Flory Lattice Model

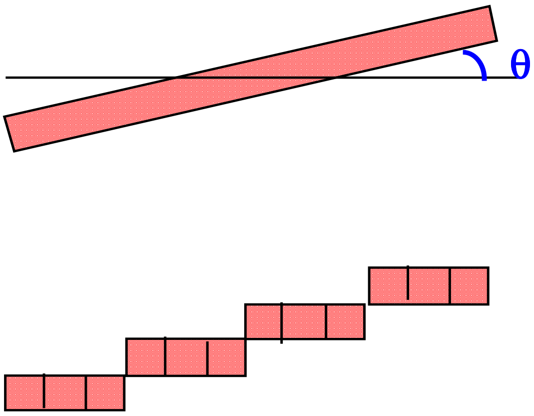
Works out distributions and averages by usaing a lattice; monomer and solvent each occupy one lattice site.

Particularly good for lyotropic polymers, i.e. ones where there are small solvent molecules present, as well as the stiff polymer chains themselves.

Partition function can be written as the product of two terms:

$$Z = Z_{comb} \times Z_{orient}$$

combinatoric **orientation**



Z_{comb} describes the number of ways of arranging identical rod-like molecules on a lattice, with a fixed misorientation to the director.

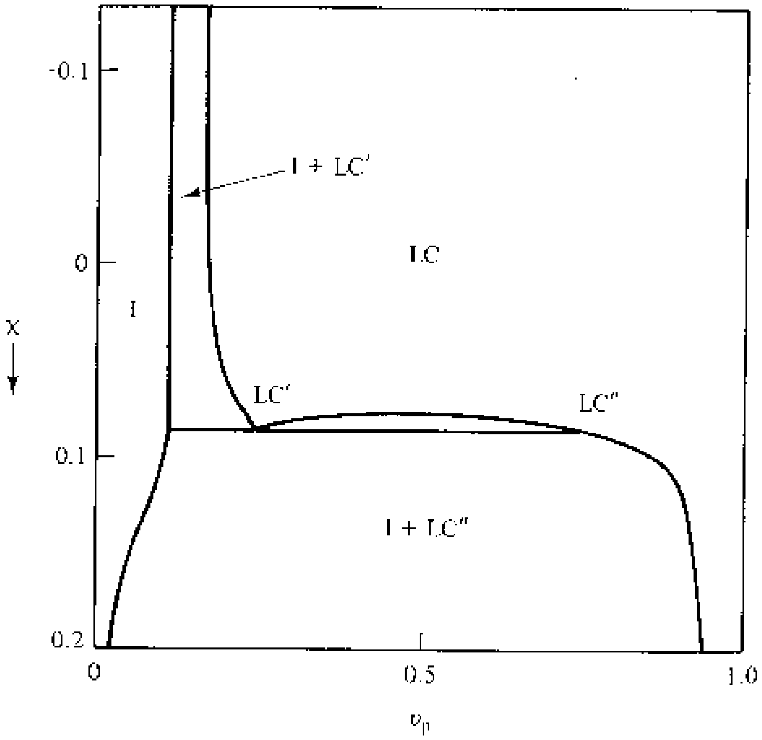
Z_{orient} takes into account the many additional arrangements possible when allowance is made for the possible different orientations.

Based on this approach the following key points emerge.

- There is a critical axial ratio (i.e. length/width ratio) ~ 6.4.
- For values smaller than this an LC phase never forms.
- LC and I phases can coexist.

In its simplest form the theory is athermal, but molecular interactions – and hence T – can be built in.

Then a phase diagram can be plotted.



