

*Lab week 2*

**Quantifying Thermodynamic Properties**

**Module  $\alpha$ -1: Switching Energy for a Liquid Crystal Display<sup>1</sup>**

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**1. Objectives**

- Visualize the molecular structure of liquid crystals and understand how this structure gives rise to anisotropic properties
- Understand the thermodynamics of phase transitions in liquid crystals
- Understand the interaction of liquid crystals with polarized light

**2. Summary of tasks**

- Quantify the enthalpy of transition from a liquid crystalline nematic phase to an isotropic liquid using differential scanning calorimetry
- Prepare and observe a sample of nematic liquid crystal under a polarized light microscope
- Induce an orientational change of domains in the liquid crystal via application of an electric field, and quantify the energy required for this transition

**3. Introduction**

A crystal consists of a periodic arrangement of the component atoms or molecules in all three dimensions. For molecular crystals, the molecules also have fixed orientations. We can say that crystals *long-range order*; both the positions and orientations of the

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<sup>1</sup> Acknowledgement: Lab Notes courtesy of Gretchen DeVries with minor modifications.

components are defined over a large range of space. Crystallographically, we can determine a unit cell that captures all the positional and orientational information of the components. By contrast, an isotropic liquid possess only a *short-range order*. The components are randomly located and oriented and there is no long-range repeat of the structure.

A group of materials with more order than in liquids but less order than typical of crystals are called *liquid crystal* since they share properties normally associated with both liquids and crystals. There are more accessible degrees of freedom of molecular rotation, translation, and conformation than in crystals, but there is more order than is found in a truly random material. Thus, liquid crystals are characterized and classified in terms of the degrees of *positional* and *orientational* order of their molecular components. Liquid crystals are just one phase of matter; the same molecules that form liquid crystals can also form crystalline solids or isotropic liquids under different conditions (such as at lower and higher temperatures, respectively).

#### 4. Structure of liquid crystals<sup>1-3</sup>

Liquid crystals are categorized based upon the shape of their molecular component and the conditions required for their existence. There are many classes of liquid crystals; a few main classifications are listed below.

- *Calamitic*: composed of rod-like or cylindrical molecules with one dimension much larger than the other two. Many different phases are possible.
- *Discotic*: composed of disc-like molecules
  
- *Thermotropic*: the liquid crystal state exists within certain temperature regimes. At lower temperatures the substance is in a solid crystalline phase; at higher temperatures (above the clearing temperature,  $T_c$ ) it is an isotropic liquid.
- *Lyotropic*: the liquid crystal phase is formed only when mixed with a solvent. Concentration of the solution is more important than temperature.

In this class, we will discuss two types of *thermotropic calamitic* liquid crystals: the *nematic* and the *smectic* phases.

##### 4.1. Nematic liquid crystals

The nematic phase of calamitic liquid crystals is the simplest liquid crystal phase. In nematic liquid crystals the molecules have no positional order, but they do have long-range orientational order. They are composed of elongated linear molecules that are

depicted as either rods or high aspect ratio cylinders. Typical molecules are composed of ring systems (either aromatic or not) that are linked directly or via rigid linking groups, plus hydrocarbon chains at each end. Terminal and side functionalization modify the properties of the molecule and thus the structure and properties of the liquid crystal. A common molecule that forms nematic liquid crystals is shown in Figure 1:

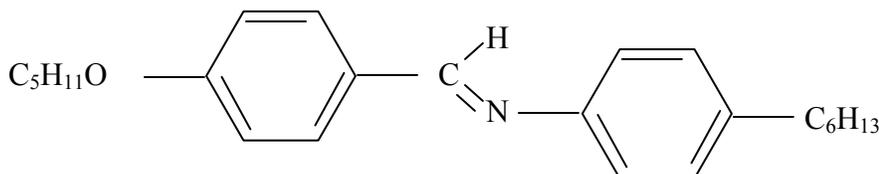


Figure 1: Typical nematic liquid crystal molecule.

