Liquid crystals; another state of matter

Solid – Liquid Crystals – liquid – gas
Applications

Liquid crystals - history

Several scientists observed liquid crystal behaviour without understanding the implications or the underlying structure.

From 1850 – 1888:

1) Microscopy studies of biological specimens: e.g. covering of nerve fibers. Soft flowing forms and polarizing effects in liquid states…

2) Crystallization studies: **Otto Lehmann**: Heating stage on a microscope with polarizing filters. Crystallization studies during cooling. Observed formation of an “amorphous state” between liquid and crystalline state.

3) Unusual melting behaviour in stearin. (W. Heintz ~1850): Cloudy at 52°C, opaque at 58°C and becomes clear at 62.5°C.
The discovery

An Austrian botanist, Friedrich Reinitzer, studied cholesterol in plants. In 1888 he reported two melting points in a compound related to cholesterol: Melts to a cloudy liquid at 145.5°C, turned to a clear liquid at 178.5°C. (cholesteryl benzoate)

What is this? Might it be a form of matter different from solids or liquids?

By asking the question, instead of just observing, he qualified to be remembered as the discoverer of liquid crystals.

Otto Lehmann became the leading figure in the early days of liquid crystal research.

Otto Lehmann

Microscope with heating stage and polarizing filters (1900)

From a letter to Reinitzer:

"…my new results confirm your [previously] declared view, that the [substance] consists of very soft crystals … It is absolutely homogeneous, and another liquid - as you assumed formerly - is not present … It is of a high interest for the physicist that crystals exist which are of such a considerable softness that one could almost call them liquid."
Types and classification of liquid crystals

Water, H₂O

solid | liquid | gas
--- | --- | ---
0°C | 100°C

Cholesteryl myristate

C₄₁H₇₂O₂

CH₂(CH₂)₄CH₂-O

3β-Hydroxy-5-cholestene 3-tetradecanoate 5-Cholesten-3β-ol 3-tetradecanoate Cholesteryl tetradecanoate

Solid to liquid crystal: 272 J/g
Liquid crystal to liquid: 29 J/g

Liquid crystals are more similar to liquids than to solids

Is a liquid crystal liquid-like or crystal-like?

Solid to liquid: endothermic

Cholesteric myristate:

Solid to liquid crystal: 272 J/g
Liquid crystal to liquid: 29 J/g

Liquid crystals are more similar to liquids than to solids
Molecules

~1 of 200 molecules form liquid crystals

Which molecules may form liquid crystals?

1) Elongated shape (anisotropic)
2) Must have some rigidity in its central region. Flexible (cooked spaghetti-like) molecules do not form a liquid crystal state.
3) Flexible ends seems to be an advantage

Calamatic:

Bridging Group $X$
- $N = N$
- $N = NO$
- $CH = CH$
- $C \equiv C$
- $CH = N(O)$
- $CH = N$
- $O - CO$

End Groups $R$, $R'$
- $C_{n}H_{2n+1}$ $n = 1$ to $9$
- $OC_{n}H_{2n+1}$ $n = 1$ to $9$
- $C \equiv N$
- $OOC - OC_{n}H_{2n+1}$ $n = 1$ to $9$
Discotic:

Kevlar - polymeric liquid crystal

Cholesterol-derivatives

5 -CB

pyrene-derivatives

OOCBP

Cholesterol

Nematic

No positional order, only rotational order.
Average direction of molecules: the director
If there is no orientational disorder the mean angle to the director is 54.74°
(3-dimensional averaging)

Order parameter: \[ S = \frac{3 \cos^2 \theta - 1}{2} \]

Variation of order parameter with temperature

KJM3100 V2008
Nematic
Crossed polarizing filters.
Defect lines:
Nematic derived from the Greek word for Thread

Chiral nematic (Cholesteric) Liquid crystals

The director is not fixed in space, but rotates through the sample.
The characteristic parameter, the pitch, is the distance along the helix, before the molecules have turned one full turn.

