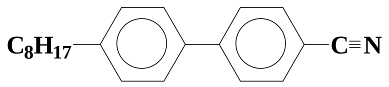
Characterization and Properties of Self-Assembled Materials

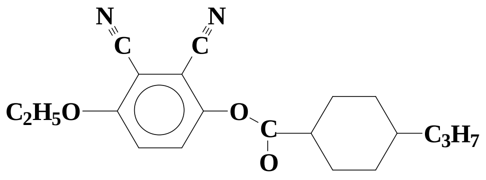
Parts 3 and 4

Liquid Crystals and Polarized Light

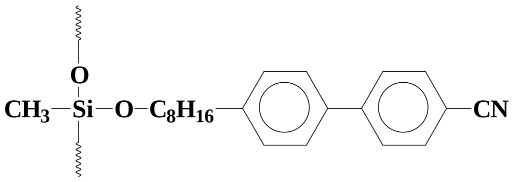
Examples of Liquid Crystal Forming (Mesogenic) Compounds



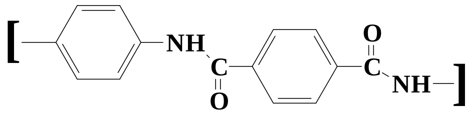
Rod-like
octyl cyanobiphenyl (8CB)
positive dielectric anisotropy
(e.g. for twisted nematic (TN) display)



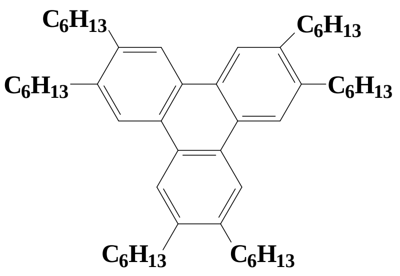
negative dielectric anisotropy
(e.g. for vertically aligned (VA) display)



Side-chain LC polymer



Main-chain LC polymer (Kevlar)



Discotic (Hexahexyl triphenylene)

Some liquid crystal phases

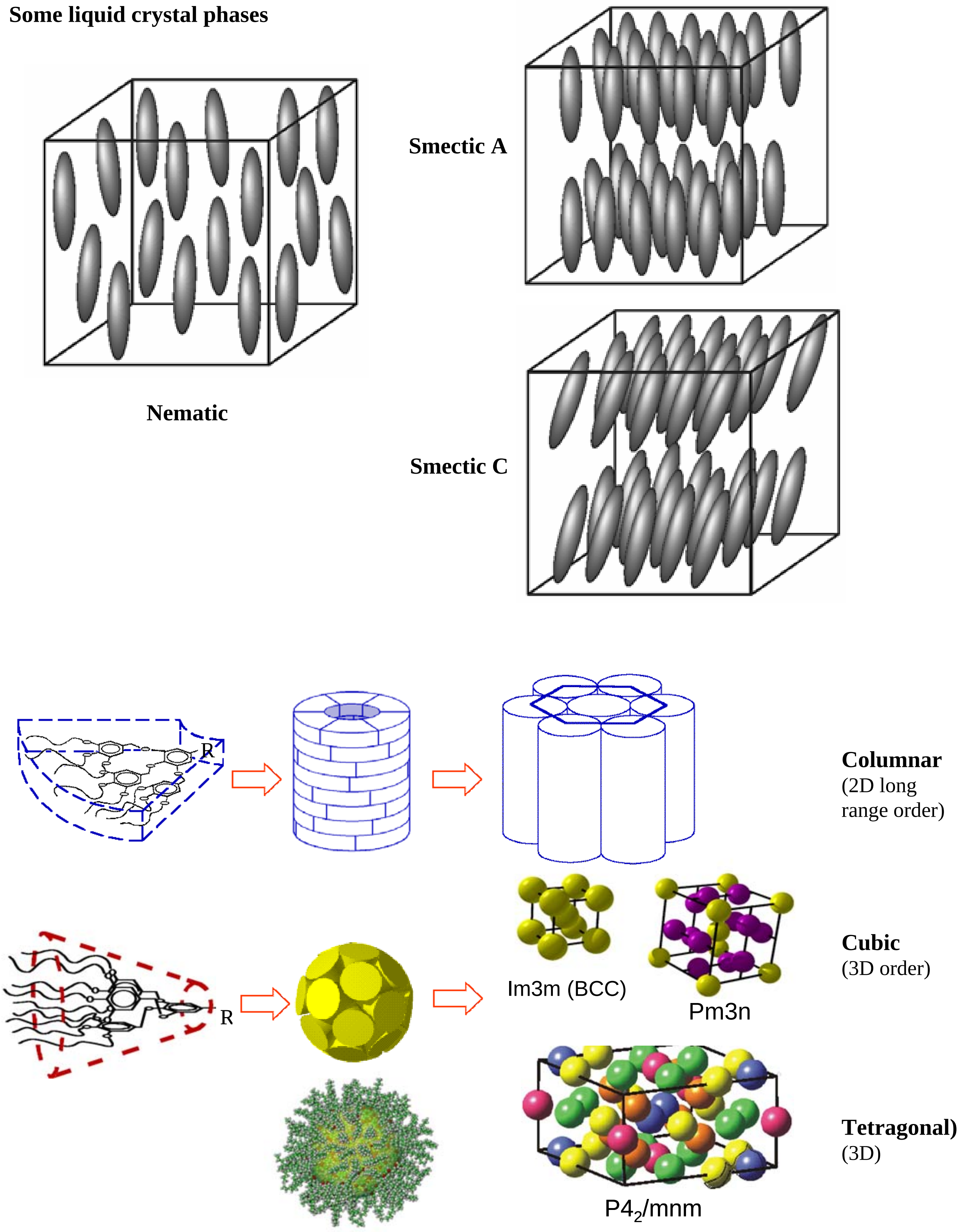


Figure 1 Different liquid crystal phases

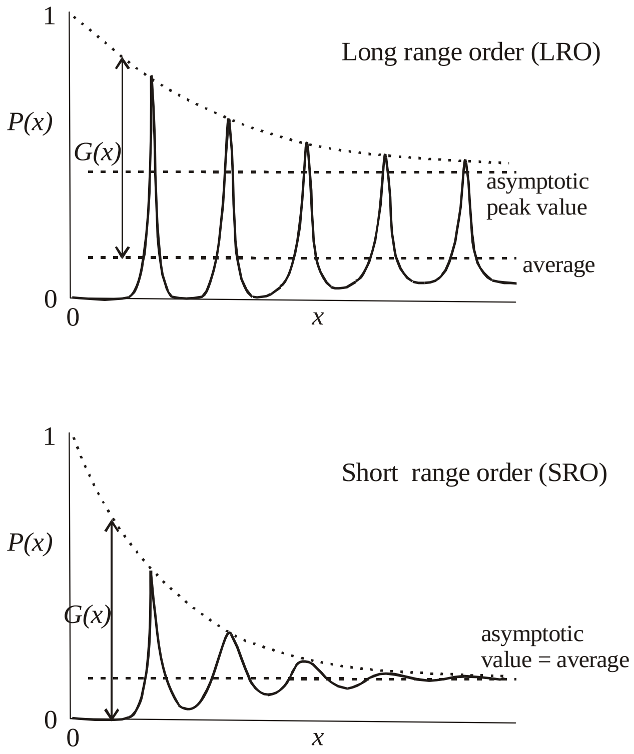
Long-Range and Short-Range Order

Crystals have long-range order in three dimensions (x,y,z). In crystals there is both **positional** and **orientational** LRO. All molecules in a crystal have a preferred position and orientation. Ordinary liquids have no LRO in any dimension, only short-range order (SRO). This applies to both positional and orientational order. All states in between are **liquid crystals**.

The difference between LRO and SRO is fundamental. It is defined by the type of decay of the **correlation function** G with distance. $G(x) = P(x) - P_{average}$ (see Figure 2). $P(x)$ is the probability of finding a particle (e.g. centre of a molecule) at a distance x from a reference particle (hence positional correl. f.). Alternatively, the orientational c.f. is related to the probability that a molecule is oriented parallel to the axis of preferred orientation, called **director** (**n**).

For LRO, the envelope of G decays asymptotically towards a **finite value** as $x \rightarrow \infty$. In the case of SRO, it decays exponentially to **zero**, i.e. as $\exp(-x/\xi)$, where ξ is the correlation length. The peaks in $P(x)$ are of constant height and width, independent of x, only in a perfect crystal at 0 K (even this is not strictly true due to quantum effects).

Correlation Function G(x)



$P(x)$ = probability that the centre of a particle is at x
(positional order)
= probability that molecule is oriented parallel to director **n**
(orientational order)

Figure 2 Long- and short-range order

Classification of l.c. phases by symmetry

Phase		**Dimensionality of positional LRO**	**Dimensionality of orientational LRO**	**Comment**
Isotropic liquid		**0**	**0**	
Nematic	**uniaxial**	**0**	**1**	
	(biaxial)		3	unconfirmed
Smectic	**A**	**1**	**1**	***n* normal to layers**
	C		**3**	***n* tilted**
	B (Hexatic)		1	*n* normal
	F, I (Hexatic)		3	*n* tilted
Columnar	**hexagonal**	**2**	**1**	different plane group symmetries
	rectangular		1,3	
	oblique		1,3	
3-D	**cubic**	**3**	**3**	different space-group symmetries
	hexagonal			
	tetragonal			
Crystal		**3**	**3**	molecules have preferred positions

(Items in bold should be remembered!)

The difference between 3D liquid crystals and 3D crystals is that in the former individual molecules don’t have a preferred position in space, only their aggregates have.

