7 Molecular order in soft condensed matter—liquid crystallinity

7.1 Introduction

Most of the materials that are studied in the field of 'hard' condensed matter physics—metals, semiconductors, and ceramics—are crystalline; the atoms or molecules of which they are composed are arranged with near-perfect long-ranged order over distances that are many orders of magnitude greater than the distance between molecules. Single crystals of metals or semiconductors of macroscopic size are not uncommon, but even where these materials are described as 'polycrystalline' the fraction of the molecules that does not partake in the long-ranged order is very small (though, of course, this small fraction of atoms associated with grain boundaries and defects such as dislocations may have an effect on bulk properties out of proportion to their number).

The situation in soft condensed matter is rather different. Crystallinity—involving full long-ranged positional order—is important in soft matter, but in most soft matter systems the degree of molecular ordering falls somewhere between the full positional order of a single crystal and the complete positional disorder of a liquid or a glass. In fact, there are two distinctly different types of intermediate order in soft matter systems:

1. **Liquid crystallinity.** These are **equilibrium** phases in which molecules are arranged with a degree of order intermediate between the complete disorder of a liquid and the long-ranged, three-dimensional order of a crystal.
2. **Partial crystallinity.** This is a **non-equilibrium** state of matter in which the system is prevented from reaching its equilibrium state of full long-ranged order for kinetic or other reasons, and in which microscopic regions of crystalline order coexist with disordered regions, often in a complex hierarchical structure.

Liquid crystalline phases are found in

- certain organic compounds with highly anisotropic molecular shapes—these are the materials used in liquid crystalline displays;
- polymers composed of units having a high degree of rigidity, either in the backbone or attached to the backbone as side chains;
- polymers or molecular aggregates which form rigid rod-like structures in solution.

Partial crystallinity is typical of many flexible polymers, such as polyethylene or poly(ethylene terephthalate).

In this chapter we discuss liquid crystallinity, and move on to consider partial crystallinity in polymers in Chapter 8.

7.2   Introduction to liquid crystal phases

A crystal has long-ranged, three-dimensional, positional order, while a liquid has neither positional order nor orientational order. Liquid crystalline phases possess order intermediate between these two extremes. The most disordered type of liquid crystalline phase is the **nematic** phase, which has no positional order, but in which the molecules are, on average, oriented about a particular direction, called the **director**. The transition between the isotropic phase and the nematic phase is sketched in Fig. 7.1. The absence of positional order in a nematic phase means that if one plotted the centres of mass of the molecules the arrangement would be indistinguishable from an isotropic liquid; the only ordering is in the orientation of the molecules, and even this ordering is, as sketched, not perfect. This point will emerge more clearly when we consider statistical mechanical theories of the transition from an isotropic to a nematic liquid, in the next section.

A variant of the nematic phase occurs in systems where the system is composed of molecules which are **chiral**; that is, in which the molecule differs from its own mirror image. In these systems there may be a slight tendency for neighbouring molecules to align at a slight angle to one another. This weak tendency leads the director to form a helix in space, with a well-defined pitch which is much longer than the size of a single molecule. These phases are called **chiral nematics**, or perhaps more commonly **cholesterics**. In many cases the pitch of the helix is of the same order as the wavelength of light, and so these materials can display striking optical effects.

There are still more phases that are intermediate in order between nematics and crystals. In a **smectic** phase, the molecules arrange themselves in sheets. Within each layer, the molecules are aligned, but have no positional order. Thus in going from a nematic to a smectic phase, we go from a situation of no positional order to long-range positional order in one dimension only (Fig. 7.2). Two common subclasses of smectic ordering are the **smectic A** phase, in which the director is parallel to the layer normal, and the **smectic C** phase, in which

Increasingly ordered

Isotropic
liquid

Nematic liquid
crystal
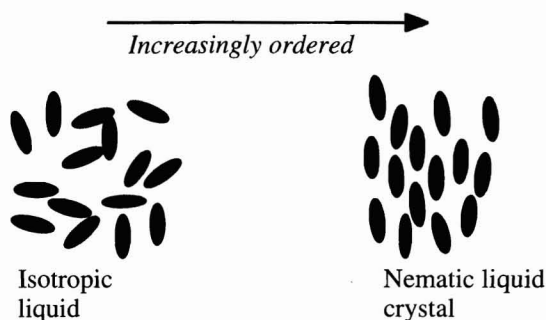
Fig. 7.1 A sketch of the transition between the isotropic liquid phase, in which there is neither positional nor orientational order, and a nematic phase, in which there is orientational order, but still no positional order.

Increasingly ordered

Nematic liquid
crystal

Smectic A liquid
crystal
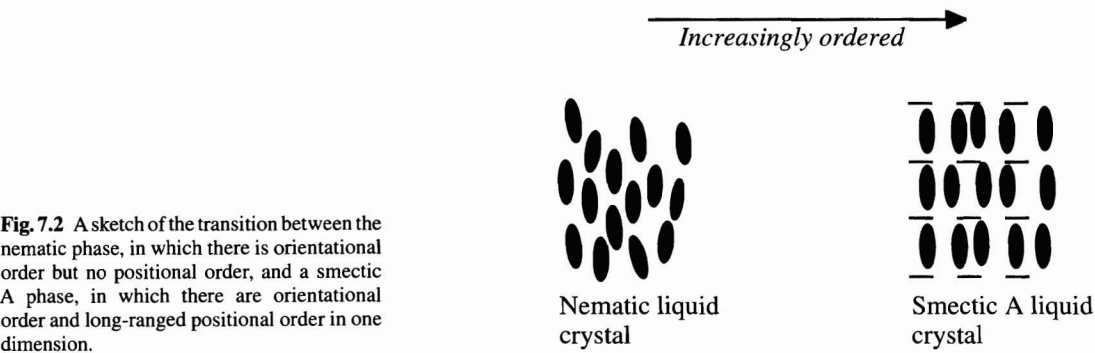
Fig. 7.2 A sketch of the transition between the nematic phase, in which there is orientational order but no positional order, and a smectic A phase, in which there are orientational order and long-ranged positional order in one dimension.
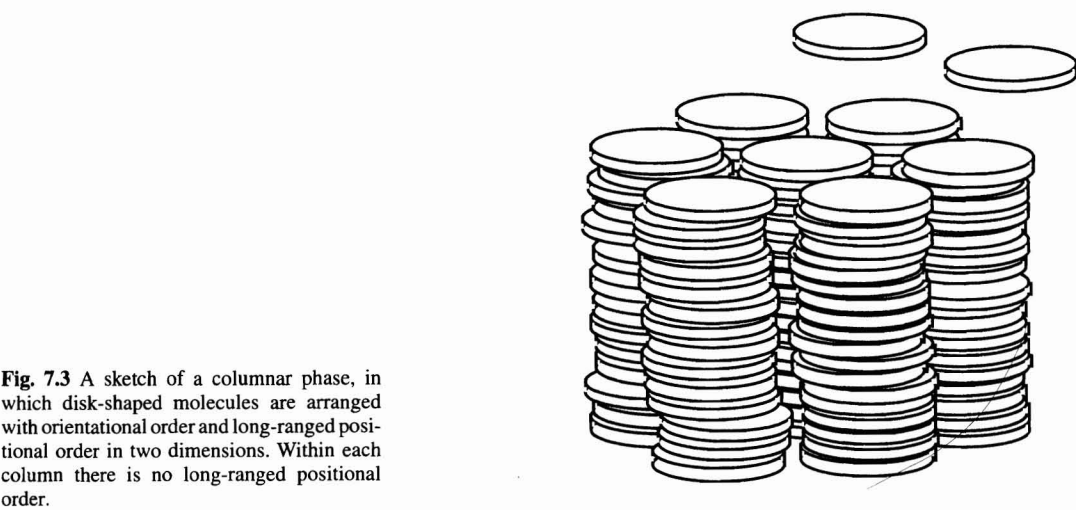
Fig. 7.3 A sketch of a columnar phase, in which disk-shaped molecules are arranged with orientational order and long-ranged positional order in two dimensions. Within each column there is no long-ranged positional order.

Table 7.1 Degrees of order in liquid crystalline phases.

Phase	Positional order	Orientational order
Liquid	None	None
Nematic	None	Yes
Smectic	One-dimensional	Yes
Columnar	Two-dimensional	Yes
Crystalline	Three-dimensional	Yes

the director and the layer normal make an angle. Thus a smectic C phase is made up of layers of tilted molecules.

Finally, it is possible to have a phase which has positional order in two dimensions as well as orientational order. This kind of phase is found in molecules that are disk-like, rather than rod-like; in a **columnar** (or **discotic**) phase such molecules stack into long columns. There are a number of different columnar phases in which there are different degrees of long-ranged order in the arrangement of the columns. One such phase is illustrated in Fig. 7.3. Within each column there is no long-ranged order in the position of the molecules, but the columns arrange themselves into a regular two-dimensional hexagonal lattice.

These different levels of positional and orientational order are summarised in Table 7.1.

7.3 The nematic/isotropic transition

The simplest and least ordered liquid crystal phase is the nematic phase, in which there is no positional order, but in which there is long-ranged order of the direction of the molecules. In going from an isotropic state, in which both position and orientation are random, to a nematic state, in which position is random but there is a preferred orientation, there must be a reduction in the orientational entropy of the system. So in order for the nematic state to have a lower free energy than the isotropic state, there must be another term in the free energy which favours orientation. Then, as the temperature changes, the relative importance of the two terms changes, leading to a phase transition.

