The Physics of Soft Matter

Lecture on „Liquid crystals“ (26.4.2012)

F.Kremer and M. Jasiurkowska

Outline

1. What are Liquid Crystals (LC)

Experiment: Phases of thermotropic LC

2. Classification of LC

3. Orientation of LC

4. Structural and optical properties of LC

Experiment: How does a LC display work?

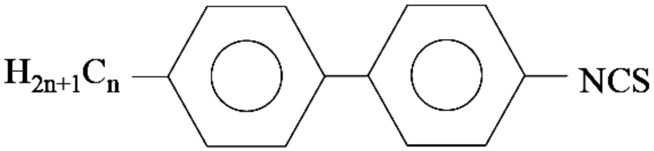
5. Textures of LC

6. Dynamics of LC

7. Ferroelectric LC

1. What are liquid crystals?

A typical LC molecule:



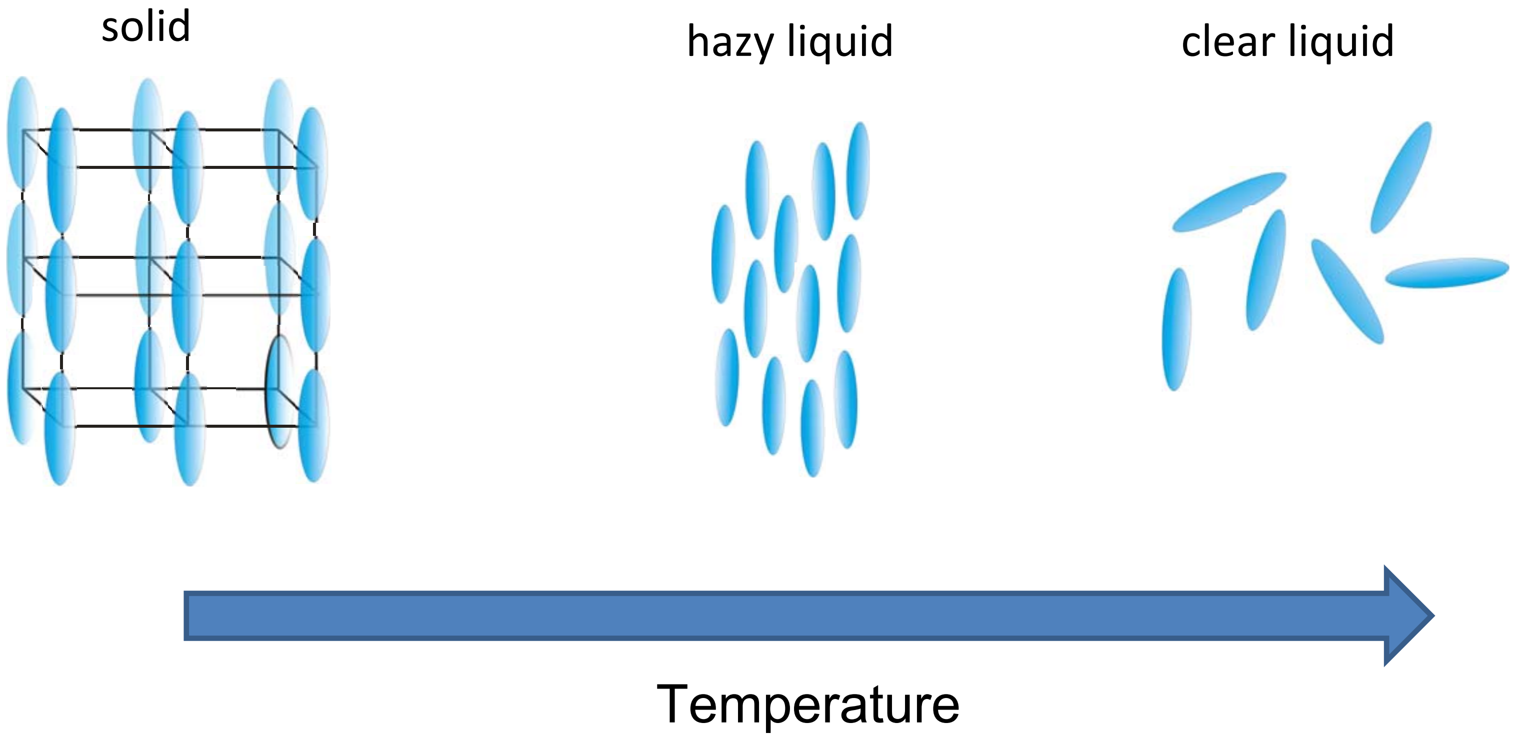
aliphatic tail

rigid core, „mesogen“

the core alone has a strong tendency to crystallize, but this is counterbalanced by the tendency of the aliphatic tails to form a glass.

Thermotropic LC

The botanist Reinitzer observed 2 melting points in cholesteryl benzoate (1888)



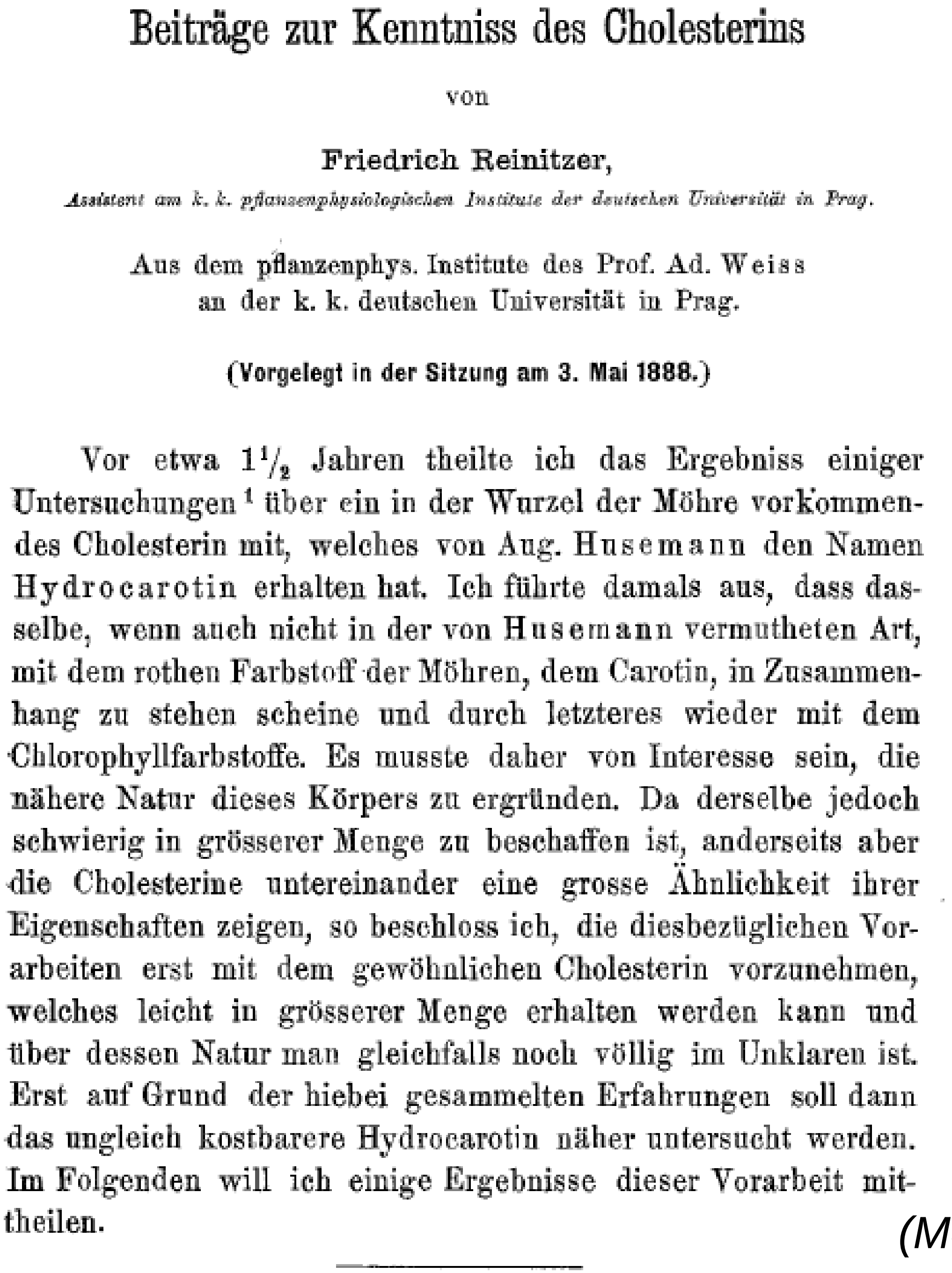
solid

hazy liquid

clear liquid

Temperature

Liquid crystals are an intermediate state between ordered three-dimensional crystalline arrays and isotropic disorder.



Beiträge zur Kenntniss des Cholesterins

von

Friedrich Reinitzer,

Assistent am k. k. pflanzenphysiologischen Institute der deutschen Universität in Prag.

Aus dem pflanzenphys. Institute des Prof. Ad. Weiss
an der k. k. deutschen Universität in Prag.

(Vorgelegt in der Sitzung am 3. Mai 1888.)

Vor etwa 1½ Jahren theilte ich das Ergebniss einiger Untersuchungen[1] über ein in der Wurzel der Möhre vorkommendes Cholesterin mit, welches von Aug. Husemann den Namen Hydrocarotin erhalten hat. Ich führte damals aus, dass dasselbe, wenn auch nicht in der von Husemann vermutheten Art, mit dem rothen Farbstoff der Möhren, dem Carotin, in Zusammenhang zu stehen scheine und durch letzteres wieder mit dem Chlorophyllfarbstoffe. Es musste daher von Interesse sein, die nähere Natur dieses Körpers zu ergründen. Da derselbe jedoch schwierig in grösserer Menge zu beschaffen ist, anderseits aber die Cholesterine untereinander eine grosse Ähnlichkeit ihrer Eigenschaften zeigen, so beschloss ich, die diesbezüglichen Vorarbeiten erst mit dem gewöhnlichen Cholesterin vorzunehmen, welches leicht in grösserer Menge erhalten werden kann und über dessen Natur man gleichfalls noch völlig im Unklaren ist. Erst auf Grund der hiebei gesammelten Erfahrungen soll dann das ungleich kostbarere Hydrocarotin näher untersucht werden. Im Folgenden will ich einige Ergebnisse dieser Vorarbeit mittheilen.

(Monatshefte für Chemie 9:421–41)

Summary concerning the question, what are LC?

1. LC molecules are allways characterized by a rigid core (mesogen) and a typically aliphatic tail.

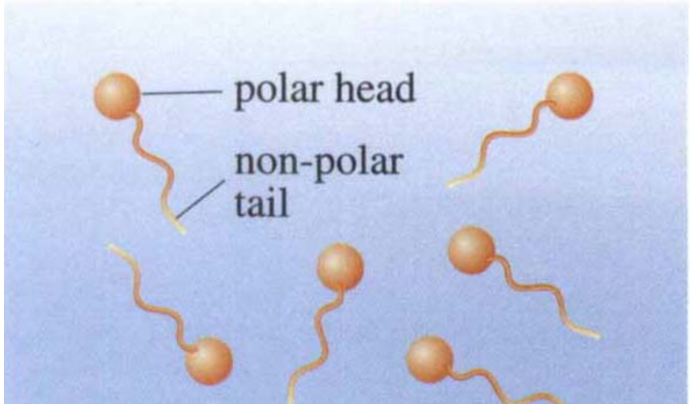
2. The mesogen may have very different shapes.