Nematics possess no long-range positional order, meaning that the molecules have three translational degrees of freedom. They possess only long-range orientational order; the long axes of the molecules are arranged parallel to one another, on average. The molecules of a nematic are free to rotate about their long axis (hence the description of the molecules as cylinders). A nematic liquid crystal can be characterized by a parameter known as the director,  $\vec{n}$ , which is the average direction in which the long axes of the molecular components point.

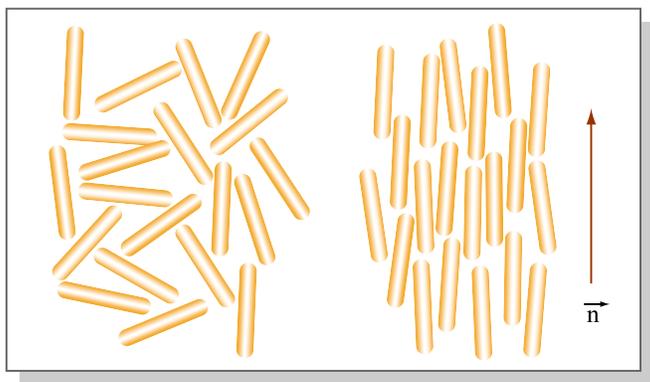


Figure by MIT OCW.

Figure 2. (Left) Schematic of molecular positions and orientations in an isotropic liquid. (Right) In a nematic liquid crystal, the positions are random but the molecules are aligned to point along a common direction, denoted by the director,  $\vec{n}$ . (From reference 1).

We introduce the concept of an *order parameter*,  $S$ , to describe the degree of order in a substance. A high order parameter indicates a well-ordered material; a low order parameter is indicative of increased disorder. The order parameter is defined as

$$S = \frac{1}{2} \langle 3 \cos^2 \beta - 1 \rangle$$

where  $\beta$  is the angle between the director of the crystal ( $\vec{n}$ ) and the long axis of each molecule. The triangular brackets indicate that  $S$  is an average over all the molecules in

the liquid crystal. By this definition, isotropic liquids have an order parameter  $S = 0$ , because of the random molecular orientations (Figure 2). Molecular crystalline solids, on the other hand, have  $S = 1$ , because the molecules are constrained to have a particular orientation direction. For nematic liquid crystals,  $S$  ranges from 0.3 near the clearing temperature to 0.7 at low temperature.

#### 4.2. Smectic liquid crystals

Smectics are another class of calamitic liquid crystals in which the rod-like molecules form into a layered structure (Figure 3). Because the molecules are constrained to be situated within a layer, they only possess two degrees of translational freedom (within the plane of the layer, but not normal to it). The orientational freedom is similar to that of the nematic phase: the molecules are free to rotate around their long axis. A variety of smectic phases exist, some of which have even fewer translational or orientational degrees of freedom.

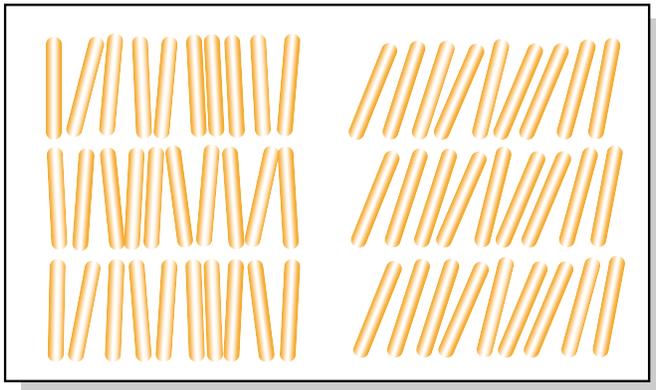


Figure 3. Smectic liquid crystals are composed of rod-like molecules that arrange into a stratified structure. (Left) In the smectic A phase, the molecules lie within the layer. (Right) In the smectic C phase, the molecules are tilted relative to the layer normal (from reference 1).

Figure by MIT OCW.

The *smectic A phase* and the *smectic C phase* can be thought of as layers of two-dimensional nematics. That is, within each layer the molecules are on average parallel but possess no long-range positional order, and they are allowed to rotate about their long axis. In the smectic A phase, the molecules lie perpendicular the layers; in the smectic C phase, the molecules are tilted relative to the layer normal.

