Liquid Crystal Phases

The liquid crystal state is a distinct phase of matter observed between the crystalline (solid) and isotropic (liquid) states. There are many types of liquid crystal states, depending upon the amount of order in the material. This section will explain the phase behavior of liquid crystal materials.

Nematic Phases

The nematic liquid crystal phase is characterized by molecules that have no positional order but tend to point in the same direction (along the director). In the following diagram, notice that the molecules point vertically but are arranged with no particular order.

Liquid crystals are anisotropic materials, and the physical properties of the system vary with the average alignment with the director. If the alignment is large, the material is very anisotropic. Similarly, if the alignment is small, the material is almost isotropic.

The phase transition of a nematic liquid crystal is demonstrated in the following movie provided by Dr. Mary Neubert, LCI–KSU. The nematic phase is seen as the marbled texture. Watch as the temperature of the material is raised, causing a transition to the black, isotropic liquid.

A special class of nematic liquid crystals is called chiral nematic. Chiral refers to the unique ability to selectively reflect one component of circularly polarized light. The term chiral nematic is used interchangeably with cholesteric. Refer to the section on cholesteric liquid crystals for more information about this mesophase.

Smectic Phases

The word "smectic" is derived from the Greek word for soap. This seemingly ambiguous origin is explained by the fact that the thick, slippery substance often found at the bottom of a soap dish is actually a type of smectic liquid crystal.

The smectic state is another distinct mesophase of liquid crystal substances. Molecules in this phase show a degree of translational order not present in the nematic. In the smectic state, the molecules...
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maintain the general orientational order of nematics, but also tend to align themselves in layers or planes. Motion is restricted to within these planes, and separate planes are observed to flow past each other. The increased order means that the smectic state is more "solid-like" than the nematic.

Many compounds are observed to form more than one type of smectic phase. As many as 12 of these variations have been identified, however only the most distinct phases are discussed here.

In the smectic–A mesophase, the director is perpendicular to the smectic plane, and there is no particular positional order in the layer. Similarly, the smectic–B mesophase orients with the director perpendicular to the smectic plane, but the molecules are arranged into a network of hexagons within the layer. In the smectic–C mesophase, molecules are arranged as in the smectic–A mesophase, but the director is at a constant tilt angle measured normally to the smectic plane.

As in the nematic, the smectic–C mesophase has a chiral state designated C*. Consistent with the smectic–C, the director makes a tilt angle with respect to the smectic layer. The difference is that this angle rotates from layer to layer forming a helix. In other words, the director of the smectic–C* mesophase is not parallel or perpendicular to the layers, and it rotates from one layer to the next. Notice the twist of the director, represented by the green arrows, in each layer in the following diagram.
In some smectic mesophases, the molecules are affected by the various layers above and below them. Therefore, a small amount of three dimensional order is observed. Smectic–G is an example demonstrating this type of arrangement.

**Cholesteric Phases**

The **cholesteric** (or chiral nematic) liquid crystal phase is typically composed of nematic mesogenic molecules containing a chiral center which produces intermolecular forces that favor alignment between molecules at a slight angle to one another. This leads to the formation of a structure which can be visualized as a stack of very thin 2–D nematic–like layers with the director in each layer twisted with respect to those above and below. In this structure, the directors actually form in a continuous helical pattern about the layer normal as illustrated by the black arrow in the following figure and animation. The black arrow in the animation represents director orientation in the succession of layers along the stack.

The molecules shown are merely representations of the many chiral nematic mesogens lying in the slabs of infinitesimal thickness with a distribution of orientation around the director. This is not to be confused with the planar arrangement found in smectic mesophases.