LCs can be thermotropic and lyotropic. **Thermotropics** change phase through heating or cooling, and do not contain a solvent. **Lyotropic** LCs contain a solvent for the whole or a part of the molecule, and phase transitions can be induced by changing the concentration. Typical lyotropics are surfactant (soap) – water systems, lipids – water systems (living cell membranes), Kevlar solution, many components of living organisms and of food.

The main emphasis of this series of lectures is on thermotropic LCs for displays. In displays, the most important LCs are nematic and smectic. Columnar LCs containing discotic molecules are also used; e.g. a thin discotic layer often covers an LCD in order to increase the viewing angle.

A nematic LC is essentially an anisotropic liquid. There is no positional LRO, but there is a degree of 1D orientational LRO, i.e. a preference for molecules to align spontaneously along a direction (the nematic director **n**). For clarity, when we talk about the ordinary liquid phase, we shall refer to it as the **isotropic liquid** (*isotropic* = same in all directions).

BIREFRINGENCE IN OPTICALLY ANISOTROPIC MEDIA

- In optically isotropic media (liquids, cubic crystals) refractive index $n = c/v$
  (c, v = speed of light in vacuum and in material)
  [Question: Explain, using a sketch, why light is refracted as it enters a transparent material.]

- In optically anisotropic (birefringent) materials light beam splits in two, an ordinary ray and an extraordinary ray. Indices are n_o and n_e.

- Both *e* and *o* rays are plane-polarized (linearly polarized). The planes are ⊥ to each other. The plane of *e* light contains the unique axis.

- Optical indicatrix = ellipsoid describing angular dependence of n_e. In uniaxial systems indicatrix is cylindrically symmetrical around the unique axis. (U.a. = nematic director, *c*-axis of a hexagonal or tetragonal crystal, flow direction of polymer melt or solution, stretch direction, etc). n_o is independent of direction of incident light.

- Cross-section through indicatrix ⊥ to light ray is generally an ellipse. Electric vectors $\mathbf{E}_e$ and $\mathbf{E}_o$ are ∥ to the principal axes of the ellipse. The lengths of the principal axes give n_e and n_o.
  [Q: (a) Explain why we see a double image when looking through some birefringent crystals. (b) (for those familiar with Huygens representation of refraction and diffraction) Explain why in birefringent materials light can be refracted even if it is incident perpendicular to the crystal surface.]

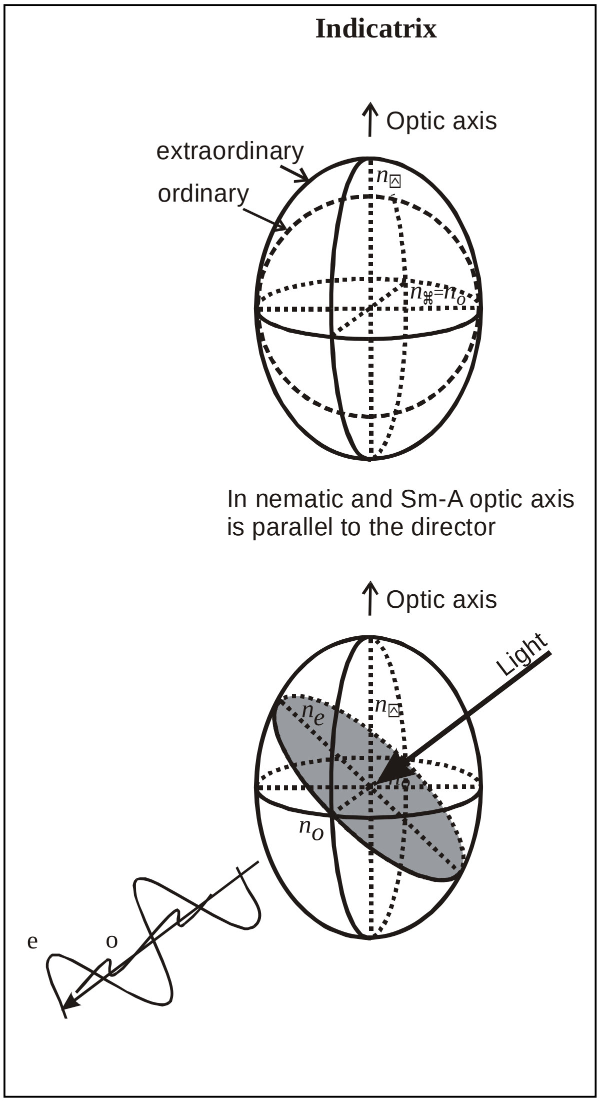


Figure 3 Top: Index ellipsoid (extraordinary indicatrix) and index sphere (ordinary indicatrix). Bottom: Determining n_e, n_o and the direction of polarization of *o* and *e* beams.

∥

- ***Birefringence*** of a material: $\Delta n = n_{\parallel} - n_{\perp}$
  $n_{\parallel}$ parallel to optic axis (length of unique axis of indicatrix),
  $n_{\perp}$ perpendicular to o.a. (radius of circular cross-section); $n_{\perp} = n_o$
  [Q: When is $n_{\parallel} = n_e$ in a uniaxial birefringent material?]

- Prolate (elongated) indicatrix ($n_e > n_o$): ***positive birefringence***. (e.g. typical polymer crystals, nematic or smectic phase of rod-like molecules).
  Oblate (squashed) indicatrix ($n_e < n_o$): ***negative birefringence***. (e.g. nematic or columnar phase of discotic molecules). (Discotic l.c. used e.g. as compensator in nematic LCD for optical correction and improved viewing angle).

- The two beams, generated by splitting of incident beam, propagate independently through material at speeds $v_e = c/n_e$ and $v_o = c/n_o$. To find the resultant electric vector $\mathbf{E}$ at a given position in the material,

$\mathbf{E}_e$ and $\mathbf{E}_o$ must be added (vector summation):

$$\mathbf{E} = \mathbf{E}_e + \mathbf{E}_o$$

- If incident light is linearly polarized, at any point after entering a birefringent material the resultant **E**-vector generally describes elliptical motion. Light becomes ***elliptically polarized***. In special cases it is linearly or circularly polarized. Phase difference (in radians) between the two components at depth *d* is:

$$\Gamma = \frac{2\pi}{\lambda}(n_e - n_o)d$$

[Q: Is the material in Figure 3 positively or negatively birefringent?]

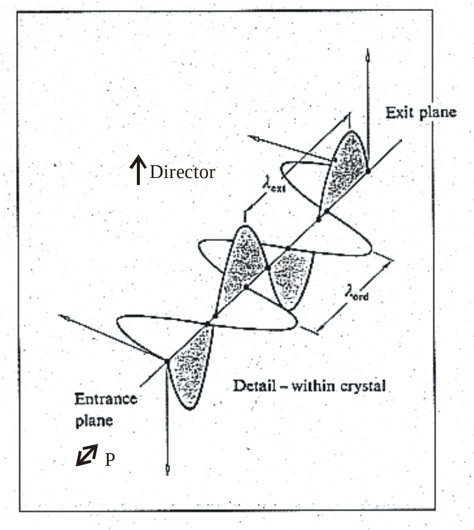


Figure 4 Electric displacement $\mathbf{E_e}$ (vertical) and $\mathbf{E_o}$ (horizontal) as a function of distance from the entrance plane at a given moment in time. Note that, since the frequency (colour) of light is unchanged, $\lambda_e/\lambda_o = n_o/n_e$. Here incident light is polarized (**P**) at 45° to the plane of the director, hence amplitudes of *e* and *o* beam are equal.

- ***Optic axis*** = axis perpendicular to which the section through the indicatrix is circular.
  - Light incident along optic axis is not split (Explain why!). If incident light is linearly polarized, it remains linearly polarized. To the light incident along optic axis the material appears optically isotropic.
  - In uniaxial systems, optic axis = unique axis.

- Fig. 5 (top) is a view along the beam at the point of incidence, where the **E** vector of the linearly polarized light (**E** vertical) is resolved into **e** component (in the plane of the optic axis) and **o** component (normal to it). The bottom part shows the situation at depth *d* within the material where the *e* wave lags behind the *o* wave by a phase angle $\Gamma = \pi/2$ (90°) (path difference $\lambda/4$). The resultant **E** is constructed for four successive times, separated by a quarter of a cycle. In a full cycle **E** is seen to describe an ellipse.