3. The structure of the LC molecule causes mesophases between the crystalline and the liquid state.

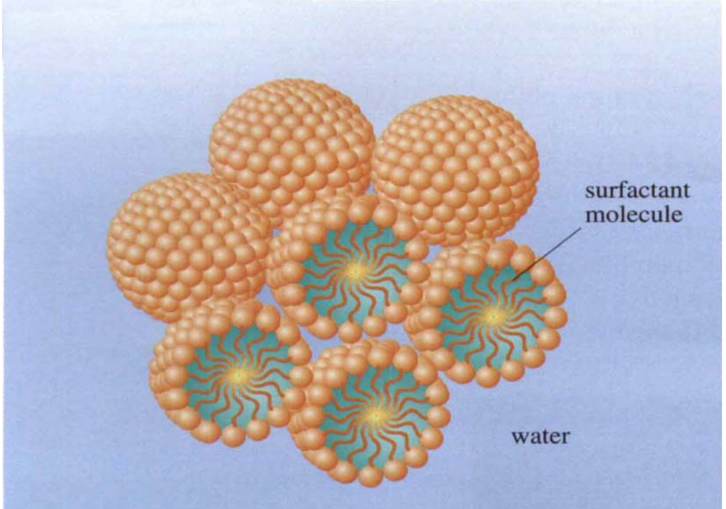
2. Classification of liquid crystals

- **Thermotropic LCs -** obtained by heating up the crystalline solid or cooling the isotropic liquid
- **Lyotropic LCs -** obtained by dissolving the LC in an appropriate solvent under given concentration and temperature conditions

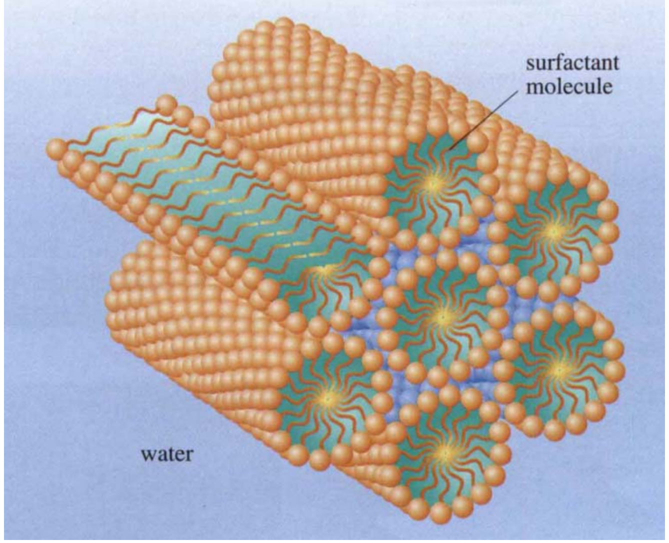
Lyotropic liquid crystal



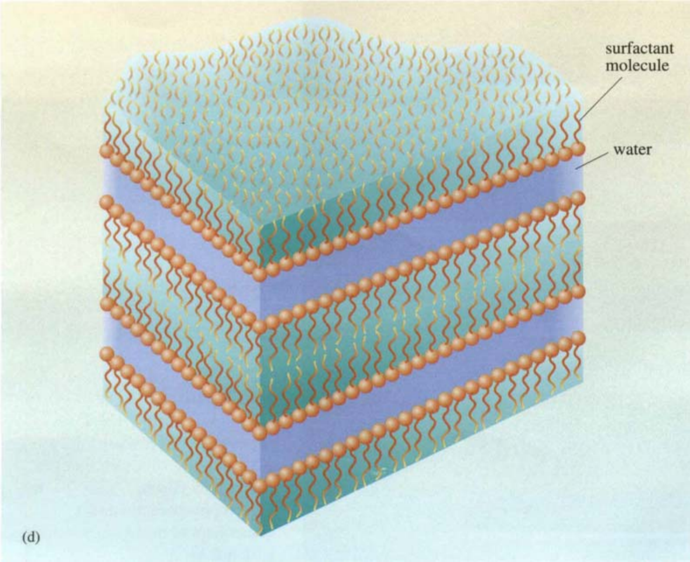
isolated molecules



spherical micelles,



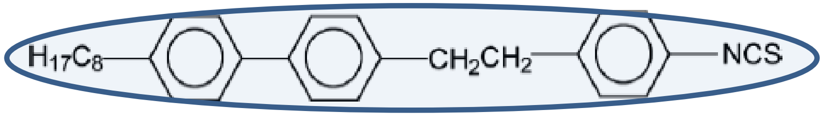
rod-like micelles packed
in a hexagonal arrangement,

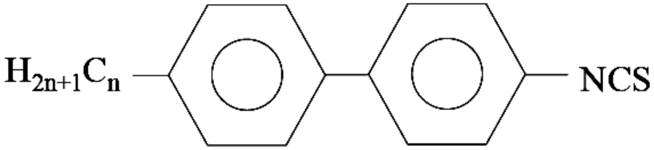


a lamellar phase.

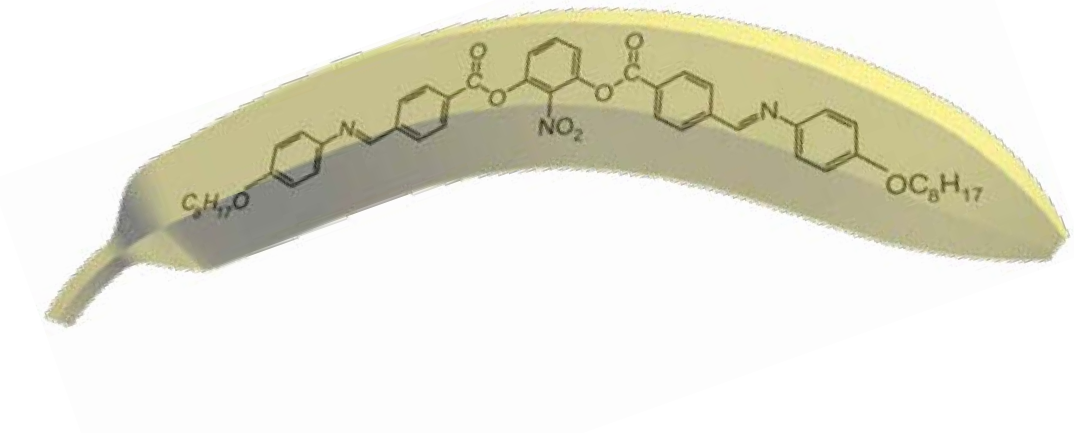
Shape of LC molecules

calamitic (rod-like molecules)

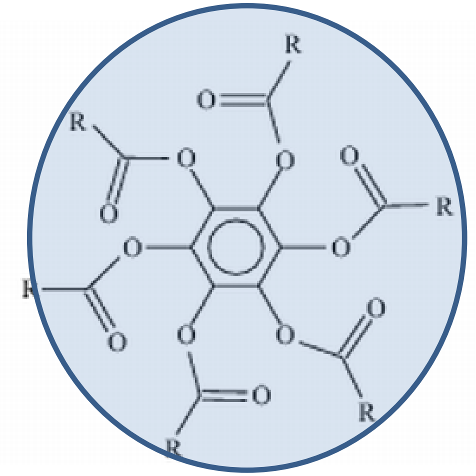


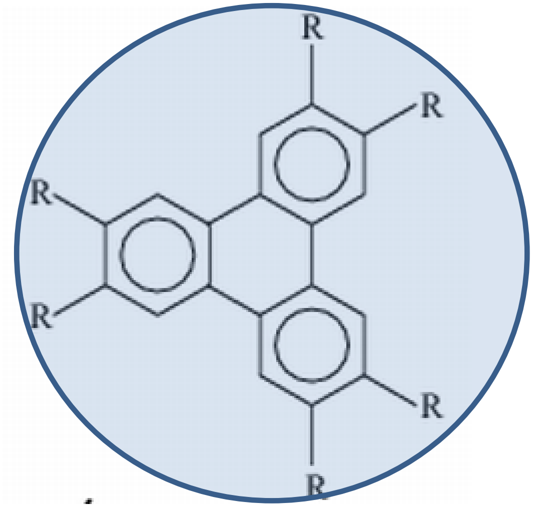


banana-shaped liquid crystal



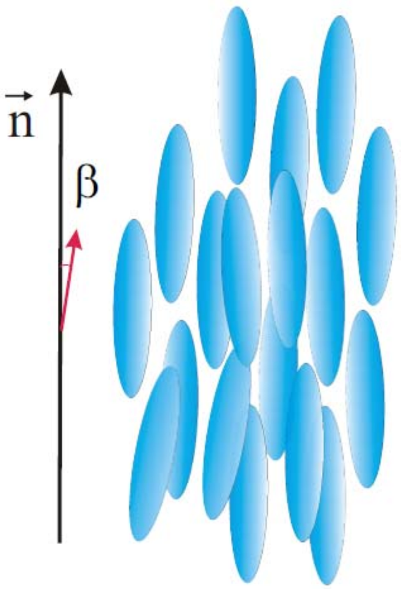
discotic (disc-like)