How can we describe the state of orientational order of a molecule in a quantitative way? For a rod-like molecule we can introduce a single preferred direction, the director, and we introduce an **orientation function** $f(\theta)$; $f(\theta)\,d\Omega$ is the fraction of molecules in a solid angle $d\Omega$ which are oriented at an angle of θ to the director. For a completely randomly oriented molecule, there is an equal chance that the molecule points anywhere in a solid angle of 4π, and $f(\theta)$ is constant. For a more ordered system the function becomes more peaked around the angles 0 and π, as shown in Fig. 7.4. In all known nematics, the directions 0 and $+\pi$ are identical, so $f(\theta) = f(\pi - \theta)$.

The distribution function contains all the information about the state of order in the material, but it would be convenient to represent this state of order not as a function but as a simple number—an **order parameter**—which took the value 0 for complete disorder, and 1 for complete order. One might think of taking the average of $\cos\theta$, but this is zero because $f(\theta) = f(\pi - \theta)$. Instead we must take another average: $\frac{1}{2}\langle 3\cos^2\theta - 1\rangle$ has the right properties. Thus we define the order parameter S by

$$S = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle = \int \frac{1}{2}(3\cos^2\theta - 1)f(\theta)\,d\Omega. \qquad (7.1)$$
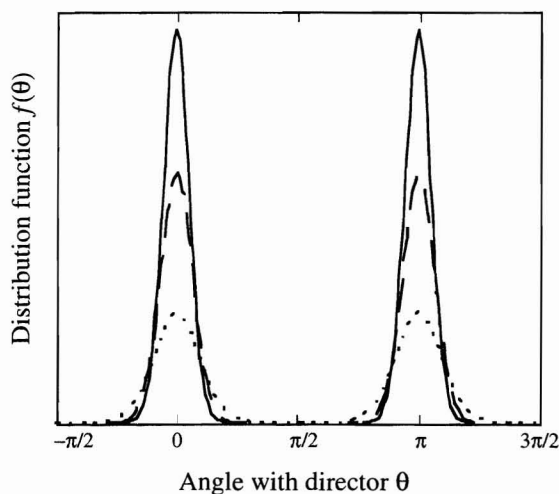

Fig. 7.4 The distribution function $f(\theta)$ for a nematic phase with various degrees of order. The order parameter S takes the value 0.82, 0.71, and 0.44 for the solid, dashed, and dotted lines respectively.

Why should a liquid adopt a nematic phase? In going from an isotropic state to a state of orientational order, there must be a loss of the entropy associated with the freedom of a molecule to be oriented in any arbitrary direction. If the nematic phase is to be at equilibrium, the positive contribution to the free energy arising from this loss of orientational entropy must be outweighed by some other factor that causes the free energy to be lowered when the molecules are aligned. This is likely to occur in melts of rod-like objects for two reasons:

(1) favourable attractive interactions arising from van der Waals forces between the molecules will be maximised when they are aligned;
(2) it is easier to pack rod-like molecules when they are aligned.

The first factor is perhaps most important for melts of relatively small molecules which form nematic phases; the second factor is the major factor underlying the transitions that occur as a function of concentration for very long rigid molecules and supramolecular assemblies. In both cases, simple statistical mechanical theories can be formulated on the basis of these ideas. These theories, which yield predictions about the nature of the transition between the isotropic and nematic states, are both mean field theories, and as such are similar in spirit to theories introduced elsewhere in this book to describe other phase transitions.

The starting point for both theories is to write down an expression for the entropy lost when molecules become oriented. We can write the contribution to the entropy of a molecule due to its orientational freedom using the Boltzmann formula as

$$S_{\text{orient}} = -k_B \int f(\theta) \ln f(\theta) \, d\Omega. \tag{7.2}$$

In the isotropic state, $f(\theta) = 1/4\pi$, so the change in entropy per molecule on going from the isotropic state to an ordered state is given by

$$\Delta S = -k_B \int f(\theta) \ln[4\pi f(\theta)] \, d\Omega. \tag{7.3}$$

In the first theory we consider, which is known as the **Maier–Saupe theory**, we make the phenomenological assumption that the energetic interaction between molecules is simply a quadratic function of the order parameter, so we write the total free energy change per molecule on going from the isotropic to the nematic state as

$$\Delta F = -uS^2/2 + k_B T \int f(\theta) \ln[4\pi f(\theta)] \, d\Omega, \tag{7.4}$$

where u is a parameter that expresses the strength of the favourable interaction between two neighbouring molecules. Of course, S is defined in terms of the distribution function $f(\theta)$. What we now need to do is find the function $f(\theta)$ which minimises the free energy.

We do this in two stages. Firstly, for a given value of the order parameter S, we find the most probable distribution function $f(\theta)$ by maximising the entropy associated with $f(\theta)$ subject to the constraint of a fixed value of S. From this most probable distribution function we can calculate the entropy. In this way we can find the orientational entropy as a function of the order parameter.
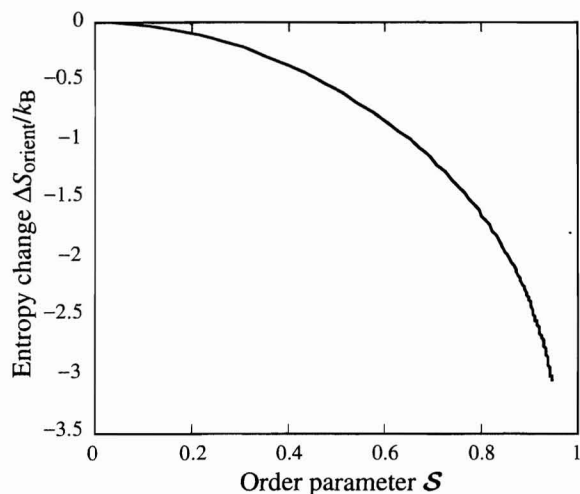
Fig. 7.5 The change in orientational entropy per molecule on going from an isotropic state to an ordered state as a function of the order parameter S.

Thus we need to find the function $f(\theta)$ that gives a stationary value of the integral $\int f(\theta) \ln f(\theta) \sin \theta \, d\theta$ subject to the constraint that the integral $\int \frac{1}{2}(3\cos^2\theta - 1) f(\theta) \sin \theta \, d\theta = S$ is a constant. The Euler–Lagrange equation resulting from this problem in the calculus of variations is

$$\ln f + \frac{3\lambda}{2} \cos^2 \theta + 1 - \frac{\lambda}{2} = 0, \tag{7.5}$$

which has the solution

$$f(\theta) = \exp(3 \lambda \cos \theta^2), \tag{7.6}$$

where λ is the Lagrange multiplier that sets the value of the order parameter S. Now, for a given value of λ, and thus a given value of S, we can evaluate the entropy using eqn 7.3. The resulting curve showing the change in orientational entropy per molecule ΔS_{orient} on going to an oriented state with order parameter S is shown in Fig. 7.5.

We can now plot the free energy as predicted by eqn 7.4 as a function of order parameter for various values of $u/k_B T$. This is shown in Fig. 7.6. For relatively small values of $u/k_B T$, the minimum free energy is found for a value of the order parameter of zero; here the free energy is dominated by the orientational entropy term, and the equilibrium state is isotropic. But as the coupling parameter is increased a minimum of the free energy is found for a non-zero value of S: the equilibrium phase is nematic. The critical value of $u/k_B T$ for the transition is around 4.55.

By calculating the value of the order parameter S as a function of $u/k_B T$ we can investigate the character of the transition. This is shown in Fig. 7.7; at a value of $u/k_B T = 4.55$ there is a discontinuous change of the order parameter from $S = 0$ to $S = 0.44$. This is the nematic–isotropic phase transition; because it is a discontinuous change it is a **first-order** phase transition. However, as the minimum in free energy at the transition is rather shallow, fluctuations at the transition will be important. The transition should therefore be considered to be only weakly first order, and the change in degree of order at the transition is usually not very great.
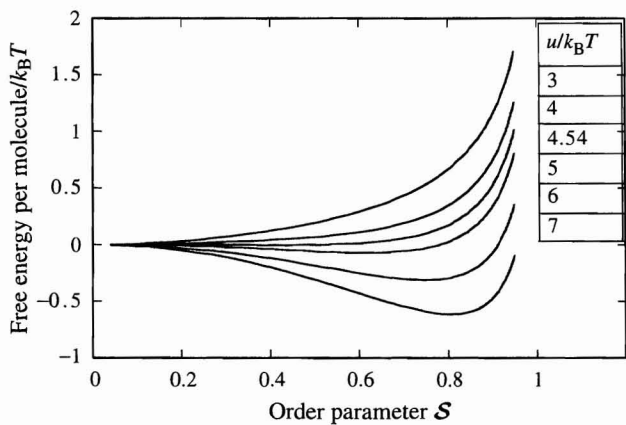
Fig. 7.6 The free energy as a function of the order parameter S for various values of the coupling parameter $u/k_B T$, as given by the Maier–Saupe theory (eqn 7.4).
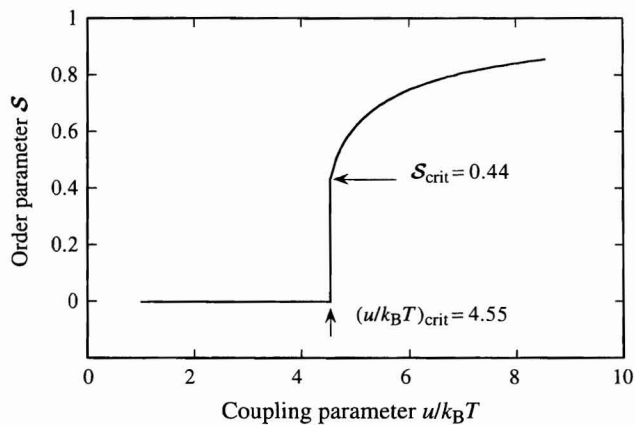
Fig. 7.7 The order parameter S as a function of the coupling parameter $u/k_B T$, as given by the Maier–Saupe theory. There is a weak first-order phase transition at $u/k_B T = 4.55$.