Semiflexible Chains

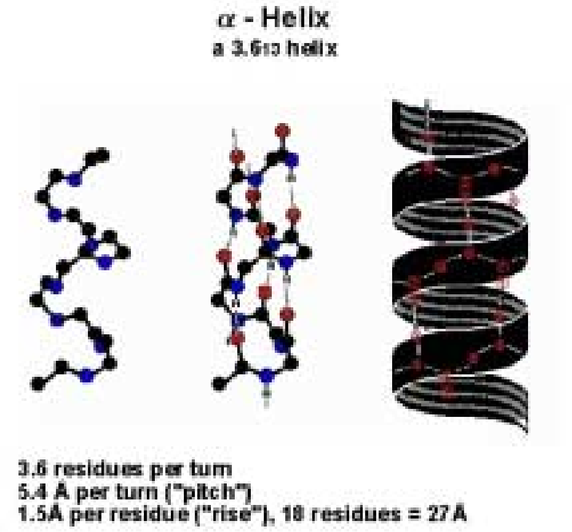
These theories assume a completely stiff rod; in practice molecules deviate from this to a greater or lesser extent.

In particular, temperature may increase molecular flexibility.

Modifications to Flory theory to take this into account have been developed.

However, more drastic changes can also occur – in particular biological molecules can undergo a helix-coil transition.

e.g. proteins have internal hydrogen bonding which favours the formation of the α-helix.



These favourable interactions can overcome the unfavourable loss of entropy.

However as the temperature is raised, the gain in energy no longer is sufficient to overcome the entropic term, and a transition occurs.

Imagine chain of N units existing as sections of coil and helix, with h units in helical regions and g units of each type (so 2g junctions between coil and helix).

ΔF_{hc} is change in free energy when coil moves from a coil to helix state.

ΔF_g is free energy associated with junction – it represents the fact that neighbouring hydrogen bonds are easier to form once one is in place i.e. represents cooperativity.

Number of ways of arranging h out of the N units into g helical regions

$$\Omega_h = \frac{h!}{g!(h-g)!}$$

Similarly there are Ω_c ways of arranging the (N-h) coil segments into g units

$$\Omega_c = \frac{(N-h)!}{g!(N-h-g)!}$$

Entropy associated with these arrangements $\Delta S(h,g,N) = k_B \ln(\Omega_c \Omega_h)$ which can be expanded via Stirling's approximation.

Total free energy

$F(h,g) = h\Delta F_{hc} + 2g\Delta F_g - T\Delta S_c(h,g,N)$

This needs to be minimised wrt h and g to yield

$$\frac{c(h-g)}{h(c-g)} = \exp\left(-\frac{2\Delta F_{hc}}{k_B T}\right) = s$$

$$\frac{g^2}{(c-g)(h-g)} = \exp\left(-\frac{2\Delta F_g}{k_B T}\right) = \sigma$$

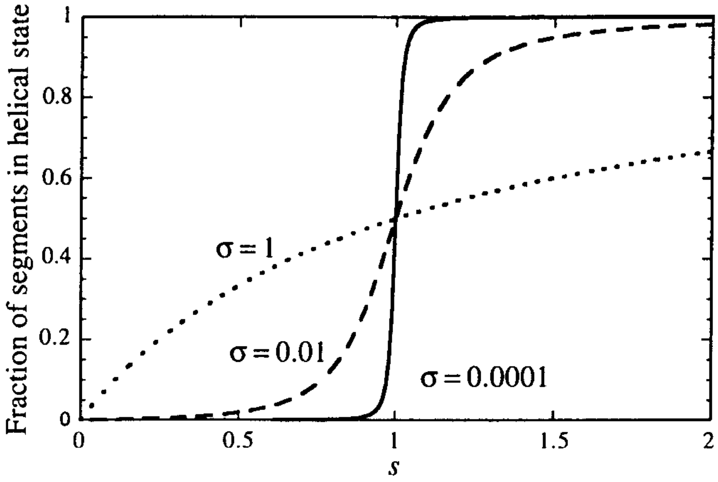
where c=N-h the number of coil regions.

s represents the preference for a given segment to be in the helix state, and will be temperature dependent: s<1 means the coil state is preferred; s>1 the helix.

σ is a measure of the cooperativity of the transition; σ = 1 implies no cooperativity; σ=0 implies junctions are forbidden.

Put $f_h = h/N$, the fraction of units in the helix state, and substitute for g gives

$$f_h = \frac{1}{2} + \frac{(s-1)}{2\sqrt{(s-1)^2 + 4s\sigma}}$$



s<1 means the coil state is energetically favoured.

Breadth of transition depends on σ.

Note that this is <u>not</u> a first order phase transition, which cannot exist in 1D.

