http://plc.cwru.edu/tutorial/enhanced/files/textbook.htm

Introduction to Liquid Crystals

Definition:

Liquid crystals are <u>substances</u> that exhibit a <u>phase of matter</u> that has properties between those of a conventional <u>liquid</u>, and those of a <u>solid crystal</u>. For instance, a liquid crystal (LC) may flow like a liquid, but have the <u>molecules</u> in the liquid arranged and/or oriented in a crystal-like way. There are many different types of LC phases, which can be distinguished based on their different <u>optical</u> properties (such as <u>birefringence</u>). When viewed under a <u>microscope</u> using a <u>polarized light</u> source, different liquid crystal phases will appear to have a distinct <u>texture</u>. Each "patch" in the texture corresponds to a domain where the LC molecules are oriented in a different direction. Within a domain, however, the molecules are well ordered. Liquid crystal materials may not always be in an LC phase (just as <u>water</u> is not always in the liquid phase: it may also be found in the solid or <u>gas phase</u>). Liquid crystals can be divided into <u>thermotropic</u> and <u>lyotropic</u> LCs. Thermotropic LCs exhibit a <u>phase</u> <u>transition</u> into the LC phase as <u>temperature</u> is changed, whereas lyotropic LCs exhibit phase transitions as a function of <u>concentration</u> of the <u>mesogen</u> in a <u>solvent</u> (typically water) as well as <u>temperature</u>

The study of liquid crystals began in 1888 when an Austrian botanist named Friedrich Reinitzer observed that a material known as cholesteryl benzoate had two distinct melting points. In his experiments, Reinitzer increased the temperature of a solid sample and watched the crystal change into a hazy liquid. As he increased the temperature further, the material changed again into a clear, transparent liquid. Because of this early work, Reinitzer is often credited with discovering a new phase of matter - the *liquid crystal* phase.

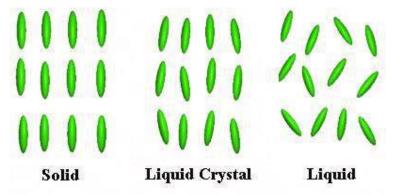
Liquid crystal materials are unique in their properties and uses. As research into this field continues and as new applications are developed, liquid crystals will play an important role in modern technology. This tutorial provides an introduction to the science and applications of these materials.

What are Liquid Crystals?

Liquid crystal materials generally have several common characteristics. Among these are a rod-like molecular structure, rigidness of the long axis, and strong <u>dipoles</u> and/or easily polarizable substituents.

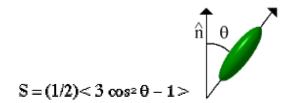
The distinguishing characteristic of the liquid crystalline state is the tendency of the molecules ($\underline{mesogens}$) to point along a common axis, called the $\underline{director}$. This is in

contrast to molecules in the liquid phase, which have no intrinsic order. In the solid state, molecules are highly ordered and have little translational freedom. The characteristic orientational order of the liquid crystal state is between the traditional solid and liquid phases and this is the origin of the term mesogenic state, used synonymously with liquid crystal state. Note the average alignment of the molecules for each phase in the following diagram.

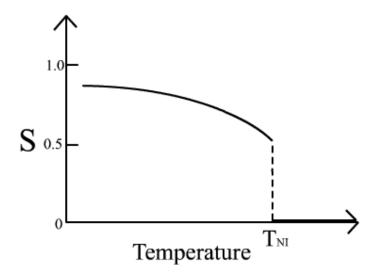


It is sometimes difficult to determine whether a material is in a crystal or liquid crystal state. *Crystalline* materials demonstrate long range periodic order in three dimensions. By definition, an *isotropic* liquid has no orientational order. Substances that aren't as ordered as a solid, yet have some degree of alignment are properly called liquid crystals.

To quantify just how much order is present in a material, an <u>order parameter</u> (S) is defined. Traditionally, the order parameter is given as follows:



where *theta* is the angle between the director and the long axis of each molecule. The brackets denote an average over all of the molecules in the sample. In an isotropic liquid, the average of the cosine terms is zero, and therefore the order parameter is equal to zero. For a perfect crystal, the order parameter evaluates to one. Typical values for the order parameter of a liquid crystal range between 0.3 and 0.9, with the exact value a function of temperature, as a result of kinetic molecular motion. This is illustrated below for a nematic liquid crystal material (to be discussed in the next section).



The tendency of the liquid crystal molecules to point along the director leads to a condition known as *anisotropy*. This term means that the properties of a material depend on the direction in which they are measured. For example, it is easier to cut a piece of wood along the grain than against it. The anisotropic nature of liquid crystals is responsible for the unique optical properties exploited by scientists and engineers in a variety of applications.

Characterizing Liquid Crystals

The following parameters describe the liquid crystalline structure:

- Positional Order
- Orientational Order
- Bond Orientational Order

Each of these parameters describes the extent to which the liquid crystal sample is ordered. *Positional order* refers to the extent to which an average molecule or group of molecules shows translational symmetry (as crystalline material shows). *Orientational order*, as discussed above, represents a measure of the tendency of the molecules to align along the director on a long-range basis. *Bond Orientational Order* describes a line joining the centers of nearest-neighbor molecules without requiring a regular spacing along that line. Thus, a relatively long-range order with respect to the line of centers but only short range positional order along that line. (See discussion of hexatic phases in a text such as Chandrasekhar, *Liquid Crystals*)

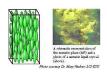
Most liquid crystal compounds exhibit *polymorphism*, or a condition where more than one phase is observed in the liquid crystalline state. The term *mesophase* is used to describe the "subphases" of liquid crystal materials. Mesophases are formed by changing the amount of order in the sample, either by imposing order in only one or two dimensions, or by allowing the molecules to have a degree of translational motion. The following section describes the mesophases of liquid crystals in greater detail.