In order to compare the predictions of the Maier–Saupe theory with experiment we would need to have some theory about the way in which the coupling parameter u varied with temperature. The simplest assumption is that u is independent of temperature; this would be the case if the coupling arose entirely from van der Waals forces. This turns out to be quite a reasonable first approximation for small-molecule liquid crystals. Figure 7.8 compares experimentally measured ordered parameters for the molecule p-azoxyanisole (PAA) with the prediction of Maier–Saupe theory assuming that u takes the temperature-independent value that reproduces the experimentally observed transition temperature (i.e. this is a one-parameter fit). There is quite good qualitative agreement. While the theory captures the relatively small degree of order at the transition and gives a good account of the development of order with decreasing temperature, there are clearly systematic deviations from the predictions of theory, particularly close to the transition.
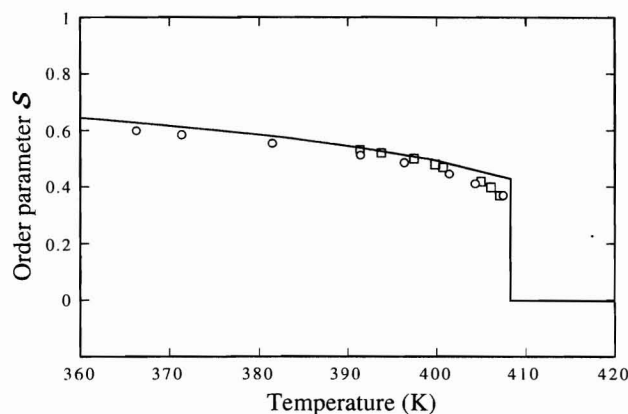
Fig. 7.8 The order parameter S as a function of temperature for p-azoxyanisole (PAA), as measured by refractive indices (circles, from S. Chandrasekhar and N.V. Madhusudana, *Appl. Spectrosc. Rev.*, **6**, 189 (1972)) and diamagnetic anisotropy (squares, from H. Gasparoux, B. Regaya, and J. Prost, *C.R. Acad. Sci.*, **272B**, 1168 (1971)). The solid line is the prediction of Maier–Saupe theory assuming u is independent of temperature and takes a value which reproduces the experimental transition temperature.

There are a number of reasons why there are discrepancies between the experimental data and the predictions of Maier–Saupe theory. Two such possible factors are:

1. Intrinsic temperature dependence of u. This could arise, for example, because the excluded volume interaction is significant.
2. Neglect of fluctuations. The Maier–Saupe theory is a mean field theory, and like all such theories it neglects the effects of fluctuations in the order parameter. These are likely to become important close to the transition point.

7.4 Distortions and topological defects in liquid crystals

7.4.1 Generalised rigidity and the elastic constants of a nematic liquid crystal

Why is it that when one pushes the end of a lever or a beam, the force applied is transmitted from this end to the other? We are so used to the idea that solids are rigid that we forget that the property of rigidity is rather mysterious. After all, we now know that a solid beam is mostly empty space, with atoms or molecules locked into their positions by a subtle balance of forces. It is not just the strength of the interatomic interactions that allows macroscopic forces to be transmitted over macroscopic distances. After all, the density of a solid is usually very similar to the density of its melt, and the total interaction energies in the two situations are very similar, yet the difference in behaviour is qualitative: solids are rigid, and liquids are not. The difference is in the long-ranged order of the solid; if one moves the position of an atom at one end of a rod, an atom at the other end somehow knows it has to try and move in order to maintain the
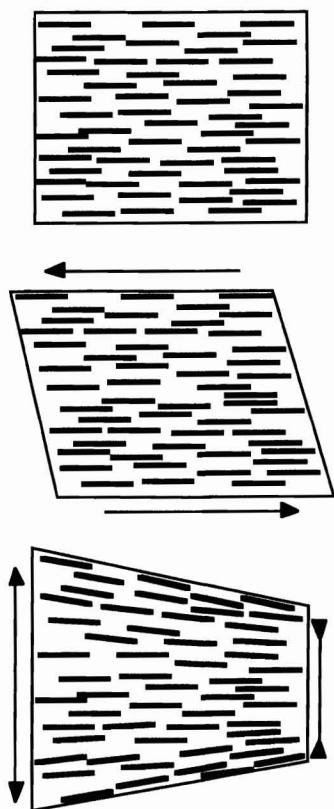
Fig. 7.9 Deformations of a nematic liquid crystal. The shear deformation (middle) does not perturb the long-ranged orientational order, and thus is not opposed by any increase in elastic energy. The splay deformation (bottom) does perturb the long-ranged order, and is opposed by an increase in elastic energy.

absolute precision of the crystalline order. Thus whenever one has long-ranged order of any kind, one has some kind of rigidity which ensures that the system does its best to maintain its long-ranged order when a part of it is perturbed.

In a solid, this rigidity is described by the theory of elasticity. If we apply a stress to a crystal it will deform in response, but this deformation leads to a perturbation of its long-ranged order. This deformation leads to an increase in the energy of the solid proportional to the square of the size of the deformation, as long as the deformation is relatively small (Hooke's law), and if we release the stress the crystal will relax back to its original shape. This elastic behaviour is in contrast to the behaviour of a liquid, which shows no rigidity; if we apply a stress the liquid flows.

In a liquid crystal if an applied stress leads to a deformation that perturbs any long-ranged order that the system possesses, then the deformation will be opposed by an increase in elastic energy. On the other hand, if the applied stress leads to a deformation that does not perturb the long-ranged order, then there will be no increase in elastic energy and the material will respond by flow. Thus the essence of the mechanical response of a liquid crystal is that it has an elastic response to some types of deformation, and a liquid-like response to others. This is illustrated for a nematic liquid crystal in Fig. 7.9. This shows that a nematic liquid crystal will flow like a liquid in response to a simple shear stress, because the resulting deformation leaves the long-ranged orientational order unchanged. On the other hand, more complicated types of deformation, such as the splay deformation illustrated, do lead to an increase in elastic energy. We can define elastic constants for this type of deformation.

In the continuum limit, we can characterise a nematic liquid crystal in a state of deformation by the vector field $\mathbf{n}(\mathbf{r})$ giving the director at every point $\mathbf{r}$. In analogy to Hooke's law, we expect the elastic energy to be proportional to terms in the square of space derivatives of $\mathbf{n}(\mathbf{r})$. Formally, we can enumerate the space derivatives of $\mathbf{n}(\mathbf{r})$, which form a second-rank tensor; by exploiting symmetry properties one can show that there are only three independent elastic constants (de Gennes and Prost 1993). We shall merely state the result, and then discuss the physical significance of the terms.

The elastic energy of distortion per unit volume of a nematic liquid crystal, F_d, can be written

$$F_d = \frac{1}{2}K_1(\nabla \cdot \mathbf{n})^2 + \frac{1}{2}K_2(\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + \frac{1}{2}K_3((\mathbf{n} \cdot \nabla) \cdot \mathbf{n})^2, \quad (7.7)$$

where K_1, K_2, and K_3 are the three elastic constants. These three constants correspond to three fundamental types of deformation in nematic liquid crystals: **splay**, **twist**, and **bend**. These are illustrated in Fig. 7.10.

In practice, we find that values for the elastic constants in typical small-molecule liquid crystals are of order 10^{-12} N. All three constants are of the same order of magnitude, though the bending constant K_3 is generally somewhat larger than the other two.

7.4.2 Boundary effects

In discussing the elastic constants of nematic liquid crystals, we glossed over the important practical question of how it is that one can impose a distortion on a nematic liquid crystal. It turns out that an easy and practically important method

is to exploit the property that many surfaces have of imposing a preferential state of ordering on the nematic liquid crystal.

In fact, virtually any surface will impose some sort of ordering on the director of an adjacent liquid crystal. There are two important cases:

1. **Homeotropic**—alignment perpendicular to the surface. This can be achieved by arranging for the surface to be coated by a surfactant molecule.
2. **Homogeneous**—alignment parallel to the surface. This is the more usual case. For a free surface any direction in the plane of the surface may be allowed, while for a solid substrate a particular direction in the plane may be imposed by the crystalline structure of the surface. A direction may also be imposed simply by rubbing a glass or plastic surface. The mechanism by which this rubbing process works is still a little obscure. In the case of the most technologically important process, in which polymers of the polyimide family are rubbed with a velvet cloth, it seems that the rubbing causes an alignment of the polymer chains. The molecules of the liquid crystal then tend to be aligned with the chain direction.

The important general point to remember about these effects is that the sensitivity to alignment at the boundary is a consequence of the **broken symmetry** of the nematic phase. In the bulk, the energy of a nematic monodomain is independent of the orientation of the director. Thus the smallest perturbation that can change the relative energies of the different orientations will be sufficient to impose this preference on the material.

### 7.4.3 Disclinations, dislocations, and other topological defects

Up to this point, we have assumed that the director in a nematic phase always varies through space in a smooth way. In fact, experimental samples of liquid crystals will often contain points or lines where the orientation of the sample changes discontinuously. These topological defects are known as **disclinations**.

