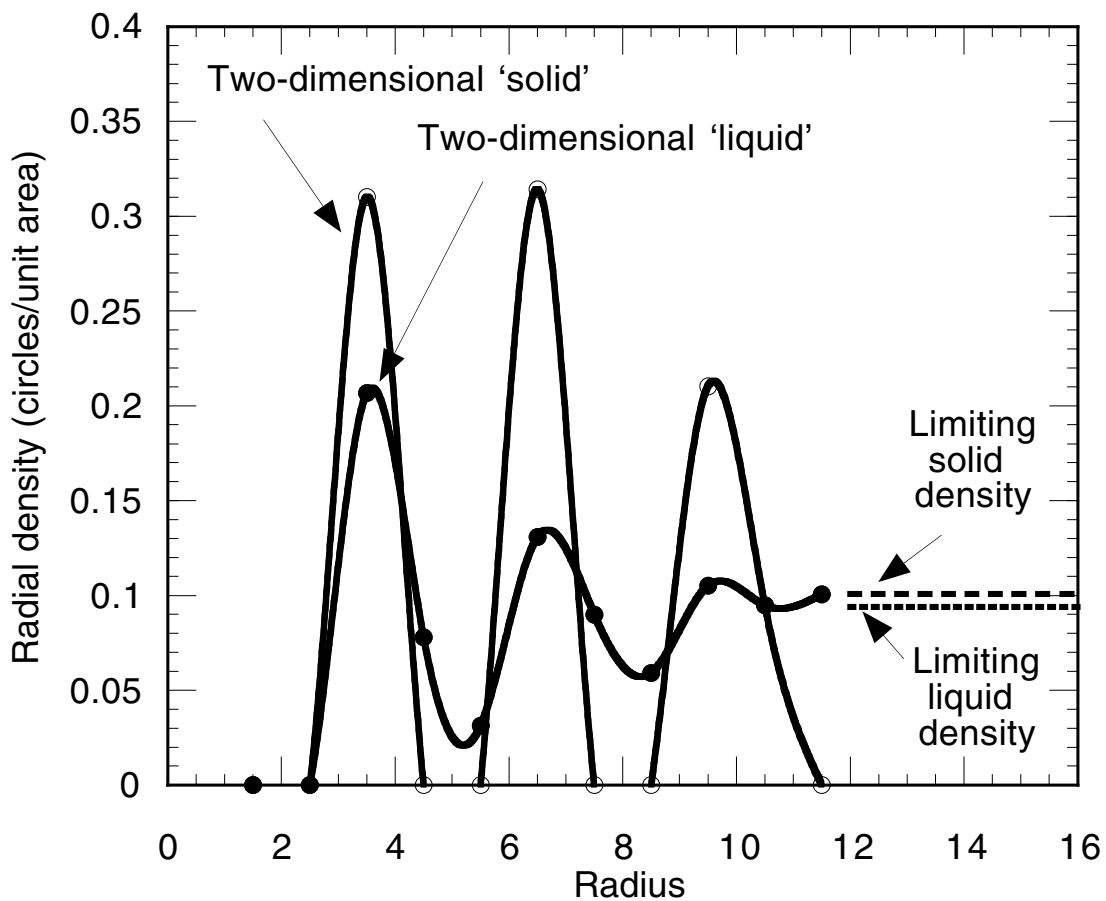


Figure 8.7 A representation of an asymmetric molecule with relatively fixed shape.

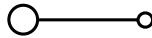


Figure 8.8 Five possible arrangements of pairs of the molecules from Figure 8.7.