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 <u>anisotropic</u> 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. <u>Chiral</u> 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 <u>translational order</u> not present in the nematic. In the smectic state, the molecules 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.

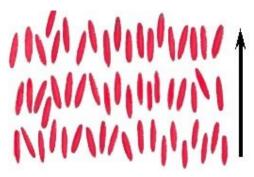


Photo courtesy Dr. Mary Neubert LCI-KSU

Photo of a smectic phase (using polarizing microscope)

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.



Picture of the smectic A phase

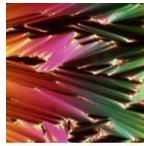


Photo courtesy of Dr. Mary Neubert LCI-KSU

Photo of the smectic A phase (using polarizing microscope)



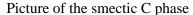
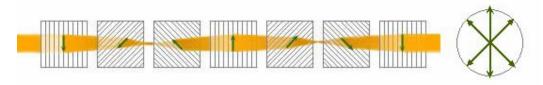




Photo courtesy Dr. Mary Neubert LCI-KSU

Photo of the smectic C phase
(using polarizing microscope)

As in the nematic, the smectic-C mesophase has a chiral state designated C*. Consistent with the smectic-C, the <u>director</u> 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.

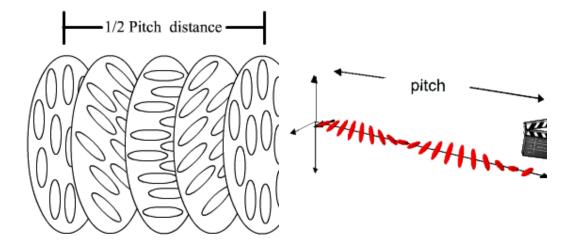


A schematic representation of a smectic C* phase (left), and a view of the same phase, but along the axis (right).

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 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.



Macroscopic View

Optical polarizing microscopy is a standard tool in the identification of liquid crystal phases and 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.



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.

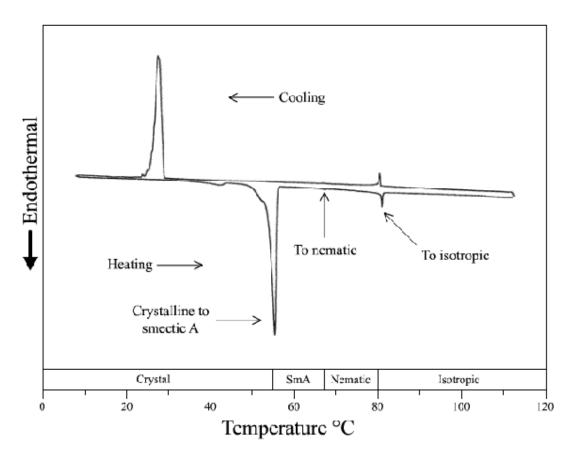


Figure (a): DSC plot with phase diagram

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.

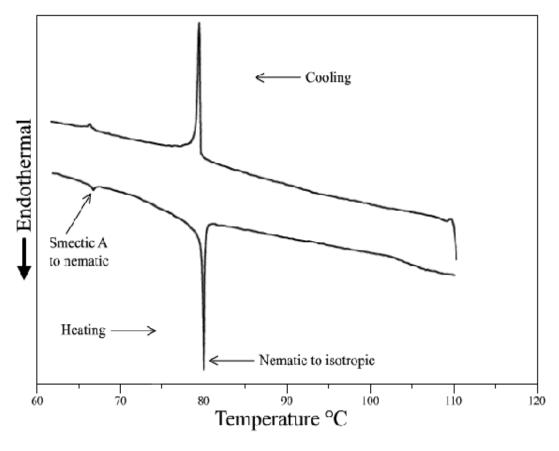


Figure (b): DSC plot

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

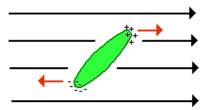
The next section describes the effects of an external field on a liquid crystal sample.

External Influences on Liquid Crystals

Scientists and engineers are able to use liquid crystals in a variety of applications because external *perturbation* can cause significant changes in the macroscopic properties of the liquid crystal system. Both electric and magnetic fields can be used to induce these changes. The magnitude of the fields, as well as the speed at which the molecules align are important characteristics industry deals with. Finally, special surface treatments can be used in liquid crystal devices to force specific orientations of the *director*.

Electric and Magnetic Field Effects

The response of liquid crystal molecules to an electric field is the major characteristic utilized in industrial applications. The ability of the director to align along an external field is caused by the electric nature of the molecules. *Permanent electric dipoles* result when one end of a molecule has a net positive charge while the other end has a net negative charge. When an external electric field is applied to the liquid crystal, the dipole molecules tend to orient themselves along the direction of the field. In the following diagram, the black arrows represent the electric field vector and the red arrows show the electric force on the molecule.



Even if a molecule does not form a permanent dipole, it can still be influenced by an electric field. In some cases, the field produces slight re-arrangement of electrons and protons in molecules such that an *induced electric dipole* results. While not as strong as permanent dipoles, orientation with the external field still occurs.

The effects of magnetic fields on liquid crystal molecules are analogous to electric fields. Because magnetic fields are generated by moving electric charges, permanent magnetic dipoles are produced by electrons moving about atoms. When a magnetic field is applied, the molecules will tend to align with or against the field. (See Chandrasekhar, 1992 for further discussion)

Surface Preparations

In the absence of an external field, the director of a liquid crystal is free to point in any direction. It is possible, however, to force the director to point in a specific direction by introducing an outside agent to the system. For example, when a thin polymer coating (usually a polyimide) is spread on a glass substrate and rubbed in a single direction with a cloth, it is observed that liquid crystal molecules in contact with that surface align with the rubbing direction. The currently accepted mechanism for this is believed to be an epitaxial growth of the liquid crystal layers on the partially aligned polymer chains in the near surface layers of the polyimide.