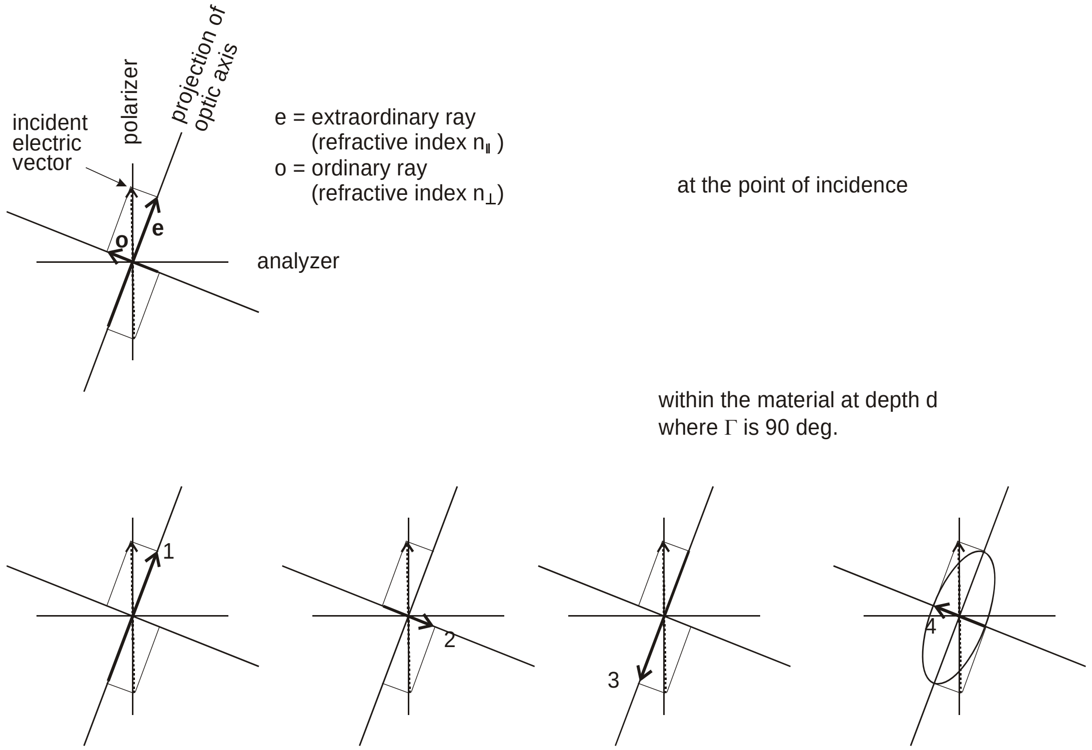


Fig. 5 Construction of electric vector of elliptically polarized light at four different times

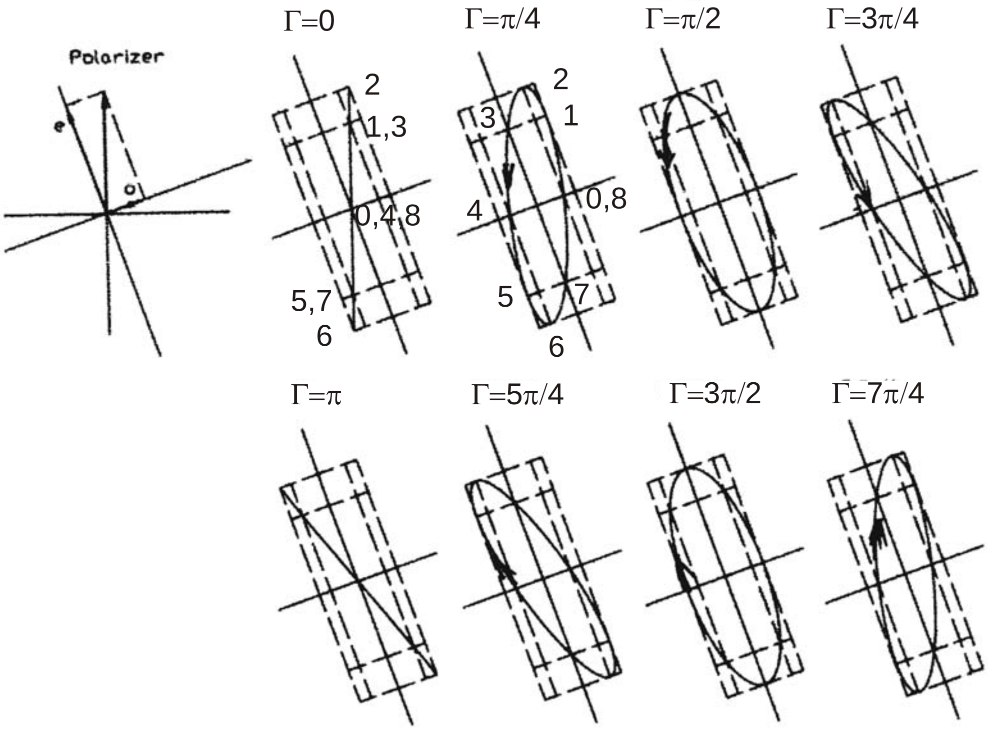


Figure 6 Motion of the electric vector of light at 8 different depths in a birefringent material corresponding to the *o*-*e* phase differences Γ indicated. The numerals indicate the positions of the vector at 8 successive times separated by 1/8 of the cycle. [Q: What determines the sense of rotation of the electric vector?]

- Figure 6 shows the construction of the ellipse at different depths in the birefringent sample. Note the special cases of $\Gamma = k\pi$ (k is an integer), where the light is linearly polarized. After leaving the sample the light retains the state of polarization as at the exit (i.e. generally elliptical).

- In most LCD applications and in most optical studies of birefringent materials (e.g. polarized optical microscopy), the material is placed between two polarizers crossed at 90° to each other. A polarizer (now typically a film of iodine-doped poly(vinyl acetate)) selectively absorbs light with **E** along a specific direction while transmitting the perpendicular component (such selective absorption is called *dichroism*). Thus a polarizer transmits ca. 50% of unpolarized light intensity.

- If there is no sample or there is an optically isotropic sample between crossed polarizers, the plane polarized light transmitted by the first polarizer is not altered, hence is fully absorbed in the second polarizer (“analyzer”). However, if a birefringent material is placed between the polarizers, aliptically polarized light is created in the sample. The component of such light which is parallel to the analyzer is transmitted. Thus in general, when viewed through crossed polarizers, a birefringent sample looks bright and coloured on a black background. The colour comes from the fact that components of the white light with different λ have different phase delays Γ as they leave the birefringent sample.

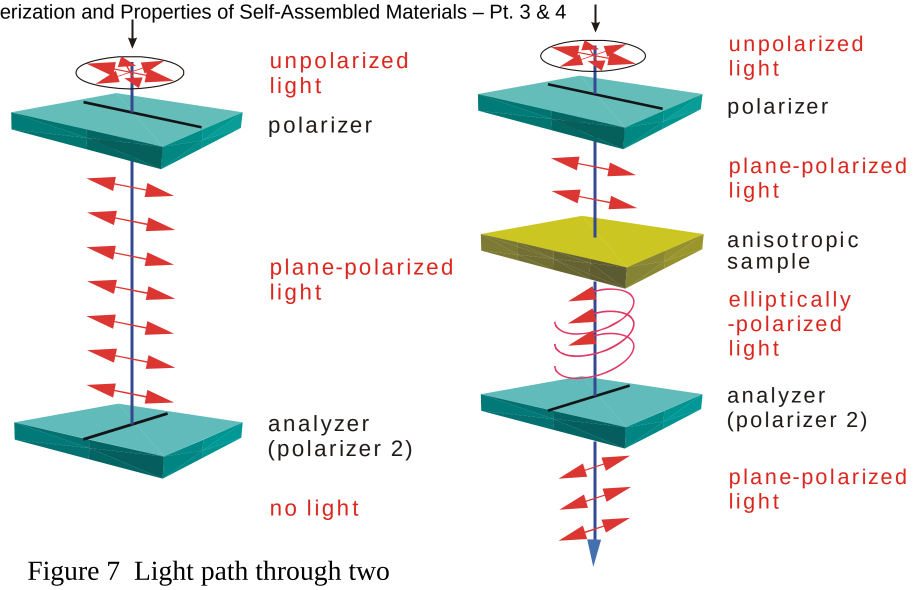


Figure 7 Light path through two crossed polarizers

THREE CAUSES OF EXTINCTION OF LIGHT PASSING THROUGH ANISOTROPIC MEDIUM BETWEEN CROSSED POLARIZERS

1.) Thickness is such that at the exit the phase difference $\Gamma = 2k\pi$ (path difference = $k\lambda$).

- Exiting light is linearly polarized parallel to **P**, i.e. is in the same state as at the point of incidence ("***coincidental extinction***"). For this type of extinction light must be monochromatic.
- Figure 8 shows a nematic droplet on a glass surface between crossed polarizers. The black concentric rings are positions where $\Gamma = k*2\pi$.
- If the incident light is polychromatic (white), coloured rather than dark rings will be seen – a sequence of pale rainbows. This is because the extinction condition will apply only to one λ, eliminating that wavelength from the white spectrum. “Coincidental extinction” causes liquid crystals and crystals to appear coloured between crossed polarizers. However, note that below a minimum thickness of the sample no colour is seen, only shades of grey. This is because, even for the shortest λ (blue), d is not sufficient to build up a Γ of 360°.

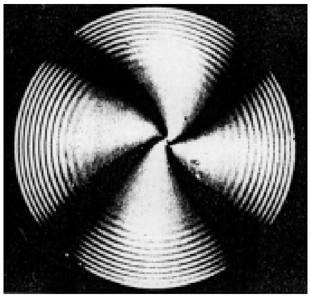


Figure 9 Droplet of nematic LC between crossed polarizers viewed in monochromatic light.

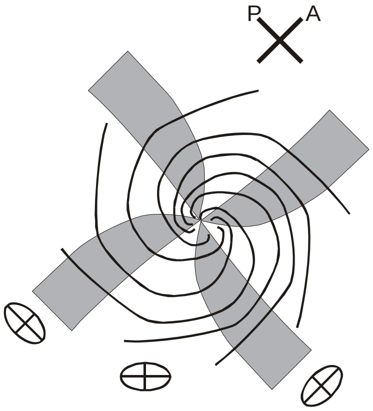


Figure 9 Director lines spiral out of the centre of the droplet.

2.) One of the principal axes of the elliptical section through the indicatrix is parallel to **P**. In other words, the projection of the unique axis is ∥ or ⊥ to **P**.

- Incident light is not split into two components (intensity of the second component = 0) Hence light remains plane-polarized throughout the sample thickness and is absorbed by the analyser.
- This extinction type accounts for the dark “propeller blades” in Figure 8 and also for the Maltese cross in polymer spherulites. The cross in Figure 8 is explained by the vortex of

spiralling director lines as in Figure 9. Note that the curvature of the cross is due to the vortex. In contrast, in spherulites (Figure 10) the arms of the cross are straight, since polymer chains, hence also the long axis of the optical ellipse, are exactly tangential.