Ordering in Electrical and Magnetic Fields

Have so far described the orientation in terms of the scalar order parameter

$$\mathbf{S} = 1/2\langle 3\cos^2\theta - 1\rangle$$

However, in the presence of external fields which may not be aligned with the director, need a more formal analysis.

Nematic phases either have an inversion centre, or equal probabilities of pointing up or down – do not get ferroelectric nematics.

If ν^α is the unit vector pointing along the molecular axis of the molecule at $\underline{x}^\alpha$, then both ν^α and $-\nu^\alpha$ contribute to the order (i.e. quadrupolar not dipolar order): any order parameter must be even in ν^α, and a vector order parameter is insufficient.
Try a second rank tensor $\underline{\underline{Q}}$

$$= \begin{pmatrix} \frac{2}{3}S & 0 & 0 \\ 0 & -\frac{1}{3}S & 0 \\ 0 & 0 & -\frac{1}{3}S \end{pmatrix}$$ **with S defined as before.**

$$\langle Q_{ij}\rangle = \mathbf{S}\,(n_i n_j - 1/3\delta_{ij})$$

$\underline{\underline{Q}}$ has the properties that its trace is zero, but in the nematic phase $\langle Q\rangle \neq 0$ (unlike the isotropic).

Put the nematic fluid in an electric field, macroscopic susceptibility will depend on $\underline{\underline{Q}}$ (and similarly for other properties).

If $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the diamagnetic susceptibilities along and perpendicular to each molecule's axis and there are N mols/unit vol, then the component of the susceptibility along z (parallel to $\underline{n}$) will be

$$\chi_z = N(\alpha_{\parallel}\langle\cos^2\theta\rangle + \alpha_{\perp}\langle\sin^2\theta\rangle)$$

and $\langle\cos^2\theta\rangle = 1/3\,(2S+1)$ and $\langle\sin^2\theta\rangle = 2/3\,(1-S)$

Hence can write

$\chi_z = N(\alpha^{\dagger} + 2/3(\alpha_{\parallel} - \alpha_{\perp})S)$ where $\alpha^{\dagger} = 1/3(\alpha_{\parallel} + 2\alpha_{\perp})$

Similarly can show

$\chi_x = \chi_y = N(\alpha^{\dagger} - 1/3\,(\alpha_{\parallel} - \alpha_{\perp})S)$

and hence overall

$$\underline{\underline{\chi}} = N(\alpha^{\dagger}\underline{\underline{\delta}} + 1/3\,(\alpha_{\parallel} - \alpha_{\perp})\underline{\underline{Q}})$$

thus showing the linkage between $\underline{\underline{Q}}$ and macroscopic parameters.

Role of $\underline{\underline{Q}}$ in Phase Transitions

In general, for any system, can construct an expansion of the order parameter to express the free energy (Landau free energy).

For a dipolar system, this will mean only even terms are present, but for the nematic with its quadrupolar ordering, can have odd terms.

NB 1st order term corresponds to Tr $\underline{\underline{Q}}$ which is identically zero, and so this term is absent.

$F = 1/2\, AQ^2 - 1/3\, BQ^3 + 1/4\, CQ^4$ **and** $A = (T - T^*)$

There are qualitatively different free energy curves as the temperature changes.

$T_{N \to I}$ **occurs when F at Q=0 and at finite Q are identical for the first time.**

