

Lab Week 3 – Module γ_1

DSC and Polarized light microscopy study of liquid crystals

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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

Summary of tasks

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

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*; the positions and orientations of the 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 *short-range order*. The components are randomly located and oriented and there is no long-range repeat of the structure.

The term *liquid crystal* refers to a wide range of molecular structures and compositions that all possess a higher degree of order than isotropic liquids but that are less ordered than crystalline solids. 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).

Structure of liquid crystals¹⁻³

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 that have one long axis and negligible dimensions in the other two directions

Discotic: composed of disc-like molecules

Sanidic: composed of “rectangular” molecules that have substantial size in two dimensions

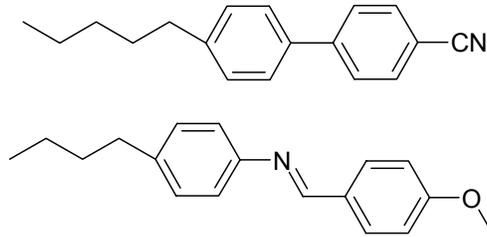
Thermotropic: the liquid crystal state exists within certain temperature regimes. At lower temperatures the substance is in a solid crystalline phase; at higher temperatures (above the clearing temperature, T_c) it is an isotropic liquid.

Lyotropic: the liquid crystal state is driven by interactions between certain amphiphilic molecules and some polar solvents.

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

Nematic liquid crystals

Nematic liquid crystals belong to the calamitic family; 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 to give approximately linear molecules. Terminal and side functionalization modify the properties of the molecule and thus the structure and properties of the liquid crystal. Two common molecules that form nematic liquid crystals are shown below:



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 removed for copyright reasons

(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 disorder. The order parameter is defined as

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

where β 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. 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.

Smectic liquid crystals

Smectics are another class of calamitic liquid crystals in which the rod-like molecules form into a layered structure. 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.

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.

Figure removed for copyright reasons

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).

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	1
Nematic LC	3	1
Isotropic liquid	3	3

Optical properties of liquid crystals¹⁻³

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, electronic and magnetic susceptibilities, electronic 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.

Definitions

Refractive index: The refractive index, n , describes the speed of light propagation in a material: $n = c/v$, where c = velocity of light in vacuum and v = phase velocity of light in the material. The refractive index also controls the angle of refraction that light experiences when entering or exiting a material (Snell's law). It is related to the dielectric constant, ϵ , and the magnetic permeability, μ : $n = \sqrt{\epsilon\mu}$.

Birefringence (double refraction): A birefringent material has two different indices of refraction depending on the polarization of the incident light.

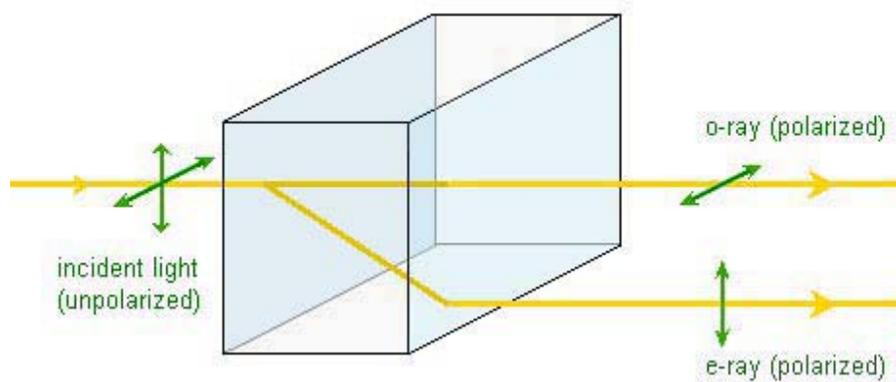
Optically uniaxial: Materials in which there is one propagation direction (called the *optic axis*) in which birefringence does not occur

Optically biaxial: Materials in which there are two propagation directions that do not exhibit birefringence.

Optical anisotropy in liquid crystals

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.)



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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.

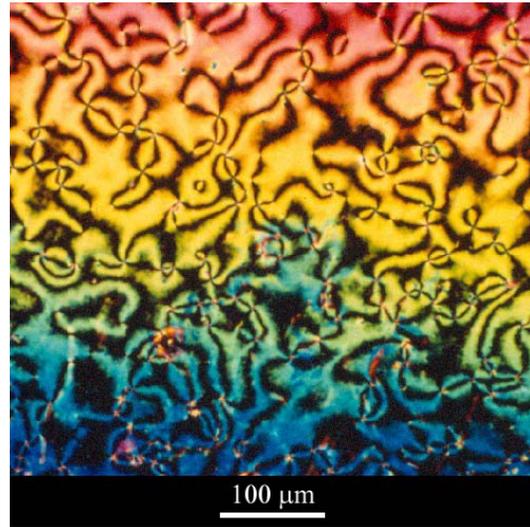
From <http://plc.cwru.edu/tutorial/enhanced/files/lc/biref/biref.htm>

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 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*. 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.



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.

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Phase transitions in liquid crystals

Thermally driven phase transitions¹⁻³

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 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.