Two important types of disclination are illustrated in Fig. 7.11. Here the local directions of the director are drawn in the plane perpendicular to the disclination line. One can define the **strength** of the disclination by a construction illustrated in this diagram. If one draws a loop round the defect core, and one goes round the loop drawing an arrow in the direction of the local director, in disclination (a) the arrow rotates π radians in the same sense as the direction of traverse of the loop. This disclination has strength $s = +\frac{1}{2}$. In disclination (b) the rotation is also π radians, but the sense of rotation is opposite to that of the traverse of the loop; the disclination has strength $s = -\frac{1}{2}$.

Disclinations should not be present in a macroscopic sample of a liquid crystal at equilibrium, because they lead to an increase in the free energy proportional to the length of disclination line present. The origin of this energy is two-fold: there is a certain elastic energy associated with the long-ranged distortion of the director field, while right at the core of the disclination there is an increase in energy associated with the complete loss of orientational order there. Accurate calculation of the disclination energy is complex, particularly

(a)

(b)

(c)
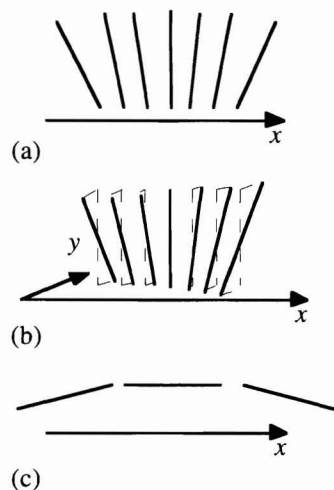
Fig. 7.10 The three fundamental deformations of a nematic liquid crystal. (a) Splay, $(\nabla \cdot \mathbf{n}) \neq 0$. (b) Twist, $\nabla \times \mathbf{n}$ parallel to $\mathbf{n}$. (c) Bend, $\nabla \times \mathbf{n}$ perpendicular to $\mathbf{n}$.

(a)

(b)
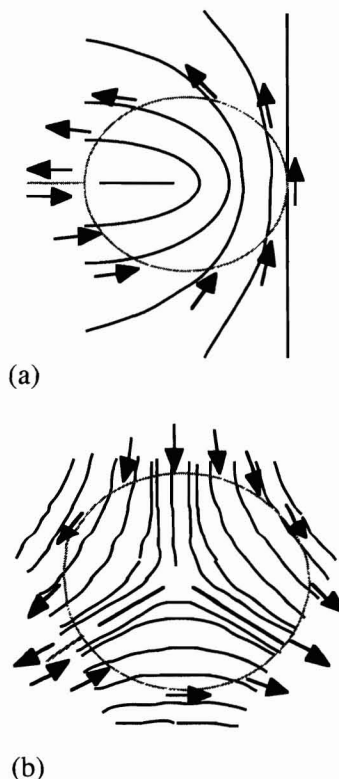
Fig. 7.11 Disclinations in a nematic liquid crystal. The disclination in (a) has strength $s = +\frac{1}{2}$, the disclination in (b) has strength $s = -\frac{1}{2}$.

if one goes beyond an approximation in which the three elastic constants, K_1, K_2, and K_3, are treated as equal. In this approximation, if we can write $K = K_1 = K_2 = K_3$, then we can show that the energy E of length L of disclination is given by

$$\frac{E}{L} = \pi K s^2 l, \tag{7.8}$$

where l is a factor which varies only logarithmically with quantities such as the size of the disclination core and the average separation of disclinations. An energy per unit length corresponds to a **line tension**; thus we can consider a disclination in some respects as behaving like a string under tension.

Disclinations correspond to defects in the state of orientational order. If we have a liquid crystal that has some degree of translational order, such as a smectic one, then we can expect also defects in translational order. Such defects, which are familiar from crystalline solids, are known as **dislocations**.

7.5   The electrical and magnetic properties of liquid crystals

The anisotropic nature of liquid crystal phases manifests itself in particularly striking ways in regard to their interaction with electromagnetic fields. This is the basis not only of the very striking optical effects that are characteristic of liquid crystal phases, but also of their crucial role in display technologies. Our discussion will mostly be confined to effects in nematics, which are by far the most important systems for practical applications.

Most of the molecules that form nematic phases have a permanent dipole, but it is found that in the absence of an applied field there is an equal probability that the dipole points in either direction—nematics are never **ferroelectric**. When a nematic phase is put in an electric field $\mathbf{E}$ the field induces a polarisation $\mathbf{P}$ which is given, in an isotropic system, by $\mathbf{P} = (\epsilon - 1)\epsilon_0 \mathbf{E}$, where ϵ is the dielectric constant. In a nematic liquid crystal, the degree to which the material can be polarised depends on whether the field is applied parallel or perpendicular to the director.

This is illustrated in Fig. 7.12, which sketches the response to an applied field of a nematic liquid crystal in which the molecules have a dipole parallel to their long axis. Much more polarisation can be induced when the applied field is in the same direction as the director. The consequence is that the dielectric coefficient parallel to the director $\epsilon_\parallel$ is larger than the dielectric coefficient perpendicular to the director $\epsilon_\perp$. The situation is reversed if the dipole moment lies perpendicular to the long axis of the molecule; then we find $\epsilon_\parallel < \epsilon_\perp$.

The consequence of this is that electric fields are able to align nematic liquid crystals rather efficiently. In the case of a parallel dipole, if the director adjusts to be parallel to the applied field, the electric field within the material is reduced by the polarisation effect and as a result the total energy of the system is reduced. For a field applied in some general direction, we can write the energy in terms of the displacement $\mathbf{D}$. This is given by

$$\mathbf{D} = \epsilon_\perp \mathbf{E} + (\epsilon_\parallel - \epsilon_\perp)(\mathbf{n} \cdot \mathbf{E})\mathbf{n}, \tag{7.9}$$
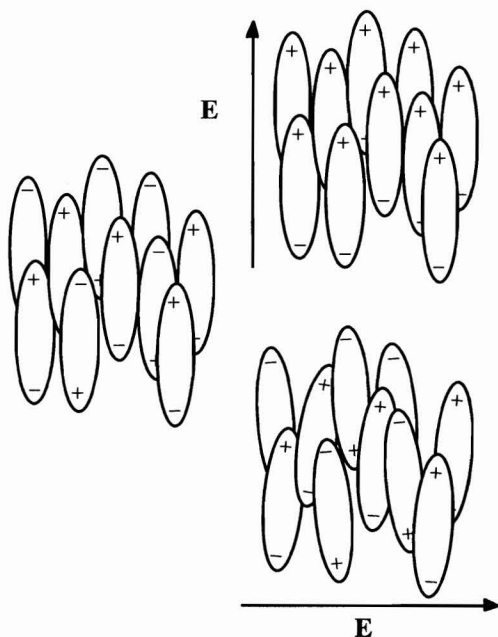
Fig. 7.12 Dielectric anisotropy in a nematic liquid crystal, in which there is a permanent electric dipole parallel to the long axis of the molecule. In the absence of field (left) there is no net dipole moment. If the field is applied parallel to the director (top right), it is relatively easy to acquire a large induced dipole, while if the field is perpendicular to the director (bottom right) the degree of polarisation is smaller. Thus the dielectric coefficient parallel to the director $\epsilon_\parallel$ is larger than the dielectric coefficient perpendicular to the director $\epsilon_\perp$.

so we can write the energy per unit volume associated with the field, F_{el}, as

$$F_{\text{el}} = -\frac{1}{4\pi} \int \mathbf{D} \cdot \mathbf{dE} = -\frac{\epsilon_\perp}{8\pi} E^2 - \frac{\epsilon_a}{8\pi} (\mathbf{n} \cdot \mathbf{E})^2, \qquad (7.10)$$

where $\epsilon_a = \epsilon_\parallel - \epsilon_\perp$ and the director is along the unit vector $\mathbf{n}$. Thus for dipoles parallel to the long axis ϵ_a is positive and the energy is reduced when the nematic liquid crystal aligns along the field.

The response of a nematic liquid crystal to a magnetic field is similarly anisotropic. Most liquid-crystal-forming molecules are **diamagnetic**; an applied magnetic field H causes a molecular current which produces a magnetic field opposing the applied field. The coefficient relating the induced magnetisation M to the field H is the susceptibility $\chi = M/H$. The susceptibility takes different values according to whether the field is applied parallel to the director ($\chi_\parallel$) or perpendicular to the director ($\chi_\perp$). Usually the difference between the two susceptibilities, $\chi_a = \chi_\parallel - \chi_\perp$, is **positive**; the director tends to line up with the direction of the magnetic field. Entirely analogously to the electrical case, we can write down the energy per unit volume associated with the magnetic field, F_{mag}, as

$$F_{\text{mag}} = -\int \mathbf{M} \cdot \mathbf{dH} = -\frac{1}{2}\chi_\parallel H^2 - \frac{1}{2}\chi_a (\mathbf{n} \cdot \mathbf{H})^2, \qquad (7.11)$$

where the director is along the unit vector $\mathbf{n}$.

7.6   The Frederiks transition and liquid crystal displays

We have seen that the alignment of liquid crystals is highly sensitive to external fields; these fields include electric and magnetic fields in the bulk, and the effects of surfaces in imposing alignment. There is a class of interesting transition effects that occur when two antagonistic aligning influences compete—these are known as **Frederiks transitions**.