3.) Sample is viewed along the optic axis.

• Cross-section through the indicatrix is circular → Any two components of light propagate with same velocity.

• Light leaves the sample with same polarization as on entry (i.e. ∥ to P).

This extinction type is responsible for the concentric dark rings in banded spherulites (light parallel to polymer chains - Figure 10). In liquid crystals this is responsible for dark regions of ***homeotropic*** alignment (i.e. where the director is normal to the glass slide). The latter is common in S_A LCs, and in some nematics.

Figure 10 Two ringed polymer spherulites between crossed polarizers

DEFECTS IN LIQUID CRYSTALS

Unless the LC is subjected to external field (shear, electric or magnetic field, grooved surface) the director will change direction throughout the sample. The curvature will tend to be minimal due to ***curvature elasticity*** of LCs. This will inevitably result in occasional defects, where the mismatch in director orientation will tend to concentrate. The centre of the droplet in Figure 8 and Figure 9 is an example of such a defect, called ***disclination*** (originally termed dis-inclination, in analogy with dislocations in crystals). A disclination in LC textures between crossed polarizers is identified as the point of convergence of either 2 or 4 dark brushes Figure 12 and Figure 11.

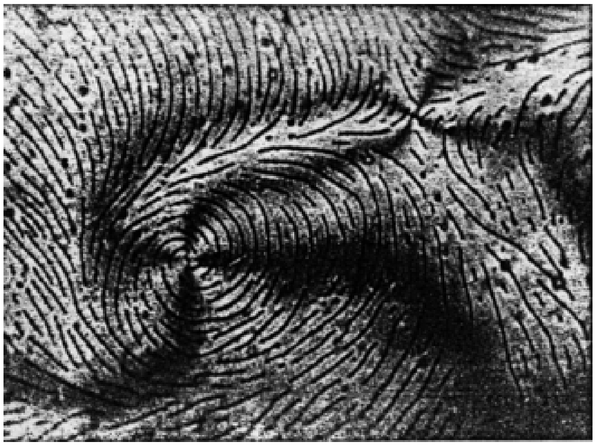


Figure 12 Four-brush disclinations of two different types. Director lines are made visible by bubble decoration.

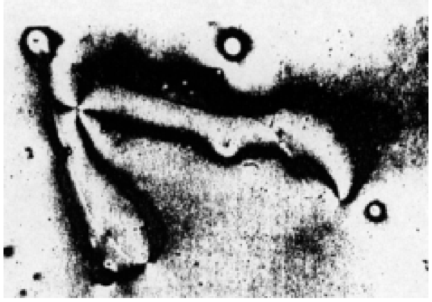


Figure 12 A typical nematic texture between crossed polarizers. [Q: Identify the two disclinations where two brushes meet and try to explain their origin (draw the director lines)].

TWISTED NEMATIC LC DISPLAY

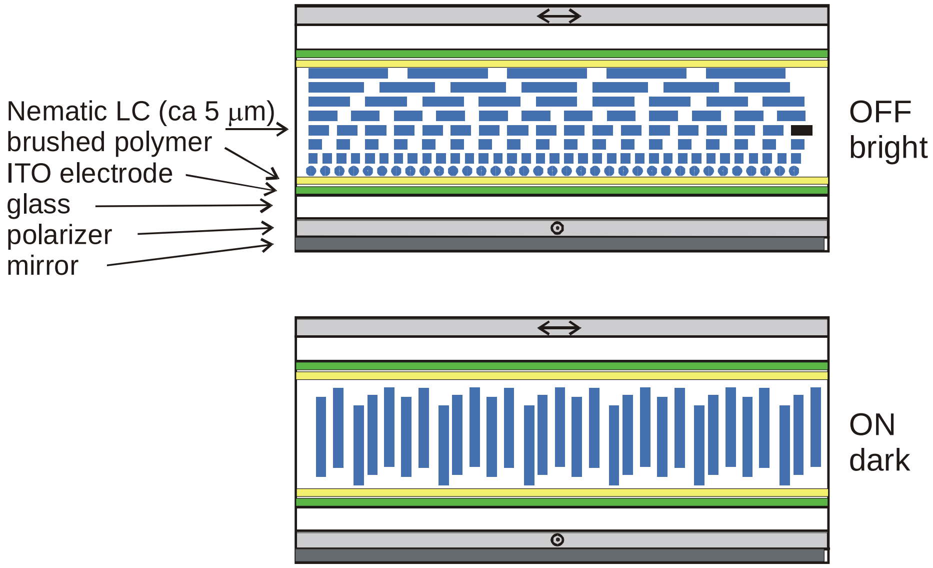


Figure 13 Cross-section through a “normally bright” TN LC cell in the Off and On states

Figure 13 show the TN cell in cross-section. In the absence of an electric field (**OFF** state, Figure 13 top and Figure 15), the rod-like molecules at the top surface are oriented horizontally in the plane of the paper (long horizontal lines), while those at the bottom surface lie perpendicular to the plane of the paper (dots). This twist in the liquid crystal (90^{o}) is enforced by alignment on rubbed polymer-coated glass surfaces: molecules orient parallel to the rubbing direction and the two glass slides are rotated with respect to each other. The result is that the plane of light polarization follows the rotation of the director. Imagine that the LC is divided in an ∞ number of thin layers, each rotated to the previous by an infinitesimal angle. At each “boundary” the **E** vector is “split” into 2 components, the nearly perpendicular component being effectively zero. Thus the width of the ellipse (elliptical polarization) is infinitesimal, the light effectively remains linearly polarized but with a slightly rotated plane of polarization. Thus the plane of polarization is guided to follow the director and rotates by a total of 90^{o} (see Figure 16). Light is therefore transmitted completely through the second polarizer, which is rotated through 90^{o} relative to the first. In a reflective cell light is then reflected on the back mirror and transmitted again through both polarizers, giving rise to a bright field. See also Fig. 12.

However, when the electric field is **ON**, the molecules, which contain a dipole parallel to their long axis (Figure 14), are forced to stand up (homeotropic alignment). The dipole is typically introduced by a polar group such as –CN, -F or -NO$_2$. In the ON state the twist is absent. Light now travels along the optic axis, and retains its original state of polarization. Thus none of it passes through the second polarizer and the field is black.

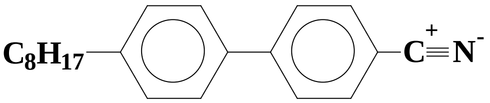


Figure 14 Octyl cyanobiphenyl (8CB) - a typical nematogen. The cyano group provides a strong axial dipole.

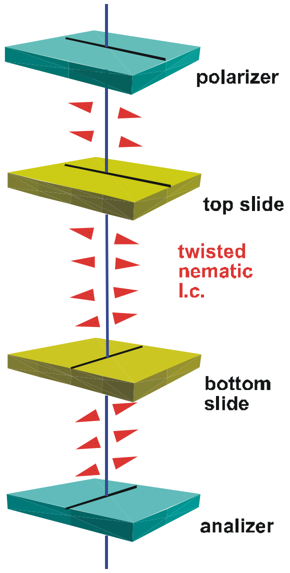
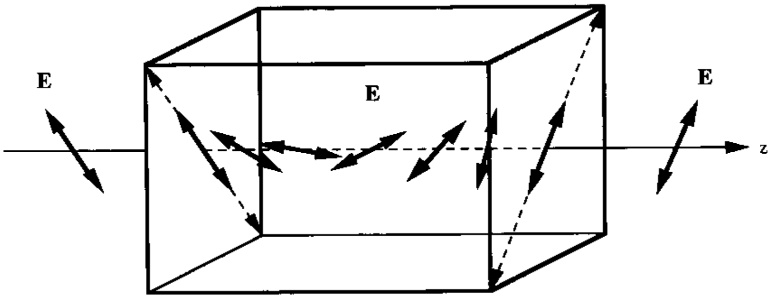


Figure 15 Passage of light through an E-mode TN cell. Polarizers and rubbed glass windows are shown. Field is off.

In a common LCD used in watches and calculators the electrodes are deposited as thin films of transparent and conductive indium tin oxide (ITO) on glass surface; the electrodes are shaped as characters or their segments (Figure 17). The state is ON when both electrode are under voltage (typically +1 and -1V, respectively.

The switch between planar and homeotropic alignment is relatively sharp and occurs at the **threshold voltage**, typically between 1 and 2V, through **Fredericksz transition** (Figure 18).

Question: How would you construct a “normally black” TN cell?



(a) E-mode Waveguiding

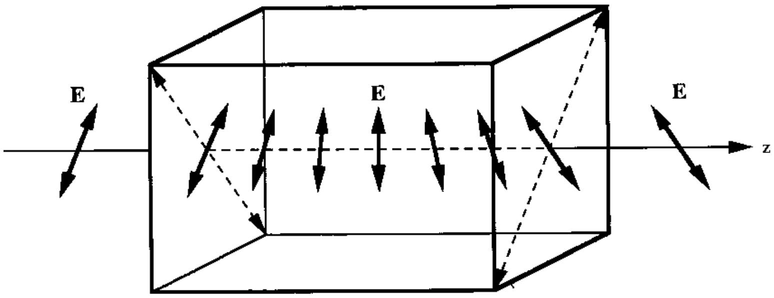


Figure 16 E-mode and O-mode waveguiding in a TN LCD cell. The first polarizer is either parallel (E-mode waveguiding) or perpendicular (O-mode) to the rubbing direction on the front glass slide, hence to the nematic director at the point of incidence.

Fredericksz transition is sharp because the state where molecular alignment is neither planar nor homeotropic (i.e. they are tilted) is sterically very unfavourable in a twisted nematic. A sharp switch transition is essential (a) for high contrast, and (b) for multiplex addressing (a pixel should remain white both when none and when only one electrode is charged).