Freedericksz Transition

The competition between orientation produced by surface anchoring and by electric field effects is often exploited in liquid crystal devices. Consider the case in which liquid crystal molecules are aligned parallel to the surface and an electric field is applied perpendicular to the cell as in the following diagram. At first, as the electric field increases in magnitude, no change in alignment occurs. However at a threshold magnitude of electric field, *deformation* occurs. Deformation occurs where the director changes its orientation from one molecule to the next. The occurrence of such a change from an aligned to a deformed state is called a *Freedericksz transition* and can also be produced by the application of a magnetic field of sufficient strength.



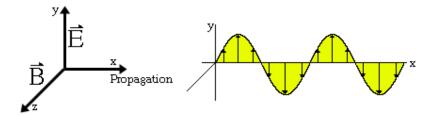
The Freedericksz transition is fundamental to the operation of many liquid crystal displays because the director orientation (and thus the properties) can be controlled easily by the application of a field. Refer to the <u>Applications</u> section for more information about liquid crystals used in displays.

Light and Polarization

This section will introduce some of the basic concepts that are important in understanding the optical behavior of liquid crystals. This is by no means a complete discussion of the topic; it is only intended to be used in the context of liquid crystal optical behavior. Please refer to <u>Jenkins and White</u> for a detailed treatment.

Light and Polarization

Light can be represented as a transverse electromagnetic wave made up of mutually perpendicular, fluctuating electric and magnetic fields. The left side of the following diagram shows the electric field in the xy plane, the magnetic field in the xz plane and the propagation of the wave in the x direction. The right half shows a line tracing out the electric field vector as it propagates. Traditionally, only the electric field vector is dealt with because the magnetic field component is essentially the same.

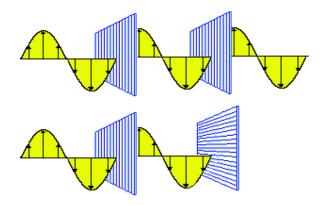


This sinusoidally varying electric field can be thought of as a length of rope held by two children at opposite ends. The children begin to displace the ends in such a way

that the rope moves in a plane, either up and down, left and right, or at any angle in between.

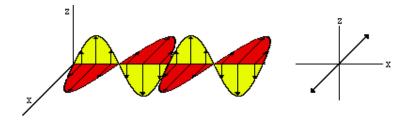
Ordinary white light is made up of waves that fluctuate at all possible angles. Light is considered to be "linearly polarized" when it contains waves that only fluctuate in one specific plane. It is as if the rope is strung through a picket fence -- the wave can move up and down, but motion is blocked in any other direction. A *polarizer* is a material that allows only light with a specific angle of vibration to pass through. The direction of fluctuation passed by the polarizer is called the "easy" axis.

If two polarizers are set up in series so that their optical axes are parallel, light passes through both. However, if the axes are set up 90 degrees apart (crossed), the polarized light from the first is extinguished by the second. As the angle rotates from 0 to 90 degrees, the amount of light that is transmitted decreases. This effect is demonstrated in the following diagram. The polarizers are parallel at the top and crossed at the bottom.

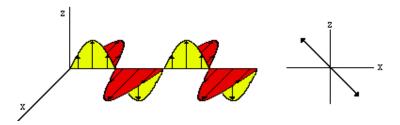


Polarized Light

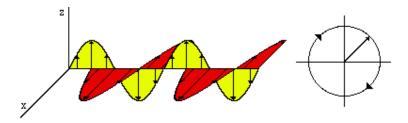
Linear polarization is merely a special case of <u>circularly polarized</u> light. Consider two light waves, one polarized in the YZ plane and the other in the XY plane. If the waves reach their maximum and minimum points at the same time (they are in phase), their vector sum leads to one wave, linearly polarized at 45 degrees. This is shown in the following diagram.



Similarly, if the two waves are 180 degrees out of phase, the resultant is linearly polarized at 45 degrees in the opposite sense.



If the two waves are 90 degrees out of phase (one is at an extremum and the other is at zero), the resulting wave is circularly polarized. In effect, the resultant electric field vector from the sum of the components rotates around the origin as the wave propagates. The following diagram shows the sum of the electric field vectors for two such waves.



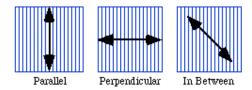
The most general case is when the phase difference is at an arbitrary angle (not necessarily 90 or 180 degrees.) This is called elliptical polarization because the electric field vector traces out an ellipse (instead of a line or circle as before.)

These concepts can be rather abstract the first time they are presented. The following simulation allows the user to change the phase shift to an arbitrary value to observe the resultant polarization state.

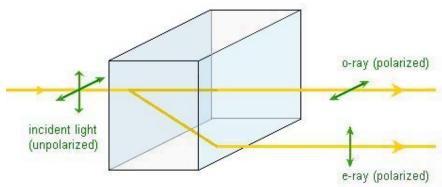
Birefringence in Liquid Crystals

The previous section introduced the concepts of polarized light and *polarizers*. This section will show how these ideas are important to liquid crystals.

Liquid crystals are found to be birefringent, due to their *anisotropic* nature. That is, they demonstrate double refraction (having two indices of refraction). Light polarized parallel to the director has a different index of refraction (that is to say it travels at a different velocity) than light polarized perpendicular to the director. In the following diagram, the blue lines represent the director field and the arrows show the polarization vector.



Thus, when light enters a birefringent material, such as a nematic liquid crystal sample, the process is modeled in terms of the light being broken up into the fast (called the ordinary ray) and slow (called the extraordinary ray) components. Because the two components travel at different velocities, the waves get out of phase. When the rays are recombined as they exit the birefringent material, the polarization state has changed because of this phase difference.



Light traveling through a birefringent medium will take one of two paths depending on its polarization.