A summary of the degrees of translational and rotational freedom for various phases and structures of liquid crystals is given:

|                   | Translational freedom | Rotational freedom |
|-------------------|-----------------------|--------------------|
| Crystalline solid | 0                     | 0                  |
| Smectic LC        | 2                     | 2                  |
| Nematic LC        | 3                     | 2                  |
| Isotropic liquid  | 3                     | 3                  |

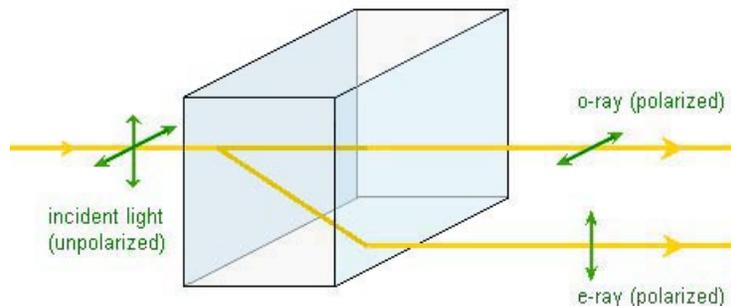
## 5. Optical properties of liquid crystals<sup>1-3</sup>

Because of the uniform orientation of the component molecules along a particular axis, most properties of liquid crystals are anisotropic. For example, viscosity, elastic modulus, electrical and magnetic susceptibilities, electrical and thermal conductivity, and refractive index differ along different directions in a liquid crystal. Here, we will study the refractive index and the implications that an anisotropic refractive index has for the optical properties of liquid crystals.

### 5.1. Definitions

- *Refractive index*: The refractive index,  $n$ , describes the phase velocity of light in a material relative to its velocity in a vacuum:  $n = c/v$ , where  $c$  = velocity of light in vacuum and  $v$  = phase velocity of light in the material. The refractive index also describes the angle of refraction that light experiences when entering or exiting a material (Snell's law). It is related to the dielectric constant,  $\epsilon$ , and the magnetic permeability,  $\mu$ :  $n = \sqrt{\epsilon\mu}$ .
- *Birefringence (double refraction)*: A birefringent material has two different indices of refraction depending on the polarization of the incident light.
- *Optically uniaxial*: Materials in which there is one propagation direction (called the *optic axis*) in which birefringence does not occur.
- *Optically biaxial*: Materials in which there are two propagation directions that do not exhibit birefringence.

### 5.2. Optical anisotropy in liquid crystals



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Figure 4. Schematic showing unpolarized light incident on a liquid crystal sample. On entering the sample, the light is split into two rays, the ordinary (in the direction of the director) and the extraordinary, because of the birefringent nature of the material. On exiting, the rays recombine and generate a new polarization state, because they have traveled different distances at different speeds. From <http://plc.cwru.edu/tutorial/enhanced/files/lc/biref/biref.htm>

The refractive index of a birefringent material (such as liquid crystals) is dependent on the polarization of the incident light. Thus, incident light of arbitrary polarization will be split into two components, traveling at different speeds and in different directions. The

*ordinary ray* is the fast component that is polarized along the director of the liquid crystal; the *extraordinary ray* is slower and polarized perpendicular to the director.

Upon exiting the material, the ordinary and extraordinary rays recombine. However, these two rays are now out of phase, because they have propagated at different speeds through the material. Thus, the recombined beam has a different polarization than that of the incident light. (Note that this change in polarization is not exclusively a material property – it depends on the width of the material as well as its birefringence.) Note that if the light is incident along the optic axis of a birefringent material, the beam is not split into two components. Thus, there is no change in polarization on exiting the sample.

It is useful to study liquid crystals between crossed polarizers (see Polarized Light Microscopy section below for a full explanation). Isotropic samples appear dark when viewed through crossed polarizers, because the sample does not change the polarization of the incident light. However, due to the birefringent nature of nematic liquid crystals, a change in polarization occurs when light exits the sample. Thus, there is (in general) a component of light that can pass through the second polarizer. Liquid crystals therefore will appear bright through crossed polarizers. For light incident along (or perpendicular to) the optic axis, however, the sample will appear dark because there is no change in the polarization of the light.