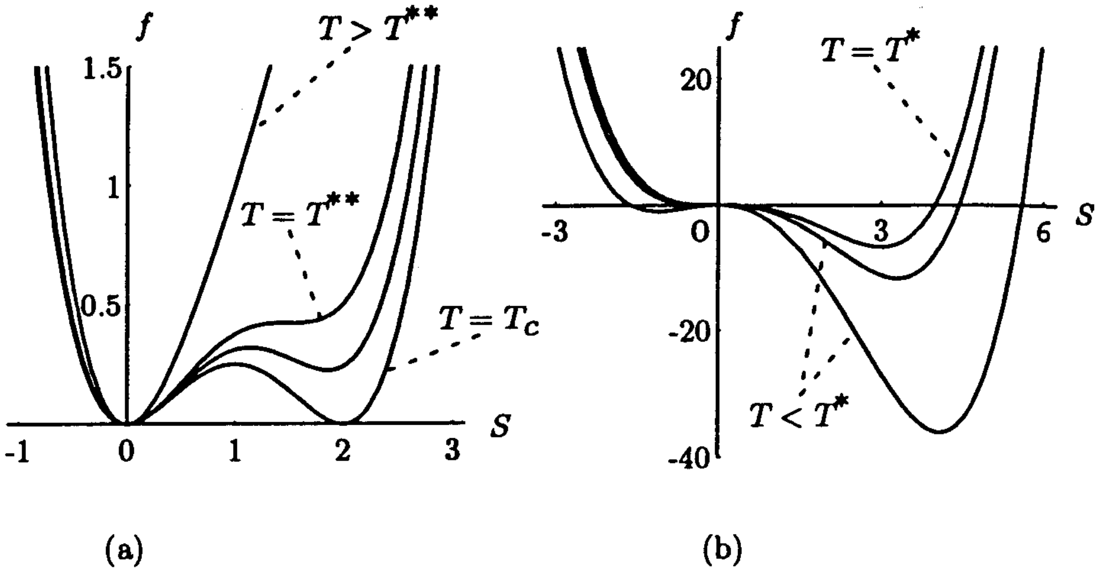


Fig. 4.5.2. Free energy density f as a function of order parameter S for different T for the isotropic-nematic transition. The transition is first order. Note the limits of metastability for supercooling (T^*) and superheating (T^{**}).

Properties of Liquid Crystalline Phases

The phases are inherently anisotropic – this shows up in many of their properties.

1. **Optically anisotropic i.e. birefringent.**

However they are rarely uniformly oriented, and the director will vary over space.

Different phases have different characteristic textures which arise from the permitted symmetry of the defects which occur in the packing.

The textures can be used to identify the phases (and often are).

However in the case of the 'fingerprint' texture seen in cholesterics, the structure arises simply from its helical structure.

Light is rotated by the director – as long as the rate of twist is not too great compared with λ.

Then there are systematic extinctions which give rise to the fingerprint texture.

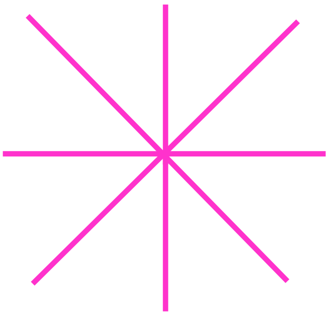
Defects

Whereas dislocations are discontinuities in translation of atoms, disclinations in LC phases are

discontinuities in orientation i.e. within the director field.

There are various types of disclinations characterised by their 'strength' s.

strength = no of multiples of 2π director rotates in a complete circuit around the disclination core.



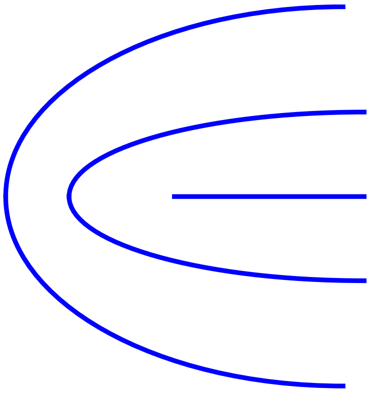
s= +1

Lines represent local direction of the director around the core.

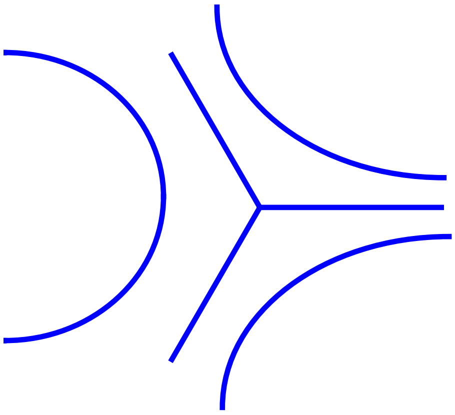
Under crossed polars, 4 dark 'brushes' are seen where the director is parallel to one of the polarisers and extinction occurs.