The birefringence of a material is characterized by the difference, Δn , in the indices of refraction for the ordinary and extraordinary rays. To be a little more quantitative, since the index of refraction of a material is defined as the ratio of the speed of light in a vacuum to that in the material, we have for this case, $n_e = c/V_{||}$ and $n_o = c/V_{\perp}$ for the velocities of a wave travelling perpendicular to the director and polarized parallel and perpendicular to the director, so that the maximum value for the birefringence, $\Delta n = n_e - n_o$. We won't deal here with the general case of a wave travelling in an arbitrary direction relative to the director in a liquid crystal sample, except to note that Δn varies from zero to the maximum value, depending on the direction of travel. The condition $n_e > n_o$ describes a positive uniaxial material, so that nematic liquid crystals are in this category. For typical nematic liquid crystals, n_o is approximately 1.5 and the maximum difference, Δn , may range between 0.05 and 0.5.

The length of the sample is another important parameter because the phase shift accumulates as long as the light propagates in the birefringent material. Any polarization state can be produced with the right combination of the birefringence and length parameters.

It is convenient here to introduce the concept of optical path in media since for the above two wave components travelling with different speeds in a birefringent material, the difference in optical paths will lead to a change in the polarization state of the wave as it progresses through the medium. We define the optical path for a

wave travelling a distance L in a crystal as nL so that the optical path difference for the two wave components mentioned above will be L $(n_e - n_o) = L\Delta n$. The resultant phase difference between the two components (the amount by which the slow, extraordinary component lags behind the fast, ordinary one) is just $2\pi L\Delta n/\lambda v$ where λv is the wavelength in vacuum.

The following simulation demonstrates the optical properties of a birefringent material. A linearly polarized light wave enters a crystal whose extraordinary (slow) index of refraction can be controlled by the user. The length of the sample can also be varied, and the outgoing polarization state is shown. The concept of optical path difference and its influence on polarization state can also be explored here. This leads to a discussion of optical retardation plates or phase retarders, in the context of the simulation.



Application to Polarized Light Studies of Liquid Crystals

Consider the case where a liquid crystal sample is placed between crossed polarizers whose transmission axes are aligned at some angle between the fast and slow direction of the material. Because of the birefringent nature of the sample, the incoming linearly polarized light becomes elliptically polarized, as you have already found in the simulation. When this ray reaches the second polarizer, there is now a component that can pass through, and the region appears bright. For monochromatic light (single frequency), the magnitude of the phase difference is determined by the length and the birefringence of the material. If the sample is very thin, the ordinary and extraordinary components do not get very far out of phase. Likewise, if the sample is thick, the phase difference can be large. If the phase difference equals 360 degrees, the wave returns to its original polarization state and is blocked by the second polarizer. The size of the phase shift determines the intensity of the transmitted light.

If the transmission axis of the first polarizer is parallel to either the ordinary or extraordinary directions, the light is not broken up into components, and no change in the polarization state occurs. In this case, there is not a transmitted component and the region appears dark.

In a typical liquid crystal, the birefringence and length are not constant over the entire sample. This means that some areas appear light and others appear dark, as shown in the following microscope picture of a nematic liquid crystal, taken between crossed polarizers. The light and dark areas that denote regions of differing director orientation, birefringence, and length.



Image courtesy of E. Merck Company

The Schlieren texture, as this particular arrangement is known, is characteristic of the nematic phase. The dark regions that represent alignment parallel or perpendicular to the director are called brushes. The next section will describe the textures of liquid crystals in greater detail, but before going there lets see how birefringence can lead to multicolored images in the examination of liquid crystals under polarized white light.

Colors Arising From Polarized Light Studies

Up to this point, we have dealt only with monochromatic light is considering the optical properties of materials. In understanding the origin of the colors which are observed in the studies of liquid crystals placed between crossed linear polarizers, it will be helpful to return to the examples of retarding plates discussed in the Birefringence Simulation. They are designed for a specific wavelength and thus will produce the desired results for a relatively narrow band of wavelengths around that particular value. If, for example, a full-wave plate designed for wavelength is λ' is placed between crossed polarizers at some arbitrary orientation and the combination illuminated by white light, the wavelength λ' will not be affected by the retarder and so will be extinguished (absorbed) by the analyzer. However, all other wavelengths will experience some retardation and emerge from the full-wave plate in a variety of polarization states. The components of this light passed by the analyzer will then form the complementary color to λ' .

Color patterns observed in the polarizing microscope, together with the extinctions already noted in the connection with the Birefringence Simulations are very useful in the study of liquid crystals in many situations, including the identification of textures, of liquid crystal phases and the observations of phase changes.

The following simulation illustrates the role of birefringence in the formation of colored images by a liquid crystal sample located between crossed linear polarizers when observed, for example, in a microscope. The simulation allows you to adjust the birefringence, the length, and the orientation, θ , of the liquid crystal sample. Here, θ is the angle between the director and the vertical direction (The transmission direction of the polarizer).



Temperature Dependence of Birefringence

Recall that the birefringence of a material results from its anisotropy and the anisotropy of liquid crystals show a strong temperature dependence, vanishing at the nematic to isotropic phase transition. Hence, the birefringence shows a significant temperature dependence. This is discussed and illustrated in the following simulation.

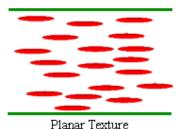
Textures and Defects

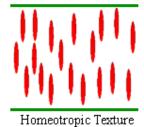
The unique optical properties of liquid crystals enable them to be used in a variety of applications. This section explains how these characteristics arise.

Liquid Crystal Textures

The term texture refers to the orientation of liquid crystal molecules in the vicinity of a surface. Each liquid crystal mesophase can form its own characteristic textures, which are useful in identification. We consider the nematic textures here, postponing discussion of cholesteric textures until the section on polymer stabilized cholesteric liquid crystals.

