

Liquid Crystals

Books

S Chandrasekhar Liquid Crystals 2nd edition, 1992, CUP

P-G de Gennes The Physics of Liquid Crystals, OUP
1974

AM Donald and AH Windle, Liquid Crystalline
Polymers, CUP 1992.

Introduction

Crystals have 3 dimensional periodic structures.

Amorphous materials including liquids are disordered.

Liquid crystals have **intermediate order**, and are
consequently sometimes known as **mesophases**.

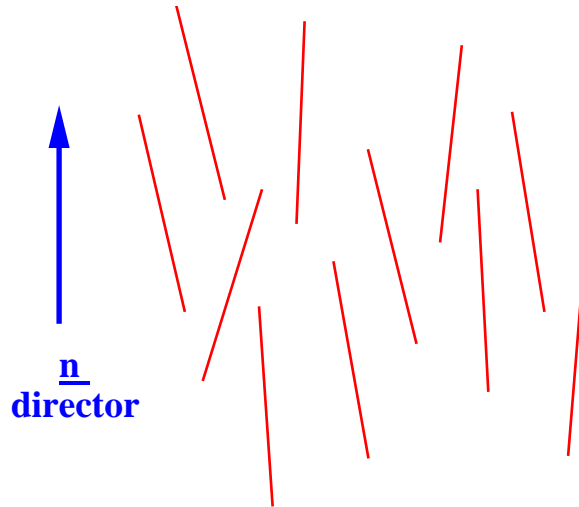
They have orientational but not positional order.

They are neither true liquids nor crystals.

There are various different types with differing
symmetries.

Friedelian Classes

Nematic – lowest symmetry



n is the preferred direction, known as the **director**

Alignment with the director is not perfect.

Can be characterised by the order parameter

$$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle \quad \text{2nd Legendre polynomial}$$

where θ is the angle each molecule makes with **n**.

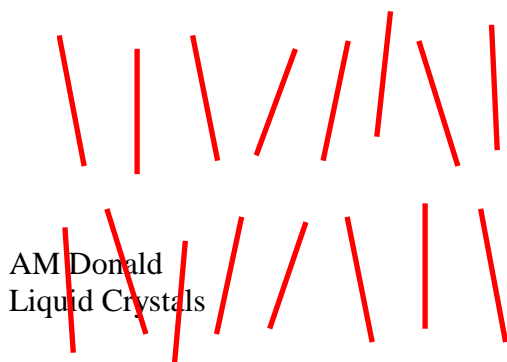
S = 1 for perfect alignment

S = 0 for random alignment (as in isotropic liquid) and

S = -1/2 for molecules lying randomly in plane \perp ar to director

Smectic – from Greek for soap.

Layer structure – with nematic order within layers.



Smectic A

n parallel to layer

normal



Smectic C

**n inclined to layer
normal**

There are a whole series of smectic phases, with different degrees of symmetry.

Some of them are really equivalent to low-dimensional crystals.

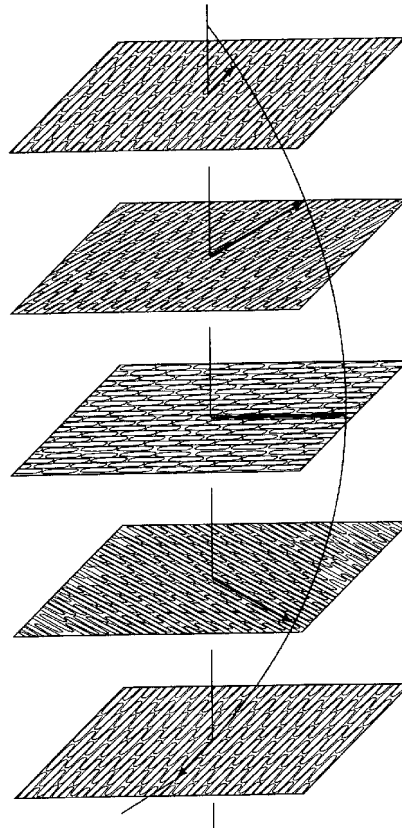
All have layer structures.