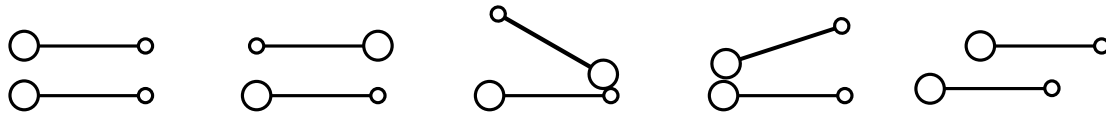
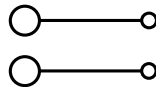
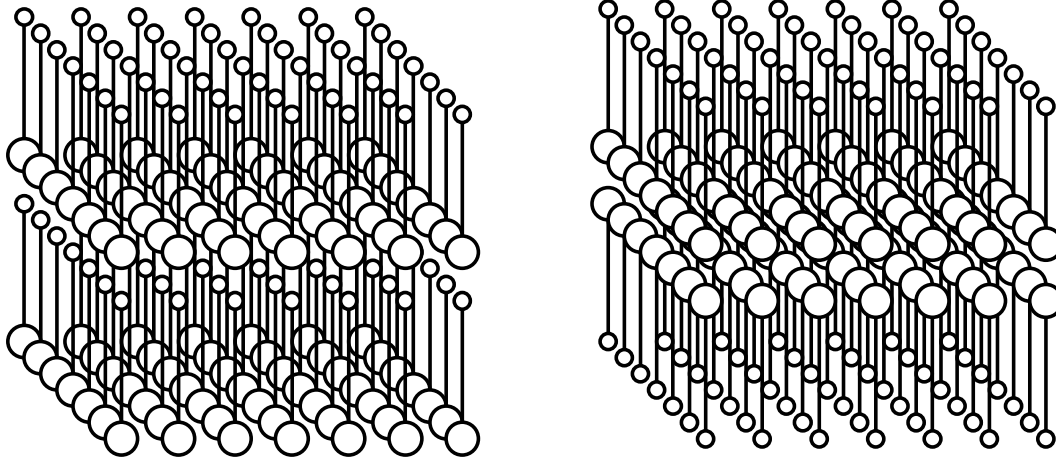


Figure 8.9 We suppose that the molecules illustrated in Figure 8.7 have their lowest energy when they are oriented as shown



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



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

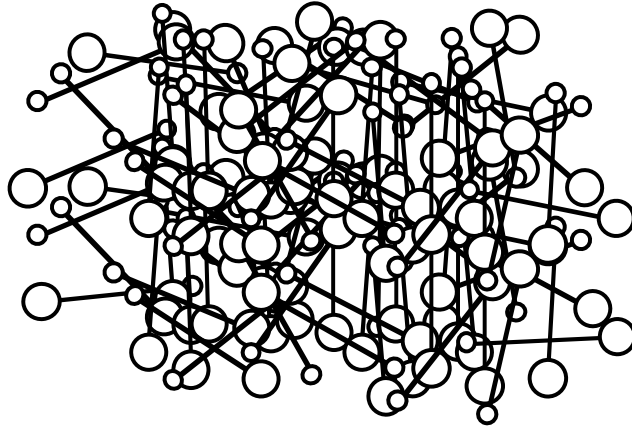


Figure 8.12 Conceivable nematic liquid crystal structure of molecules which have a minimum energy configuration like that illustrated in Figure 8.9. In (a) the vector \mathbf{n} is the *director* which describes the direction of the texture of the structure, while (b) illustrates a region in which two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