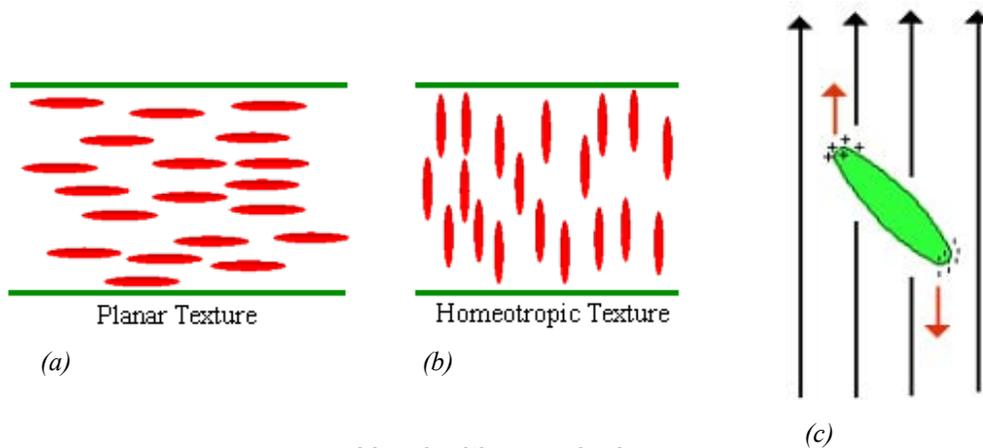
A polymorphic material is one that can exist in more than one structural phase. For example, there are liquid crystal molecules that possess a nematic phase and a variety of smectic phases. In these cases, the low-temperature phases are always more ordered than the high-temperature phases; this is required 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.

Electric field driven phase transitions^{4,5}

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. Liquid crystal molecules generally have slight dipole moments, which will tend to align along an external electric field. In a solid, this reorientation is not possible because the dipoles are fixed too strongly 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 “phase transition” and change the orientation of the director.



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- (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 phase transition 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>

We can calculate the energy of this rotational phase transition:

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

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

where V is the voltage at which the phase transition occurs 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

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

where θ is the angle between the unrotated molecule and the applied field.

This energy is per molecule. Convert to a molar energy to compare with values for the thermally-driven nematic \rightarrow isotropic phase transition measured in DSC.

Experimental techniques

Differential scanning calorimetry (DSC)^{6,7}

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 (ΔH) as we change the temperature (T) at a constant rate, we can directly determine thermodynamic quantities such as:

- The enthalpy of melting, ΔH_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
- The thermal degradation temperature

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, ΔH_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 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:

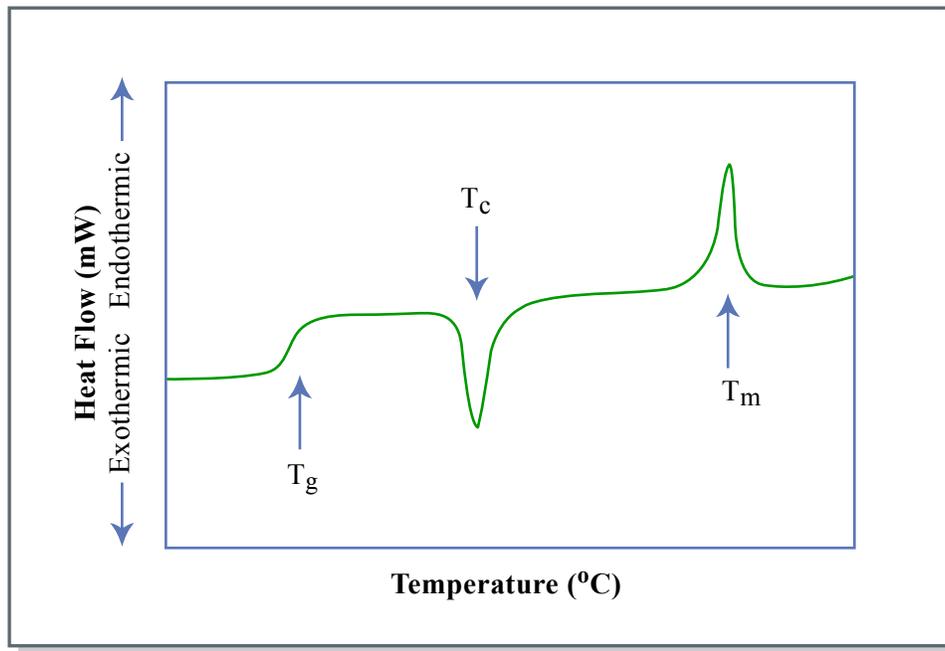


Figure by MIT OCW.

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 (ΔH) can be determined by integrating the peak.

To calculate the heat capacity C_p and the entropy change ΔS , you must use the initial and final peak temperatures and the area under the peak:

$$C_p: \begin{cases} \Delta H = \int_{T_1}^{T_2} C_p dT \\ \Delta H = C_p (T_2 - T_1) \\ C_p = \frac{\Delta H}{(T_2 - T_1)} \end{cases}$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} dT = C_p \ln(T_2 - T_1)$$

To calculate ΔG of transition, you must use the peak temperature, the ΔH from the thermogram, and the ΔS from calculations as given above:

$$\Delta G = \Delta H - T\Delta S$$

Polarized Light Microscopy^{8,9}

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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