Schematic diagram of a chiral nematic phase with a helical pitch, $P$. $n$ is the nematic director for each of the layers shown in the diagram.
Partial orientational and positional order

Tendency to organization in planes. Usually no positional order within a plane.

Smectic liquid crystals are turbid and viscous substances “goo”. Their molecules are arranged into equidistant two-dimensional sheets. The long axis of the molecules is perpendicular to or tilted by a certain angle to the face of the layers. The lateral spacing between the molecules within a layer may be regular or random. Hydrogen-bonding between the polar groups link the molecules laterally and cooperatively to form head-to-head tail-to-tail bilayers. This class is further separated into several subclass, due to subtle differences.
Phase transitions

Higher symmetry: decreasing order

I - isotropic liquid
N - nematic
N_A - chiral nematic (formally Ch for cholesteric)
A, F
C, G
C*H
B
E
K - crystals
K_1 - highest temperature crystals
K_2 - second highest temperature crystals

decreasing order
Characterization: thermal analysis

DTA: Differential Thermal Analysis
DSC: Differential Scanning Calorimetry
Determine enthalpy of phase transitions

DTA and DSC graphs showing phase transitions:
- **PAA, p-azoxyanisole**
  - Solid: 118°C
  - Nematic: 135°C
- **4-n-pentylbenzen-4'-n-decylxybenzoate**
  - Solid: 60°C
  - Smectic C: 63°C
  - Smectic A: 80°C
  - Nematic: 86°C
- **Cholesteryl myristate**
  - C_{41}H_{72}O_{2}
  - Solid: 71°C
  - Smectic A: 79°C
  - Chiral nematic: 85°C

KJM3100 V2008
**Discotic phases**

Disc-shaped molecules
Columnar organized liquid crystals
Nematic or smectic organization

**Hexatic smectic**

**Smectic B**
Two distinct smectic B phases have been identified. Both of these phases, molecules are aligned perpendicular to smectic layers. Three dimensional crystal, **crystalline B** phase, has short range positional correlation among layers with molecules in hexatic two dimensional lattice. Hexatic B forms layers with short range positional correlation and week correlation between layers.

**Smectic D**
This phase occur between SC and SA or between SC and the isotropic phase. The mechanism of structural formation and the detail molecular arrangement is not known but assumed to be micelle type. At present only 4 compounds are known to exhibit this phase.

**Smectic E**
Three dimensional crystal, orthorhombic with interlayer herringbone arrangement of the molecules.

**Smectic F**
This is the tilted version of the hexatic B phase. There are two types of smectic F, chiral and achiral. Achiral Smectic F has the C- centered monoclinic symmetry with in-plane short-range positional correlation and weak or no interlayer positional correlation. Chiral Smectic F is formed with a twist axis normal to the layers.

**Smectic G**
It has a C- centered monoclinic symmetry.

**Smectic H**
There are two types, chiral and achiral. Three dimensional crystal, monoclinic, with herringbone arrangement of the molecules. Chiral Smectic H is form with a twist axis normal to the layers.

**Smectic I**
There are two types, chiral and achiral. Achiral Smectic F has the C- centered monoclinic symmetry and tilted hexatic with slightly greater in-plane correlation than smectic F. Chiral Smectic F is form with a twist axis normal to the layers.

**Smectic J**
There are two types, chiral and achiral. Three dimensional crystal, monoclinic, with herringbone arrangement of the molecules. Chiral Smectic F is form with a twist axis normal to the layers.

**Smectic K**
There are two types, chiral and achiral. Three dimensional crystal, monoclinic, with herringbone arrangement of the molecules. Chiral Smectic F is form with a twist axis normal to the layers.
Lyotropic Liquid Crystals

Lyotropic liquid crystals are multi component systems formed in mixtures of amphiphilic molecules and a polar solvent. Amphiphilic molecules are consisted of a hydrophilic polar head attached to a hydrophobic hydrocarbon tail containing one or two alkyl chains.