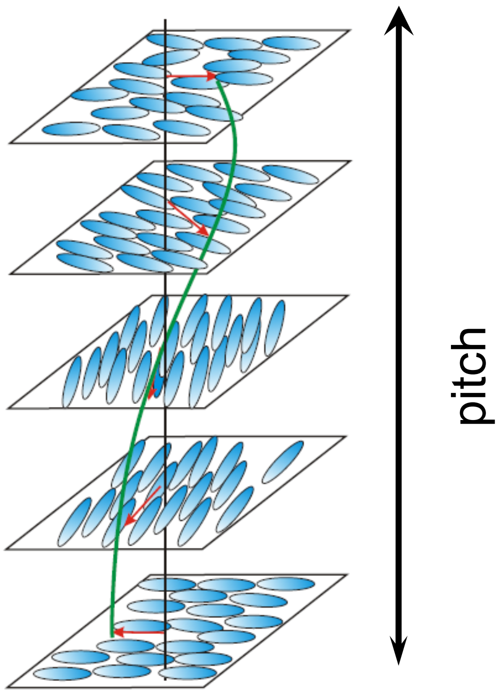
Calamitic liquid crystals

Nematic

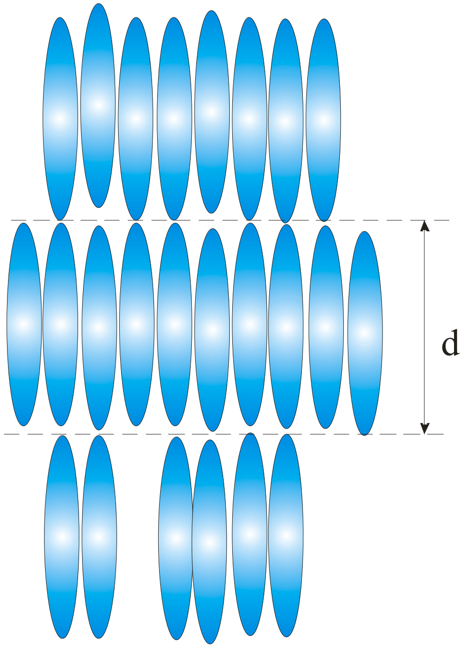


$\vec{n}$ - director

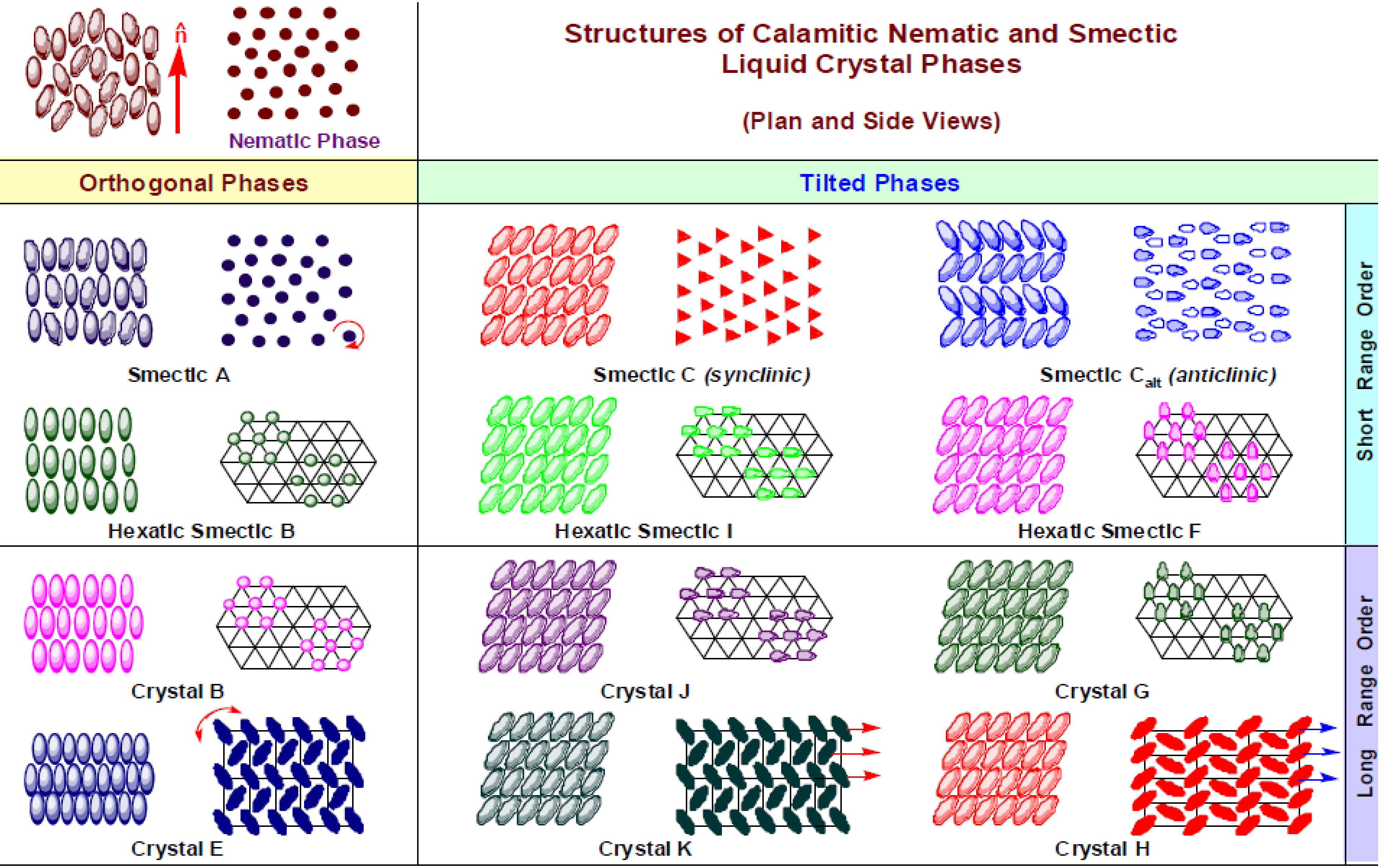
Cholesteric phase
(chiral nematic)

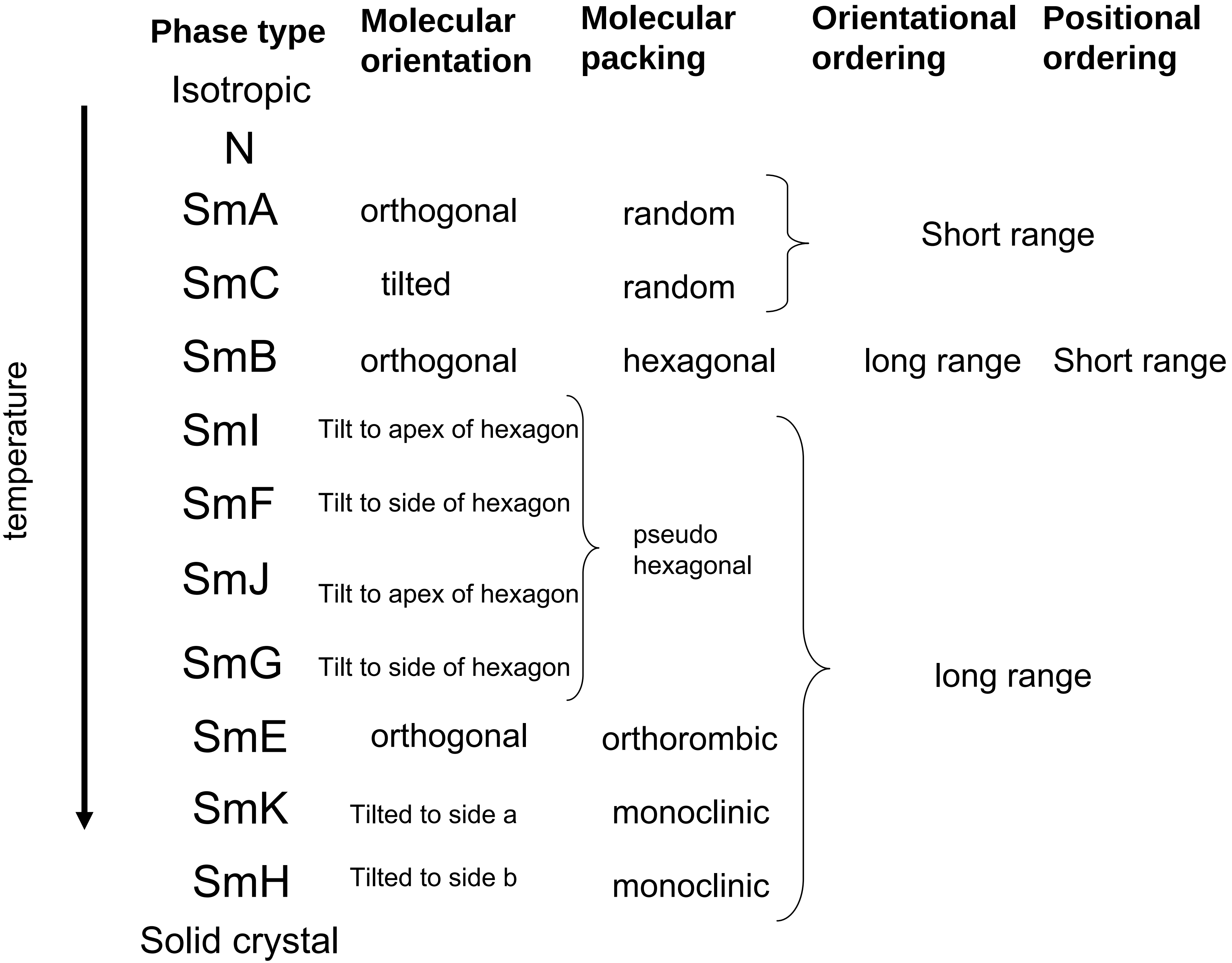


Smectic



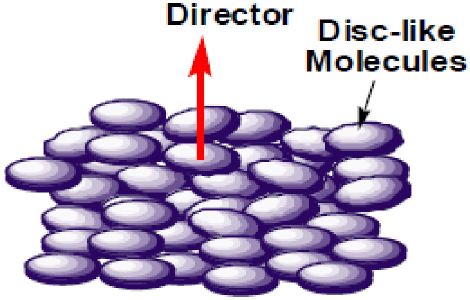
Mesophase polymorphism



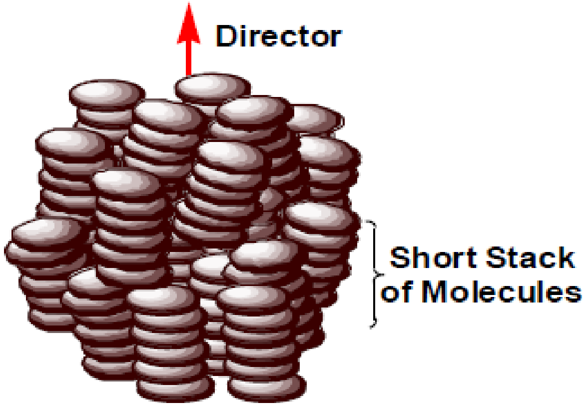


<table>
<tr><th>Phase type</th><th>Molecular orientation</th><th>Molecular packing</th><th>Orientational ordering</th><th>Positional ordering</th></tr>
<tr><td>Isotropic</td><td></td><td></td><td></td><td></td></tr>
<tr><td>N</td><td></td><td></td><td></td><td></td></tr>
<tr><td>SmA</td><td>orthogonal</td><td>random</td><td colspan="2" rowspan="2">Short range</td></tr>
<tr><td>SmC</td><td>tilted</td><td>random</td></tr>
<tr><td>SmB</td><td>orthogonal</td><td>hexagonal</td><td>long range</td><td>Short range</td></tr>
<tr><td>SmI</td><td>Tilt to apex of hexagon</td><td rowspan="4">pseudo hexagonal</td><td colspan="2" rowspan="7">long range</td></tr>
<tr><td>SmF</td><td>Tilt to side of hexagon</td></tr>
<tr><td>SmJ</td><td>Tilt to apex of hexagon</td></tr>
<tr><td>SmG</td><td>Tilt to side of hexagon</td></tr>
<tr><td>SmE</td><td>orthogonal</td><td>orthorombic</td></tr>
<tr><td>SmK</td><td>Tilted to side a</td><td>monoclinic</td></tr>
<tr><td>SmH</td><td>Tilted to side b</td><td>monoclinic</td></tr>
<tr><td>Solid crystal</td><td></td><td></td></tr>
</table>

