Physics & Astronomy Faculty Works   Physics & Astronomy

2002

Liquid Crystals: Nature's Delicate Phase Of Matter

Peter J. Collings
Swarthmore College, pcollin1@swarthmore.edu

Recommended Citation

Peter J. Collings. (2002). 2nd ed. "Liquid Crystals: Nature's Delicate Phase Of Matter". *Liquid Crystals: Nature's Delicate Phase Of Matter*.
https://works.swarthmore.edu/fac-physics/194

Chapter 1

WHAT ARE LIQUID CRYSTALS?

ONE FAMOUS SCIENTIST once remarked that he found liquid crystals to be quite mysterious. Certainly the name itself is confusing. After all, how can something be both liquid and crystalline? We shall see in this chapter that in some cases a very interesting compromise spontaneously occurs in the natural world, and that the name used to describe the result of this compromise is quite appropriate. It will also be evident that liquid crystals come in a number of forms, creating an area of study rich in new and exciting phenomena.

STATES OF MATTER

We are all aware of the fact that many substances can exist in more than one state of matter. The most familiar example is water, which is a solid below 0°C (32°F), a liquid between 0 and 100°C (212°F), and a gas above 100°C. Solids, liquids, and gases are the most common states of matter, but in spite of what many children learn in school, they are not the only states of matter.

These three common states of matter are different from each other because the molecules in each state possess different amounts of order. The solid state consists of a more or less rigid arrangement of molecules because each molecule occupies a certain place in the arrangement and remains there. Not only are the molecules constrained to occupy a specific position, but they are also oriented in a specific way. The molecules might vibrate a bit, but on average they constantly maintain this highly ordered arrangement. There are large attractive forces holding the molecules of a solid in place, because the arrangement causes the forces between individual molecules to add together. It therefore takes large external forces to disrupt the structure, so solids are hard and difficult to deform.

The liquid state is quite different in that the molecules neither occupy a specific average position nor remain oriented in a particular way. The molecules are free to diffuse about in a random fashion, constantly bumping into one another and abruptly changing their direction of motion. The amount of order in a liquid is therefore much less than in a solid. Attractive forces still exist in a liquid, but the random motion of the molecules does not allow the forces between individual molecules to add together. The result is that the forces holding liquid molecules together tend to be much weaker than the forces in solids. These forces are strong enough, however, to keep

the molecules fairly close to each other. A liquid, therefore, maintains a constant density, even though it takes the shape of its container. The lack of a rigid arrangement allows liquids to be deformed quite easily. Liquids flow and will change their shape in response to weak outside forces. The fact that the molecules are held close together is evident when one tries to compress a liquid. Liquids are difficult to compress, a characteristic that is put to successful use in the hydraulic systems of automobile brakes and earth-moving equipment.

In the gaseous state, the more chaotic motion of the molecules causes the attractive forces between them to add together even less than in the liquid state. The amount of order is therefore less than in liquids, and the forces are not strong enough to hold the molecules close together. The molecules move about in the same fashion as in liquids, but they eventually spread evenly throughout the container no matter how large it is. Thus, the liquid and gaseous states are very similar; the motion of the molecules is random and disorganized in both states. But in the liquid state the molecules maintain a specific average distance between each other, while in the gaseous state the average intermolecular distance is determined by the number of molecules and the size of the container. A gas can be deformed even more easily than a liquid. In fact, a gas can be significantly compressed since it takes much less force to move the molecules a little closer together.

I should mention that the description I have given for the solid state is really appropriate for a crystalline solid. Some substances in the liquid state change into an amorphous solid rather than a crystalline solid when cooled. The molecules in an amorphous solid are fixed in place, but there is no overall pattern to the arrangement of these molecules. The molecules are arranged more or less randomly (similar to a snapshot taken in a liquid), but unlike in the liquid state, they do not diffuse throughout the substance. Some of the substances discussed in this book possess crystalline solid states while others possess amorphous solid states.

To understand why different substances form certain phases, we must consider the effects due to temperature. Temperature is a measure of the random motion of molecules. The higher the temperature, the more the molecules are moving and vibrating in a random way. Since the attractive forces between the molecules of a substance in a certain state of matter do not change with temperature (although the random motion of molecules does increase with temperature), the ability of the attractive intermolecular forces to keep the molecules ordered in any way must decrease as the temperature increases. Consider water for example. Below 0°C the attractive forces between the water molecules when arranged so rigidly are strong enough to hold the molecules firmly in place, even though they all possess random motion due to the temperature. Above 0°C, however, the random motion becomes too violent and the intermolecular forces cannot hold the molecules in place,

causing the solid to melt. The random motion causes the molecules to wander around, which reduces the forces holding the molecules together because the forces between molecules no longer add together as in the solid state. These forces, however, are still great enough to keep the molecules from wandering completely away from each other. The liquid takes up a specific amount of space. At a temperature above 100°C the random motion is so violent that the attractive forces are not even capable of keeping the molecules next to one another. The water is now in the gas phase, and the intermolecular forces are even weaker than in the liquid phase, because the forces between molecules add together even less. The molecules spread out to fill the available volume.

I can now make a generalization from our discussion concerning water. Every substance possesses intermolecular forces of some kind, so at any temperature, a substance exists in a specific state of matter. Scientists also use the word *phase* to describe a specific state of matter, and refer to the specific state as the stable phase at that temperature. For example, water at 20°C (68°F) is stable in the liquid phase. Carbon dioxide is stable in the gas phase at this temperature, and salt (sodium chloride) is stable in the solid phase. The intermolecular forces are different in these three substances, in each case causing a different phase to be stable at the same temperature.