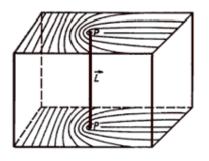
If mesogenic materials are confined between closely spaced plates with rubbed surfaces (as described above) and oriented with rubbing directions parallel, the entire liquid crystal sample can be oriented in a *planar texture*, as shown in the following diagram. Mesogens can also be oriented normal to a surface with the use of appropriate polymer films, or in the presence of an electric field applied normal to the surface, giving rise to the *homeotropic texture*, as illustrated below.

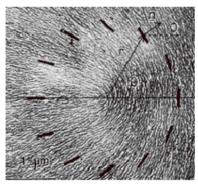




Defects Under the Microscope

The abrupt changes in brightness seen in the pictures from the previous section on birefringence signal a rapid change in director orientation in the vicinity of a line or point singularity known as a disclination. A disclination is a region where the director is undefined. The following is a diagram that shows the orientation of the director around a disclination.





Director topology around a line disclination in a liquid crystal (left), and an electron micrograph of the same type of disclination. Crystalline lamellae are seen edge on and appear dark. The director field lines lie normal to the lamellae as illustrated by the vector n for a highlighted lamellae.

Focal conic defects are responsible for many of the structures in smectic liquid crystals. The following is a TEM micrograph of a focal conic.



The diagram and micrographs in this section were provided by Professor Steven Hudson of the Macromolecular Science Department, CWRU.

Chemical Properties of Liquid Crystals

Liquid crystals can be classified into two main categories: thermotropic liquid crystals, and lyotropic liquid crystals. These two types of liquid crystals are distinguished by the mechanisms that drive their self-organization, but they are also similar in many ways.

Thermotropic transactions occur in most liquid crystals, and they are defined by the fact that the transitions to the liquid crystalline state are induced thermally. That is, one can arrive at the liquid crystalline state by raising the temperature of a solid and/or lowering the temperature of a liquid. Thermotropic liquid crystals can be classified into two types: enantiotropic liquid crystals, which can be changed into the

liquid crystal state from either lowering the temperature of a liquid or raising of the temperature of a solid, and monotropic liquid crystals, which can only be changed into the liquid crystal state from either an increase in the temperature of a solid or a decrease in the temperature of a liquid, but not both. In general, thermotropic mesophases occur because of anisotropic dispersion forces between the molecules and because of packing interactions.

In contrast to thermotropic mesophases, lyotropic liquid crystal transitions occur with the influence of solvents, not by a change in temperature. Lyotropic mesophases occur as a result of solvent-induced aggregation of the constituent mesogens into micellar structures. Lyotropic mesogens are typically amphiphilic, meaning that they are composed of both lyophilic (solvent-attracting) and lyophobic (solvent-repelling) parts. This causes them to form into micellar structures in the presence of a solvent, since the lyophobic ends will stay together as the lyophilic ends extend outward toward the solution. As the concentration of the solution is increased and the solution is cooled, the micelles increase in size and eventually coalesce. This separates the newly formed liquid crystalline state from the solvent.

A very large number of chemical compounds are known to exhibit one or several liquid crystalline phases. Despite significant differences in chemical composition, these molecules have some common features in chemical and physical properties. There are two types of thermotropic liquid crystals: discotics and rod-shaped molecules. Discotics are flat disc-like molecules consisting of a core of adjacent aromatic rings. This allows for two dimensional columnar ordering. Rod-shaped molecules have an elongated, anisotropic geometry which allows for preferential alignment along one spatial direction.

The rod-like low molar mass (LMM) liquid crystals, such as 5CB shown in the following diagram:

5CB p-n pentyl-p'-cyanobiphenyl (PCB)

require an extended conformation of the molecule which must be maintained through the rigidity and linearity of its constituents. That is, in order for a molecule to display the characteristics of a liquid crystal, it must be rigid and rod-shaped. This is accomplished by the interconnection of two rigid cyclic units. The interconnecting group should cause the resulting compound to have a linear planar conformation. Linking units containing multiple bonds such as -(CH=N)-, -N=N-, -(CH=CH)n-, -CH=N-N=CH-, etc. are used since they restrict the freedom of rotation. These groups can conjugate with phenylene rings, enhancing the anisotropic polarizability. This increases the molecular length and maintains the rigidity

Applications of Liquid Crystals

Effect of chirality

As already described, <u>chiral</u> mesogens usually give rise to chiral mesophases. For molecular mesogens, this means that the molecule must possess some form of asymmetry, usually a <u>stereogenic</u> center. An additional requirement is that the system not be <u>racemic</u>: a mixture of right- and left-handed versions of the mesogen will cancel the chiral effect. Due to the cooperative nature of liquid crystal ordering, however, a small amount of chiral dopant in an otherwise achiral mesophase is often enough to select out one domain handedness, making the system overall chiral.

Chiral phases usually have a helical twisting of the mesogens. If the pitch of this twist is on the order of the wavelength of visible light, then interesting optical interference effects can be observed. The chiral twisting that occurs in chiral LC phases also makes the system respond differently to right- and left-handed circularly polarized light. These materials can thus be used as polarization filters.

It is possible for chiral mesogens to produce essentially achiral mesophases. For instance, in certain ranges of concentration and molecular weight, DNA will form an achiral line hexatic phase. A curious recent observation is of the formation of chiral mesophases from achiral mesogens. Specifically, bent-core molecules (sometimes called banana liquid crystals) have been shown to form liquid crystal phases that are chiral. In any particular sample, various domains will have opposite handedness, but within any given domain, strong chiral ordering will be present. The appearance mechanism of this macroscopic chirality is not yet entirely clear. It appears that the molecules stack in layers and orient themselves in a tilted fashion inside the layers. These liquid crystals phases are ferroelectric and anti-ferroelectric, both of which are of interest for applications.

Applications of liquid crystals

1) Liquid Crystal Displays LCD: The most common application of liquid crystal technology is liquid crystal displays (LCDs.) This field has grown into a multi-billion dollar industry, and many significant scientific and engineering discoveries have been made. Please refer to the LCD chapter for more detail.