Perhaps the simplest of these transitions occurs when one has a thin film of a nematic liquid crystal sandwiched between two plates. If these plates impose a strong parallel alignment effect on the liquid crystals then the liquid crystal will form a single domain. Let us now impose a field (either electric or magnetic) perpendicular to the plates that has a tendency to align the director in that direction. The surface constraint forces the director to lie parallel to the plates at the edge of the cell, while the field tends to impose a perpendicular orientation towards the centre. The only way both can be satisfied is if there is a distortion of the director field that will cost a splay energy. It is this splay energy that means that the cell will only change from one configuration to the other when a certain critical field has been applied.

To see this we can carry out a simple linear stability analysis. Let us suppose that the unperturbed director is $\mathbf{n}_0$, and that towards the centre of the cell the director is slightly perturbed and lies in the direction $\mathbf{n}_0 + \delta\mathbf{n}(z)$, where $\delta\mathbf{n}(z)$ is a small vector perpendicular to the plates. We can now write the total free energy per unit volume in terms of an elastic contribution and a contribution to the field. This has the form

$$F_{\text{total}} = F_{\text{elastic}} + F_{\text{field}}$$
$$= \frac{1}{2}K_1 \left(\frac{\partial \delta\mathbf{n}(z)}{\partial z}\right)^2 - \frac{\epsilon_a E^2}{8\pi}\delta\mathbf{n}(z)^2, \tag{7.12}$$

where K_1 is the splay elastic modulus and ϵ_a is the difference in dielectric coefficients perpendicular and parallel to the field. At the boundaries $z = 0$ and $z = d$ (where d is the thickness of the cell), $\delta\mathbf{n} = 0$ because of the alignment properties of the surface, which we assume to be strong. So consider a distortion of the form

$$\delta\mathbf{n}(z) = \delta n \sin\left(\frac{\pi z}{d}\right). \tag{7.13}$$

If we substitute this into eqn 7.12 and integrate from $z = 0$ to $z = d$ we get the following expression for the energy:

$$\int_0^d F_{\text{total}}\, \mathrm{d}z = \delta n^2 \left[\left(\frac{K_1 \pi^2}{4d}\right) - \left(\frac{\epsilon_a E^2 d}{16\pi}\right)\right]. \tag{7.14}$$

So any small distortion of the director will lead to a lowering of the free energy if the field exceeds a critical value E_{crit}, which is given by

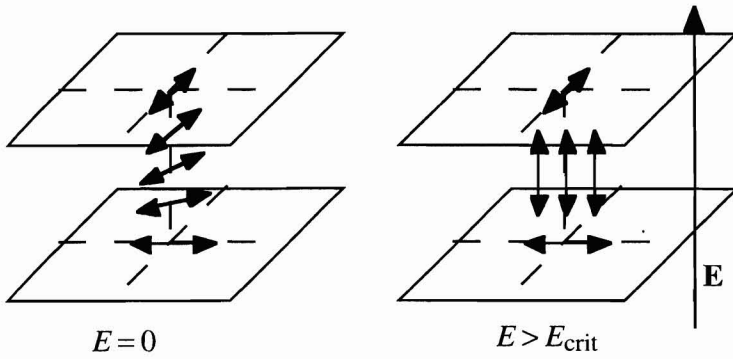$$E_{\text{crit}} = \frac{2\pi}{d}\sqrt{\frac{\pi K_1}{\epsilon_a}}; \tag{7.15}$$

Fig. 7.13 The twisted nematic display.

for values of applied field less than E_{crit} the director remains parallel to the cell walls right through the cell, while for values greater than E_{crit} the director distorts in the centre of the cell to align with the field.

Very similar calculations can be made for the case of a liquid crystal in a magnetic field. In fact, observations of magnetic Frederiks transitions provide the best way experimentally to determine the elastic constants for twist, splay, and bend.

Frederiks transitions, in slightly more complicated geometries, form the basis for **liquid crystal displays**. For example, in a **twisted nematic display**, a nematic liquid crystal is confined between two plates, typically around $10\,\mu m$ apart. The plates are treated to impose a parallel alignment on the liquid crystal, but the alignment directions of the two plates are perpendicular to each other. This forces the director to twist round by $90°$ between the top and bottom plate. Now if a field is applied perpendicular to the plates, above the Frederiks transition the director towards the centre of the plates will swing into alignment with the applied field (Fig. 7.13).

The critical field for the Frederiks transition in the twisted nematic geometry can be calculated by a linear stability argument similar to the one given above; the situation is slightly more complicated because bend and twist distortions are involved as well as splay distortions. The result is that the critical field is given by

$$E_{crit} = \frac{2\pi}{d}\sqrt{\frac{\pi}{\epsilon_a}}\left[K_1 + \frac{1}{4}(K_3 - 2K_2)\right]^{1/2}. \tag{7.16}$$

To use the twisted nematic cell as a display device, the cell is sandwiched between crossed polarisers. In the voltage-off state, the polarisation state of incoming light is twisted round through $90°$ as it follows the changing orientation of the director through the cell. When a field substantially greater than the critical field is applied, the director through most of the cell is perpendicular to the plates and has no effect on the polarisation state of the light; the polarised light is blocked by the polariser as it leaves the cell, which appears dark.

7.7   Polymer liquid crystals

7.7.1   Rigid polymers

Polymers form an important subclass of liquid-crystal-forming materials. Polymer liquid crystal phases are important in the processing of advanced high-modulus engineering materials, like Kevlar, and they may also occur in nature in solutions of some biopolymers.

We can distinguish between two classes of liquid crystal polymer:

thermotropic   liquid crystal polymers, in which the transition from an isotropic to a liquid crystalline phase is driven by changes in temperature;
lyotropic   liquid crystal polymers, in which a liquid crystal phase is formed in solution, with a transition from isotropic to liquid crystalline phase driven by a change in concentration.

A polymer will have a propensity to form a liquid crystalline phase if its backbone is relatively **rigid**; liquid crystal phases are also possible for polymers with a flexible backbone with rigid units attached, but these **side-chain liquid crystals** are rather different. Such rigidity in the main chain can be achieved in one of two ways:

1. The polymer itself is made up of mesogenic monomer units which allow for restricted rotation between the units, resulting in a tendency to a rigid or semi-rigid rod conformation.
2. The polymer has a flexible backbone, but strong interactions between nearby monomers cause a transition from a random coil state to a rigid **helix**.

As an example of a polymer in the first category, Fig. 7.14 shows the chemical structure of an aromatic polyamide, poly(p-phenyleneterephthalamide) or PPTA, which forms a liquid crystal phase in solution. If fibres are spun from this liquid crystalline solution, they will have a high degree of molecular alignment resulting in very good mechanical properties; this material in fact forms the basis for the commercial material Kevlar (du Pont), which is very stiff and strong.
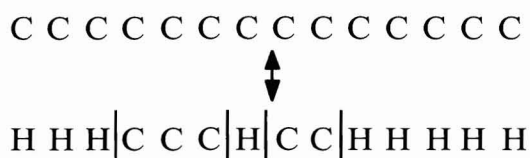
7.7.2   Helix–coil transitions

The classic case of a polymer which adopts a helical rigid rod structure stabilised by strong interactions between nearby monomers is provided by the α-helix structure of polypeptides. This is illustrated in Fig. 7.15; a hydrogen bond is formed between the C=O group on the ith monomer and the N–H group on the $(i+4)$th monomer.
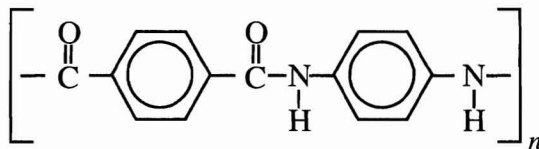
Fig. 7.14 The chemical structure of poly (p-phenyleneterephthalamide), or PPTA, a typical semi-rigid polymer.
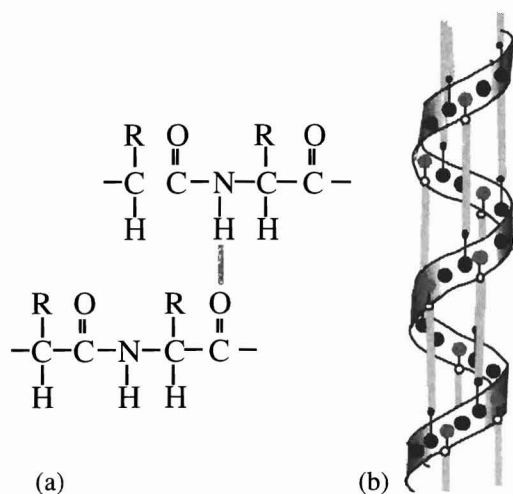
Fig. 7.15 The formation of an α-helix in a polypeptide. (a) The chemical structure of a polypeptide, illustrating the hydrogen bond that can be formed between nearby monomers. (b) The α-helix that results when hydrogen bonds are formed between the ith and $(i + 3)$th monomer units.

Fig. 7.16 A simple model for the helix–coil transition. We imagine our chain to be made up of units that are in either the helix state (H) or the coil state (C). The free energy change when a single specified coil unit transforms to a helix state is ΔF_{hc}; in addition there is a free energy associated with each junction between helix and coil segments ΔF_g.

What drives the formation of such a helical structure is the lowering of free energy that results from the formation of the hydrogen bonds. What opposes it is the loss of entropy that is a result of the loss of flexibility of the chain. Thus we would expect a transition to take place as the temperature is increased, with the lower energy helix conformation favoured at low temperatures, and the higher entropy coil conformation favoured at higher temperatures. What is the nature of this transition?