When the temperature is changed so that the phase that was stable no longer is stable, the substance changes phase. The change of phase occurs at a precise temperature because at that temperature the ability of the inter-molecular forces to cause that phase to exist is no longer sufficient. We say a *phase transition* occurs at that temperature. The important change that takes place at a phase transition is the amount of order among the molecules of the substance.

In most cases the process is reversible. A liquid to solid phase transition occurs at 0°C for water if it is being cooled. The fact that any substance has phases that are stable over certain temperature ranges allows us to draw a single diagram for each substance summarizing its phase behavior. A horizontal line represents temperature, with higher temperature to the right. Phase transitions are indicated by short vertical lines at the proper temperature, and the names of the stable phases are written between the appropriate phase transition lines. The diagram for water is shown in figure 1.1.
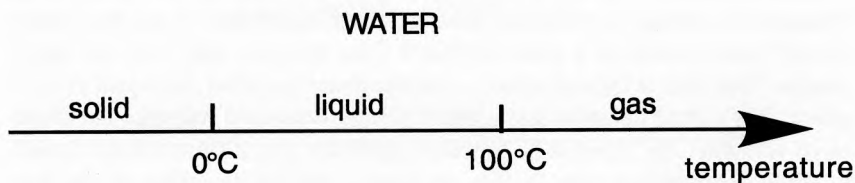
WATER

Fig. 1.1. Phase diagram of water. The stable phases of water are given above the temperature axis, with the phase transition temperatures shown below the axis.

Before I proceed, let me digress and mention a fourth state of matter called the *plasma* phase. It has nothing to do with liquid crystals, but it is a true state of matter just as the solid, liquid, and gaseous states are. If a substance is heated to a high enough temperature (and I do mean very high), the random motion becomes so violent that electrons that are normally bound to the atoms get knocked off. This phase of matter is composed of positively charged ions (atoms that have lost one or more electrons) and negatively charged electrons, which normally attract each other so strongly that the ions and electrons bind together. The temperature is so high, however, that the rate the ions and electrons bind together is equal to the rate the electrons are being knocked off atoms. Thus the substance exists in this state with unbound ions and electrons. It is a new phase of matter, one that normally exists in and around stars. Scientists presently create a plasma in their experiments on nuclear fusion. The temperatures of these plasmas are so high that scientists continue to learn new things about how matter behaves under these conditions.

THE LIQUID CRYSTAL PHASE

I will now complicate this picture one more time and discuss liquid crystals. Instead of doing an experiment with water, let's imagine that we have a substance called cholesteryl myristate and wish to investigate its phases. Cholesteryl myristate is a complicated molecule, composed mostly of carbon and hydrogen atoms. It is a fairly common substance, however, and can be found in our cell membranes and also in those nasty deposits that cause hardening of our arteries. At room temperature (20°C) it is in the solid phase, so we heat it up slowly and observe what takes place. At 71°C the solid melts, but the resulting "liquid" is very cloudy and not like other liquids such as water, alcohol, or cooking oil. If we keep raising the temperature, we notice that another change takes place at 85°C; here the cloudy "liquid" turns clear, now looking like other familiar liquids. We continue to heat up the substance; nothing further happens, and we reach the maximum temperature of our apparatus (200°C).

Based on what I have discussed, you may be thinking that these sharp changes at a specific temperature must be phase transitions. If so, the cloudy "liquid" must represent a phase different from both the solid and the liquid phases. This idea is indeed correct, and the phase is called the *liquid crystal* phase. It is a fluid phase in that a liquid crystal flows and will take the shape of its container. Its cloudiness, however, indicates that it differs from liquids in some fundamental way. It was no simple job for scientists of the late nineteenth and early twentieth centuries to put together a proper conception of this new state of matter. But through lots of experimentation and some

good creative thinking, a useful picture of the liquid crystal phase began to emerge. Before going any further, let us draw a diagram showing the phases of cholesteryl myristate (see figure 1.2). I am certain a gas phase of cholesteryl myristate exists at some high temperature, but the molecules begin to break apart at high temperatures. Therefore, it might be impossible to obtain a gas phase of the pure compound.

The molecules in a solid are constrained to occupy only certain positions. We describe this condition by saying that the solid phase possesses *positional order*. In addition, the molecules in these specific positions are constrained in the ways they orient themselves with respect to one another. We say the solid phase also possesses *orientational order*. When a solid melts to a liquid, both types of order are lost completely; the molecules move and tumble randomly. When a solid melts to a liquid crystal, however, the positional order may be lost although some of the orientational order remains. The molecules in the liquid crystal phase are free to move about in much the same fashion as in a liquid, but as they do so they tend to remain oriented in a certain direction. This orientational order is not nearly as perfect as in a solid; in fact, the molecules of a liquid crystal spend only a little more time pointing along the direction of orientation than along some other direction. Still this partial alignment does represent a degree of order not present in liquids and thus requires that we call this condition a new phase or state of matter. Figure 1.3 illustrates the order present in the solid, liquid crystal, and liquid phases.