A common texture for nematic liquid crystals is known as the *Schlieren texture* (Figure 5). The black regions are where the optic axis is either parallel or perpendicular to the incident light. Points where the black regions meet are known as *disclinations*. The colors result from different orientations of the liquid crystal relative to the incident light.

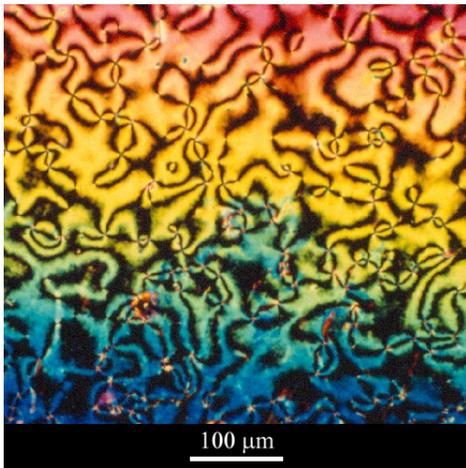


Figure 5. Nematic Schlieren texture seen through crossed polarizers. From University of Cambridge Micrograph Library, micrograph 612, <http://www.doitpoms.ac.uk/miclib/index.php>

Courtesy of DoITPoMS, University of Cambridge. © DoITPoMS Micrograph Library, University of Cambridge.

## 6. Phase transitions in liquid crystals

### 6.1. Thermally driven phase transitions<sup>1-3</sup>

In ordinary solids, a phase transition occurs from solid to liquid at the melting temperature,  $T_m$ . At this temperature, the system has enough energy for interatomic (or intermolecular) bonds of the solid to be broken, and for the arrangement of the component atoms or molecules to be randomized. This solid  $\rightarrow$  liquid phase transition entails the destruction of both translational (positional) and long-range orientational order.

For liquid crystals, order is only partially destroyed at each phase transition. The enthalpy of each transition depends on the amount of change in order that occurs (the greater the change in order, the larger the enthalpy of the transition). For example, a thermotropic nematic liquid crystal will undergo a solid  $\rightarrow$  liquid crystal transition, in which 3 degrees of translational order and 2 degrees of rotational order are destroyed (e.g. the same number of degrees of freedom are created). The next transition, from nematic  $\rightarrow$  isotropic liquid (which occurs at the clearing temperature,  $T_c$ ) destroys only 1 degree of rotational order. Thus, the latter involves a much smaller enthalpy change than the former.

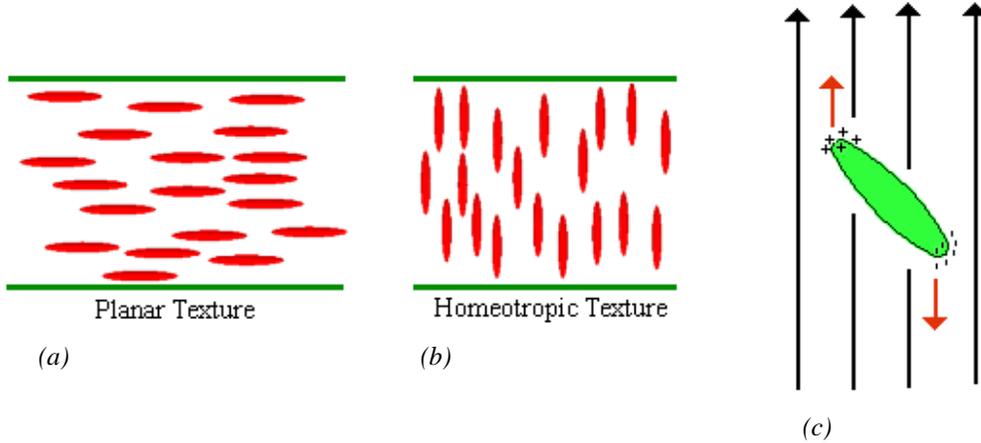
A polymorphic material is one that can exist in more than one structural phase. For example, there are liquid crystal molecules that possess a nematic phase and a variety of smectic phases. In these cases, the low-temperature phases are always more ordered than the high-temperature phases; this is required by entropic contributions to the free energy. Thus, a smectic phase may transform to a nematic with increasing temperature but never the reverse, because order must be destroyed with increasing temperature.