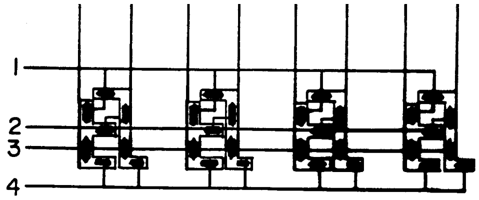


Figure 17 ITO electrodes evaporated on each glass surface of a calculator display. Vertical and horizontal wires connect electrodes on top and bottom slide, respectively. This arrangement (“multiplexing”) reduces the total number of electrical contacts.

Matrix multiplexing is shown in Figure 19. Each intersection between a row electrode (top glass slide) and a column electrode (bottom slide) is a pixel. In a small matrix display electrodes can stay at a constant voltage between switches. However, for larger displays, pixels are scanned, line by line, at video refresh rate (full screen 25 times per second). For a computer screen with a million pixels, each pixel receives a very short pulse. The response of the LC must be slow enough (ca. 100 ms), so that the pixel remains ON until the next pulse arrives. This means that the LC will experience only a time-averaged voltage. The difference between average voltages of ON and OFF states will thus be < 0.1 V. Fredericksz transition of a conventional TN LCD is too broad to provide adequate contrast under such conditions. However, a solution has been found in “supertwisted” nematic (STN) LCD.

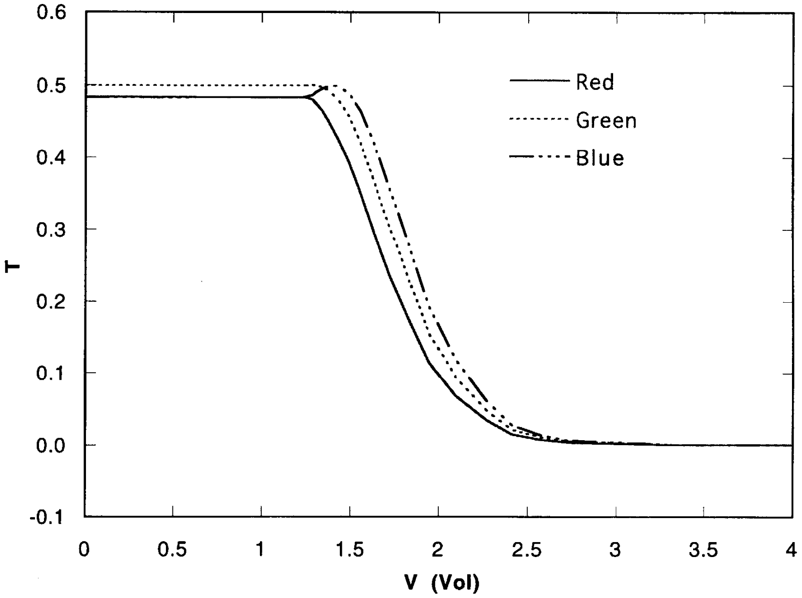


Figure 18 Light transmission through a "normally white" TN LCD as a function of applied voltage. The abrupt drop in light transmission with increasing voltage is due to the Freedericksz transition (molecular orientation turning from planar to homeotropic).

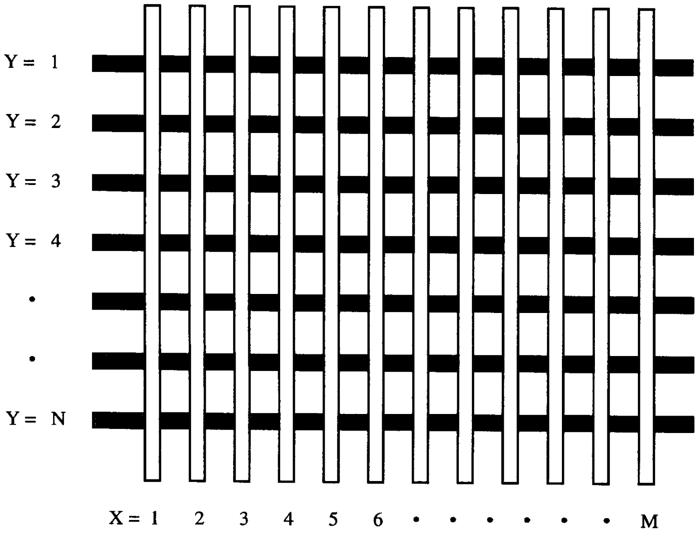


Figure 19 Multiplexing of a passive matrix TN LCD. Using multiplexing the number of contacts for m×n pixels decreases from m×n to m+n.

SUPERTWISTED NEMATIC LCD

Increasing the twist angle from 90° to 180° (Figure 20a) and, particularly, to 270° (Figure 20b), sharpens the transition sufficiently (Figure 21) for the LCD to satisfy the requirement of a VGA computer screen. The contrast ratio of 100:1 can be achieved even for a small change in average voltage. STN also increases the viewing angle compared to TN LCD. STN is found today in many displays, e.g. in cheaper laptops.

How is the 180° STN made to twist? How is the 270° STN made to twist by 270° and not by 90°? Answer: the compound used is chiral, inducing a spontaneous twist - see section on chiral nematic (cholesteric) LC below.

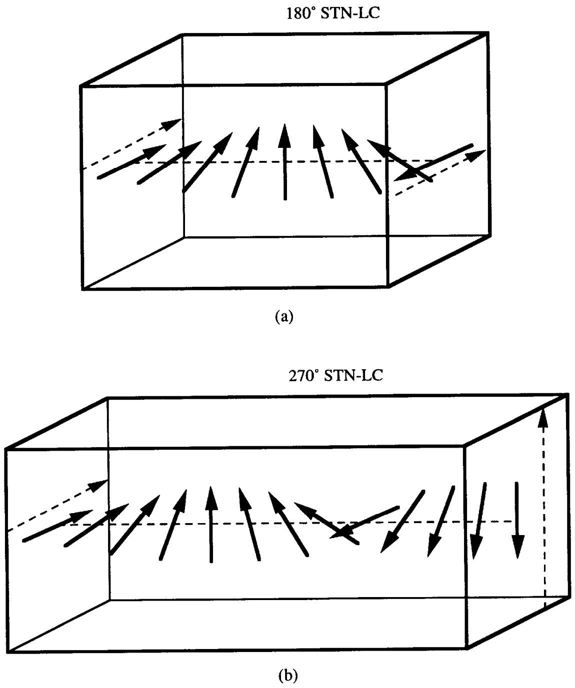


Figure 20 Supertwisted Nematic (STN) display waveguiding: (a) 180°, (b) 270° twist

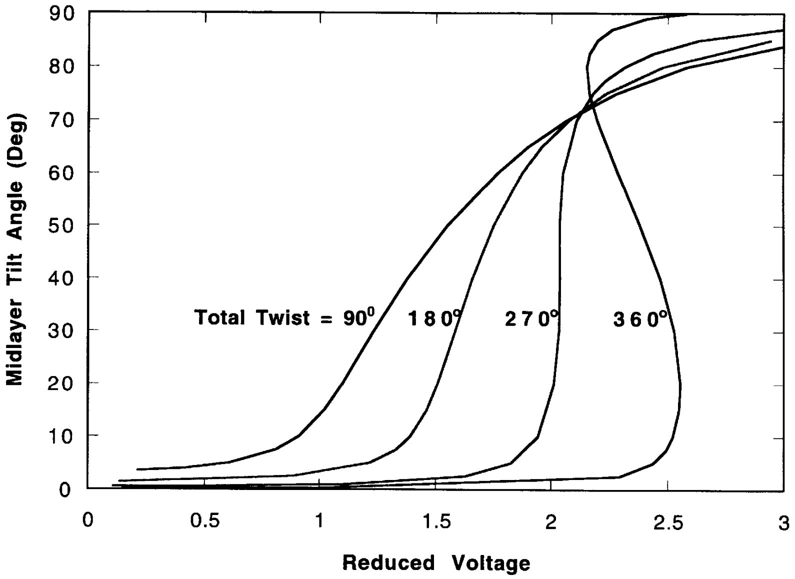


Figure 21 Tilt angle of molecules in the central layer of a STN LCD. The 270° twist device gives the highest contrast.