Liquid crystals find wide use in <u>liquid crystal displays</u>, which rely on the <u>optical</u> properties of certain liquid crystalline molecules in the presence or absence of an <u>electric field</u>. In a typical device, a liquid crystal layer sits between two <u>polarizers</u> that are crossed (oriented at 90° to one another). The liquid crystal is chosen so that its relaxed phase is a twisted one. This twisted phase reorients light that has passed through the first polarizer, allowing it to be transmitted through the second polarizer and reflected back to the observer. The device thus appears clear. When an electric field is applied to the LC layer, all the mesogens align (and are no longer twisting). In this aligned state, the mesogens do not reorient light, so the light polarized at the first polarizer is absorbed at the second polarizer, and the entire device appears dark. In this way, the electric field can be used to make a pixel switch between clear or dark on command. Color LCD systems use the same technique, with color filters used to generate red, green, and blue pixels. Similar principles can be used to make other liquid crystal based optical devices.

2) Liquid Crystal Thermometers:

As demonstrated earlier, chiral nematic (cholesteric) liquid crystals reflect light with a wavelength equal to the pitch. Because the pitch is dependent upon temperature, the color reflected also is dependent upon temperature. Liquid crystals make it possible to accurately gauge temperature just by looking at the color of the thermometer. By mixing different compounds, a device for practically any temperature range can be built.

More important and practical applications have been developed in such diverse areas as medicine and electronics. Special liquid crystal devices can be attached to the skin to show a "map" of temperatures. This is useful because often physical problems, such as tumors, have a different temperature than the surrounding tissue. Liquid crystal temperature sensors can also be used to find bad connections on a circuit board by detecting the characteristic higher temperature.

Thermotropic chiral LCs whose pitch varies strongly with temperature can be used as crude thermometers, since the color of the material will change as the pitch is changed. Liquid crystal color transitions are used on many aquarium and pool thermometers. Other liquid crystal materials change color when stretched or stressed. Thus, liquid crystal sheets are often used in industry to look for hot spots, map heat flow, measure stress distribution patterns, and so on. Liquid crystal memory units with extensive capacity were used in Space Shuttle navigation equipment.

Note: It is also worth noting that many common fluids are in fact liquid crystals. Soap, for instance, is a liquid crystal, and forms a variety of LC phases depending on its concentration in water.

3) Optical Imaging

An application of liquid crystals that is only now being explored is optical imaging and recording. In this technology, a liquid crystal cell is placed between two layers of photoconductor. Light is applied to the photoconductor, which increases the material's conductivity. This causes an electric field to develop in the liquid crystal corresponding to the intensity of the light. The electric pattern can be transmitted by an electrode, which enables the image to be recorded. This technology is still being developed and is one of the most promising areas of liquid crystal research.

4) Other Liquid Crystal Applications

Liquid crystals have a multitude of other uses. They are used for nondestructive mechanical testing of materials under stress. This technique is also used for the visualization of RF (radio frequency) waves in waveguides. They are used in medical applications where, for example, transient pressure transmitted by a walking foot on the ground is measured. Low molar mass (LMM) liquid crystals have applications including erasable optical disks, full color "electronic slides" for computer-aided drawing (CAD), and light modulators for color electronic imaging.

As new properties and types of liquid crystals are investigated and researched, these materials are sure to gain increasing importance in industrial and scientific applications.

Introduction to Liquid Crystal Displays



The most common application of liquid crystal technology is in liquid crystal displays (LCDs). From the ubiquitous wrist watch and pocket calculator to an advanced VGA computer screen, this type of display has evolved into an important and versatile interface.

A liquid crystal display consists of an array of tiny segments (called pixels) that can be manipulated to present information. This basic idea is common to all displays, ranging from simple calculators to a full color LCD television.

Why are liquid crystal displays important? The first factor is size. As will be shown in the following sections, an LCD consists primarily of two glass plates with some liquid crystal material between them. There is no bulky picture tube. This makes LCDs practical for applications where size (as well as weight) are important.

In general, LCDs use much less power than their cathode-ray tube (CRT) counterparts. Many LCDs are reflective, meaning that they use only ambient light to

illuminate the display. Even displays that do require an external light source (i.e. computer displays) consume much less power than CRT devices.

Liquid crystal displays do have drawbacks, and these are the subject of intense research. Problems with viewing angle, contrast ratio, and response time still need to be solved before the LCD replaces the cathode-ray tube. However with the rate of technological innovation, this day may not be too far into the future.

We will restrict this discussion to traditional nematic LCDs since the major technological advances have been developed for this group of devices. Other LC applications, such as those employing polymer stabilization of LC structure, are discussed in the appropriate section covering those materials.

For a more detailed look at liquid crystal displays, follow this link.

Twisted Nematic (TN) Displays

There are many types of liquid crystal displays, each with unique properties. The most common LCD that is used for everyday items like watches and calculators is called the *twisted nematic* (TN) display. This device consists of a *nematic* liquid crystal sandwiched between two plates of glass. A special surface treatment is given to the glass such that the molecules are homeotropic yet the *director* at the top of the sample is perpendicular to the director at the bottom. This configuration sets up a 90 degree twist into the bulk of the liquid crystal, hence the name of the display. The twist is visible in the following animation.

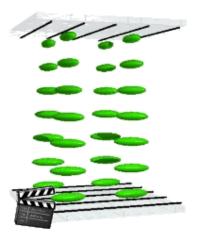


This structure is similar to the <u>cholesteric</u> state, and sometimes a small amount of a chiral material is added to ensure a uniform twist.

The underlying principle in a TN display is the manipulation of <u>polarized</u> light. When light enters the TN cell, the polarization state twists with the director of the liquid crystal material. For example, consider light polarized parallel to the director at the

top of the sample. As is travels through the cell, its polarization rotates with the molecules. When the light emerges, it's polarization has rotated 90 degrees from when it entered.