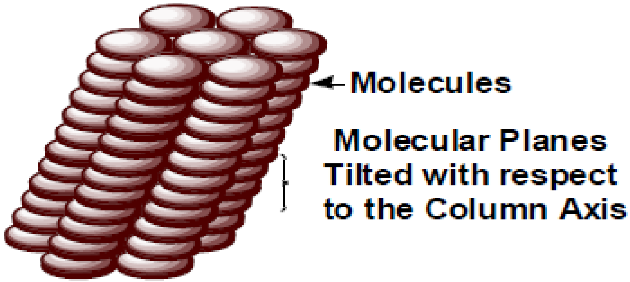
Structures of discotic LC phases



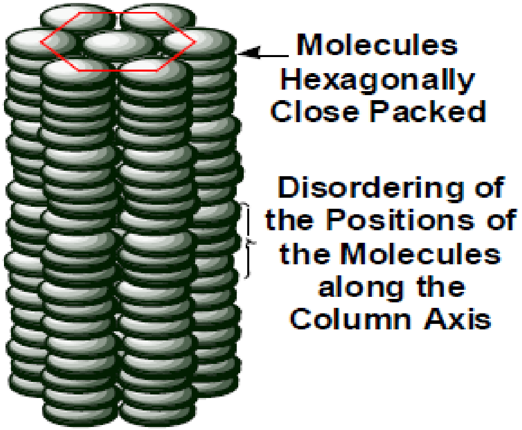
Nematic Discotic Phase



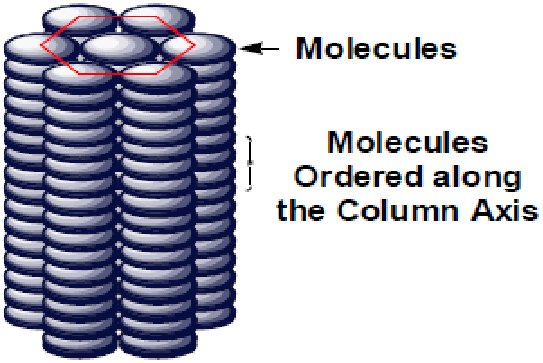
Short-Stacked Nematic Discotic Phase



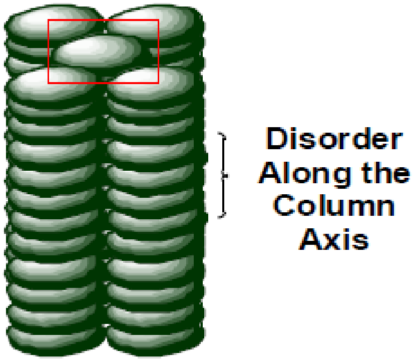
Tilted Columnar Phase Col$_t$



Disordered Hexagonal Columnar Phase Col$_{hd}$



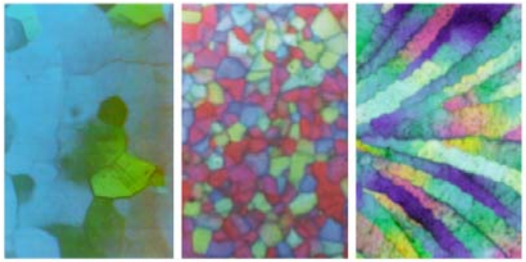
Ordered Hexagonal Columnar Phase Col$_{ho}$



Disordered Rectangular Phase Col$_{rd(C2/m)}$

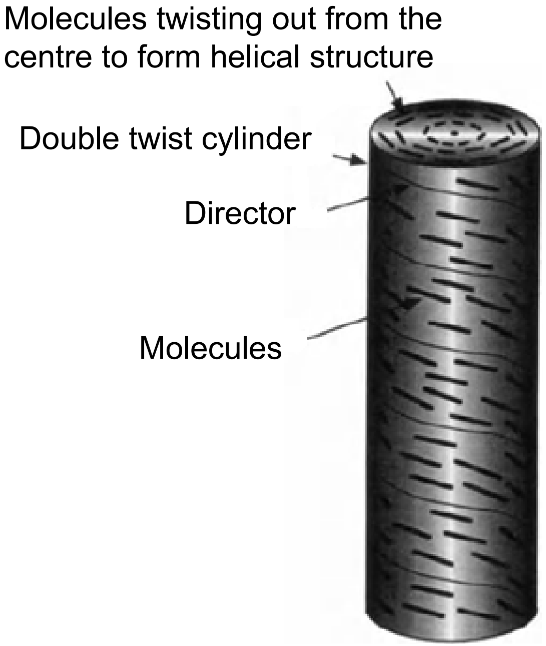
Blue phases

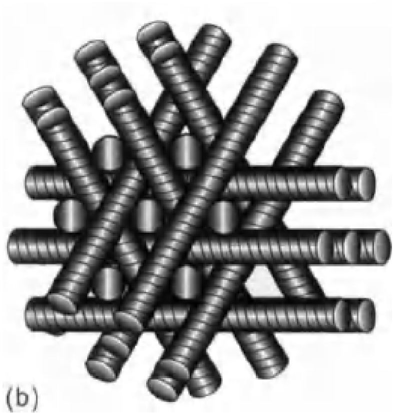
- special types of liquid crystal phases that appear in the temperature range between a chiral nematic phase and an isotropic liquid phase



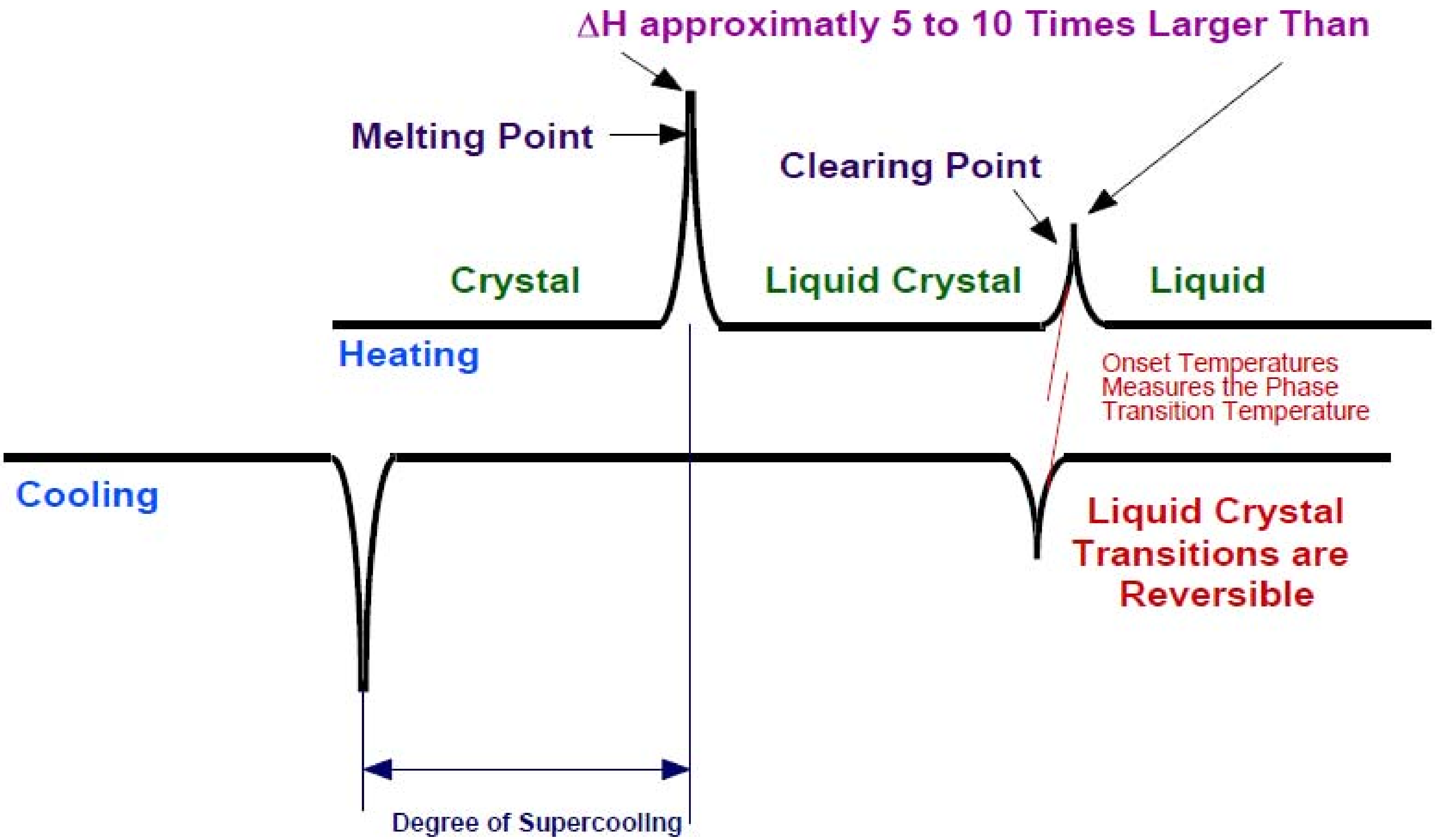
- have a regular three-dimensional cubic structure of defects with lattice periods of several hundred nanometers