ACTIVE MATRIX TN DISPLAY

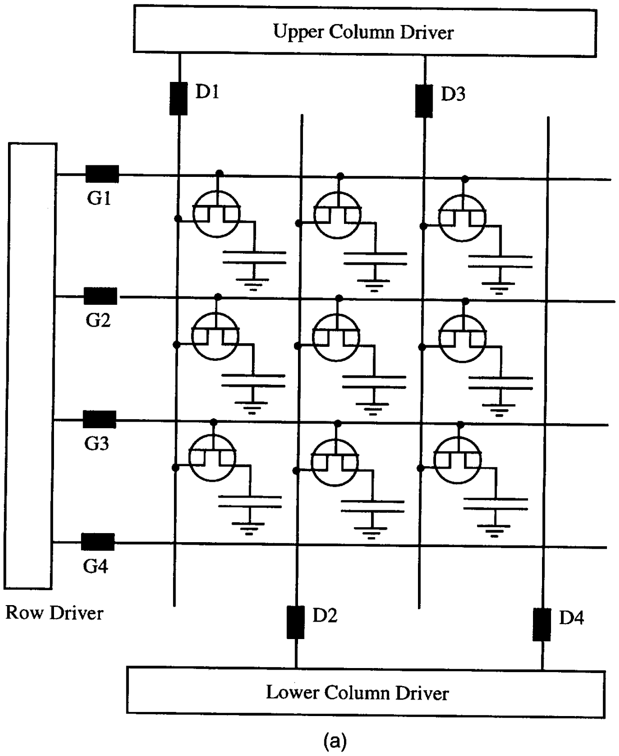


Figure 22 Circuit diagram of a portion of an active matrix of thin film transistors (TFT)

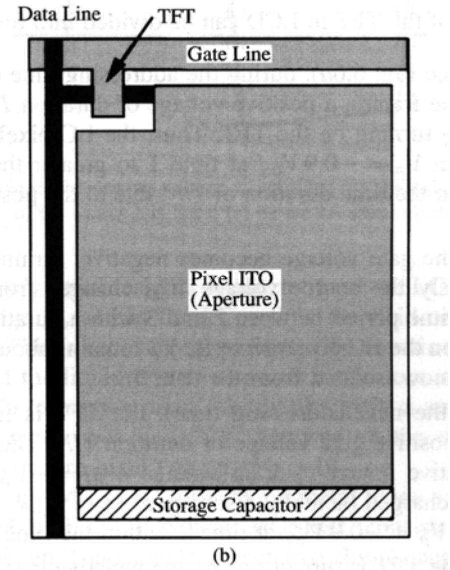


Figure 23 An individual pixel of an active matrix display is a self-contained TN LCD

Instead of relying on sluggishness of STN LC switching to hold the ON or OFF state between electric pulses, an active matrix TN display is an array in which each pixel is an individual TN display, containing a thin film transistor (TFT) (Figure 22 through Figure 24). While the voltage of a column is switched on, the rows are scanned in sequence, delivering a short pulse of current where required. The pulse is delivered to the gate of an individual TFT, which allows the column current to charge the capacitor associated with each pixel. The capacitor then maintains the ON voltage throughout the cycle, increasing considerably the average voltage difference between ON and OFF. This improves the contrast. Also, since faster response LC material can be used, faster scanning rates are possible, making AM TFT displays suitable for video and fast graphics applications. However, active matrix displays are much more expensive to manufacture than passive matrix STN LCD.

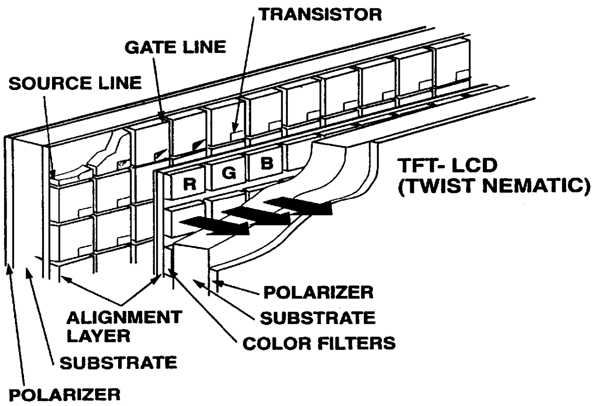


Figure 24 A section through an active matrix display

Projector Display

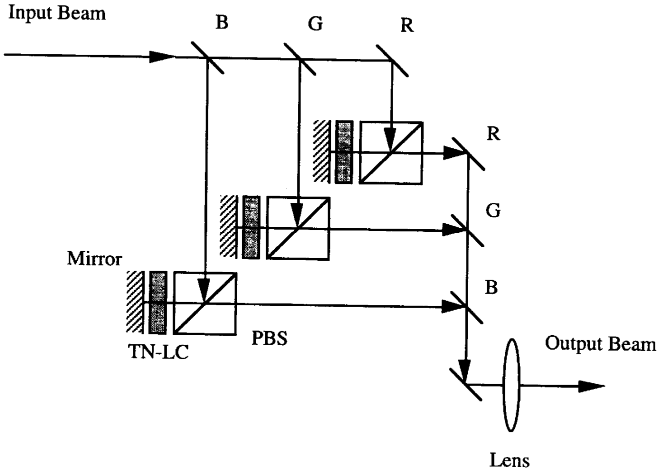


Figure 25 In high definition LCD projector displays the red, green and blue light beams from the three reflective TN LCDs are recombine to form one coloured pixel. Note the use of mirrors and beamsplitters (semitransparent mirrors).

MORE RECENT NEMATIC DISPLAYS

Recent developments have brought about two new types of displays using nematic LCs: the *in-plane swicthing* (IPS) and the *vertically aligned nematic* (VAN) displays. These are compared with TN LCD in Figure 26.

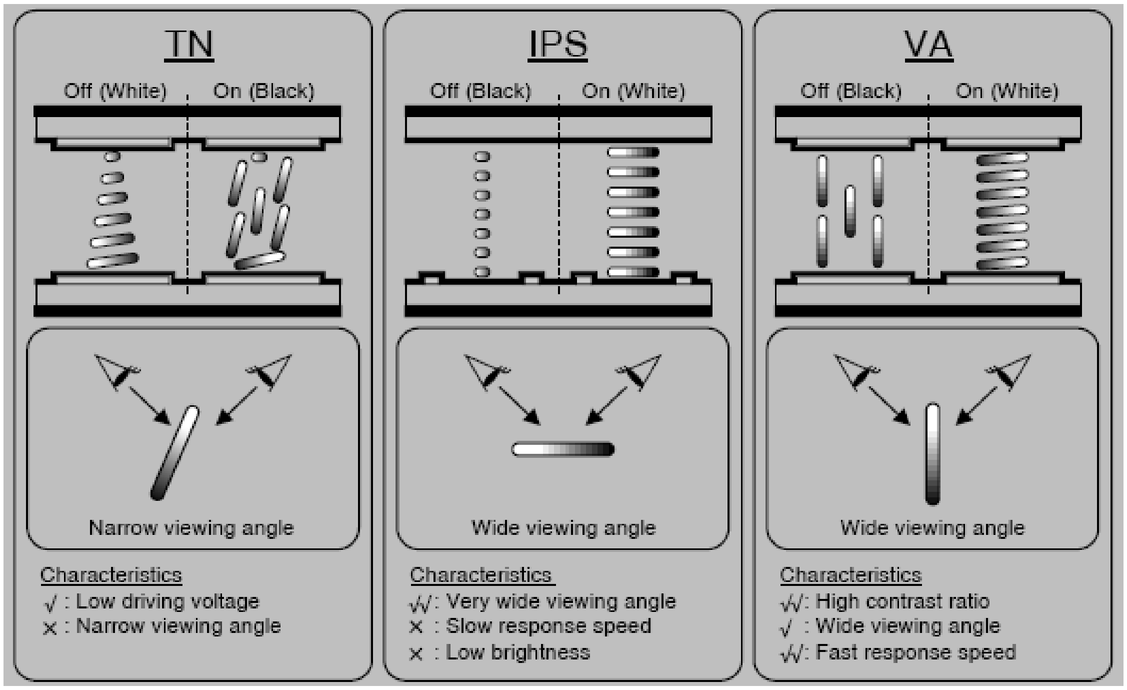


Figure 26 Comparison of the three main types of nematic LCDs: twisted nematic (TN), in-plane swithing (IPS) and vertically aligned (VAN). All three types use crossed polarizers.

An IPS cell has electrodes only on one glass surface and the electric field is generated in the plane of the display rather than normal to it. Molecules always lie parallel to the glass surface. Without the field they align ∥ to the rubbing direction, which is also ∥ to one of the polarizers – hence the field of view is dark (which of the 3 cases of extinction is this?). When the electric field is ON the molecules are rotated in plane by ca 45° - the view is now the brightest, but still not as bright as in TN LCD (why?).

Most new large LCDs used in flat panel displays employ VAN-type cells. They have a wide viewing angle and fast response. You can identify them by applying pressure on the screen, which in case of VAN LCD will cause change of contrast around the affected area. With no electric field, the LC molecules normally lie perpendicular to the glass surface ("homeotropic" alignment) and have negative dielectric anisotropy, i.e. have the dipole moment ⊥ to the molecular long axis (see example at bottom left on p. 1). In this state the area appears dark (which of the 3 causes of extinction is responsible?). When the electric field is applied across (⊥) the LC display, the molecular electric dipole follows, which means that the molecular long axis (and with it the optic axis) is forced to lie parallel to the glass. The rubbing direction is at 45° to the polarizers, thus maximising the brightness of the ON state.

Both IPS and VAN are normally used with TFT active matrix.

FERROELECTRIC LIQUID CRYSTAL (FLC) DISPLAY

How to devise a LCD based on in-plane rotation of molecules (director) from parallel to polarizer (dark) to 45° to polarizer (bright) (Figure 27)?

Answer: Employ a smectic-C liquid crystal (Figure 1) with chiral molecules (molecules with no mirror plane). In Figure 28 such a molecule is represented schematically as a fish with only one side fin and an asymmetric tail. The fin represents the polar group (-C=O, -F, -NO_2) with a dipole component perpendicular to the plane of paper. The asymmetry of the tail determines the tilt.