Most thermally driven phase transitions of liquid crystals are first order. In general, a first order phase transition displays a discontinuity in some physical property, such as the heat capacity. For liquid crystals, this property is the order parameter. For example, the nematic  $\rightarrow$  isotropic liquid transition that we will observe is of first order because of the discontinuous change in the order parameter (from some finite value to 0) at  $T_c$ . Although most liquid crystal transitions are first order, a few (such as smectic C  $\rightarrow$  smectic A) are second order, meaning that the order parameter undergoes a continuous change through the transition region.

### 6.2. Electric field driven phase transitions<sup>4,5</sup>

Liquid crystals placed between two horizontal surfaces tend to align in a planar texture with the long axis of the molecules parallel to the surface. It is possible to align them perpendicular to the surfaces as well, through the application of an electric field (Figure 6). Liquid crystal molecules have slight dipole moments (permanent or induced by an external electric field), which will tend to align along an external electric field. In a solid, this reorientation is difficult because the molecules are strongly bonded to other

molecules to be turned by an applied field. In a liquid, the thermal motion of the molecules opposes their alignment by an electric field. However, for liquid crystals, we can induce this transition and change the orientation of the direction.



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Figure 6. (a) Planar texture, in which the director of a liquid crystal points parallel to the confining surface. (b) Homeotropic texture, in which the director is perpendicular to the surface. (c) It is possible to induce a reorientation from planar to homeotropic texture via application of an electric field, which induces the dipoles of the liquid crystal molecules to align with the field.

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

The electric field across a parallel plate capacitor (such as our sample) is

$$E = \frac{V}{d}$$

where  $V$  is the voltage and  $d$  is the thickness of the capacitor.

The dipole moment per molecule of our liquid crystal sample is  $\mu = 4.4$  Debyes (1 Debye =  $3.3 \times 10^{-30} \text{ C} \cdot \text{m}$ ). The energy (in the form of a torque) to rotate a molecule with a given dipole moment into alignment with an electric field is

$$\tau = \vec{E} \times \vec{\mu} = |\vec{E}| |\vec{\mu}| \sin \theta$$

where  $\theta$  is the angle between the unrotated molecule and the applied field. Convert to a molar energy to compare with values for the thermally-driven nematic  $\rightarrow$  isotropic phase transition measured in DSC.

## 7. Experimental techniques

### 7.1. Differential scanning calorimetry (DSC)<sup>6,7</sup>

DSC is a technique to measure the heat flow into or out of a sample (relative to a reference sample) as a function of temperature. By measuring the amount of heat a sample absorbs or releases ( $\Delta H$ ) as we change the temperature ( $T$ ) at a constant rate, we can directly determine thermodynamic quantities such as:

- The enthalpy of melting,  $\Delta H_m$  (and that of other phase transitions)
- The temperatures of various phase transitions (e.g. solid $\rightarrow$ liquid, liquid $\rightarrow$ vapor, and vice versa), as well as the crystallization and glass transition temperatures ( $T_c$  and  $T_g$ , respectively) of polymers

Most of the thermodynamic quantities accessible by DSC are associated with phase transitions, such as melting. Recall from class that the change in enthalpy upon melting is known as the enthalpy of melting,  $\Delta H_m$ , and that there is a discontinuity in the enthalpy at the solid-liquid phase transition. More practically, consider what happens to ice when it is heated at a constant rate. At first, its temperature rises as it is heated. When it reaches its melting temperature,  $T_m$ , the ice begins to melt and become liquid water. However, until the entire sample has melted, the temperature does not rise above  $T_m$  even though heat is still being added to the system. Only once the entire sample has become liquid does the temperature rise again. This is because heat is required to overcome the energetic barrier between the two phases and drive the solid $\rightarrow$ liquid phase transition.