We can investigate this by making a simple but effective model, illustrated in Fig. 7.16. We imagine the chain to be made up of units that can be either in the helix state or in the coil state. For each specified unit, there is a certain free energy change ΔF_{hc} when it changes from a coil to a helix state; this represents the energy of the hydrogen bond which stabilises the helix. However, there is also a free energy ΔF_g associated with the junction between helix and coil segments. It is this factor that expresses the **cooperativity** of the transition. If one hydrogen bond has been formed, it makes it easier to form neighbouring hydrogen bonds.

To find out the nature of the transition, we need to determine the free energy change on going from an all-coil state to a state with a certain number of helix segments h, and a certain number of junctions between helix and coil regions $2g$. In addition to the free energy change associated with the total number of helices and the total number of junctions there is an entropy associated with the total number of different ways of arranging a chain with N units so that it has h helix segments and $2g$ junctions.

How can we find this entropy? The $2g$ junctions define a set of g boxes in which we have to put the helix segments, with at least one segment going in each box, and another set of g boxes into which the coil segments must be put. So for the helix segments, we define as Ω_h the number of ways there are of arranging h objects in g boxes, each of which must contain at least one object. This is given by

$$\Omega_h = \frac{h!}{g!(h-g)!}. \tag{7.17}$$

Similarly, for the coil segments there are Ω_c ways of arranging the $N-h$ coil segments in the g boxes, where

$$\Omega_c = \frac{(N-h)!}{g!(N-h-g)!}. \tag{7.18}$$

The total number of arrangements is $\Omega_c \times \Omega_h$, and the entropy associated with this number of arrangements is

$$\Delta S_c(h, g, N) = k_B \ln(\Omega_c \Omega_h). \tag{7.19}$$

We can simplify this using Stirling's approximation for the factorials ($\ln x! \approx x \ln x - x$), to find

$$\begin{aligned} \Delta S_c(h, g, N)/k_B = {} & h \ln h + (N-h)\ln(N-h) - 2g \ln g \\ & - (h-g)\ln(h-g) \\ & - (N-h-g)\ln(N-h-g). \end{aligned} \tag{7.20}$$

Now we can write down the free energy relative to the coil state in terms of h and g, $F(h, g)$;

$$F(h, g) = h\Delta F_{hc} + 2g\Delta F_g - T\Delta S_c(h, g, N). \tag{7.21}$$

We need to minimise $F(h, g)$ with respect to both h and g. Taking partial derivatives with respect to each variable and setting these equal to zero gives us two equations:

$$\frac{c(h-g)}{h(c-g)} = \exp\left(-\frac{\Delta F_{hc}}{k_B T}\right) = s, \tag{7.22}$$

$$\frac{g^2}{(c-g)(h-g)} = \exp\left(-\frac{2\Delta F_g}{k_B T}\right) = \sigma. \tag{7.23}$$

Here we have written the number of coil segments $N - h = c$, and we have introduced the two parameters σ and s. The parameter s expresses the preference of a given segment for the helix state over the coil state; as the temperature changes s may change from a value less than unity, in which the coil state is energetically preferred, to a value greater than unity, in which the helix state is preferred. The parameter σ is a measure of the cooperativity of the transition. For $\sigma = 1$ there is no cooperativity; the conformational state of one segment is independent of its neighbour. As the energy associated with a junction between helical and coil regions increases, σ takes a value less than unity, with a value of $\sigma = 0$ implying that junctions between helical regions and coil regions are absolutely forbidden.
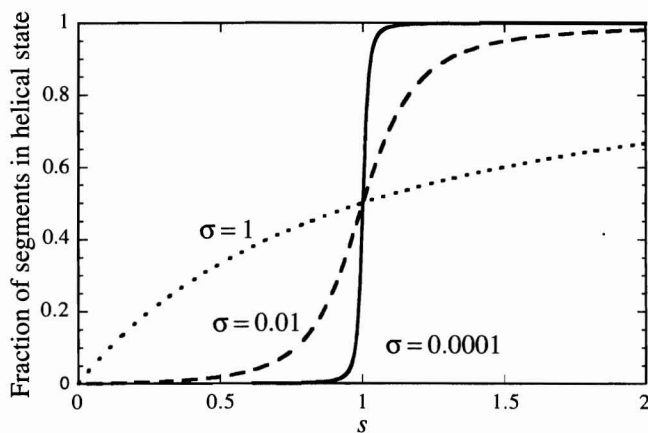
Fig. 7.17 The helix–coil transition as predicted by eqn 7.24. The coil state is favoured for $s < 1$, and the helix state for $s > 1$. For a system with no cooperativity ($\sigma = 1$), the transition is very broad, but for realistic values of the cooperativity parameter $\sigma \approx 10^{-4}$, the transition is rather sharp.

Writing $f_h = h/N$ for the fraction of segments in the coil state, we can eliminate g from the simultaneous equations 7.23 to find

$$f_h = \frac{1}{2} + \frac{(s-1)}{2\sqrt{(s-1)^2 + 4s\sigma}}. \qquad (7.24)$$

In Fig. 7.17 we plot eqn 7.24 as a function of s for various values of σ. In all cases we see that for $s < 1$, for which the coil state is energetically favourable, the molecule is predominantly in the coil state, while for $s > 1$ the molecular is predominantly helical. But the nature of the transition between the coil and helix states depends on the value of σ. For large values of σ, the transition is very broad. For $\sigma = 1$, which corresponds to a value of $\Delta f_g = 0$, eqn 7.24 reduces to $f_h = s/(1+s)$. In this limit the probability of a segment being in the helix state is given by a simple Boltzmann factor; because there is no energy penalty for junctions between coil and helix segments each segment behaves independently. As the degree of cooperativity becomes larger, corresponding to smaller values of σ, the transition becomes much sharper.

The sharpness of the transition (values of σ are found to be in the range 10^{-4}–10^{-3}) makes it tempting to think of the helix–coil transition as being analogous to **melting**. However, there is an important fundamental difference. The helix–coil transition is not a true phase transition, as the width of the transition does not tend to zero as the total size of the system becomes infinite, but instead remains finite. This is a manifestation of a general theorem in statistical physics that states that true phase transitions do not occur in one-dimensional systems in which the interactions are of short range. For any finite value of s there will always be a finite fraction of coil sections, so a long chain will always have some shorter coil sections coexisting with longer sections of helix. Fully rigid rods will only be obtained for relatively short chains.

7.7.3   The isotropic/nematic transition for ideal hard rods

An important idealisation of a lyotropic liquid crystal system consists of a solution of **hard rods**, the theory of which was developed by Onsager. This is the anisotropic analogue of the hard-sphere system we discussed in Chapter 4, where a transition to an ordered crystalline phase was driven by an effective repulsion of entropic origin arising from the effect of excluded volume. The energy of interaction between hard rods is zero except when they overlap in space, in which case it is infinite. This means that there is a reduction in translational entropy, as some space is not available to be explored by a given rod because it is already occupied by another rod. In the hard-rod system, we find that less volume is excluded if the rods tend to align, and it is this reduction of the excluded volume effect by alignment which drives a phase transition from an isotropic state to a nematic liquid crystalline state as a function of increasing concentration of the rods.

Let us recall some basic results about excluded volume from Chapter 4. In a perfect gas one can write the entropy per atom S_{ideal} of N atoms in a volume V as

$$S_{ideal} = k_B \ln \left(a \frac{V}{N} \right) \tag{7.25}$$

where a is a constant. If the gas atoms have a finite volume b this reduces the volume accessible to any given atom from V to $V - Nb$, and the entropy is modified to

$$
\begin{aligned}
S &= k_B \ln \left(a \frac{(V - Nb)}{N} \right) \\
&= S_{ideal} + k_B \ln \left(1 - \frac{bN}{V} \right) \\
&= S_{ideal} - k_B \left(\frac{N}{V} \right) b,
\end{aligned}
\tag{7.26}
$$

where we have expanded the logarithm assuming that the volume fraction of atoms is low. The corresponding free energy is

$$
\begin{aligned}
F &= F_{ideal} + k_B T \left(\frac{N}{V} \right) b \\
&= F_0 + k_B T \log c + k_B T c b,
\end{aligned}
\tag{7.27}
$$

where the concentration $c = N/V$.

In the hard-rod system another factor enters: the degree of alignment of the rods. If we describe this by an orientation function $f(\theta)$, we need to introduce two new factors to the expression for the free energy:

1. As a net orientation is introduced, there is a loss of orientational entropy ΔS, which is given by eqn 7.3 as $\Delta S = -k_B \int f(\theta) \ln[4\pi f(\theta)] \, d\Omega$.
2. The excluded volume b becomes a function of the degree of orientation; as the degree of alignment increases the excluded volume decreases.

To quantify the second point, consider two rods, each of length L and diameter D, that make an angle γ with each other. The excluded volume

is $2L^2 D |\sin\gamma|$, as shown in Fig. 7.18. If the orientation of all the rods is completely random, then the average value of $|\sin\gamma|$ can be shown to be $\pi/4$. However, as the rods become aligned then the average value of $|\sin\gamma|$ starts to decrease from this value. If we write this average value as $p[f(\theta)] = \langle |\sin\gamma| \rangle$ then in terms of the orientation function $f(\theta)$ we have

$$p[f(\theta)] = \langle |\sin\gamma| \rangle = \int\int f(\theta) f(\theta') \sin\gamma \, \mathrm{d}\Omega \, \mathrm{d}\Omega'. \qquad (7.28)$$

Thus for any given distribution function one can calculate $p[f(\theta)]$ in terms of this rather messy multiple integral.