How do we quantitatively describe the amount of orientational order present in a liquid crystal? Since the molecules are not fixed, we are forced to describe the order as some sort of average. For example, let us imagine that the direction of preferred orientation in a liquid crystal is toward the top or bottom of the page. This direction can be represented by a vertical arrow, called the *director* of the liquid crystal. There are always two choices as to which way the director points (up or down in this example). The two directions are equivalent in the liquid crystal, so either choice is fine. One way we could visualize performing an average is to take a snapshot of a rep-
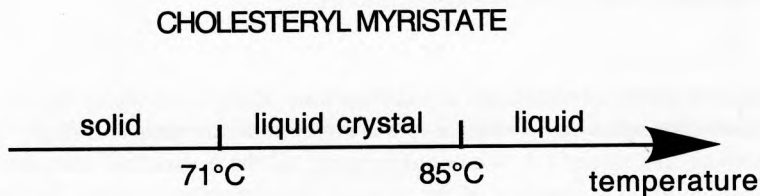
CHOLESTERYL MYRISTATE

Fig. 1.2. Phase diagram of cholesteryl myristate. A gas phase is not shown, because the molecule decomposes at high temperatures.
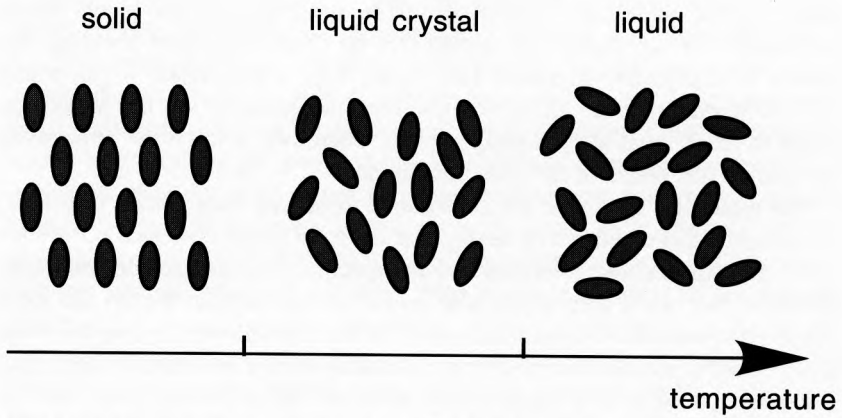
CHAPTER ONE

solid   liquid crystal   liquid

temperature

Fig. 1.3. Schematic illustration of the solid, liquid crystal, and liquid phases. The elliptical shapes represent molecules.
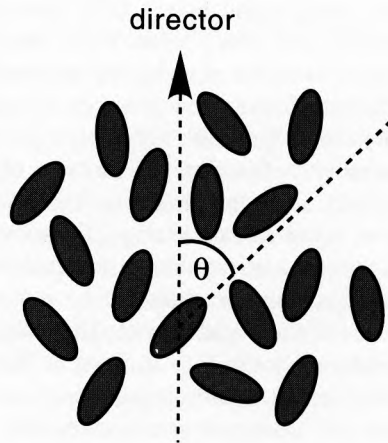
director

Fig. 1.4. A snapshot of the molecules in the liquid crystal phase. The dashed arrow (director) shows the direction of preferred orientation. Each molecule makes an angle with the director (shown for one molecule as θ).

resentative group of molecules at a certain time. Each molecule in our picture is oriented at some angle relative to the director, so our snapshot might look something like figure 1.4. We could measure all the angles and compute the average angle as a measure of the amount of orientational order. The more orientational order present, the closer the average angle would be to zero. A snapshot of the molecules in a liquid with no orientational order would

yield values for the angle between 0° and 90°, with angles representing all possible directions distributed at random. We must keep in mind that this random arrangement occurs in three dimensions. Innumerable orientations make an angle of 90° to the director, but only one makes an angle of 0°. There will therefore be many more molecules making angles of 90° with the director as compared to 0°. If we average these measurements, the larger number of molecules oriented at larger angles produces a result greater than 45° (57° to be exact). Using this scheme, therefore, no orientational order means an average angle of 57°, with smaller angles indicating the presence of orientational order. The most order possible (complete alignment) would give an average angle of 0°.

There is nothing wrong with this procedure, but for many reasons a different method is more useful. In this new procedure, the angle the molecule makes with the director is not averaged; instead, the function $(3\cos^2\theta - 1)/2$ is averaged. Since the cosine of 0° is 1, perfect orientational order (all angles equal to 0°) causes this average to equal 1. In addition, in a liquid with no orientational order, the average of this function is 0. This is a more meaningful range of values, and the average of this function is called the *order parameter* of the liquid crystal. It is an extremely important quantity. The order parameter of a liquid crystal decreases as the temperature is increased and, as can be seen in figure 1.5, typical values for the order parameter are between 0.3 and 0.9.
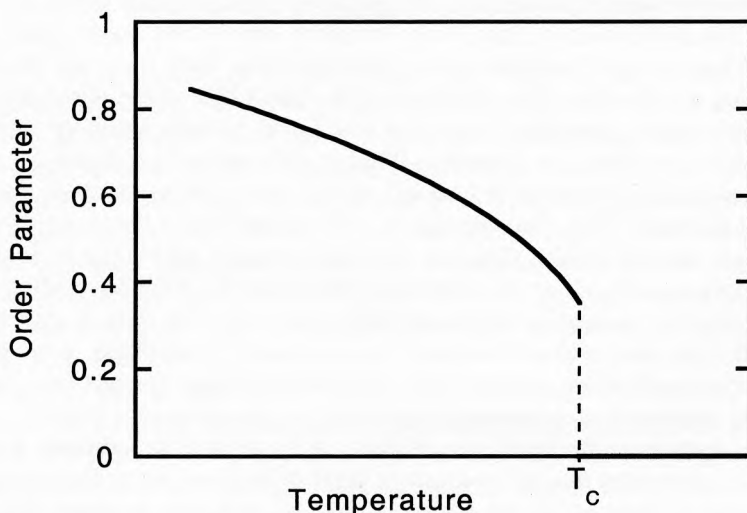

Fig. 1.5. Order parameter variation with temperature in the liquid crystal phase. T_C represents the transition temperature to the liquid phase.