The defect may be either a line or a point defect. However in practice, at least for small molecules, line defects do not occur (for energetic reasons).

s = + 1/2



s = -1/2

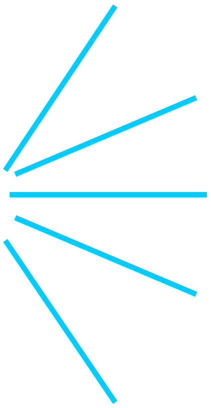


For both these two cases, two brushes are seen in the polarised light microscope.

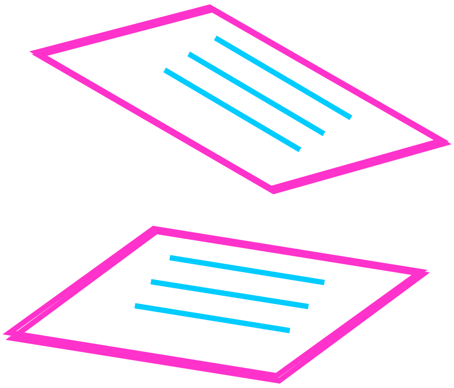
Disclinations with

- **positive strength exhibit dark brushes which rotate in the same direction as the crossed polarisers;**
- **those with negative strength rotate in the opposite direction – this is simply a sign convention.**

[This identification implies that the optic axis coincides with the molecular axis, which is usually the case.]



For the layered structures of smectics and cholesterics, the requirement of the continuity of essentially undeformed layers introduces new types of defects, known as focal conics.



2. Anisotropy of Elastic Constants

In the vicinity of defects there are various types of distortions.

Splay, K_1 – occurs e.g. around s=1 disclination. Implies a divergence in the director field.

Twist, K_2 – layers, each of which have a constant director field within, are twisted w.r.t one another. Curl $\underline{n}$ is parallel to $\underline{n}$.

Bend, K_3 – occurs around s=±1/2 disclinations. Curl $\underline{n}$ is perpendicular to $\underline{n}$.

There are 3 elastic constants, known as the Frank constants, which describe these 3 idealised types of distortions.

In practice any general distortion can be represented as an appropriate sum of these 3 types.

The 3 elastic constants are all ~10^{-12}N, but they will not have identical values.

Hence there is anisotropy of the elastic distortions.

The free energy of a general distortion can be written as

$$F_d = 1/2\ (K_1(\mathrm{div}\ \underline{n})^2) + 1/2(K_2(\underline{n}.\mathrm{curl}\ \underline{n})^2 + 1/2(K_3(\underline{n} \times \mathrm{curl}\ \underline{n})^2)$$

In general, for small molecule liquid crystals, twist is the lowest energy distortion and bend highest.

For liquid crystalline polymers, splay is thought to be highest because it will require chain end segregation, which will be increasingly difficult as the chains get longer.

For many situations, a 'one constant' approximation is used, as in the diagrams shown above for the distortions around disclinations.

However, in practice, because of the anisotropy of the elastic moduli, the director patterns around disclination cores may deviate from the symmetric patterns shown.

Indeed, this is one way of trying to estimate their relative magnitudes.

In general, the director fields will vary across the sample, with local variations in direction on the µm lengthscale.

This factor, plus the presence of defects, means that samples can look very beautiful in the polarising microscope.

However it also means that there may be scattering centres, which limit the use of LC's in optical devices.

Elimination of distortions and defects is therefore very important for applications.

3. Viscosity is Anisotropic - even more complicated!

Whereas for a isotropic fluid, a single viscosity relates stress and shear rate, six viscosities are required to describe LC flow completely (for a nematic).

These 6 viscosities, which are very hard to determine, are known as the Miesowicz viscosities.

The general equation relating the stress tensor $\underline{\sigma}$ to the director and flow fields is:

$$\underline{\sigma} = \alpha_1(\underline{n}.\underline{A}.\underline{n})\underline{nn} + \alpha_2\underline{nN} + \alpha_3\underline{Nn} + \alpha_4\underline{A} + \alpha_5\underline{nn}.\underline{A} + \alpha_6\underline{A}.\underline{nn}$$

where $\underline{A}$ is the shear strain rate tensor;
$\underline{n}$ is the director
$\underline{\sigma}$ is the shear stress tensor
and $\underline{N}$ expresses the rate at which the director orientation changes with time w.r.t background fluid.