Taking together the term for the loss of orientational entropy and the excluded volume, we find for the free energy

$$F = F_0 + k_{\mathrm{B}}T \left(\log(c) + \int f(\theta) \ln[4\pi f(\theta)] \, \mathrm{d}\Omega + L^2 Dc p[f(\theta)] \right). \qquad (7.29)$$

It is convenient to rewrite this in terms of the volume fraction of the rods $\phi = c\pi L D^2/4$; after absorbing more constant terms in F_0 this gives us

$$F = F_0' + k_{\mathrm{B}}T \left[\log\left(\frac{L}{D}\phi\right) + \int f(\theta) \ln[4\pi f(\theta)] \, \mathrm{d}\Omega + \frac{4}{\pi}\frac{L}{D}\phi p[f(\theta)] \right]. \qquad (7.30)$$

From this we can see that the phase diagram must be a function only of the combination $\phi L/D$, the product of the **volume fraction** and the **aspect ratio** L/D of the rods.

This expression is a **functional**, a function of a function, so to find the function $f(\theta)$ that minimises it soon leads us into rather difficult mathematics.[1] We can, however, get a good approximate solution by assuming a particular trial functional form for the distribution function, and then minimising the free energy with respect to a parameter in our guessed distribution function (this amounts in mathematical terms to a variational method of approximate solution).

A convenient, properly normalised, trial function is

$$f(\theta) = \frac{\alpha}{4\pi} \frac{\cosh(\alpha\cos(\theta))}{\sinh\alpha}. \qquad (7.31)$$

Here the parameter α controls the degree of orientation: for $\alpha = 0$ the distribution is uniform, and as α increases the function develops sharp peaks around the directions $\theta = 0$ and $\theta = \pi$, giving shapes similar to those shown in Fig. 7.4. Once again, we can characterise the degree of order in terms of the order parameter $\mathcal{S} = \int \frac{1}{2}\left(3\cos^2\theta - 1\right) f(\theta) \, \mathrm{d}\Omega$.

Using this function we can now use eqn 7.28 to evaluate the average value of $|\sin\gamma|$ as a function of the degree of orientation of the rods. This is shown in Fig. 7.19; for completely randomly oriented rods it takes the value $\pi/4$, and then as the rods get more aligned its value falls. We can similarly calculate the loss of orientational entropy as a function of the order parameter, and thus we can plot the contributions to the free energy. These are sketched in Fig. 7.20.

This plot summarises the physics of the hard-rod system. As the degree of ordering increases, there is an *increase* in free energy associated with the loss
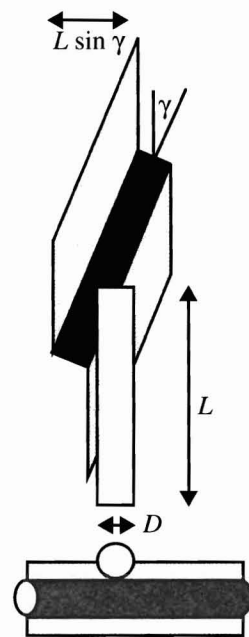

Fig. 7.18 Excluded volume in the interaction of two rods, each of length L and diameter D, with an angle γ between them. The presence of one rod means that a volume $DL^2|\sin\gamma|$ is inaccessible to the other rod.

[1] In fact it leads to an integral equation that needs to be solved numerically.
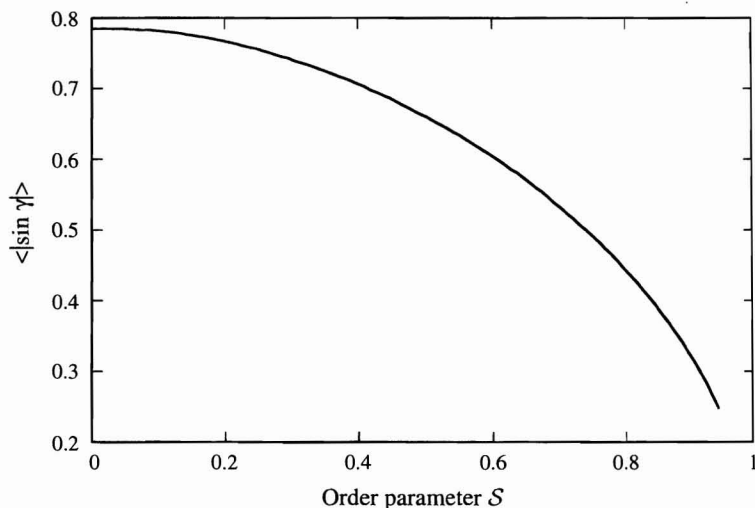
Fig. 7.19 The average value of the magnitude of the angle between two rods as a function of their degree of orientation.
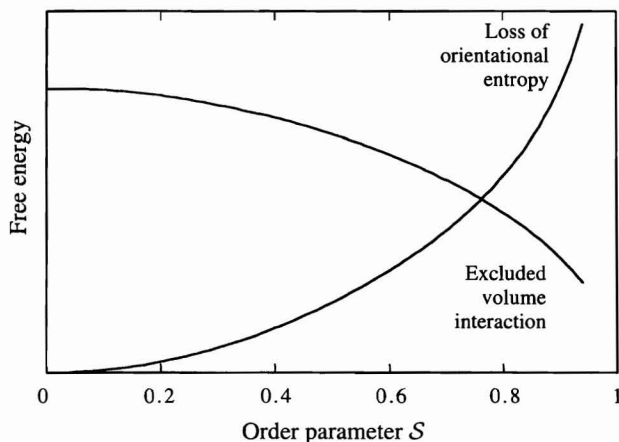

Fig. 7.20 Contributions to the free energy of a solution of hard rods as a function of their degree of orientation, as measured by the order parameter S. The relative importance of the two contributions depends on the product of the volume fraction of the rods and their aspect ratio.

of orientational entropy, but there is a *decrease* in the free energy arising from excluded volume interactions. The relative importance of the two terms depends on the quantity $\phi D/L$, the product of the volume fraction of the rods and their aspect ratio: as the volume fraction of the rods gets higher, or as the rods become more elongated, the excluded volume term becomes more important, and this can drive a phase transition into the nematic state.

This is illustrated in Fig. 7.21. For the lower value of the product $\phi L/D$, the free minimum energy state clearly occurs for $S = 0$; the equilibrium phase is an isotropic solution. But as this ratio is increased, a minimum appears in the free energy curve at a non-zero value of the order parameter S; a nematic phase has appeared. Analysis of the free energy curves reveals that there is a first-order phase transition from the isotropic to the nematic state. For values of $\phi L/D < 3.34$, the solution is isotropic. For values of $\phi L/D < 4.49$, the
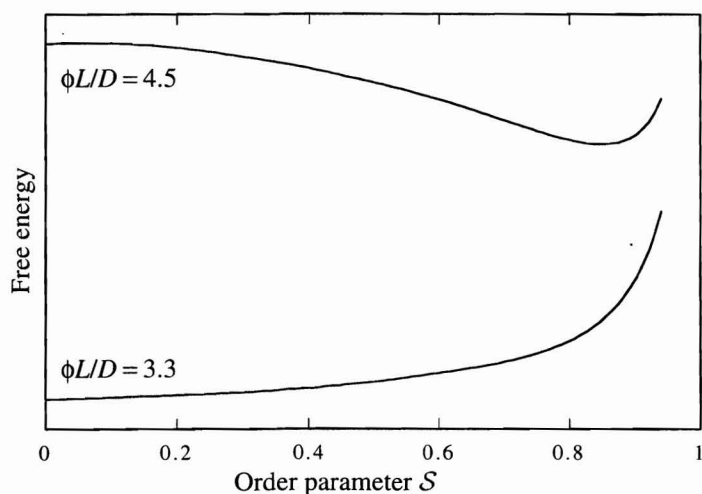
Fig. 7.21 The free energy of a solution of hard rods as a function of their degree of orientation, as measured by the order parameter S, for two values of the product of volume fraction and aspect ratio. For $\phi L/D = 3.3$, the lowest energy state is isotropic, but for the higher value of $\phi L/D = 4.5$ the equilibrium state has nematic order.
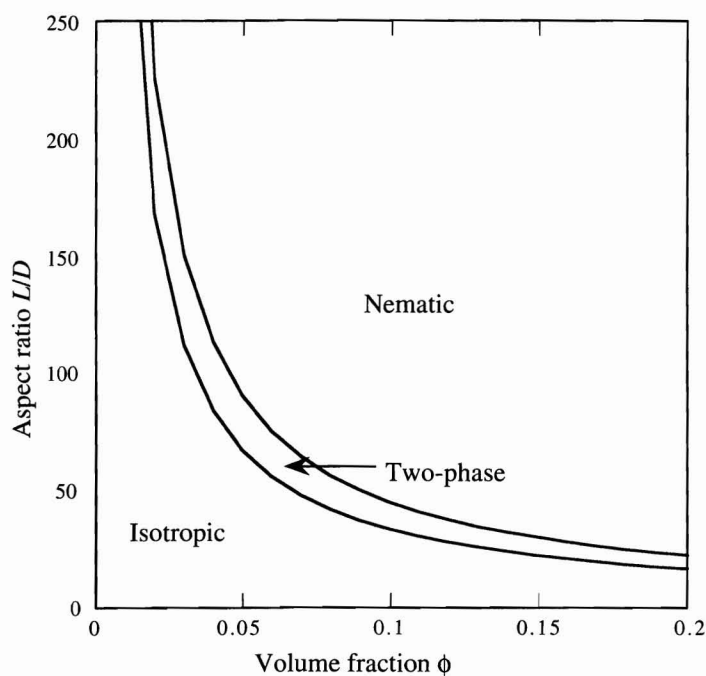
Fig. 7.22 The phase diagram of a solution of hard rods as a function of their volume fraction ϕ and aspect ratio L/D.

solution is nematic, while for values of $\phi L/D$ intermediate between these two limits, the solution separates into coexisting nematic and isotropic phases, with the order parameter in the nematic phase taking the value $S = 0.84$. The resulting phase diagram is shown as a function of ϕ and L/D in Fig. 7.22. One should note from this diagram that in order to obtain a liquid crystalline phase at a low volume fraction it is necessary to have rather a large aspect ratio.