We could have performed this average in another way. Imagine following a single molecule, taking pictures of it at regular intervals. You can imagine measuring the angle in each of these pictures and using them all to perform the average. Do you expect that the averages performed in these two different ways would yield different values for the order parameter? The answer is no if you assume that all molecules undergo the same type of random motion. If this assumption is true, the orientation one molecule has now is the same as another molecule has at some other time. Performing an average of one molecule's orientation at many times should be equivalent to performing an average of many molecules' orientations at any one time. Interestingly enough, in all the experiments performed on liquid crystals over the past one hundred years, none of the results have ever contradicted this assumption.

Is a liquid crystal more like a solid or a liquid? This question is important because it turns out that there is a definite answer. When a phase transition takes place from solid to liquid, for example, energy must be supplied to the substance to disrupt the attractive forces that hold the solid together in a highly ordered arrangement. An analogy is the energy you must supply in order to pull two magnets apart. If ice is the substance, you must supply 80 calories of energy for each gram of ice in order to melt it. Likewise, it takes energy to pull the molecules of a liquid away from each other in changing to the gas phase. For example, a gram of water must be supplied with 540 calories of energy before it will all be changed to steam. The amount of energy required to cause a phase transition is called the *latent heat* of the transition and is a useful measure of how different the two phases are. In the case of cholesteryl myristate, the latent heat of the solid to liquid crystal transition is 65 calories/gram, while the latent heat for the liquid crystal to liquid transition is 7 calories/gram. These numbers allow us to answer the question posed earlier. The smallness of the latent heat of the liquid crystal to liquid phase transition is evidence that liquid crystals are more similar to liquids than they are to solids. When a solid melts to a liquid crystal, it loses most of the order it had and retains only a bit more order than a liquid possesses. This small amount of order is then lost at the liquid crystal to liquid phase transition. The fact that liquid crystals are similar to liquids, with only a small amount of additional order, is the key to understanding the many physical properties that make them nature's delicate state of matter.

Although most molecules do not form a liquid crystal phase, it is not a rare occurrence when one does. It is said that an organic chemist indiscriminately synthesizing compounds would find out that about one in every two hundred possesses the liquid crystal phase. After years of experiments, it has become clear what type of molecule is likely to be liquid crystalline at some temperature. First of all, the molecule must be elongated in shape; that is, it must be significantly longer than it is wide. Second, the molecule must have some rigidity in its central region. A molecule that flops around like a

piece of cooked spaghetti is unlikely to have a liquid crystal phase. Finally, it seems to be advantageous if the ends of the molecule are somewhat flexible. A good model of a typical liquid crystal molecule is therefore a short pencil with a short piece of cooked spaghetti attached to each end. Why this model works is not difficult to understand. Elongated molecules usually have stronger attractive forces when they are aligned parallel to one another. In addition, elongated molecules bump into each other less when they all tend to point in the same direction, a fact that acts to stabilize aligned phases. The importance of the flexible ends is a bit more subtle. The flexibility seems to allow one molecule to position itself more easily between other molecules as they all move about.

Although it is possible to observe and identify liquid crystals in bulk samples, one of the most useful and beautiful ways to observe this phase is under a microscope. First, some liquid crystal is placed between two pieces of glass. The thickness of the liquid crystal sample usually is kept small so that light can easily pass through it. The liquid crystal sample is positioned between two polarizers, which are adjusted so that they cross each other. This arrangement would normally ensure that no light comes through to your eye; but, because of the orientational order of liquid crystals, light does reach your eye. (I will discuss polarized light at length later.) Instead, you see a collection of curved lines as shown in plate 1. The lines you see in the microscope are due to defects within the liquid crystal, which also will be discussed later. The name for the liquid crystal phase I have been discussing stems from these defect lines, which reminded some of the early scientists of threads; so the name *nematic* liquid crystal comes from the Greek word for thread.

As is often the case in science, things turn out to be more complicated than they first appear. Molecules that possess intermolecular forces and stay parallel to one another form the nematic liquid crystal phase just as I have described. Molecules with intermolecular forces that favor alignment between molecules at a slight angle to one another form a slightly different phase. In this liquid crystal phase, the director is not fixed in space as in a nematic phase; it rotates throughout the sample. A representation of this phase is shown in figure 1.6, again using elliptical shapes to represent the molecules. The molecules appear shorter at some points in the diagram because they are viewed head-on.

The best way to visualize the helical pattern formed by the director as it changes its direction is to imagine the motion of a nut as you screw it onto a bolt. As you rotate the nut around and around, the nut moves along the axis of the bolt. This is exactly what the director does in this type of liquid crystal.