This means how a system flows depends on the orientation of the director to the flow direction.

Determination of the α's has only been done for a few fluids.

There is a rich spectrum of instabilities which may occur.

Utilisation of Liquid Crystals

Small molecule LC's are mainly used in display devices, e.g watches, thermometers.

They can readily be switched, and respond to changes in temperatures, fields (electromagnetic) etc.

Recently ferroelectric LC's have started to find application.

Example: Twisted Nematic Cell

LC molecules are not only readily aligned by electric fields, they can also be aligned by surfaces, where their orientation can be fixed.

In a cell where the alignment produced by an externally applied field is different from that imposed by surfaces, there will be competition between the two senses of alignment.

In practice a threshold electric field exists at which the molecules reorient with this, at least in the centre of the cell.

This is known as the Fredericks Transition, and there is an equivalent situation for an external magnetic field.

It can be used, not only in devices, but also to extract the elastic constants.

Simple Analysis of the Fredericks Transition

The alignment produced by the surfaces is $\underline{n}_o$, cell thickness d in the z direction.

At position z the director is now $\underline{n}_o + \delta\underline{n}(z)$.

Total free energy/ unit vol at height z is

$$\overset{F_{elastic}}{\downarrow} \quad + \quad \overset{F_{field}}{\downarrow}$$

$$\frac{1}{2}K_1\left(\frac{\partial\delta n(z)}{\partial z}\right)^2 - \frac{1}{2}\varepsilon_o\delta\varepsilon E^2\delta n(z)^2$$

K_1 is the splay elastic constant and $\delta\varepsilon$ is the anisotropy in permittivity for the material (i.e $\varepsilon_{||} - \varepsilon_{\perp}$).

At the surfaces, alignment is assumed fixed by the surface properties, so that $\delta\underline{n}(0) = \delta\underline{n}(d) = 0$.

Consider a distortion of the form

$$\delta\underline{n}(z) = \Delta n \sin(\pi z/d)$$

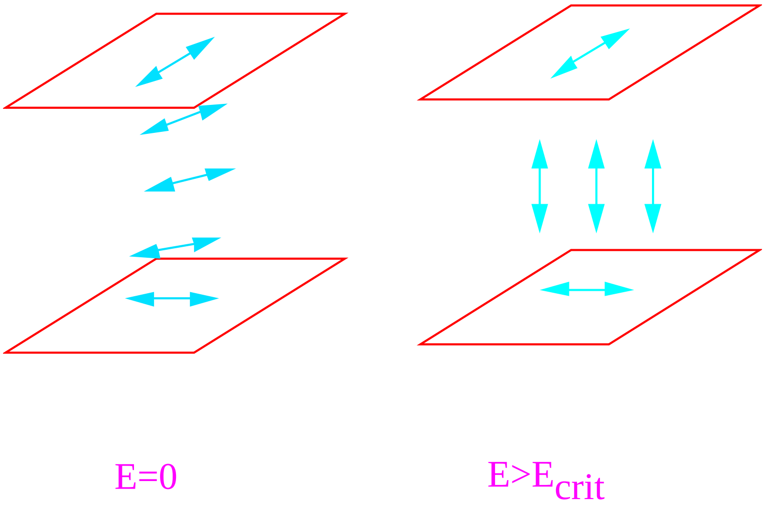
Then substitution into the free energy expression, and integrating from zero to d yields

$$\int_0^d F_{total}\,dz = \Delta n^2\left[\frac{K_1\pi^2}{4d} - \frac{\varepsilon_o\delta\varepsilon E^2 d}{4}\right]$$

Hence any small distortion of the director will lower the total free energy once a critical (threshold) field E_{crit} is exceeded, with

$$E_{crit} = \frac{\pi}{d}\sqrt{\frac{K_1}{\varepsilon_o \delta\varepsilon}}$$

Twisted nematic cells, as used for displays, actually have a slightly more complicated geometry.