Cholesteric – the name comes from cholesterol.

Chiral molecules (that is, ones with asymmetric carbon atoms, so that that is the molecule differs from its mirror image) spontaneously twist.

Nematic order in each layer, but there is a (systematic) angular twist between successive layers.

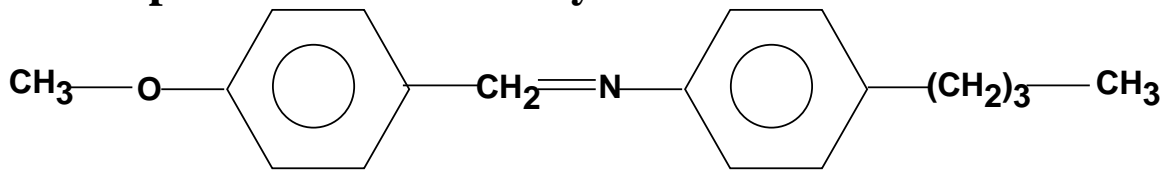
This leads to a helical structure.



Helix has a well-defined pitch.

Molecular Types

Typical molecules which form LC phases are rod-like or anisotropic in some other way.



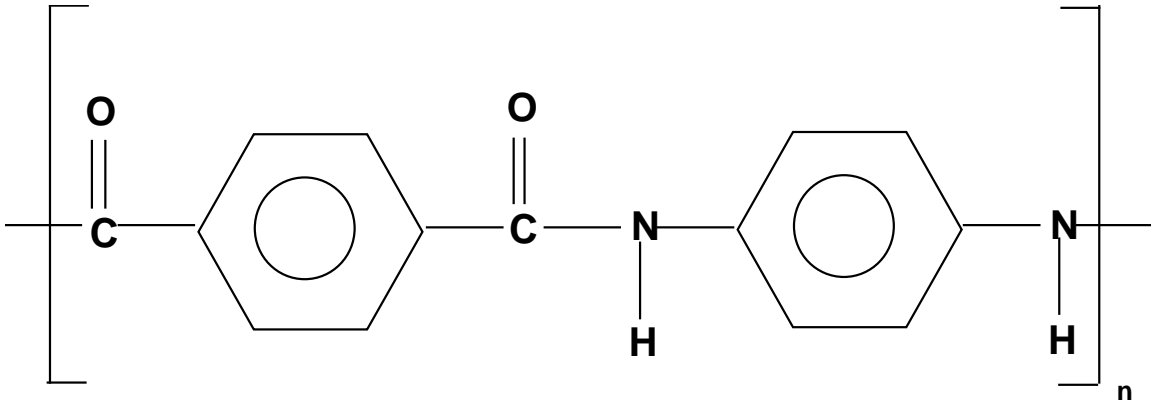
n-(4-methoxybenzylidene)-4-butylaniline **MBBA**

is a typical molecule, **para linked aromatic rings**, often with **conjugation**, to create an overall stiff molecule resembling a rod.

Para linkages mean bonding at 1 and 4 position on benzene ring to give a straight molecule.

Conjugation means alternating apparent single and double bonds along the chain promote electron delocalisation, which tends to stiffen the molecule.

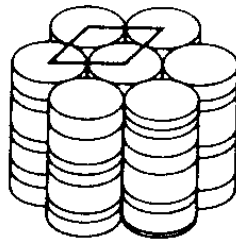
Can also have polymers with this same para linkage to give a high aspect ratio molecule.



Poly(p -phenylene terephthalamide) PPTA – **Kevlar**.

Other shaped anisotropic molecules can also form LC phases.