Notice that it takes the director a certain distance to rotate one full turn, just as the nut moves a certain distance along the axis of the bolt as it is rotated
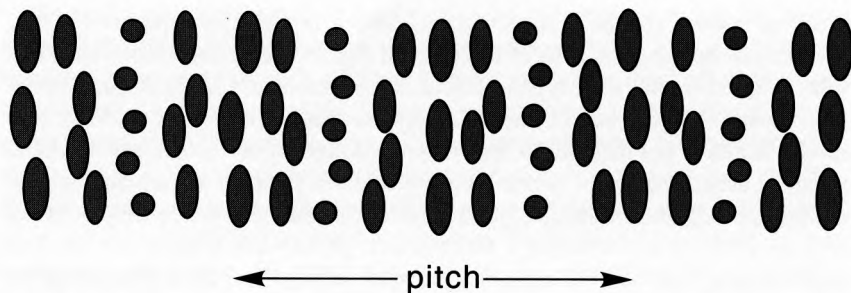
← —————— pitch —————— →

Fig. 1.6. Snapshot of the molecules in the chiral nematic liquid crystal phase. The direction of preferred orientation (director) rotates about a horizontal axis in the plane of the page. The pitch is the distance for one full director rotation.

one complete turn. This distance is called the *pitch* of the liquid crystal. In actuality, the twisted structure repeats itself over a distance equal to one-half the pitch, since the director can always be defined pointing in either direction along the preferred direction. This fact will be important when we discuss how light interacts with these twisted liquid crystals.

The most common examples of molecules forming this phase are closely associated with cholesterol, so we call them *cholesteric* liquid crystals. Cholesteryl myristate has a cholesteric liquid crystal phase. The term cholesteric is not a good one, however, since there are many cholesteric liquid crystals that have no connection with cholesterol whatsoever. A more proper name for this phase is *chiral nematic* liquid crystal (chiral simply means twisted). The twist present in chiral nematic liquid crystals produces some spectacular optical properties. I will discuss them later, but some of these properties make chiral nematic liquid crystals appear quite different under a microscope.

Plate 2 shows an example of a chiral nematic liquid crystal under the microscope; notice that defect lines are still present, but the patterns are different due to the twist inherent in the sample. The liquid crystal in plate 2 is oriented with the helical axis along the direction of viewing (perpendicular to the page). This is called the *Grandjean texture*, after the French scientist F. Grandjean, who worked with similar samples around 1920. Plate 3 shows another picture of a chiral nematic liquid crystal, but the helical axes in this sample are perpendicular to the viewing direction. The pitch of this liquid crystal is long enough to be visible under the microscope, so all the lines in the picture are points where the director rotates back to the same position. When this occurs, it is called the *fingerprint texture*.

A substance may possess either the nematic liquid crystal phase or the chiral nematic liquid crystal phase but not both. However, there is another type of liquid crystal phase that can occur as the only liquid crystal phase a

substance possesses or at a temperature below the nematic or chiral nematic phase of a substance. This third liquid crystal phase is called the *smectic* phase, from the Greek word for soap. The early investigators noticed that these liquid crystal phases possessed mechanical properties reminiscent of soaps. In fact, the thick "goo" usually found in the bottom of a soap dish is a liquid crystal phase (we will discuss this type later) and has all the properties of a smectic liquid crystal. In the smectic phase, not only is the small amount of orientational order of liquid crystals present, but there is also a small amount of positional order. Again, the molecules are free to bounce around quite randomly, but in this phase they tend to point along the director and arrange themselves in layers. To be more exact, a snapshot in time would reveal that slightly more molecules tend to be positioned in regularly spaced planes with fewer molecules in between. Likewise, following a single molecule would reveal that it spent slightly more time in these planes than between these planes. Figure 1.7 illustrates this small amount of both orientational and positional order. Notice that there are two slightly different smectic phases. In the smectic A phase the director is perpendicular to the
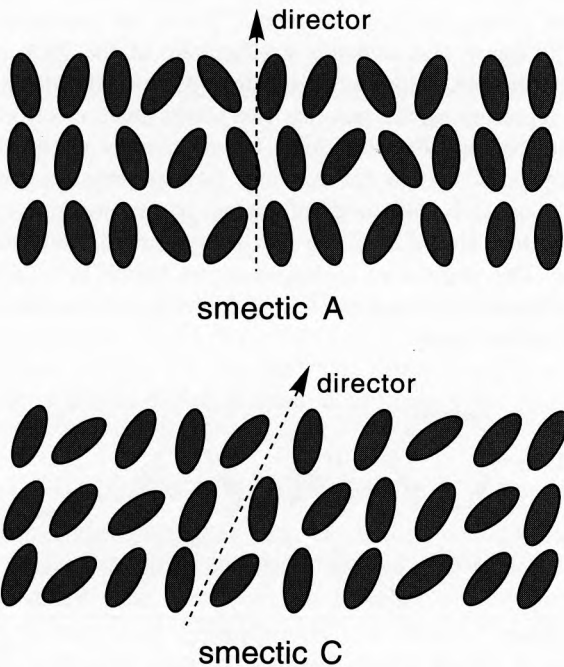

Fig. 1.7. Snapshot of the molecules in two types of smectic liquid crystal phases. The director is perpendicular to the layers in the smectic A phase but makes an angle other than 90° in the smectic C phase.

planes, while in the smectic C phase the director makes an angle other than 90° to the planes. Smectic liquid crystals have a unique appearance under the microscope; an example can be found in plate 4.