Characterization, SAXS
Small angle X-ray scattering

nematic

Smectic A

hexatic

Smectic C
Clay liquid crystals

Figure 3. Isotropic–nematic phase separation as observed between crossed polarizers, at volume fractions ranging from (a) 15.9, (b) 16.5, (c) 16.9, to (d) 17.4% (v/v). The isotropic upper phase shows streaming birefringence when the tube is slightly shaken, indicating the presence of free alignable platelets. The lower phase is permanently birefringent due to nematic ordering and shows its liquid crystalline nature by flowing like a moderately viscous liquid when the tube is tilted.
Optical effects

- Birefringence in nematic crystals
- Scattering of light
- Scattering of light polarization

Electric and magnetic field effects
Active matrix liquid crystal displays are standard on most new laptop computers. Two properties of liquid crystal is used as tiny switches to turn picture elements (pixels) off and on. First the crystals are transparent but can alter the orientation of polarized light passing through them. Second, the alignment of their molecules (and their polarization properties) is changed by applying an electric field. In a color display the liquid crystals are held between two glass plates or transparent plastics. These plates are usually manufactured with transparent electrodes, typically made of indium tin oxide, that makes it possible to apply an electric field across small areas of the film of liquid crystal. The outsides are coated with polarizing filters. Only light with a perpendicular polarization can pass through these filters. 

Inside the plates are transparent electrodes and color filters, which form very small picture element regions called subpixels. A grouping of a red, a green and a blue subpixels defines the color that the pixel transmits. Fluorescent backlighting illuminates a display from the rear. In pixels that are off, light passes through the rear polarizing filter, the crystals (b) and the color filters, only to be blocked (absorbed) by the front polarizing filter. To the eye, these pixels appear dark. When a pixel is turned on, the liquid crystals reorient their position, and they in turn repolarize the light so that it can pass through the front polarizing filter (c).

The active matrix provides a superior method of electronically addressing (turning on) an array of pixels. For an image to appear on screen, one row of pixels receives the appropriate voltage. At the same time, software in the computer dictates that voltage be applied to those columns holding active subpixels. Where an activated row and column intersect, a transistor turns on a subpixel electrode, generating an electrical field that controls the orientation of the liquid crystal. This process repeats sequentially for each of the rows in figure 3.6 above, an advanced display, which can take 16 to 33 milliseconds.
Thin nematic film on isotropic surface: 1-Dimensional periodicity

The periodic stripe structure is a spectacular consequence of the confined nature of the film. It is a result of the competition between elastic inner forces and surface anchoring forces. The surface anchoring forces want to align the liquid crystals parallel to the bottom surface and perpendicular to the top surface of the film. The elastic forces work against the resulting "vertical" distortions of the director field. When the film is sufficiently thin, the lowest energy state is surprisingly achieved by "horizontal" director deformations in the plane of the film. The current picture shows a 1-dimensional periodic pattern; 2-dimensional periodic patterns can also be observed.

Thin nematic film on isotropic surface: 2-dimensional periodicity

The periodic texture formed by a 2-D lattice of surface point defects (boojums) in a thin nematic film (0.4 micrometer). For further explanation see previous picture.
Point Defects

Schlieren texture of a nematic film with surface point defects (boojums). This picture was taken under a polarization microscope with polarizer and analyzer crossed. From every point defect emerge four dark brushes. For these directions the director is parallel either to the polarizer or to the analyzer. The colors are newton colors of thin films and depend on the thickness of the sample. Point defects can only exist in pairs. One can see two types of boojuns with "opposite sign of topological charge"; one type with yellow and red brushes, the other kind not that colorful. The difference in appearance is due to different core structures for these defects of different "charge".

KJM3100 V2008

DNA liquid crystals

With a texture resembling pencil shavings, conical-shaped structures have a color pattern that shifts from blue to purple

KJM3100 V2008
This pattern exhibits a Schlieren texture with a color transition from pinkish-purple to green. Miniature gas bubbles in the DNA specimen preparation account for "spots" seen on the focal conic textures.

KJM3100 V2008

Grown from aqueous saline solution buffered with citrate at pH 7.3, this calf thymus DNA single crystal demonstrates birefringence and the beginning of a focal conic texture.

KJM3100 V2008