- exhibit selective Bragg reflections in the wavelength range of light

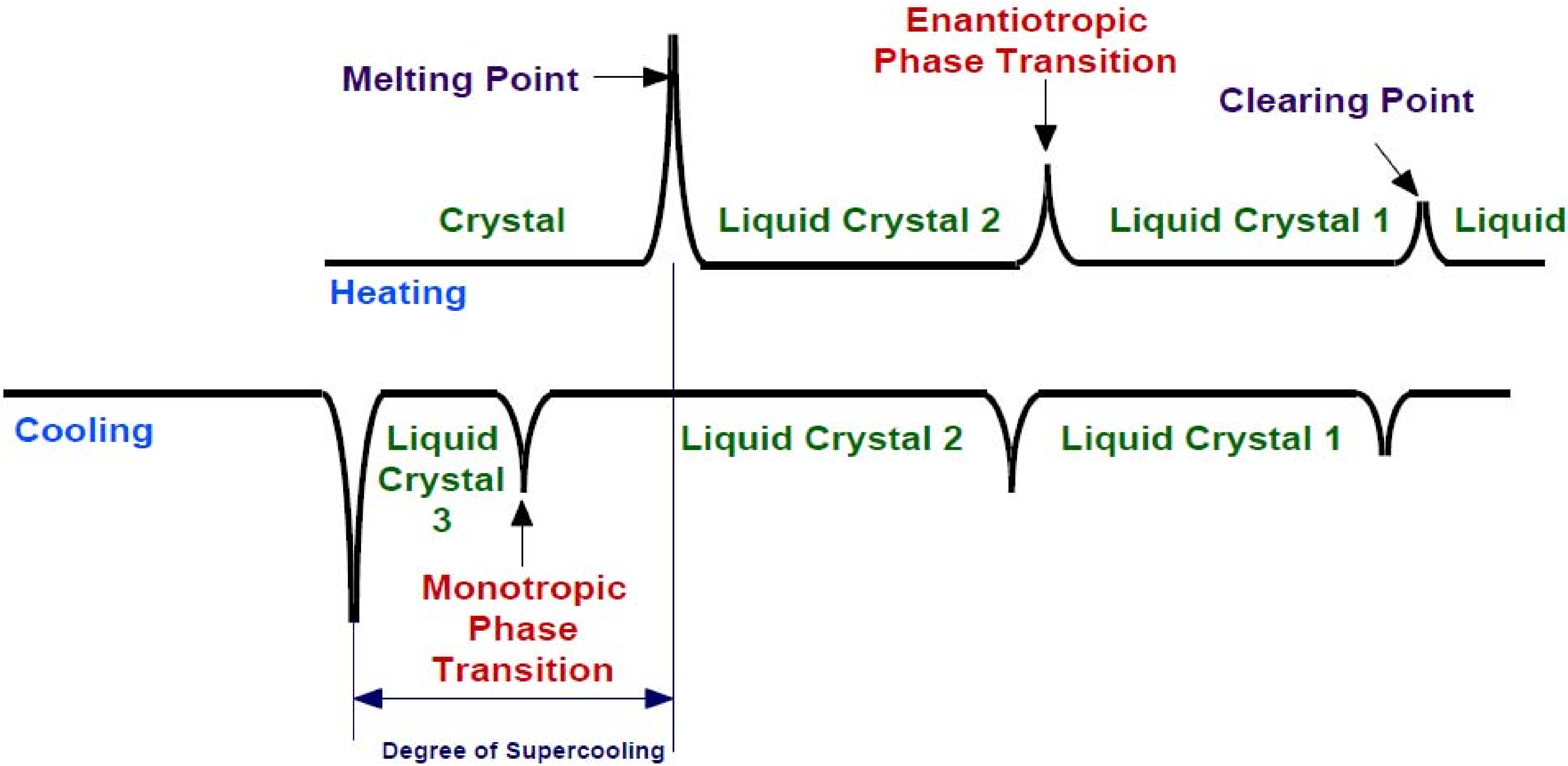




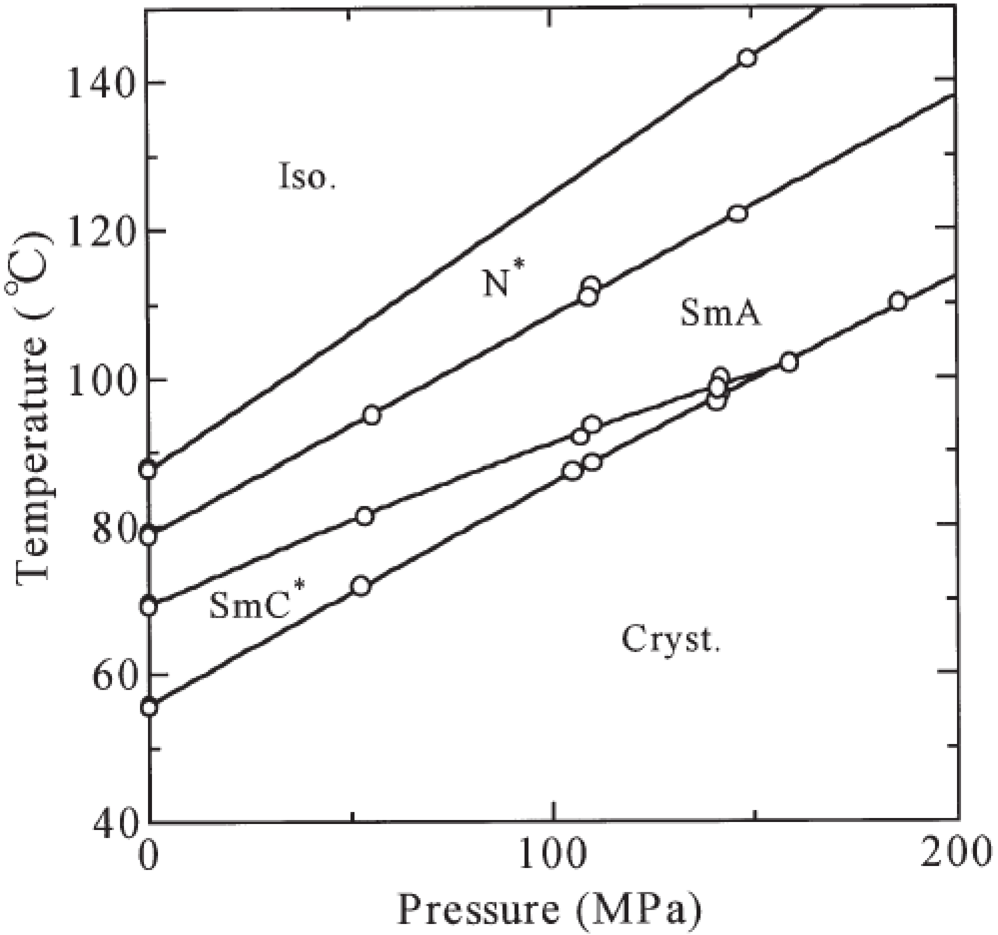
Typical DSC curve of LCs

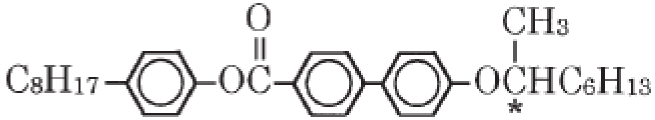


DSC curve of enantiotropic and mono-tropic liquid crystalline phases



Pressure-temperature phase diagram



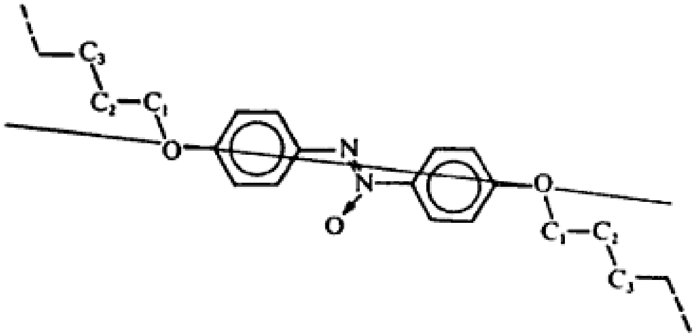


H. Uehara et al.
J. Phys. Soc. Jpn.,. 71, 2002

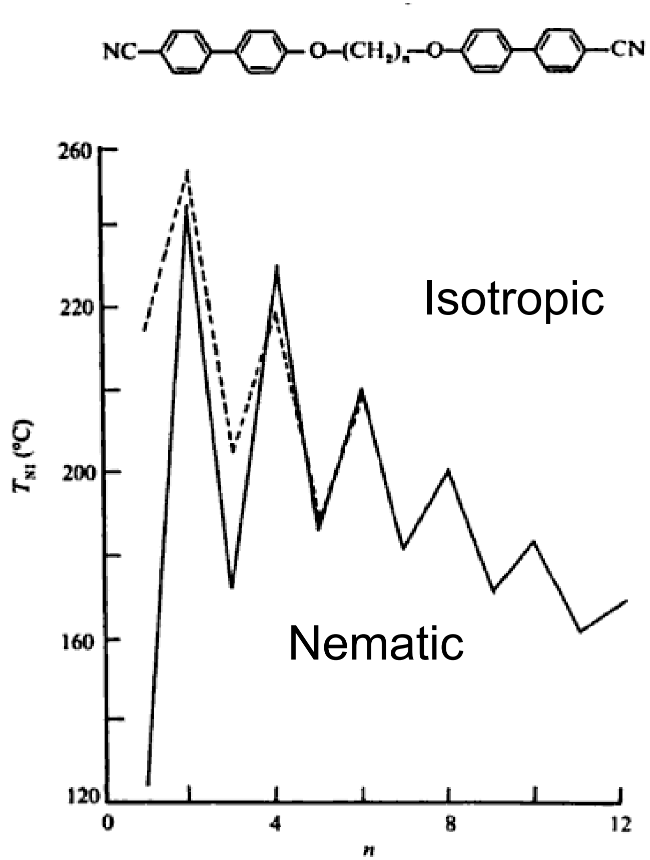
- **Liquid crystalline phase can be induced by pressure.**

The odd-even effect

- The LC properties (e.g., the phase transition temperature, the order parameter, the transition entropy show a pronounced alternation as the end-chain increases



The addition of an even-numbered carbon atome is along the major molecular axis.



When the chains become longer their flexibility increases and the odd-even effect becomes less pronounced.

Summary concerning the classification of LC

1. One separates between thermotropic and lyotropic LC
2. LC phases show a pronounced polymorphism
3. Besides temperature and concentration also pressure determines the phase sequence
4. The phase sequence depends in a subtle manner on the molecular structure, e.g. the even-odd effect

3. Orientation of LC

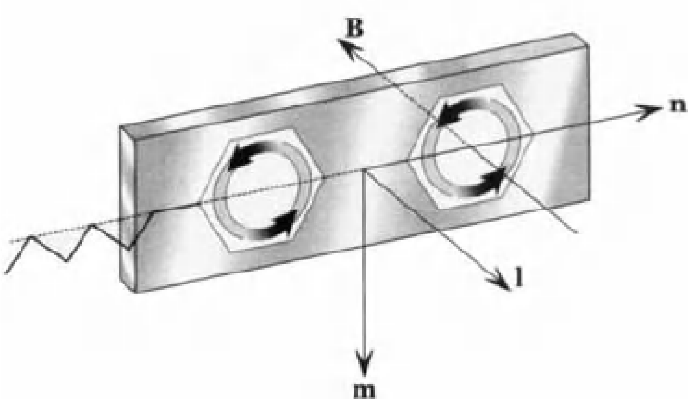
1. LC can be oriented by magnetic fields if the mesogen has a strong magnetic moment.

2. LC can be easily oriented by an external electric field if the mesogen has an electric dipolemoment

3. LC can be easily oriented due to surface interactions

Why can we order LC molecules by the external magnetic field ?

- Most liquid crystals are diamagnetic and their magnetic anisotropy arises from the electronic structure of the mesogens (delocalisation of electronic charge enhances the diamagnetic susceptibility).

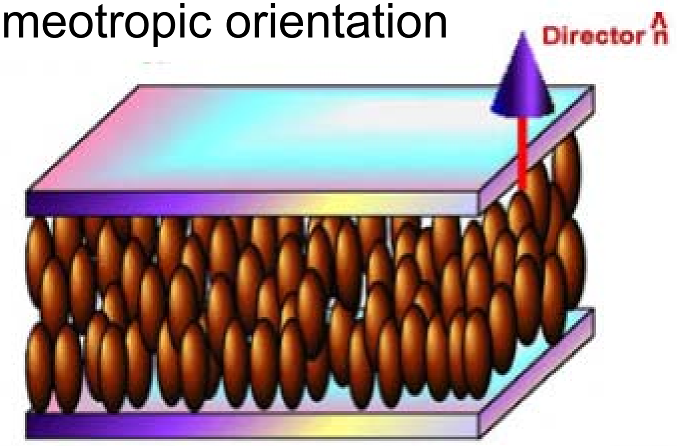


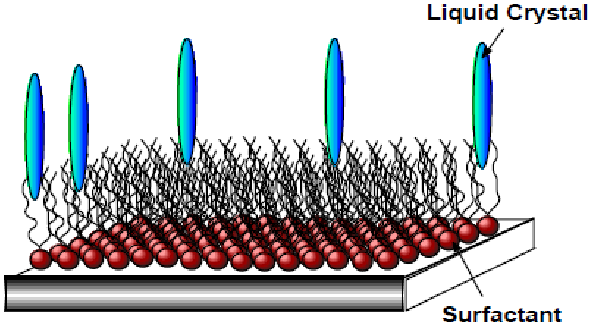
- Since the component of the diamagnetic susceptibility perpendicular to a benzene ring is greater than the in plane component, calamitic mesogens have a positive diamagnetic anisotropy.

The molecules align along the direction of an external magnetic field.