In both the smectic A and smectic C phases, the molecules randomly diffuse within each plane. No positional order exists within each plane, so in a sense the positional order is in one dimension only. However, other smectic liquid crystal phases exist in which the molecules are somewhat ordered within each plane. In other words, a molecule diffusing through the plane spends more time at special locations than at other locations. The positional order is three-dimensional now. Various arrangements of these special locations are possible, and these phases have been given names like smectic B or smectic E. The designation of smectic phases by letters is more historical than physical, in that additional letters have been used each time a new smectic phase is discovered. A recent list of these smectic phases included the letters A through K. The additional order of these smectic phases makes them appear quite different under a microscope. Plate 5 is a picture of a smectic B phase.

Although many compounds exhibit only one liquid crystal phase, it is not unusual for a single substance to possess more than one. A compound called *p*-azoxyanisole (PAA) has only a nematic phase; its phases are shown in figure 1.8. The figure also contains a schematic of the PAA molecule. In diagrams of molecules, letters are used to represent the atoms, with short straight lines representing the fact that two atoms share electrons and therefore are bound together. For simplicity, however, some of the carbon atoms are denoted by points where one or more lines (representing bonds) meet. The hydrogen atoms bound to these carbon atoms are also omitted. You can tell where they are by realizing that every carbon atom must share its four electrons. The number of hydrogen atoms bound to a carbon atom is therefore four minus the number of lines (other bonds) coming together to represent the carbon atom.
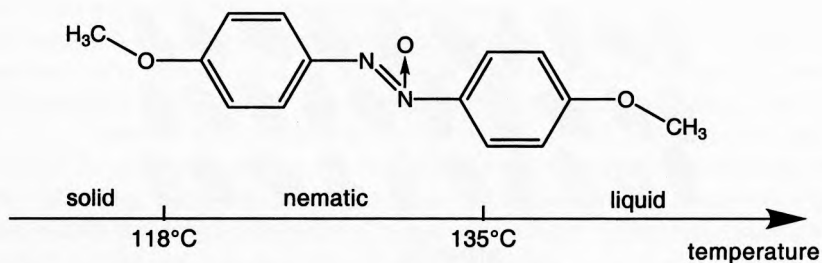

Fig. 1.8. Phase diagram for *p*-azoxyanisole (PAA). In the diagram of the molecule, intersecting lines (which represent chemical bonds) denote carbon atoms. For simplicity, the hydrogen atoms bonded to these carbon atoms have been omitted.
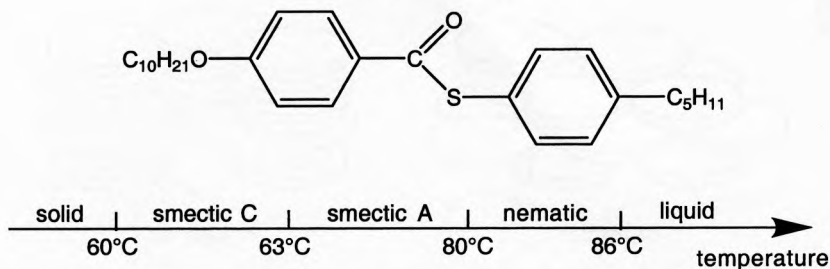
solid		smectic C		smectic A		nematic		liquid
	60°C		63°C		80°C		86°C	

temperature

Fig. 1.9. Phase diagram and molecular structure of 4-*n*-pentylbenzenethio-4'-*n* decyloxybenzoate ($\overline{10}$S5).

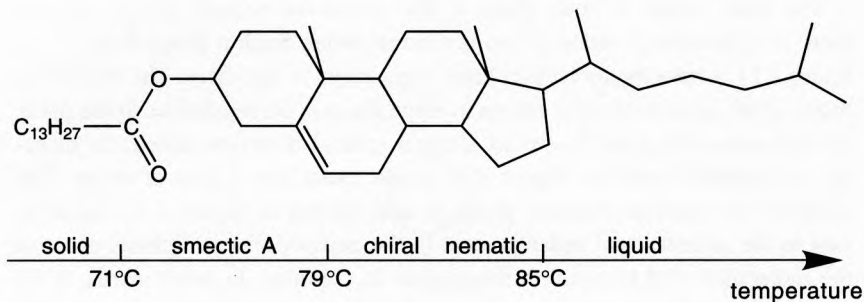| solid		smectic A		chiral nematic		liquid
	71°C		79°C		85°C	

temperature

Fig. 1.10. Complete phase diagram for cholesteryl myristate along with its molecular structure.

A compound slightly different from PAA is called 4-*n*-pentylbenzenethio-4'-*n*-decyloxybenzoate ($\overline{10}$S5 for short!). It possesses three liquid crystal phases, as shown in figure 1.9. Cholesteryl myristate has both a chiral nematic and a smectic A phase; its full diagram is in figure 1.10.

DISCOTIC LIQUID CRYSTALS

So far the entire discussion has been devoted to *calamitic* liquid crystals, that is, the phases formed by rodlike molecules. The reason for this is simple; these phases are the most common liquid crystal phases and therefore the most well-known. In 1977, however, researchers in India discovered that disclike molecules also form liquid crystal phases in which the axis perpendicular to the plane of the molecule tends to orient along a specific direction. These phases and the molecules that form them are called *discotic* liquid crystals.
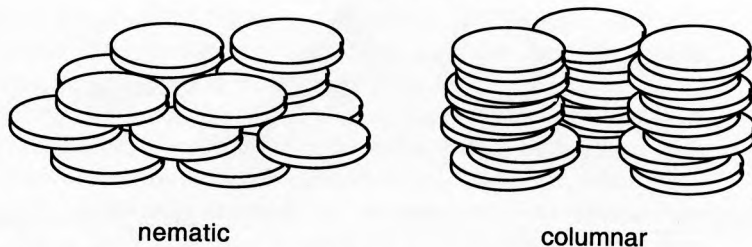
nematic   columnar

Fig. 1.11. Illustration of the nematic and columnar discotic liquid crystal phases. The flat discs represent molecules.