In DSC, the temperature of a sample is increased (or decreased) at a constant rate, and the heat flow into (or out of) the sample in order to maintain that rate is measured in comparison to a reference sample. In our above example, the heat flow is constant until we reach  $T_m$ . Then, a large amount of heat must be added in order to melt all the ice and maintain the imposed rate of temperature increase. Thus, the DSC will detect an endothermic peak (energy being put into the system) in the heat flow at  $T_m$ , from which we can calculate the enthalpy of melting.

A typical DSC curve of a crystalline polymeric material such as high density polyethylene (HDPE), for example, would look like:

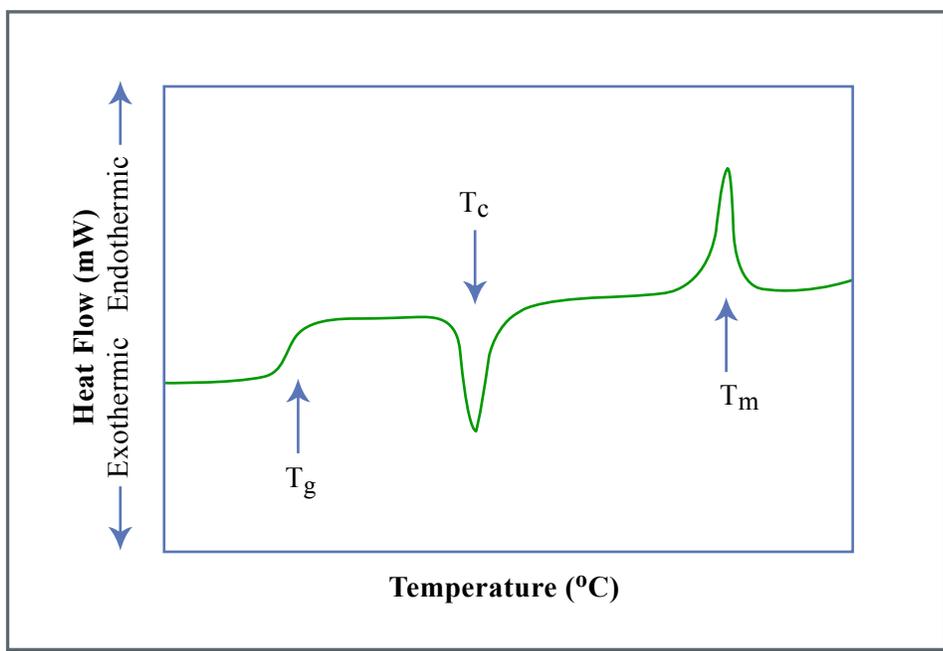


Figure by MIT OCW.

where  $T_m$  is the melting temperature,  $T_c$  is the crystallization temperature, and  $T_g$  is the glass transition temperature. Exothermic peaks, such as that of crystallization, point down, indicating that energy is being released from the sample. Endothermic peaks, such as those associated with melting, are positive because energy is being put into the sample.

General notes about data interpretation:

- Positive peaks are endothermic (a positive amount of energy is being put into the sample), and negative peaks are exothermic.
- Endothermic peaks (melting, solid-solid transitions, e.g.) are often reversible on cooling; exothermic peaks (crystallization, decomposition) are not.
- The enthalpy of a phase transition ( $\Delta H$ ) can be determined by integrating the peak.

## 7.2. Polarized Light Microscopy<sup>8,9</sup>

The polarized light microscope is an optical microscope that contains two polarizing elements in series: the *polarizer* and the *analyzer*. The analyzer is generally in a fixed orientation (meaning that it allows the transmission of light of only one particular polarization). The orientation of the polarizer can be rotated in its plane. When the polarizer is oriented at 90 degrees to the analyzer, it transmits light that is polarized at right angles to that which is able to be transmitted by the analyzer. In this arrangement, the polarizer and analyzer are said to be *crossed*. If the sample is isotropic, crossed polarizers do not allow any light to reach the eyepiece, because the linearly polarized light created by the first polarizer cannot pass through the perpendicularly oriented second polarizer. However, birefringent (anisotropic) samples such as liquid crystals do allow light through crossed polarizers at certain orientations, because the polarization of the light is changed upon transmission through the sample.

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