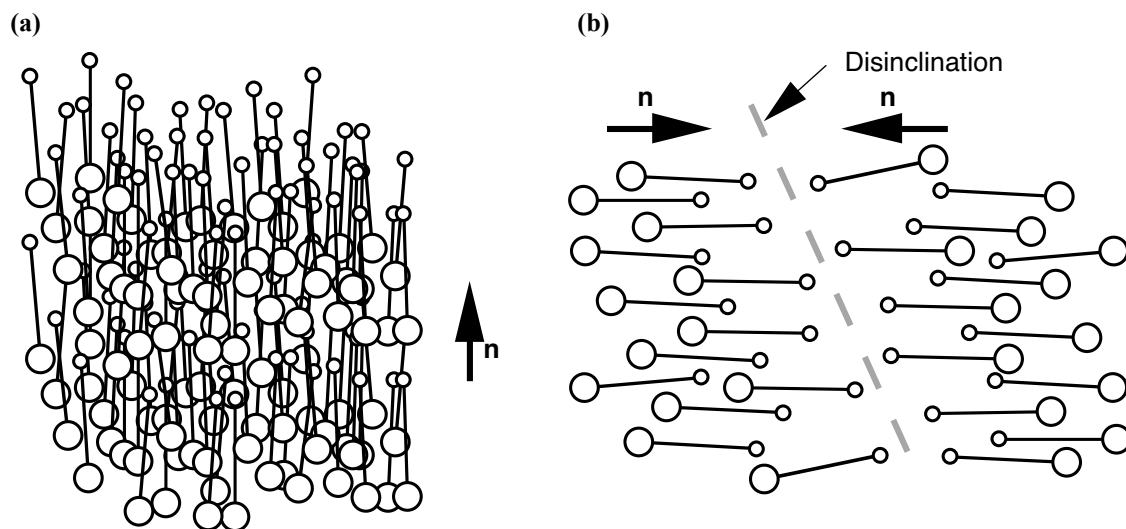


Figure 8.13 Cholesteric liquid crystal. Within any layer of the structure, the substance appears to be nematic. To appreciate the structure, consider for example the top layer on the diagram, which has a director pointed to the right. If we consider a neighbouring layer its nematic director is rotated 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.

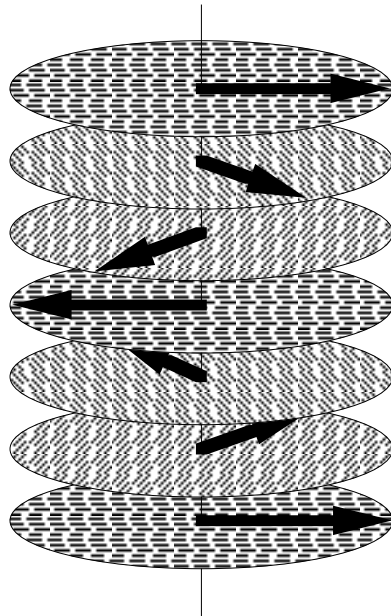
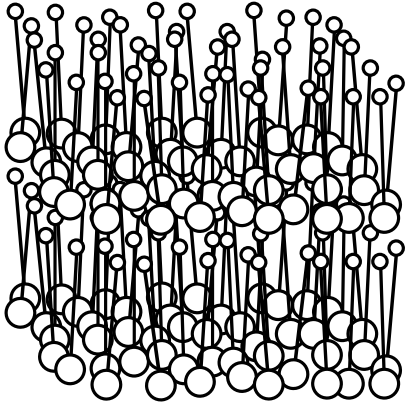
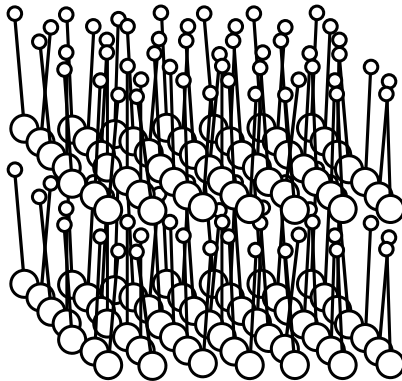


Figure 8.14 Some smectic liquid crystal structures. Smectic B is the most solid-like of the liquid crystal states, having positional order within each layer of the smectic structure. Smectic A is a structure in which this positional order *within* the layer is lost, but the orientational order within 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.

(a) Smectic A



(b) Smectic B



(c) Smectic C

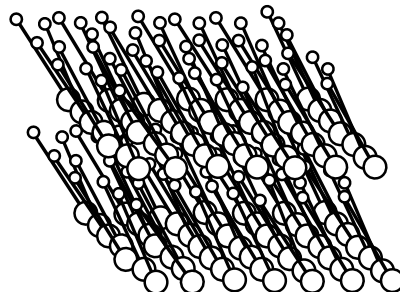


Figure 8.15 The cell model of a liquid. (a) A simple representation of a molecule. (b) The way closely-packed molecules form a cell or cage around other molecules.