A schematic of a TN cell is shown in the following animation. The black lines represent crossed polarizers that are attached to the top and bottom of the display. As light enters the cell, its polarization rotates with the molecules. When the light reaches the bottom of the cell, its polarization vector has rotated by 90 degrees, and now can pass through the second polarizer. In a reflecting TN display, a mirror is placed at the bottom of the cell to reflect the transmitted light. Once again the polarization twists as the light traverses the sample, and is able to emerge from the top of the cell. The following animation shows how light entering the cell twists along the way.



Light emerging from such a cell appears the familiar silver-gray color. As explained in the Electric and Magnetic Field Effects section, when an electric field of sufficient magnitude is applied to a sample, the molecules undergo a Freederickzs transition. The following animation shows the transition that happened in a twisted nematic cell.



Note that in this state, the twist is destroyed. The director of the bulk liquid crystal is parallel to the field and no longer twisted. When polarized light enters a cell in such a configuration, it is not twisted, and is canceled by the second polarizer. Regions where an electric field is applied appear dark against a bright background. The following animation demonstrates light traversing a cell with an applied electric field.

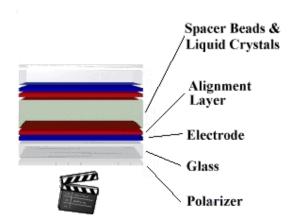


Liquid Crystal Display Construction

Before going into any further detail about the physics behind displays, it is probably best to step through the various components of a liquid crystal display and briefly mention their functions. As mentioned in the previous section, a liquid crystal display is composed of multiple layers.

First, a sheet of glass is coated with a transparent metal oxide film (shown as a blue layer in the animation below) which acts as an electrode. This film can be patterned to form the rows and columns of a passive matrix display or the individual pixels of an active matrix display. These electrodes are used to set up the voltage across the cell necessary for the orientation transition. Next, a polymer alignment layer is applied (shown in red). This layer undergoes a rubbing process which leaves a series of parallel microscopic grooves in the film. These grooves help align the liquid crystal molecules in a preferred direction, with their longitudinal axes parallel to the grooves. (see Surface Preparations) This anchors the molecules along the alignment layers and helps force the molecules between the alignment layers to twist. Two such sheets of glass are prepared and one is coated with a layer of polymer spacer beads (the slightly green glassy layer). These beads maintain a uniform gap between the sheets of glass where the liquid crystals are eventually placed. The two glass sheets are then placed together and the edges are sealed with epoxy. A corner is left unsealed so that the liquid crystal material can be injected under a vacuum. Once the display has been filled with liquid crystals, the corner is sealed and polarizers (the transparent layers with lines) are applied to the exposed glass surfaces. In a TN display (which is shown in the animation below) the alignment layers are positioned with their rubbing directions perpendicular to each other

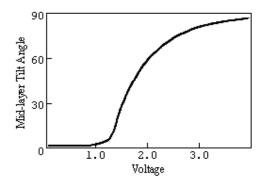
and the polarizers are applied to match the orientation of the alignment layers. In an STN (super-twisted nematic) display (which will be discussed in the next section) the alignment layers are placed with their rubbing directions at a variety of angles to one another to set up a twist from 180 to 270 degrees and the polarizers are not applied parallel to the alignment layers.



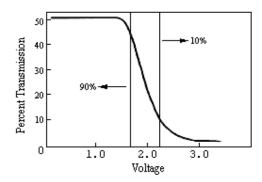
The display is finished off by completing the connections to the driving circuitry which controls the voltage applied to various areas of the display (pixels).

Optical Response

Depending on the field strength, twisted nematic displays can switch between light and dark states, or somewhere in between (grayscale.) How the molecules respond to a voltage is the important characteristic of this type of display. The response of a typical twisted nematic cell to an applied voltage is shown in the following diagram (called an electro-distortional curve). The tilt of the molecules out of the plane of the glass slides is measured as a function of the applied voltage.



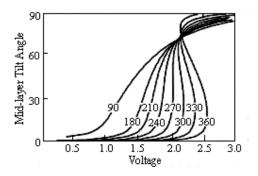
In the TN display, the electro-distortional response determines the transmission of light through the cell. Percent transmission as a function of voltage is shown in the following diagram. Keep in mind that maximum transmission for a reflective TN device is only 50 percent because polarized light must be used.



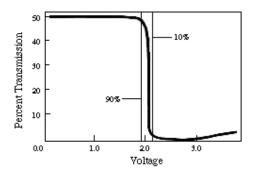
The vertical lines represent the voltages at which the cell is OFF or ON. In order to address many pixels with a multiplexing scheme (see <u>Display Addressing</u>), the differences in the OFF and ON voltages must be very small. This was difficult to achieve with the traditional TN structure. This problem was solved with the invention of the super-twisted nematic (STN) display.

Super Twisted Nematic Displays

The difference between the ON and OFF voltages in displays with many rows and columns can be very small. For this reason, the <u>TN</u> device is impractical for large information displays with conventional addressing schemes. This problem was solved in the mid 1980's with the invention of the super-twisted nematic (STN) display. In this device, the director rotates through an angle of 270 degrees, compared with the 90 degrees for the TN cell. The effect of twist angle on the electro-optical response curve is shown in the following diagram.



Note that the change in the tilt angle becomes very abrupt as the twist angle is increased. The consequence of this response curve is that the off and on voltages are much closer together, as is shown in the following figure.



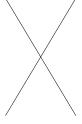
Although it is desirable to obtain a sharp electro-optic transition, grayscale images require intermediate points along the curve. For this reason, many commercial STN displays use a twist angle of 210 degrees. This broadens the transition region enough for grayscale while allowing for conventional addressing.