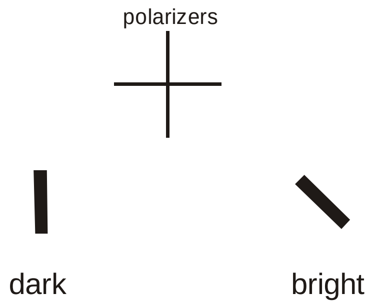


Figure 27

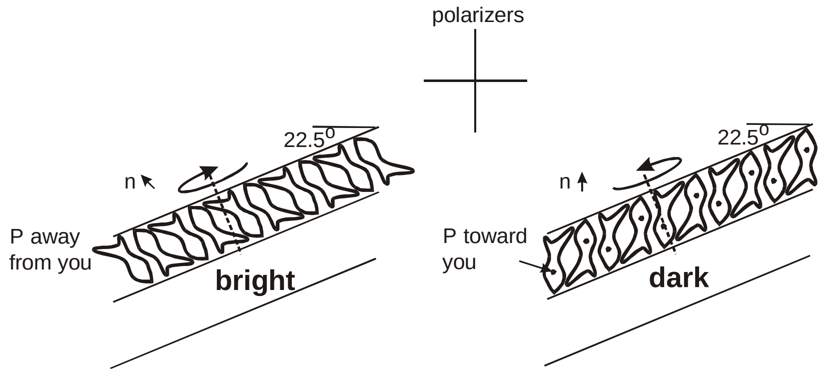


Figure 28 Schematic representation of a SSFLC cell, with “chiral fish” representing a chiral molecule. View along the light beam. Glass windows are in the plane of paper, and the layers are perpendicular to it (“bookshelf geometry”).

There is clearly a net dipole moment perpendicular to the paper. Thus the LC is ferroelectric, i.e. shows spontaneous polarization **P** (**P** is the net dipole moment). We place such a chiral smectic C (Sm-C*, or S_{C*}) LC between glass slides which have their inner surface rubbed at 22.5° to one of the crossed polarizers. For selected LCs the layers will align parallel to the rubbing direction. If we choose a S_{C*} LC with a tilt angle of around 22.5°, then the two most stable orientations of the director **n** will be parallel to one of the polarizer or at 45° to it. At such orientations the LC will appear, respectively, dark or at its brightest. To switch between the two orientations we only need to apply a short positive or negative electric pulse to the ITO electrodes on the two glass windows. The change of orientation takes place by the molecules co-operatively rotating around a cone by 180°, a rapid process with very low energy barrier. The fact that the two planar orientations are favoured over any other orientation around the cone is due to the effect of glass surfaces on the very thin LC film (typically 2-5 μm). Such a display cell is therefore called Surface Stabilized Ferroelectric Liquid Crystal (SSFLC) display.

- **Advantages of FLC display:**
    - ***faster switching*** compared to TN
    - ***bistable*** – needs no power to maintain either of the two states
      ➔ suitable for ***large displays*** without active matrix

- **Disadvantages:**
    - problems with alignment defects (“chevrons”)
    - sensitive to pressure

SURFACE STABILIZED FERROELECTRIC LCD (SSFLCD)

(View normal to layers)

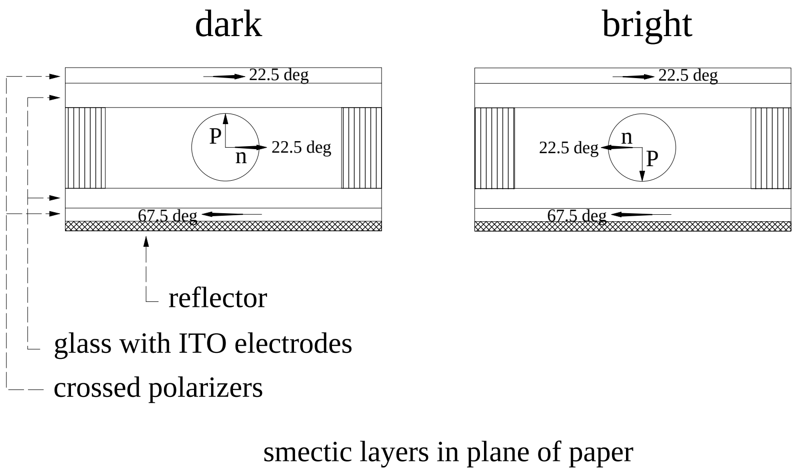


Figure 29 Cross-section of a surface-stabilized ferroelectric liquid crystal display cell

Figure 29 shows schematically a cross-section through a FLC cell, viewed normal to the layers. Figure 30 shows is a perspective view. The ITO-coated glass surface is pre-treated so that smectic layers stand up in the cell (“bookshelf” geometry). The chiral molecules are in the S_{C*} phase and the compound mixture is chosen such that the molecular tilt angle is 45/2 = 22.5^o to the layer normal, for maximum optical contrast. Molecules have a permanent dipole moment roughly normal to the molecular axis and the tilt plane, which creates spontaneous polarization **P**. By switching the polarity of the ITO electrodes, **P** is turned up or down through 180^o molecular rotation around the layer normal on the 22.5^o cone (layer orientation remains intact). There are no "on" and "off" states, the SSFLCD is a bistable device. When **P** points up the director **n** (and hence optic axis) is projected parallel to the top polarizer, hence no light passes through the analyzer which is at right angle to the polarizer. When **P** points down, **n** is at 45^o to both polarizer and analyzer, hence maximum amount of light passes through the two and is reflected back, giving a bright field. Response time of SSFLCD is much faster than that of the twisted nematic display, because molecular rotation on the S_C cone is cooperative and fast.

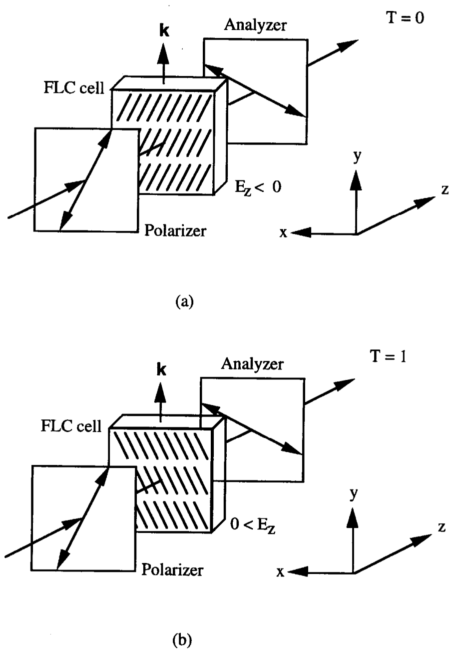


Figure 30 Ferroelectric LC display. (a) dark, (b) bright.

CHIRAL NEMATIC PHASE - THERMOCHROMIC LIQUID CRYSTALS

A special case of elliptically polarized light is ***circularly polarized light***, whereby the electric vector describes a circle.

It is sometimes useful to think of linearly polarized light as a sum of a right- and a left circularly polarized lights of equal amplitude and angular velocity (i.e. colour) – see Figure 31. One case where such representation is useful is light diffraction on chiral nematic liquid crystals.

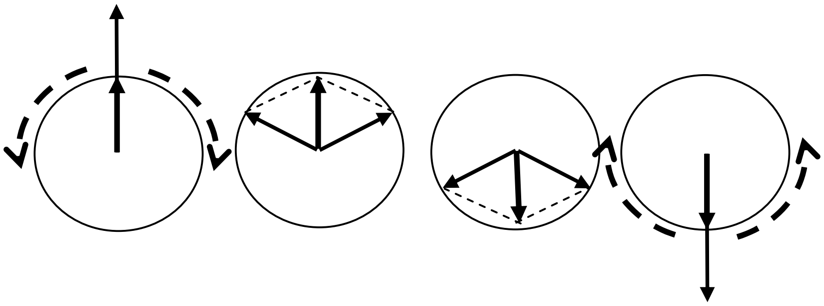


Figure 31 Splitting linearly polarized light into right and left circularly polarized components. (four instants in time are shown, within half of a oscillation period)

In the ***chiral nematic*** phase **(**also known as ***cholesteric*** phase) the director describes a helix in space – see Figure 32. The director rotates around an axis normal to it. Note that the rotation angle between successive layers of molecules is grossly exaggerated in Figure 32.

Here is where the idea of splitting linearly polarized light into two opposing circularly polarized components becomes useful. When the pitch of the cholesteric helix coincides with the wavelength of one of the colours of incident visible light, backward Bragg diffraction occurs for the appropriately handed circularly polarized component of the selected wavelength (“selective reflection”, see Figure 33). Diffraction occurs when the right-twisting electric vector of the circularly polarized light exactly matches the right twist of the nematic director in LC (replace “right” with “left” if the cholesteric helix is left handed). Thus in reflection the LC will have the colour corresponding to λ = helical pitch. In transmission the complementary colour is seen. E.g. if red is reflected, in transmission the LC would appear greenish, since it contains only half of the initial red intensity plus unpolarized transmitted light of all the other colours.

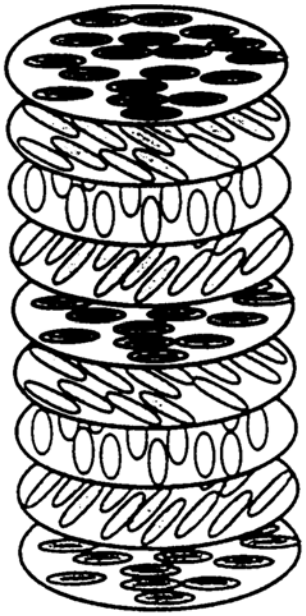


Figure 32 Molecules in a cholesteric liquid crystal

Usually the helical pitch changes with temperature, hence the colour of reflected light changes. This property is used in LC thermometers and in a number of other applications. E.g. surfaces of machinery can be painted with such ***thermochromic*** dyes to detect overheating. Painting the dye on skin can detect tumours under the skin as hot spots. “Hot shirts” contain thermochromic dyes.

Cholesteric LCs can also be used in **optical filters** where only a very narrow spectral band is removed. In this case the pitch must not change with temperature. Usually a cholesteric polymer is cross-linked to fix the pitch. To remove the whole and not just half of the light of a given wavelength, two cholesteric layers must be used, one right- and the other left-handed.

Recently cholesteric LC’s have attracted interest as potential photonic bandgap materials. Forming standing light waves, they may be used in organic lasers, particularly effectively in combination with light-emitting (LED) polymers.