Orientation due to surface interactions

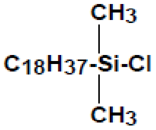
Homeotropic orientation



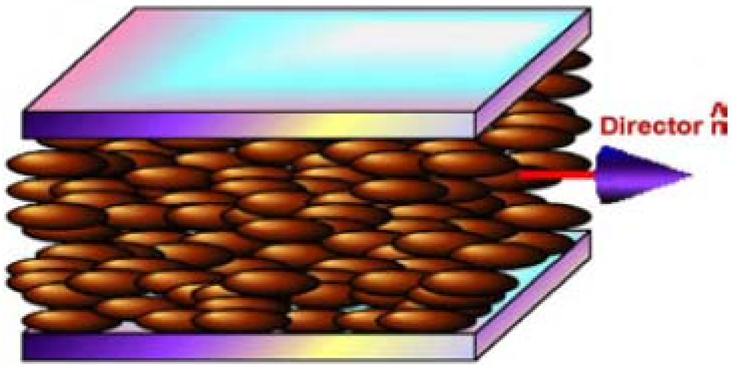

Surfactant Alignment

Lecithin - Non-permanent
Chloro-dimethyl silanes - Permanent

eg

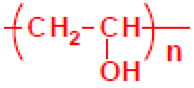

$$C_{18}H_{37}-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{Si}}}}-Cl$$

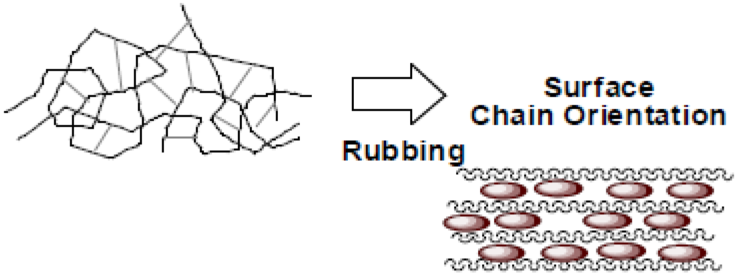
Planar orientation



The polymer solution is spin coated on the surface

Poly(vinyl alcohol)


$$\left(CH_2-\underset{OH}{\underset{|}{CH}}\right)_n$$



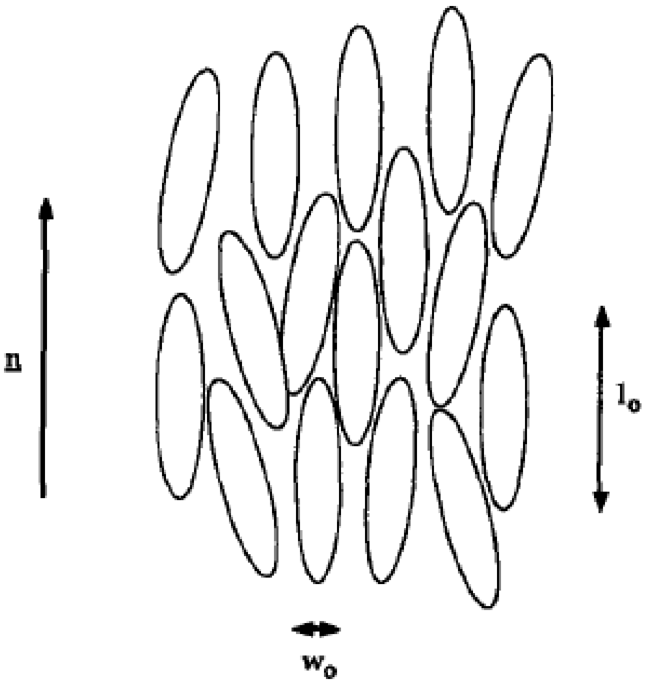
Summary concerning the Orientation of LC

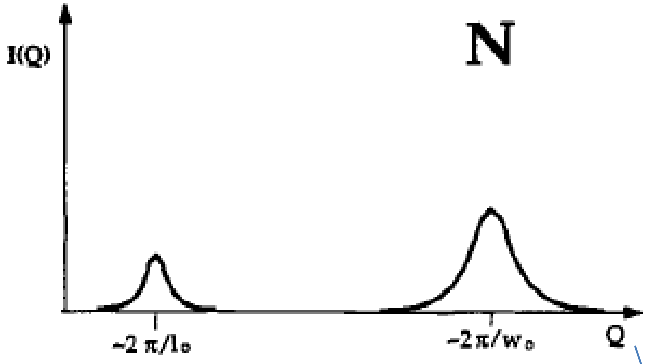
1. LC can easily oriented by different means

2. Orientation on macroscopic scales (~100cm) was for a long time not possible, but is no problem in modern technology

4. Structural and optical properties of LC

Structural studies of LCs

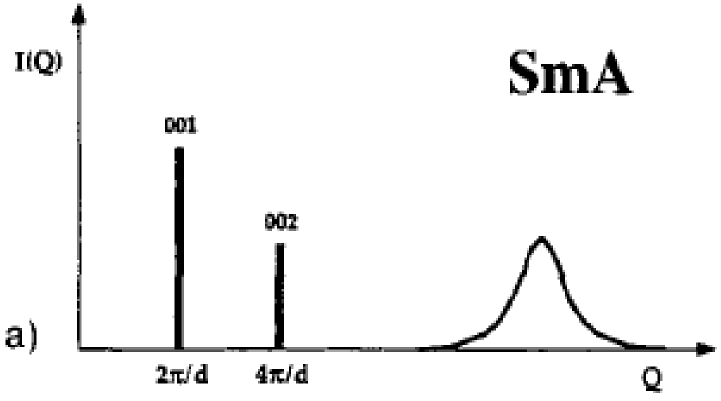


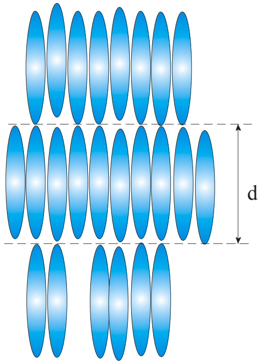


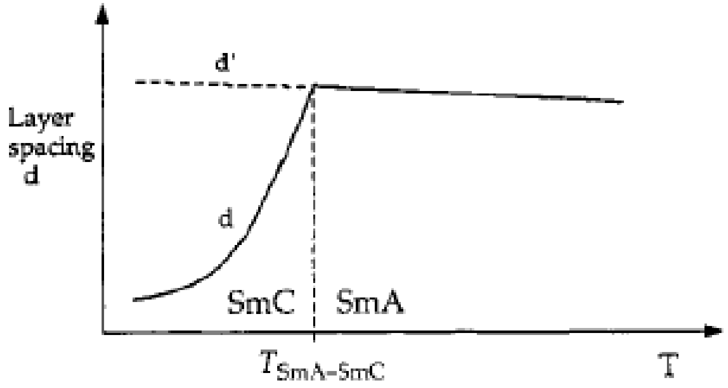
$$Q_n = n\left(\frac{2\pi}{d}\right)$$

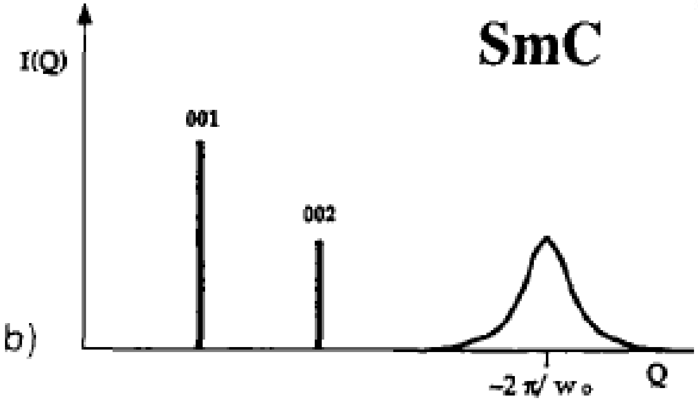
- Peaks arise from the average end-to-end and side-to- side separations of the close-packed molecules.
- The peaks are diffuse because positional correlations only extend over short distances, typically, a few molecular diameters.
- The widths of the diffuse maxima are inversely proportional to these correlation lengths