The most simple discotic phase is also called the *nematic* phase, because there is orientational order but no positional order. Such a phase is shown in figure 1.11, where the molecules have been drawn as flat discs. The molecules move about quite randomly, but on average the axis perpendicular to the plane of each molecule tends to orient along a special direction called the director. As evident from the figure, this phase looks like a pile of coins. The *columnar* or *smectic* discotic phase is also shown in figure 1.11. In addition to the orientational order present in the nematic discotic phase, most of the molecules tend to position themselves in columns. In other words, at all times more molecules are located in the columns than between columns. The columns are arranged in a hexagonal lattice. A nice analogy to this phase is a set of stacked coins, with the stacks positioned in the centers and vertices of connected hexagons. However, one must be careful about such analogies. The coins in a stack have a great deal of positional order (i.e., the distance between coins is fixed and the same for all coins), whereas the molecules of a columnar or smectic discotic liquid crystal are positioned in the stack quite randomly. The positional order in this phase is therefore two-dimensional. *Chiral nematic* discotic liquid crystals also exist. In this phase the director rotates in a helical fashion throughout the sample, just as in the case of rodlike chiral nematic liquid crystals. An example of a molecule possessing discotic liquid crystal phases is shown in figure 1.12 along with a temperature diagram of these phases. Notice that this molecule has a fairly rigid, planar center with hydrocarbon chains emanating in all directions. These features are common to just about all discotic liquid crystal molecules.

Although the structure of discotic liquid crystals is quite different from that of other types of liquid crystals, their appearance under the microscope is similar. Plate 6 shows a "crystal" of a discotic liquid crystal as it forms from the isotropic liquid.
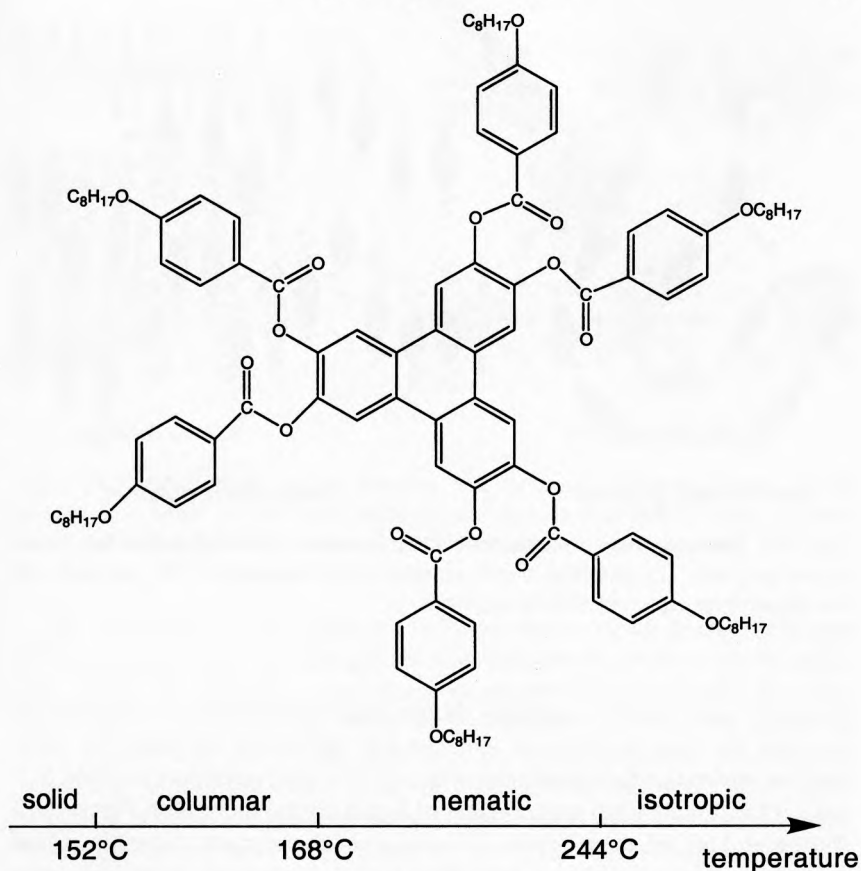
solid   columnar   nematic   isotropic

152°C   168°C   244°C   temperature

Fig. 1.12. Phase diagram and molecular structure of a typical discotic liquid crystal.