Early displays operating in the 210 degree mode suffered from undesirable coloration resulting from a shifted transmission spectrum of the device. In the ON state, the pixels tended to be yellow, while the OFF state had a bluish-purple tint. In addition to not being popular with the consumer, full color displays using filters can only be made with black and white operation. This problem was solved by adding a second STN layer with the opposite twist sense to the cell. This type of device is known as the double super-twisted nematic display (D-STN).

In the OFF state, the phase shift resulting from the first layer is compensated by the second layer. This pixel appears black. The ON state is not affected by the second STN layer, and white light emerges. Since the two layers consist of the same liquid crystal material, the behavior is constant over the entire temperature range.

Display Addressing

Addressing is the process by which pixels are turned on and off in order to create an image. There are two main types of addressing, direct and multiplexing. Direct addressing is convenient for displays where there are only a few elements that have to be activated. With direct addressing, each pixel in the display has its own drive circuit. A microprocessor must individually apply a voltage to each element. A common application of direct addressing is the traditional seven segment liquid crystal display, found in wristwatches and similar devices.



In multiplex addressing, a larger number of pixels are involved. When the elements are in a regular order, they can be addressed by their row and column instead of each element being driven separately. This reduces the complexity of the circuitry because each pixel no longer needs its own driver circuit. If you have a 10x10 matrix of pixels, with direct addressing, you need 100 individual drivers. However, if you use multiplex addressing, you only need 20 drivers, one for each row and one for each column. This is a tremendous advantage, especially as displays become larger and larger.

Passive vs. Active Matrix Displays

The passive matrix display is addressed by a set of multiplexed transparent electrodes, perpendicular to one another, above and below the liquid crystal layer in a row and column formation as seen below. The electrodes in diagram are colored red and blue so that the structure is apparent. The electrodes are typically constructed of indium tin oxide (ITO) which is a semi-transparent conducting material. The liquid crystal material is colored green in the diagram strictly for structural clarity.

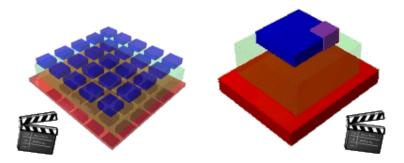
A passive pixel is addressed when there is a sufficient voltage across it to cause the liquid crystal molecules to align parallel to the electric field. A display can have more than one pixel on at any one time because of the response time of the liquid crystal material. When addressed, a pixel has a short turn-on time during which the liquid crystal molecules align in such a way as to make the pixel opaque. When the voltage is removed the pixel behaves similar to a discharging capacitor, slowly turning off as charge dissipates and the molecules return to their undeformed orientation.

Because of this response time, a display can scan across the matrix of pixels, turning on the appropriate ones to form an image. As long as the time to scan the entire matrix is shorter than the turn-off time, a multiple pixel image (like the animation below) can be displayed. The time scale of the animation has been stretched so as to see what is normally imperceptible to the human eye. The transparent electrodes momentarily revert to blue and red to signify voltage being applied. The pixel gradually becomes opaque. As the voltage is removed (as shown by the electrodes becoming colorless again) the cell remains opaque briefly before it becomes clear again.



Active Matrix Displays

Active matrix displays are currently available in high end laptop computers. In this type of display, the addressing takes place completely behind the liquid crystal film. The front surface of the display is coated with a continuous electrode while the rear surface electrode is patterned into individual pixels. A thin film transistor (TFT) acts as a switch for each pixel. The TFT is shown as the purple square at the corner of the blue electrode in the single pixel animation (below, right.) The TFT is addressed by a set of narrow multiplexed electrodes (gate lines and source lines) running along the gaps between pixels. A pixel is addressed by applying current to a gate line which switches the TFT on and allows charge from the source line to flow on to the rear electrode (shown as the starburst effect in the pixel animation below). This sets up a voltage across the pixel and turns it on. An image is created similar to the passive display as the addressing circuitry scans across the matrix. An active matrix display does not suffer from many of the limitations of the passive display. It can be viewed at an angle of up to 45 degrees and has a contrast of 40:1, meaning that the brightness of an "on" pixel is 40 times greater than an "off" pixel. It does, however, require a more intense back lighting system because the TFT's and the gate and source lines are not very transparent and therefore block a fraction of the light.



Color Displays

The techniques discussed so far have only been able to describe a simple two color display. In order to achieve color, it is first necessary to have a display which is black in one state and white in the other. This distinction is made because some displays (early STN displays for example) may have a yellow on blue appearance which will not be able to produce the full range of colors. In a white display, all wavelengths pass through and therefore, all wavelengths can be manipulated to create the desired color. To get full color, each individual pixel is divided into three subpixels: red, green and blue (RGB). That is to say that for each full color pixel, three distinct pixels are employed. These subpixels are created by applying color filters which only allow certain wavelengths to pass through them while absorbing the rest. With a combination of red, blue and green subpixels of various intensities, a pixel can be made to appear any number of different colors. This is analogous to a color cathode ray tube (CRT) like a television or computer monitor in which different phosphors glow red, green or blue when excited by an electron beam. The number of colors that can be made by mixing red, green and blue subpixels depends on the number of distinct gray scales (intensities) that can be achieved by the display.

Display Lighting

In order for a display to show information, it must have a light source. Some displays use only ambient light and employ a reflective surface mounted behind the display -- most calculators and watches are like this. These displays are not very bright because the light must pass through multiple polarizers which severely cut down on the intensity of the light, in addition to the various layers of the display which are only semi-transparent. Therefore a more intense source is employed in the form of a back lighting system. Light bulbs mounted behind and at the edges of the display replace the reflected ambient light. This results in brighter displays for two reasons: the light doesn't have to come in through the display and therefore does not lose part of the intensity, and the lighting system can be made more intense than ambient light. Back lighting has the disadvantage of being very power intensive. Back lighting systems are used in more complex displays such as laptop computer screens.