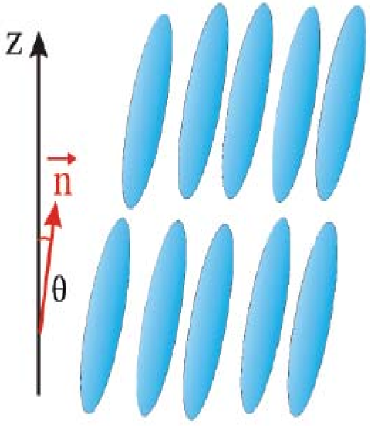
Structural studies of LCs

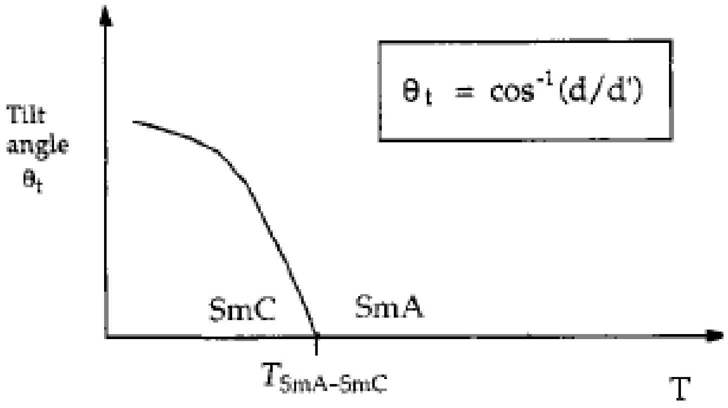






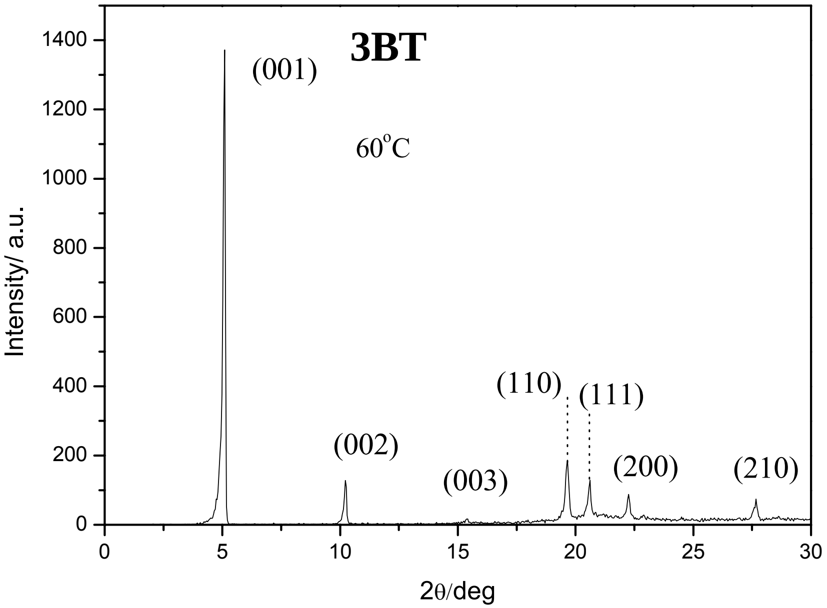


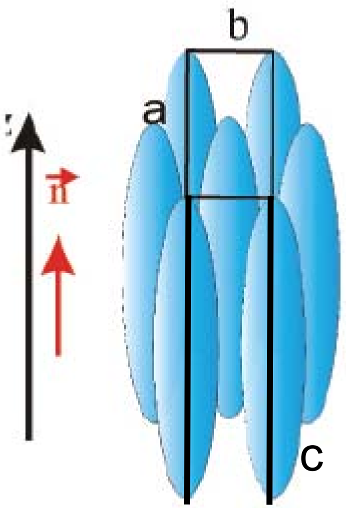


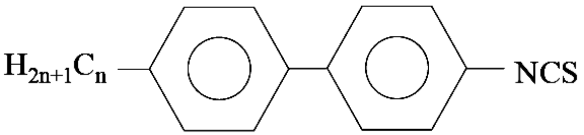


$$\theta_t = \cos^{-1}(d/d')$$

Structural studies of LCs



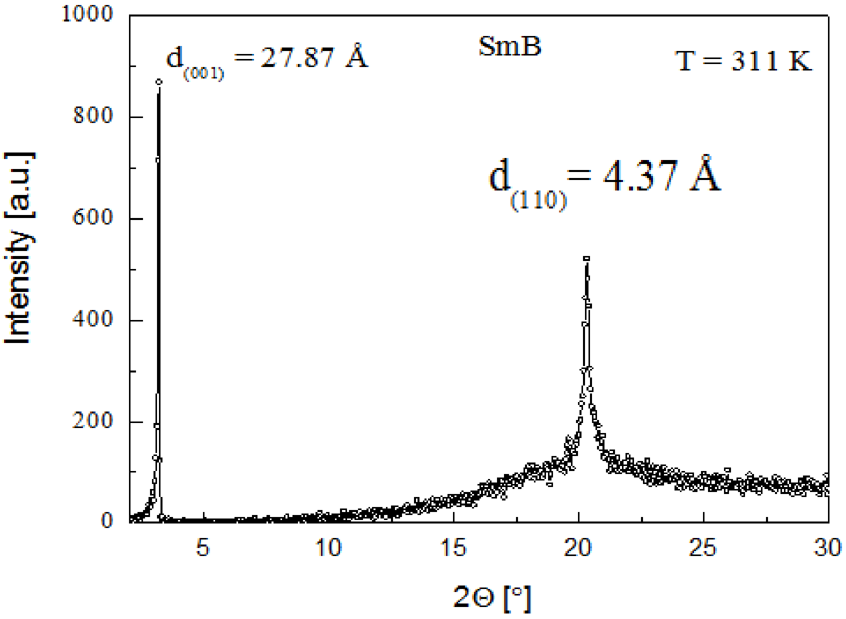


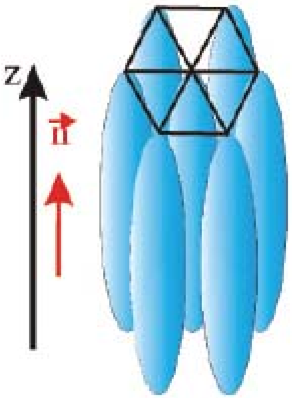


3BT 60°C

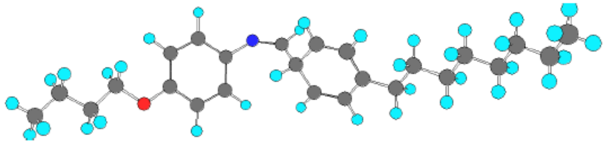
a = 8.00 ± 0,02 Å
b = 5.35 ± 0,02 Å
c = 17/36 ± 0,05Å

a – distance between two molecules
b – diameter of the molecules
c –layer thickness





BBOA

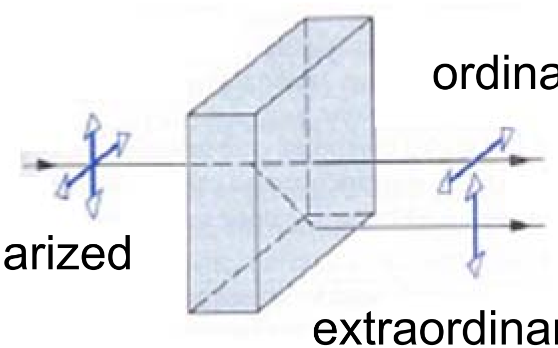


a = 5.02±0.2 °A,

c = 27.56 ± 0.05

Optical properties of LCs

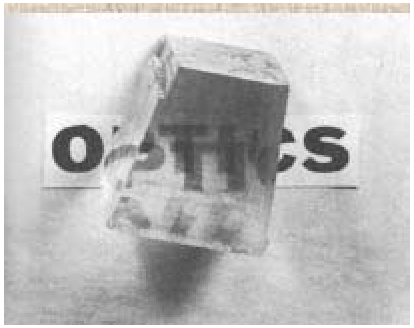
- **Birefringence** (**double refraction) -** the decomposition of a light beam into two rays (the **ordinary** and the **extraordinary** rays) when it passes through materials.
- Velocities of both components, are different and vary with the propagation direction through the specim and the waves get out of phase.



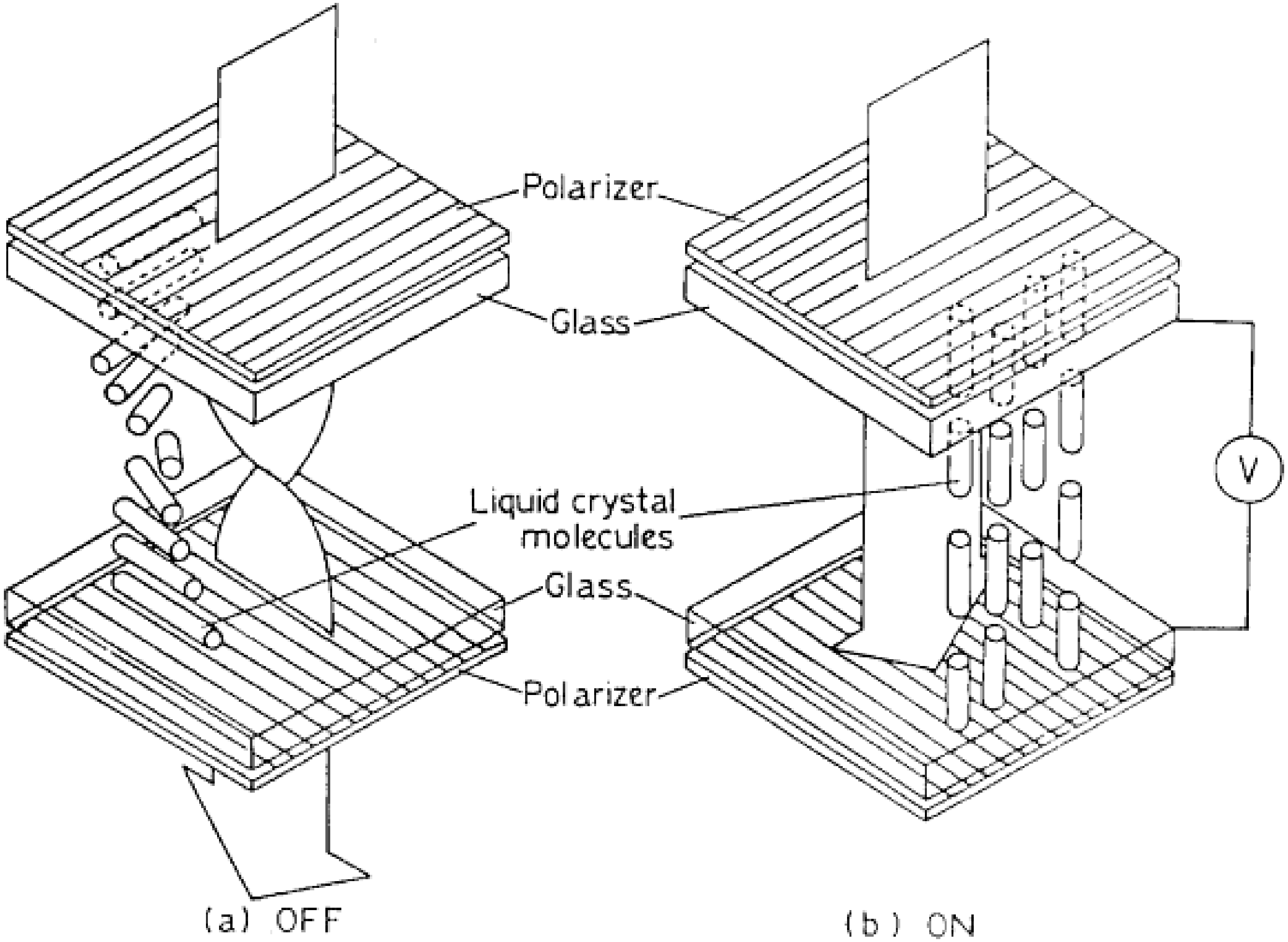
ordinary ray

Unpolarized light

extraordinary ray



Twisted nematic liquid crystal display



First LCD

- 1969 – George Heilmeier, RCA David Sarnoff Research Center, first liquid crystalline display (125 ^{o}C,)
- DSM (dynamic scattering method) :an electrical charge is applied which rearranges the molecules so that they scatter light)

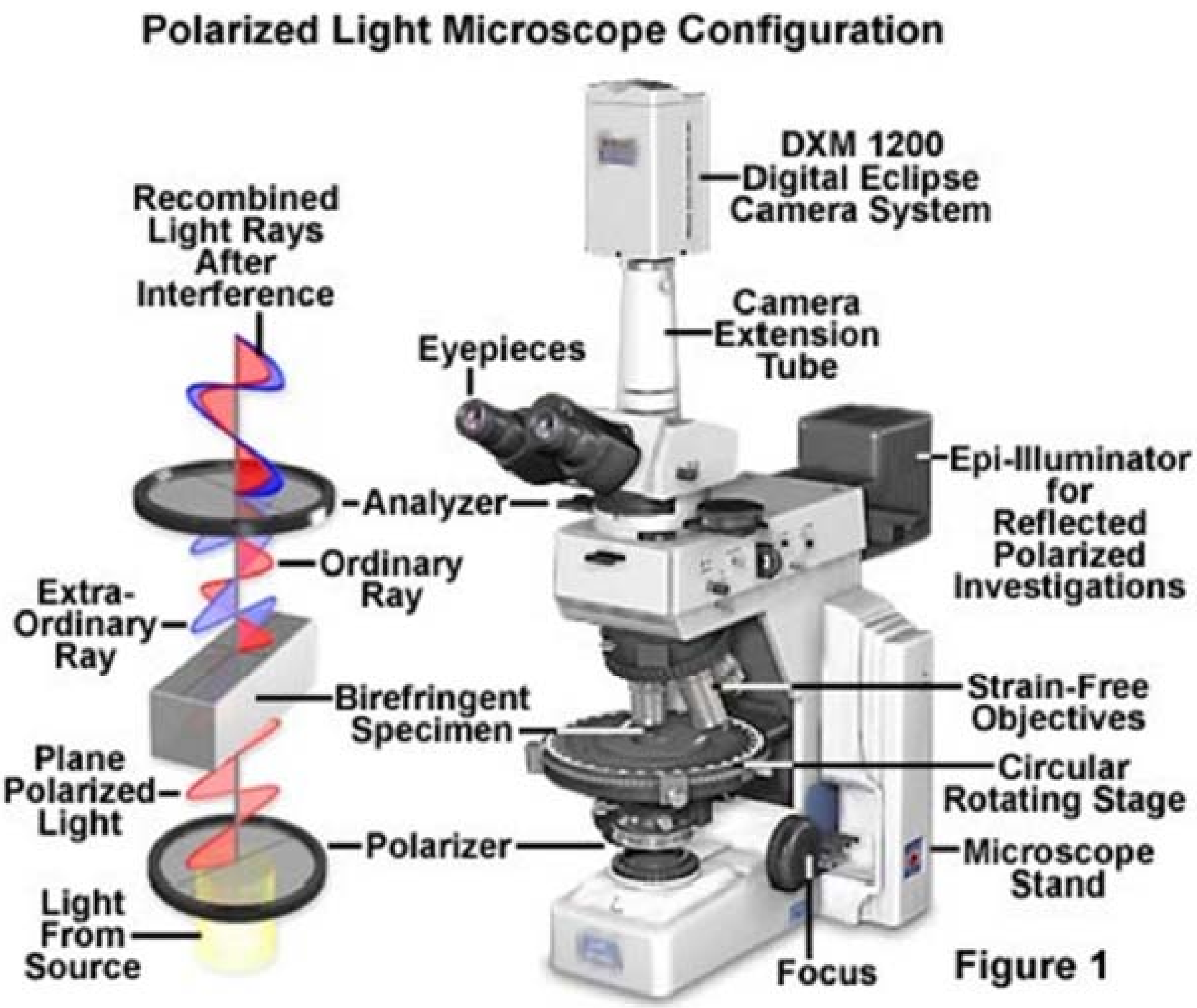
The picture above shows George Heilmeier with the first dynamic scattering method-based liquid crystal display