7.7.4   Transitions in real lyotropic systems

Real polymer systems of the kind that form lyotropic phases differ from the ideal hard-rod systems discussed above in two ways:

1. Additional interactions, either attractive or repulsive, exist between the rods over and above the simple excluded volume interaction.
2. The rods may not be completely stiff.

These two factors can make the observed phase diagrams in real lyotropic systems considerably richer than those predicted from the theory of ideal hard rods.

The effect of rod–rod interactions is perhaps the most important. One can represent the effect of these interactions by an **interaction parameter** χ of the kind introduced in Chapter 3; this parameter represents in a dimensionless way the difference in energy between rod–rod, solvent–solvent, and rod–solvent interactions. Negative values of χ correspond to net repulsive interactions between the rods, while positive values of χ correspond to net attractive interactions. If they are strong enough, these attractive interactions can lead to liquid–liquid phase separation.

The resulting phase diagram can be calculated by different theoretical approaches which are beyond the scope of this treatment. We can, however, understand this phase diagram at a qualitative level. Figure 7.23 illustrates a phase diagram, calculated using a lattice theory due to Flory (see de Gennes and Prost 1993), for rods with an aspect ratio of 100. For repulsive interactions there is a narrow 'chimney' of two-phase coexistence; in this regime the behaviour is dominated by the excluded volume interaction. For attractive interactions (which normally become more important as the temperature is lowered) there is a region of what is essentially liquid–liquid phase separation, with the high volume fraction phase being nematic. There is a very narrow window of interaction parameters in which two nematic phases at different volume fractions coexist.

As the aspect ratio of the rods decreases, we would expect on the basis of our discussion of ideal hard rods that the volume fractions defining the two-phase chimney increase.

The other important complication in practical systems arises from the fact that physical systems are not perfectly stiff. Such chains are often referred to as **semi-flexible**. By this we mean that the statistical step length introduced in the discussion of random walks in Chapter 5 is significantly larger than the diameter of the chain, but still considerably less than the total length of the chain. In this case the phase diagrams are qualitatively similar to that shown in Fig. 7.22, but the volume fractions required to enter the nematic phase are considerably higher than in the rigid rod case and the degree of ordering in the nematic phase is somewhat less.

7.7.5   Thermotropic liquid crystal phases

Although a rigid or semi-rigid polymer such as PPTA (Fig. 7.14) forms liquid crystal phases in solution, it is difficult to obtain a liquid crystalline melt of the pure polymer. The melting point of the crystalline material is too high, and if heated the material will thermally decompose before the melting point is
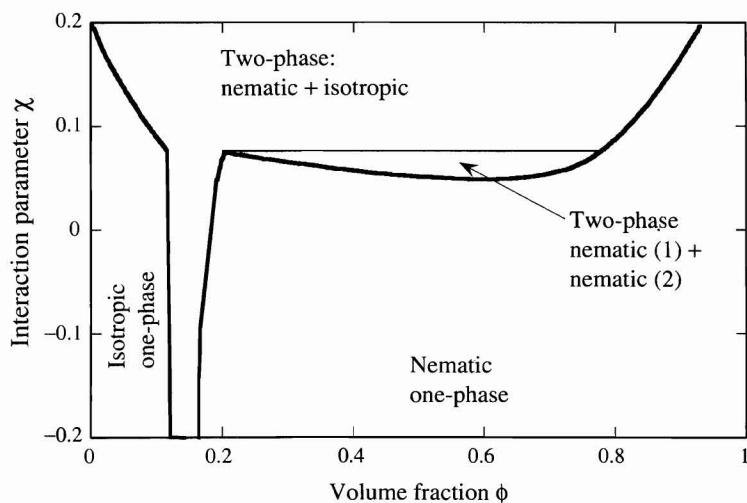
Fig. 7.23 The phase diagram of a solution of rigid rod-like polymers with an aspect ratio $L/D = 100$ as a function of their volume fraction ϕ and interaction parameter χ, as calculated from Flory's theory. Note that we would normally expect χ to decrease as the temperature is increased, so the corresponding diagram as a function of temperature would look inverted.

reached. To obtain a polymer that can be processed in the liquid crystalline melt state, one needs to be able to reduce the transition temperature from the crystal to the liquid crystal to an experimentally accessible value. Such materials are known as **thermotropic liquid crystalline polymers**. Among the strategies that can be employed to achieve this are:

- Inclusion of flexible units in the backbone. If the rigid units are separated by, for example, a $-(CH_2)_n-$ group, then the transition temperature from the crystal to liquid crystal phase is decreased as a function of increasing n.
- Use of a random copolymer. If two rigid units are copolymerised in a random way, the **quenched disorder** along the chain backbone will suppress the formation of a crystalline phase, while still permitting the formation of a liquid crystalline phase.
- Attachment of large, flexible side groups to the backbone. The melting point of a rigid polymer can be effectively reduced by attaching flexible side chains—typically aliphatic groups—to the backbone; the side chains can be thought of as acting like chemically attached solvent molecules. These materials are sometimes referred to as **hairy-rod** polymers. This approach also has the useful property that one can modify the solubility of such polymers in different solvents by modifying the chemical nature of the side groups. For an example of such a material, see Fig. 7.24.

Thermotropic liquid crystalline polymers have been explored commercially as high-specification structural materials; if they can be processed in the liquid crystalline state the high degree of molecular alignment leads to extremely high strength and stiffness. Another more recent application occurs in the field of semiconducting polymers. Such polymers have a conjugated backbone, which renders them insoluble and very difficult to process unless side groups can be attached, as in the example shown in Fig. 7.24. If, as a result of the attachment of such side groups, the materials show liquid crystalline phase behaviour then one can hope to process them in a way which maximises the degree of molecular order in the final electronic or optoelectronic device, and

Fig. 7.24 The chemical structure of a polyflu-orene, a class of conjugated polymers with a rigid rod backbone, which exhibits thermotropic liquid crystalline behaviour when aliphatic side groups of moderate length are attached (typically $m = 7$).
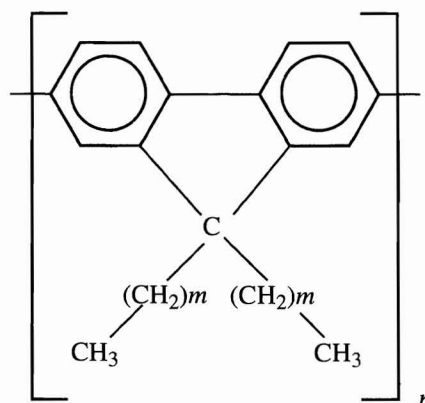
thus optimises the device parameters such as the charge carrier mobility or the degree of polarisation of emission.

Further reading

The theory of small-molecule liquid crystals is covered in de Gennes and Prost (1993); there is also much useful material in Chaikin and Lubensky (1995). Chandrasekhar (1992) is a more general monograph, covering theory, experiment, and the fundamentals of device applications. Polymer liquid crystals are described in Donald and Windle (1992).

Exercises

(7.1) In a simple model of a nematic/isotropic phase transition, the free energy change ΔF on going from the isotropic state to an ordered state with an order parameter S can be written as a function of temperature T as

$$\Delta F = \frac{1}{2}a(T - T^*)S^2 - wS^3 + uS^4,$$

where a, u, w, and T^* are positive constants.

a) Sketch curves of ΔF as a function of S for various values of temperature T for the following parameters: $a = 0.0033$; $T^* = 300$; $w = 0$; $u = 1$. What is the nature of the phase transition at $T = T^*$?

b) Sketch curves of ΔF as a function of S for temperatures T in the range 300–500 for the following parameters: $a = 0.0033$; $T^* = 300$; $w = 1$; $u = 1$. What is the nature of the phase transition now?

c) Show that for this model the nematic/isotropic transition occurs at a temperature T_c given by

$$T_c = T^* + \frac{w^2}{2au}.$$

d) Derive an expression for the order parameter at the transition S_c.

(7.2) You are asked to design a twisted nematic display, using a nematic liquid crystal whose elastic constants are given by $K_1 = 5.3 \times 10^{-12}$ N, $K_2 = 2.2 \times 10^{-12}$ N, and $K_3 = 7.45 \times 10^{-12}$ N. If the dielectric anisotropy $\epsilon_a = 0.7\epsilon_0$, what is the switching voltage?

(7.3) A biopolymer is observed to change from a helix to a coil state over a 5 K temperature interval centred on 343 K.

a) Using eqn 7.24, show that the width of the helix-coil transition in terms of the parameter s may be characterised by $\Delta s = 4\sigma^{1/2}$.

b) Assuming that s is a linear function of temperature close to the midpoint of the transition, estimate the free energy, in units of k_BT, associated with a junction between helical and coil sections, $\Delta F_g/k_BT$.

c) How would you expect the width of the transition as the length of the biopolymer is increased? What is the significance of this result?