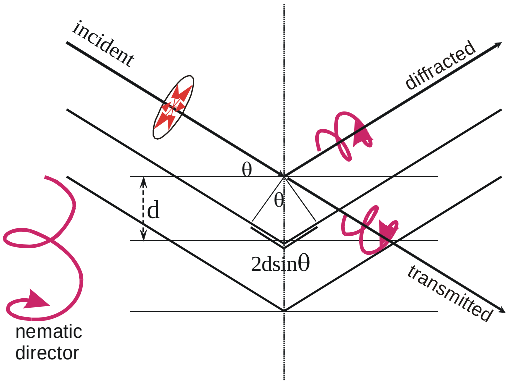


Figure 33 Bragg diffraction of light on a choletsric liquid crystal

Bragg equation:

$n\lambda = 2d \sin\theta$

Because, for a fixed *d*, λ depends on θ, the colour of a cholesteric will change somewhat with viewing angle. This causes the “irredescent” green colour of some insects, wings of butterflies etc.

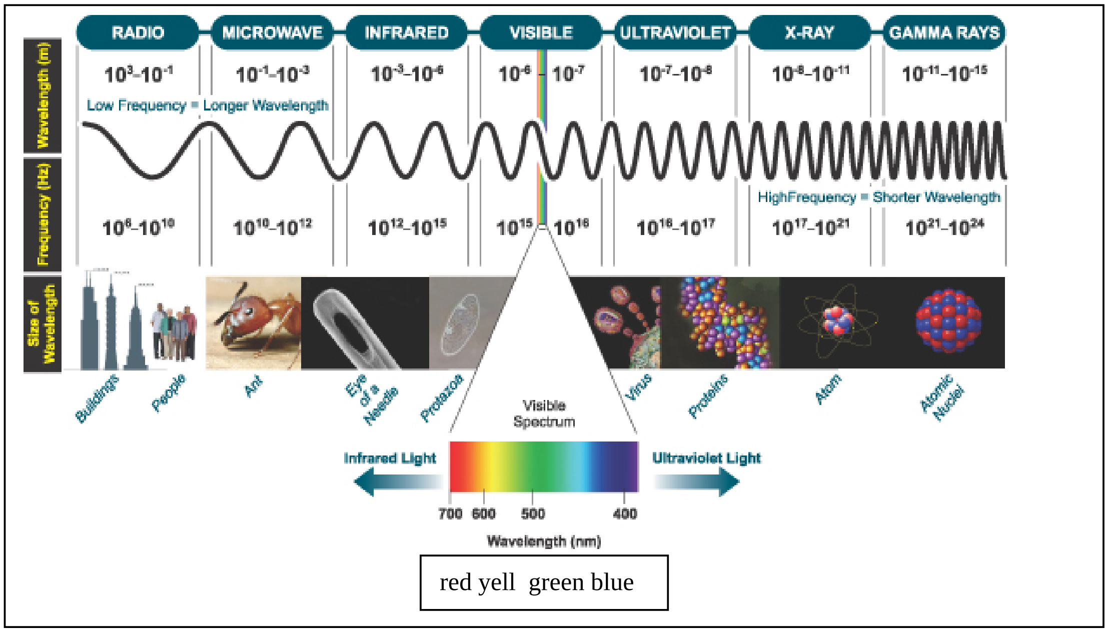


Figure 34 The electromagnetic spectrum

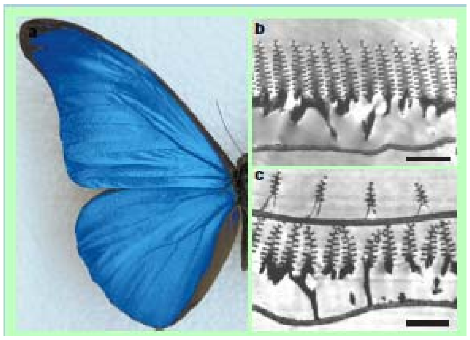


Figure 35 Wing of a butterfly is covered with microscopic helical bristles whose pitch causes the light of equivalent wavelength to diffract (“reflect”) . The colour of the wings changes with the viewing angle, according to the Bragg equation (“iridescent colour”). The colour of the green beetle is also caused by a similar diffraction effect. Bar = 1.5 µm.

POLYMER-DISPERSED LIQUID CRYSTALS

These are used for display devices or switchable transparent-opaque panels. Micron-size droplets of nematic LC are embedded in a transparent amorphous polymer matrix. Such a composite polymer film is placed between two glass panels coated with transparent electrodes (ITO). When the electric field is on, LC molecules are oriented perpendicular to the film plane (Figure 36, right); for all droplets the indicatrix is oriented with its optic axis normal to the film. When the field is off the director (and the indicatrix) reverts to its preferred radial orientation, i.e. homeotropic relative to the droplet surface (Figure 36, left). The refractive indices of the materials are chosen such that n_o of the nematic = $n_{polymer}$. Thus when the field is on, the refractive indices of the droplets and the matrix are matched for the light travelling perpendicular to the film and there is no light scattering; the film is transparent. When the field is off the light encounters the average refractive index of the droplet. This is different from the index of the polymer matrix and light is thus scattered; the film is opaque.

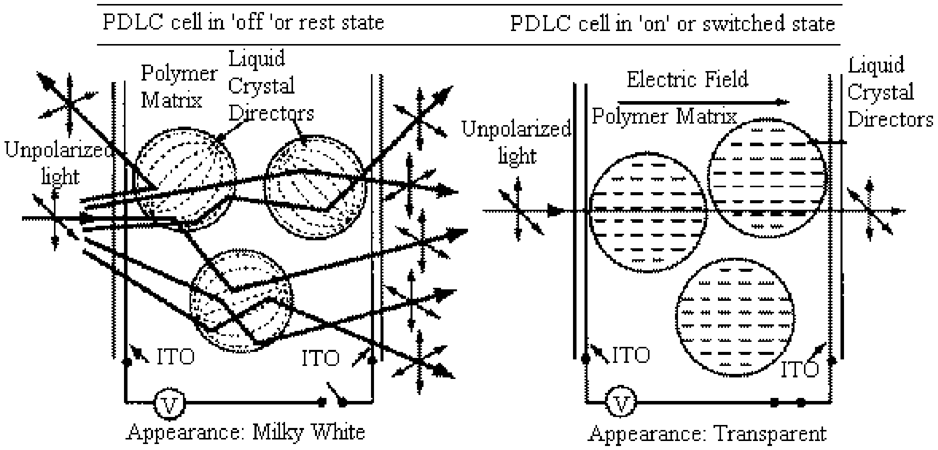


Figure 36 OFF (left) and ON (right) states of PDLC (cross-section) (from D. Lundstroem and J. Ylbar, KTH, Stockholm)

PDLCs are prepared by light-induced polymerization of a solution of the liquid crystal in the monomer. As polymerization proceeds, the polymer and the LC become immiscible and LC separates into droplets.

PDLCs are used in partition panels (e.g. in offices) and in windows, e.g. of some luxury cars. Pressing a switch the window changes from transparent to opaque and vice versa. PDLCs are also used in low-resolution large-panel displays. In the latter case ITO electrodes are shaped as letters, numbers or pixels. The display can include colour filters for colour display. Note that no polarizers are needed in PDLC devices.

LIQUID CRYSTAL ELASTOMERS

These are flexible liquid crystal polymers (polymers with rod-like groups in side-chains or in the main chain), which have been cross-linked. In other words they are rubbers with liquid crystal properties, either nematic or smectic. Mechanical stretching causes alignment of liquid crystal domains. A variety of applications can be envisaged. Placing the elastomer between crossed polarizers and applying mechanical force, LCEs can act as opto-mechanical transducers (e.g. bright when stretched, dark when relaxed). If polar groups (-CN, $-NO_2$, -F) are attached to the rod-like groups, such LCEs can be used as electro-mechanical transducers if placed between electrodes (artificial muscles for robotic components, smart skins, actuators for active noise and vibration control). LCEs can act in a way similar to piezoelectric polymers; while their response is slower, the amplitude per unit electric field can be large. LCEs are still in an experimental stage.

LIQUID CRYSTALS - PROBLEMS

Here are three problems that you should try to solve. Problem 1 is similar to that described in Fig. 6 of your handouts. There is no need to hand in your answers, but in one of the future classes you may be asked to explain your answer to the class.

Problem 1

A plane-polarized light beam enters a nematic liquid crystal. The angle between the first polarizer (i.e. plane of polarization of incident light) and the projection of the nematic director is approx. 60 degree. Construct graphically the electric vector for 4 moments in time during a cycle and draw the ellipse connecting the vector positions at three points within the sample at distances from the entry point *d* such that the phase difference Γ between the ordinary and the extraordinary ray is: a) 45^o, b) 90^o, c) 180^o. Assume the beam is normal to the plane of paper. Indicate in your diagrams the directions of the polarizer (P), the director (n), and the polarization directions of the ordinary and the extraordinary rays.

Problem 2

How would you produce circularly polarized light using (a) a pair of polarizers and a sheet of liquid crystal elastomer, and (b) a cholesteric liquid crystal? How would you check that the light is indeed circularly polarized?

Problem 3

Draw the chemical structure of a liquid crystal molecule which should be suitable for (a) TN LCD, (b) VAN LCD, and (c) ferroelectric (S_{C*} LCD). Do not copy the structures in the handouts.

Problem 4

Below is the optical micrograph of a nematic liquid crystal between crossed polarizers. Draw the trajectories of the director throughout the picture, indicate the orientation of the polarizer pair and explain the appearance of dark regions. (You have two initial choices of director orientation, differing by 90°.)