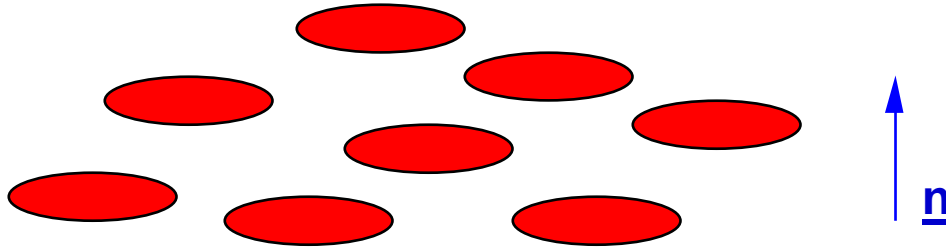
e.g. planar molecules



These may stack as columns to form **columnar phases**.

There are many variations of discotic phases depending on the symmetry of the stacks.

Or simply all the discs may align parallel to form a **discotic nematic**.



Such disc-shaped organic molecules, again with substantial para linkages, but now within a plane to form the disc, are being increasingly looked at for their ability to orient to give useful optoelectronic properties.

Amphiphilic Molecules

Have mentioned that the word smectic comes from the Greek for soap.

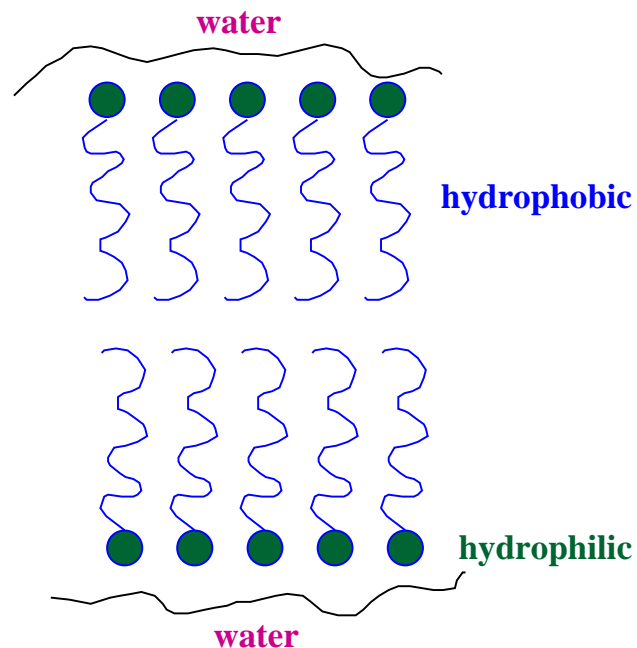
The molecules in soap (based on stearic acid) are examples of **amphiphilic molecules** (literally 'both loving').

This means they have a polar end which is hydrophilic, and a non-polar hydrophobic end.

Such molecules spontaneously order when placed in water – a process known as **'self assembly'**.