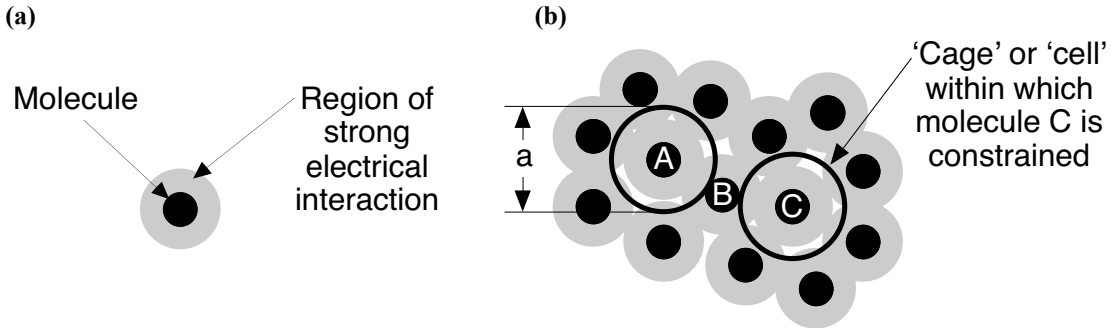


Figure 8.16 Illustration of the significance of the potential energy in the cell model of a liquid. In (a) a typical molecule *A* is shown trapped by its neighbours. This is represented on the potential energy diagram by a single *average* molecule vibrating inside a fixed *average* potential well. Occasionally, 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.

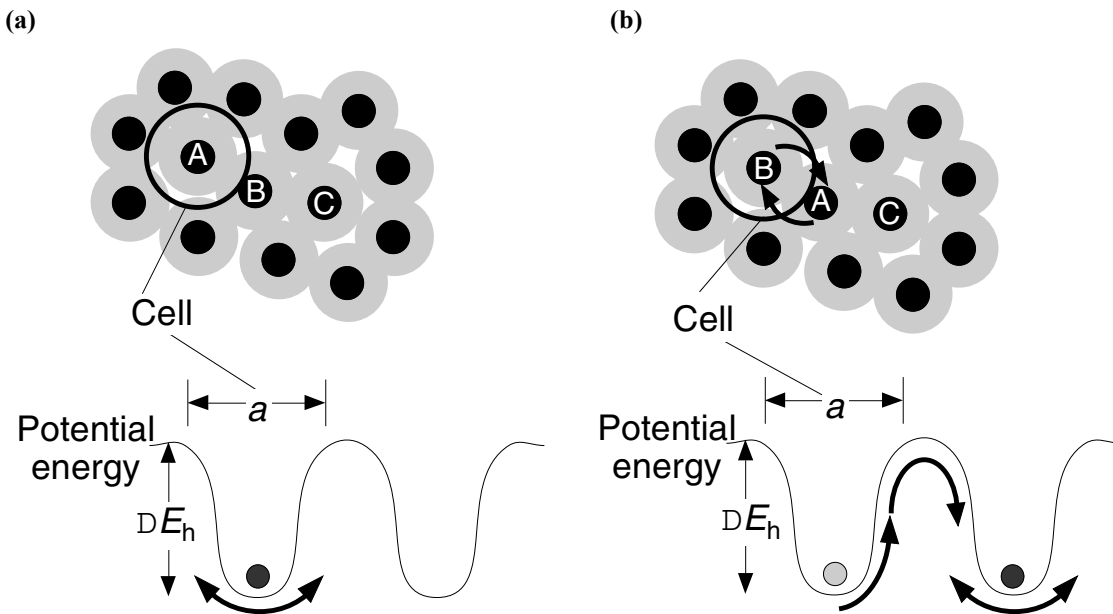


Figure 8.17 The variation of the potential energy of an average molecule with position according to the cell model of a liquid. The upper curve represents a liquid in which the ‘hopping’ process described in Figure 8.16 is more difficult than for the liquid represented by the lower curve.

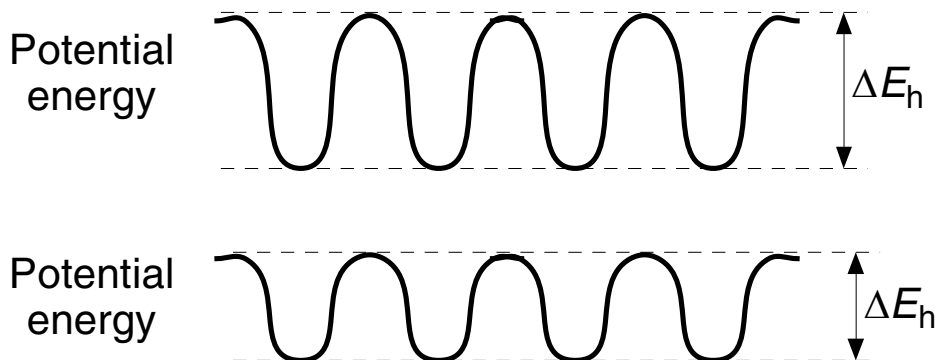


Figure 8.18 The variation of the potential energy of an average molecule with position according to the cell model of a liquid, showing the relative values of ΔE_h and ΔE_e .