An important characteristic of the cholesteric mesophase is the **pitch**. The pitch, \( p \), is defined as the distance it takes for the director to rotate one full turn in the helix as illustrated in the above animation. A byproduct of the helical structure of the chiral nematic phase, is its ability to selectively reflect light of wavelengths equal to the pitch length, so that a color will be reflected when the pitch is equal to the corresponding wavelength of light in the visible spectrum. The effect is based on the temperature dependence of the gradual change in director orientation between successive layers (illustrated above), which modifies the pitch length resulting in an alteration of the wavelength of reflected light according to the temperature. The angle at which the director changes can be made larger, and thus tighten the pitch, by increasing the temperature of the molecules, hence giving them more thermal energy. Similarly, decreasing the temperature of the molecules increases the pitch length of the chiral nematic liquid crystal. This makes it possible to
build a liquid crystal thermometer that displays the temperature of its environment by the reflected color. Mixtures of various types of these liquid crystals are often used to create sensors with a wide variety of responses to temperature change. Such sensors are used for thermometers often in the form of heat sensitive films to detect flaws in circuit board connections, fluid flow patterns, condition of batteries, the presence of radiation, or in novelties such as "mood" rings.

In the fabrication of films, since putting chiral nematic liquid crystals directly on a black background would lead to degradation and perhaps contamination, the crystals are micro–encapsulated into particles of very small dimensions. The particles are then treated with a binding material that will contract upon curing so as to flatten the microcapsules and produce the best alignment for brighter colors. An application of a class of chiral nematic liquid crystals which are less temperature sensitive is to create materials such as clothing, dolls, inks and paints.

The wavelength of the reflected light can also be controlled by adjusting the chemical composition, since cholesterics can either consist of exclusively chiral molecules or of nematic molecules with a chiral dopant dispersed throughout. In this case, the dopant concentration is used to adjust the chirality and thus the pitch.

**Columnar Phases**

![Columnar Phases](image)

Columnar liquid crystals are different from the previous types because they are shaped like disks instead of long rods. This mesophase is characterized by stacked columns of molecules. The columns are packed together to form a two–dimensional crystalline array. The arrangement of the molecules within the columns and the arrangement of the columns themselves leads to new mesophases.

**Phase Transition Simulation**

The following simulation demonstrates the phase behavior of liquid crystal materials. As has been shown, temperature determines the phase of the material.

![Phase Changes in Liquid Crystals](image)
phase transitions but requires considerable experience, particularly in the study of new and less familiar materials.

The following movie, provided by Dr. Mary Neubert, LCI–KSU, presents a view of an actual liquid crystal phase transition. Watch as the material, initially in the nematic state, changes abruptly into the solid crystalline form as the temperature is lowered.

![Movie Frame](image)

X–Rays provide a much more definitive means for the identification of mesophases but we choose not to discuss those methods here.

**Differential Scanning Calorimetry**

Differential Scanning Calorimetry (DSC) is a useful tool which complements optical methods in the study of liquid crystal phase transitions. Its utilization in determining the heat supplied or extracted during a process such as a phase transition is discussed in *Thermal Properties of Polymers*.

In the following two figures, furnished by Prof. Charles Rosenblatt (Dept. of Physics, Case Western Reserve University), DSC traces obtained with a small sample of 8 OCB (octyloxy cyanobyphenyl) at a rate of 1° C/min are displayed to illustrate its use with liquid crystals. The lower curve in Figure (a) corresponds to a heating process. This is followed by a cooling process, represented in the upper curve.

A phase diagram bar illustrating the heating process is placed just above the temperature axis (at one atmosphere pressure). This includes a crystal to liquid crystal (smectic A) transition at 55 °C followed by a barely detectable smectic A to nematic transition at 67 °C and finally the nematic to isotropic (NI) transition near 80 °C. The upper, cooling, curve shows a slight displacement of the NI transition, partially due to supercooling and partially instrumental hysteresis attributable to the temperature scan rate. The smectic A to crystal transition is depressed strongly due to supercooling of the smectic A phase. Thus, the phase diagram for the cooling process would not be identical to that for heating.

![DSC Traces](image)
Figure (a) : DSC plot with phase diagram

Figure (b) is a repeat of this run, beginning to heat at a temperature above the crystal to smectic A transition so that greater sensitivity could be employed. This makes the smectic A to nematic transition more visible and illustrates the capability of the DSC method is detecting subtle effects.

Figure (b) : DSC plot

For more information and images relating to liquid crystals, follow this link.

The next section describes the effects of an external field on a liquid crystal sample.