In this case the cell is typically ~10µm in thickness, and the alignment is rotated through 90˚ between the upper and lower surfaces.

In the absence of a field, when the cell is placed between crossed polarisers, the polarisation of the light can follow the twist of the director and light is transmitted.

Beyond a critical field, the alignment in the centre of the cell changes to align with the electric field.

The director through the bulk of the cell is therefore perpendicular to the cell surfaces, and the LC cannot affect the polarisation of light.

Light is therefore blocked by the upper polariser, and no light is transmitted.

The equation for the critical field is more complicated because both twist and bend distortions are also present.

$$E_{crit} = \frac{\pi}{d}\sqrt{\frac{K_1 + 1/4(K_3 - 2K_2)}{\varepsilon_o \delta\varepsilon}}$$

Liquid Crystalline Polymers

Two kinds of use – "main chain" which is what I have been referring to up till now, and "side chain".

Main Chain Polymers

Example: Kevlar – a lyotropic, in which the solvent is H_2SO_4.

Kevlar has very high specific strength (i.e per unit weight).

Is used in tyre cords, ropes (e.g. holding up the roof of Cambridge Bus Station), and bullet proof vests.

However Kevlar is expensive, really only can be fabricated in fibre form, susceptible to UV damage, and poor in compression.

Example: Thermotropic Copolyesters

These are melt processable, and therefore can be moulded into a variety of shapes.

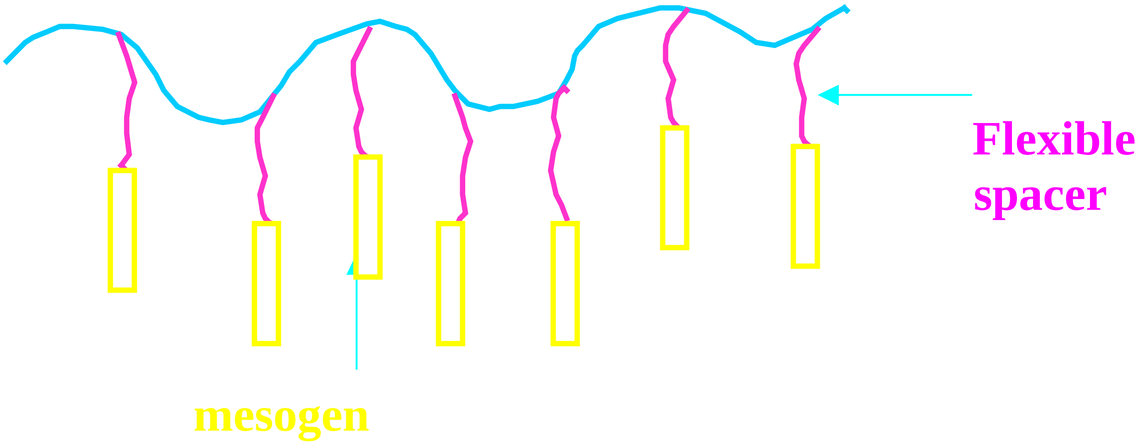
However, despite this advantage have only found a niche market in precision mouldings.

NLO applications: If the monomer in the LCP has a significant optical non-linearity, by lining up all the dipoles along the chain in the same sense can make a material with ~N times more optical non-linearity.

Theory and experiments now being worked on in this department by Prof Warner.

Side chain Liquid Crystalline Polymers

The so-called mesogenic unit is hung off the polymeric backbone.



It is the side chain units, which are often small molecule LC groups, and rod-like, which line up.

This will only work if there is sufficient decoupling between backbone and LC units.

This usually means introducing sufficiently long $(CH_2)_n$ units, with $n \geq 4$ as flexible spacers.

These polymers behave much more like SMLC's, and may also be used for display devices.

However their viscosities are much higher than the small molecule analogues, so switching times are comparatively long.

Advantage is that they can then form permanent displays since can be oriented at high temperature

and then the structure 'frozen' by dropping the temperature.

For LCP's, by comparison with SMLC's, 'domain size' over which the director is constant is much smaller.

This leads to problems for optical properties due to excess scattering at the defects.