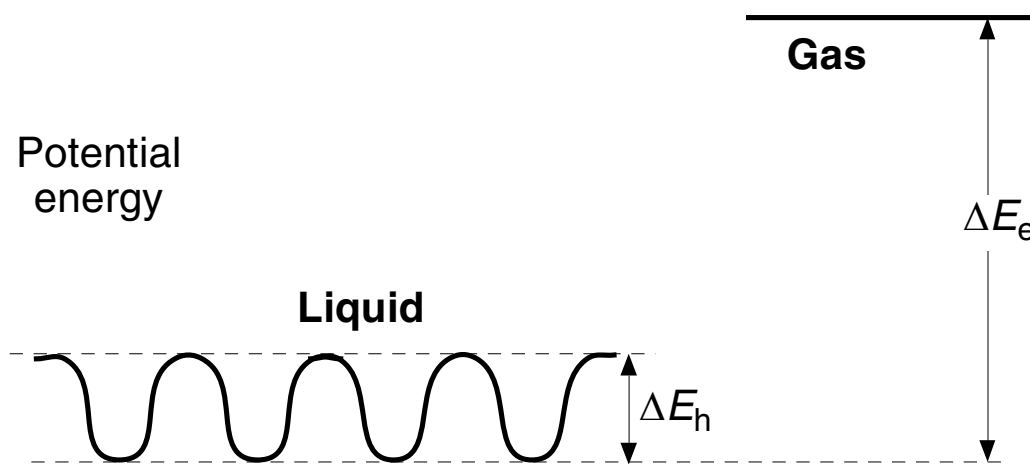


Figure 8.19 The variation of the potential energy of an average molecule with position according to the cell model of a liquid, showing the relative values of ΔE_h , ΔE_s , and ΔE_e . The curve is likely to be most appropriate to spherical molecules which can ‘hop’ past one another relatively easily.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

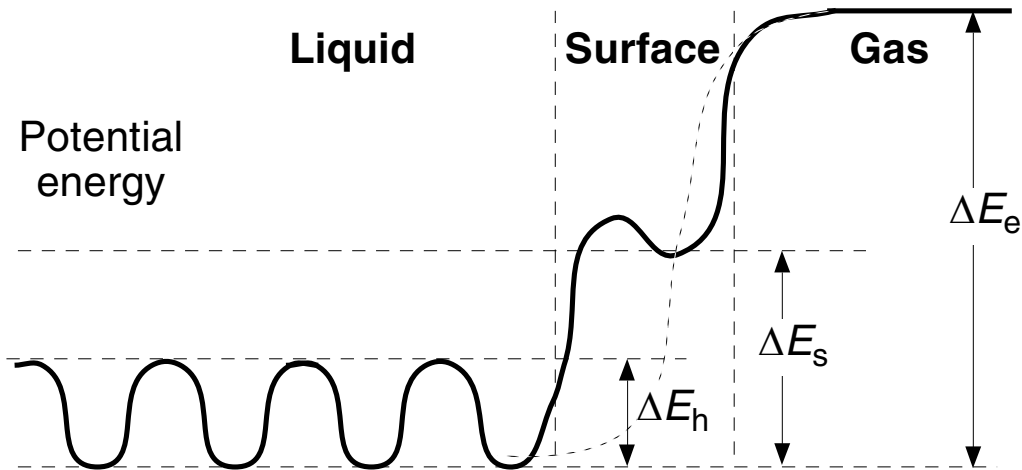


Figure 8.20 The variation of the potential energy of an average molecule with position according to the cell model of a liquid, showing the relative values of ΔE_h , ΔE_s , and ΔE_e . This curve is likely to be appropriate for non-spherical molecules which cannot ‘hop’ past one another easily. The curve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