OTHER TYPES OF LIQUID CRYSTALS

One area of modern technology that also deals with liquid crystal phases is the polymer industry. *Polymers* are extremely long and slender molecules that form when chemical reactions link shorter molecules together. A bowl of cooked spaghetti is an especially good model for most polymers. Two types of polymers give rise to liquid crystal phases. The first is composed of fairly rigid segments (like the central part of a liquid crystal molecule) connected together end to end by flexible segments (like the ends of a liquid crystal molecule). Although these long polymers move around and collide with each other in the liquid crystal phase, the rigid segments tend to remain pointing in one direction. The second type of polymer is one composed of a single, completely flexible polymer with rigid segments attached as side chains along its

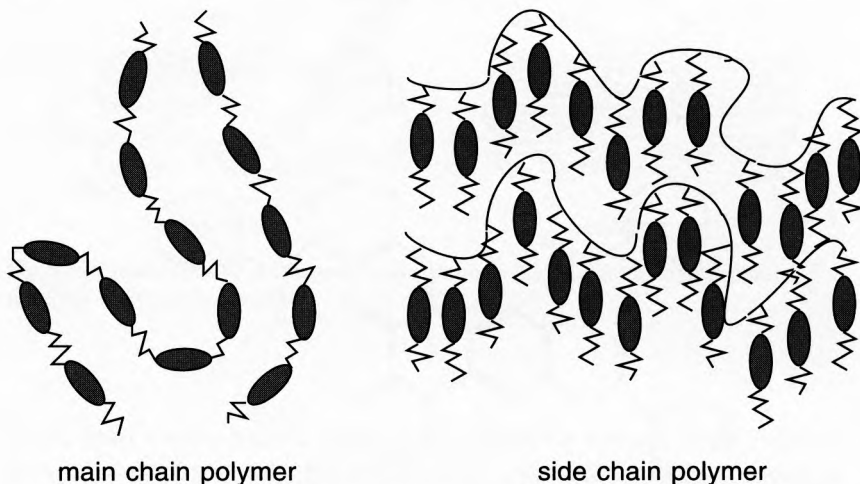main chain polymer   side chain polymer

Fig. 1.13. Illustration of the orientational order in a main chain and a side chain liquid crystal polymer. The elliptical shapes represent rigid segments of the polymer, and the zigzag lines represent flexible segments.

length by short flexible segments. In the liquid crystal phase of this type of polymer, the long flexible part winds its way throughout the substance without any orientational or positional order, but the rigid segments attached to it exhibit the orientational order typical of liquid crystal molecules. Figure 1.13 illustrates both of these types of liquid crystal polymers. Nematic, chiral nematic, and smectic phases have been found in polymers, with some possessing more than one liquid crystal phase. Their appearance under a microscope resembles that of other liquid crystals in many ways. A photograph of a nematic polymer liquid crystal is shown in plate 7. Liquid crystal polymers are an exciting new field of modern technology, which is covered in some depth in chapter 9.

Before our introduction to the liquid crystal phase can be complete, we must consider one other class of compounds in which liquid crystal phases are important. In the discussion thus far, we have considered only pure substances, and temperature changes have caused the liquid crystal phases to come and go. We call this class of liquid crystal substances *thermotropic* liquid crystals. In some cases when two different substances are mixed together, the mixture can exhibit different phases not only as the temperature is changed but also as the concentration of one component of the mixture is varied. When the liquid crystal phase is dependent on the concentration of one component in another, we call such a system a *lyotropic* liquid crystal.
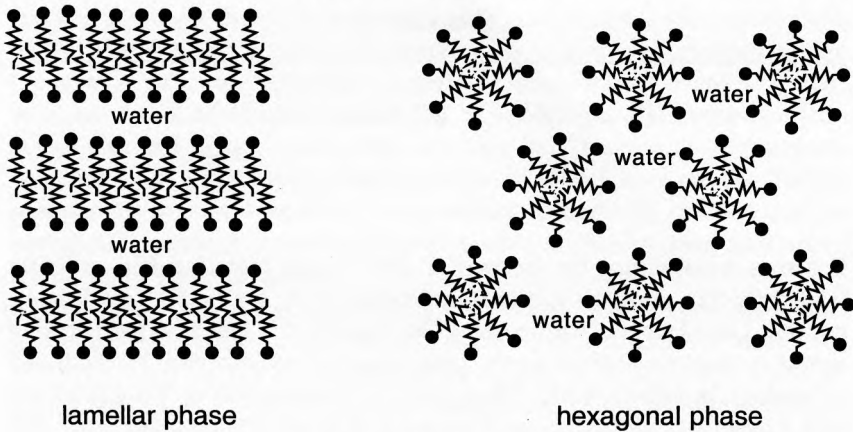
lamellar phase   hexagonal phase

Fig. 1.14. Cross-sections of the lamellar and hexagonal lyotropic liquid crystal phases. The round end of each molecule represents a hydrophilic (water-seeking) group, while the zigzag line depicts a hydrophobic (water-fearing) group.

The easiest way to put together a lyotropic liquid crystal mixture is to start with a molecule that has end groups with different properties. For example, one end of the molecule could show an affinity for water while the other end tends to exclude water. When such molecules are placed in water, the ends that exclude water tend to arrange themselves together, allowing the other end of the molecules to be in contact with the water. This effect results in structures of various shapes (spheres and cylinders are common), which themselves can be positioned in a very specific arrangement. Again the molecules are free to roam about. But as they do so, they retain the orientational and positional order due to these structures, and are therefore proper liquid crystalline phases. We can represent molecules of this type by a circle (water-seeking) connected to a tail (water-excluding). Two of the many structures these molecules form are shown in figure 1.14.

There are two important examples of molecules that behave as I have been describing. The first is soap molecules, and the ability of soap to dissolve oil and dirt is directly related to the ordered structures the soap molecules form in water. The second example is biologically important molecules called *phospholipids*. The ordered structures these molecules form are found everywhere in biological systems and include the cell membrane itself. In both of these types of molecules, one end of the molecule is charged and tends to associate with water while the other end is composed mostly of carbon and hydrogen, which tend to exclude water. Lyotropic liquid crystals are important not only for their biological significance but also because of their use as surfactants. Chapter 8 addresses both of these areas.