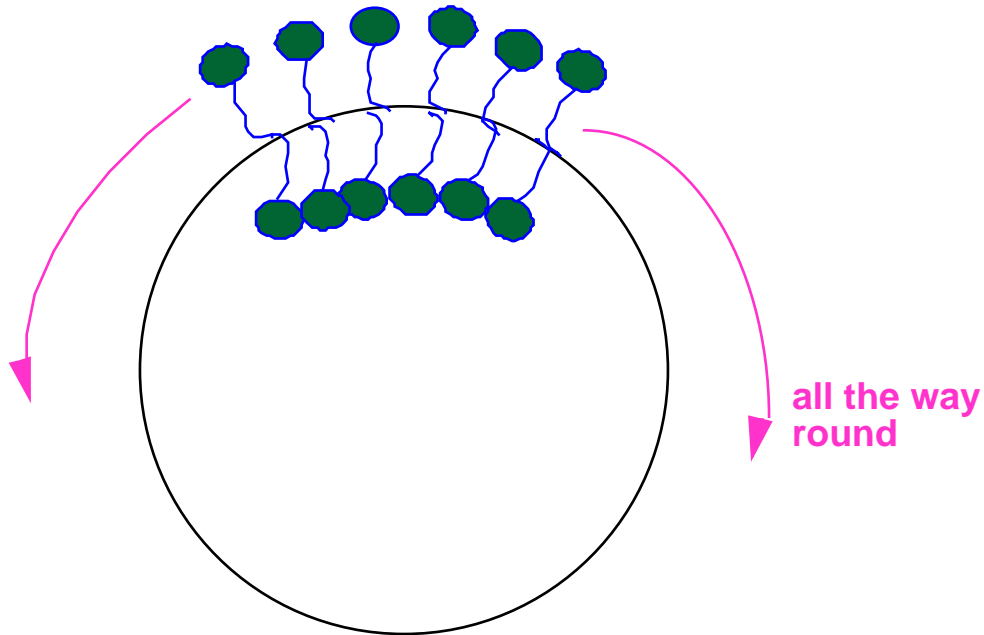
e.g. lipids

Planar bilayer Structure



These structures are very important in biology, as they form the basis of the cell membrane for all animal cells.

In this case the layers roll up to form a closed surface, with the hydrophilic head groups in contact with the aqueous environment both within and outside the cell.



Physicists are now using model bilayer structures, known as vesicles, to help understand the cell membrane's behaviour.

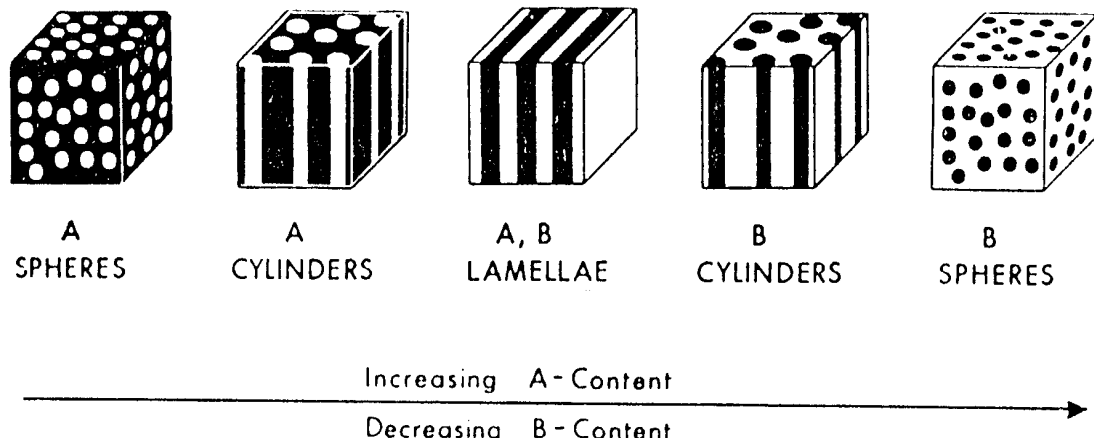
In general amphiphilic molecules can exhibit a series of different phases, with a systematic progression depending on concentration and molecular shape.

Block Copolymers

Block copolymer melts (i.e. A_nB_m type polymers) show very similar behaviour.

This is for similar reasons – the two parts of the chain do not want to mix and so the geometry of the connectedness forces particular self-assembled structures onto the system.

In this case the progression of phases occurs as a function of "concentration" (ratio of m/n) and total chain length.



Thermotropic and Lyotropic Phases

Liquid crystalline phases can form

- either over a range of temperatures – **thermotropic** phases –
- or over a range of concentrations in solution – **lyotropic**.

MBBA is an example of the former.

Crystal ----- 20°C -----> Nematic ----- 47°C -----> Isotropic

Since, as we will see, optical properties are strongly affected by the phase the system is in, such materials can be very useful for temperature sensors, by choosing materials with appropriate phase transition temperatures.

Kevlar is an example of a lyotropic material.

However, because of its para-linkages and high degree of conjugation it only dissolves in very strong acids.

When Kevlar is processed, it is dissolved in hot concentrated sulphuric acid . This makes it expensive to process.