Summary concerning the structural and optical properties of LC

1. The structural properties of LC are explored by X-ray and ν - diffraction

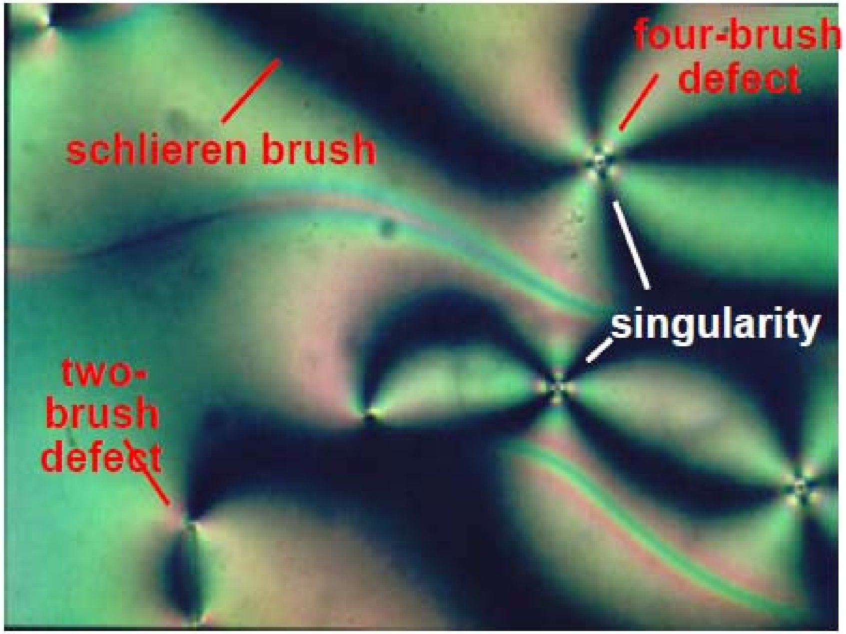
2. The pronounced optical bifringence is the basis for applications in displays

5. Textures of LC

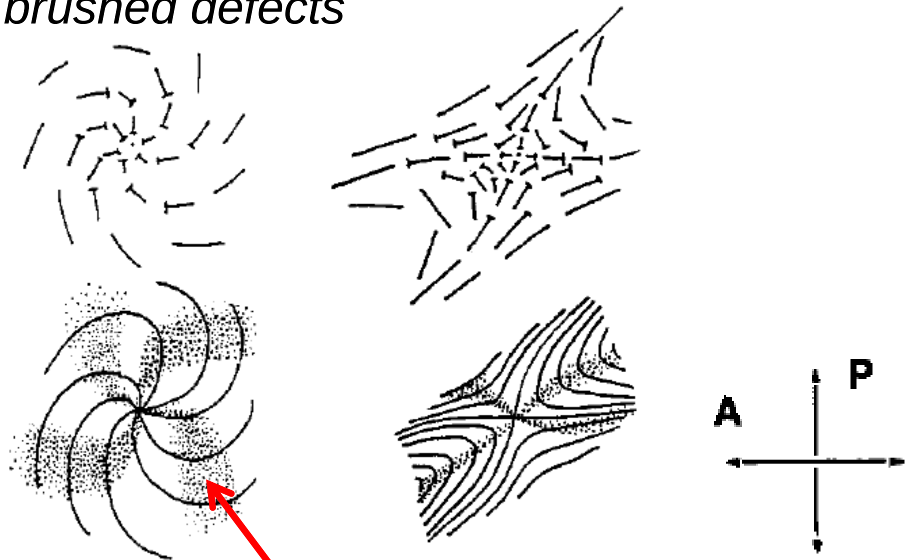


- polarization colors result from the interference of the two components of light split by the anisotropic specimen and may be regarded as white light minus those colors that are interfering destructively

Schlieren Defect Texture (Nematic)



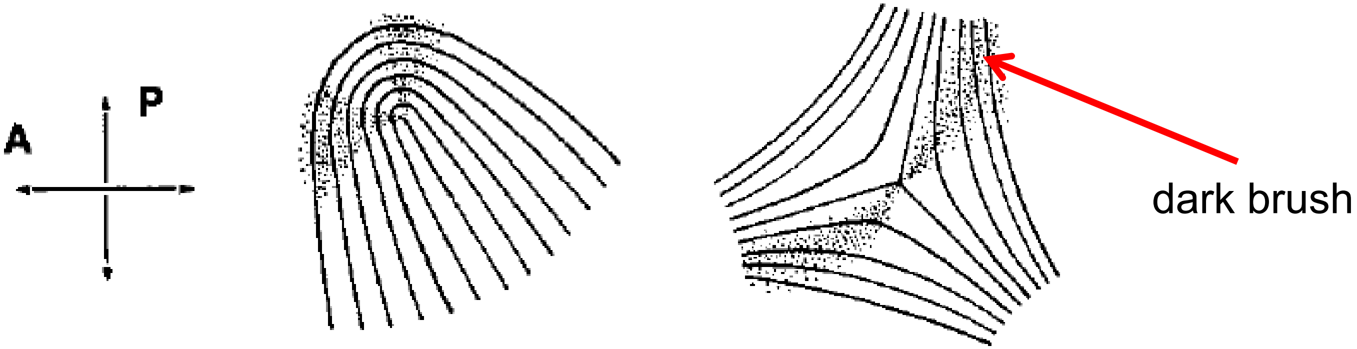
Distribution of directors in the neighborhood of 4 brushed defects



dark brush

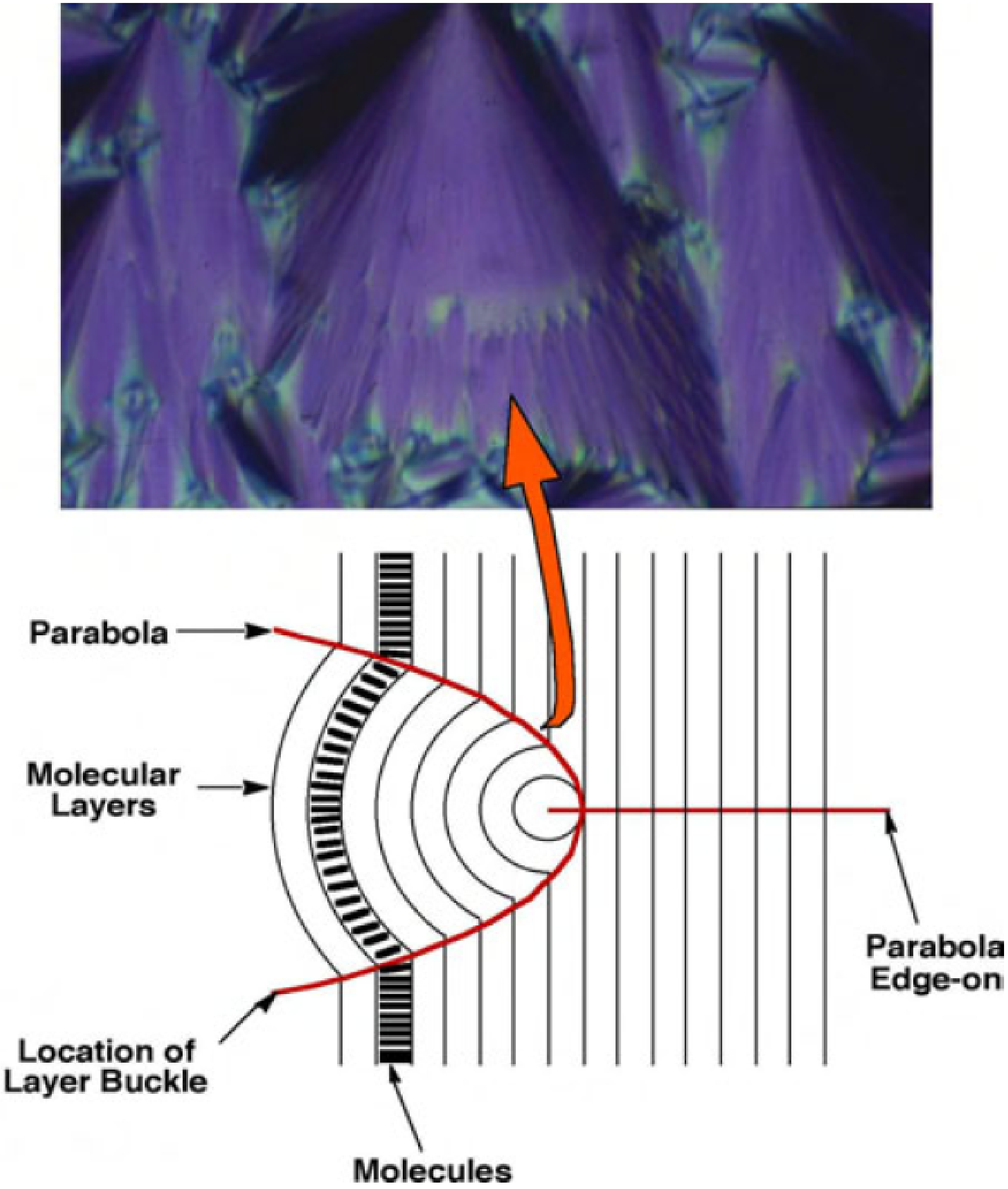
Crossed polarizers

Distribution of directors in the neighborhood of 2 brushed defects

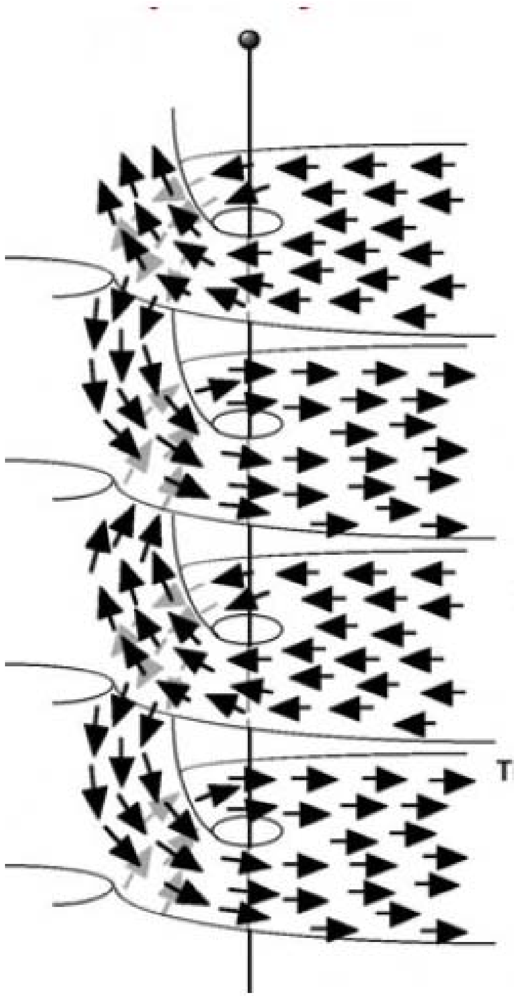


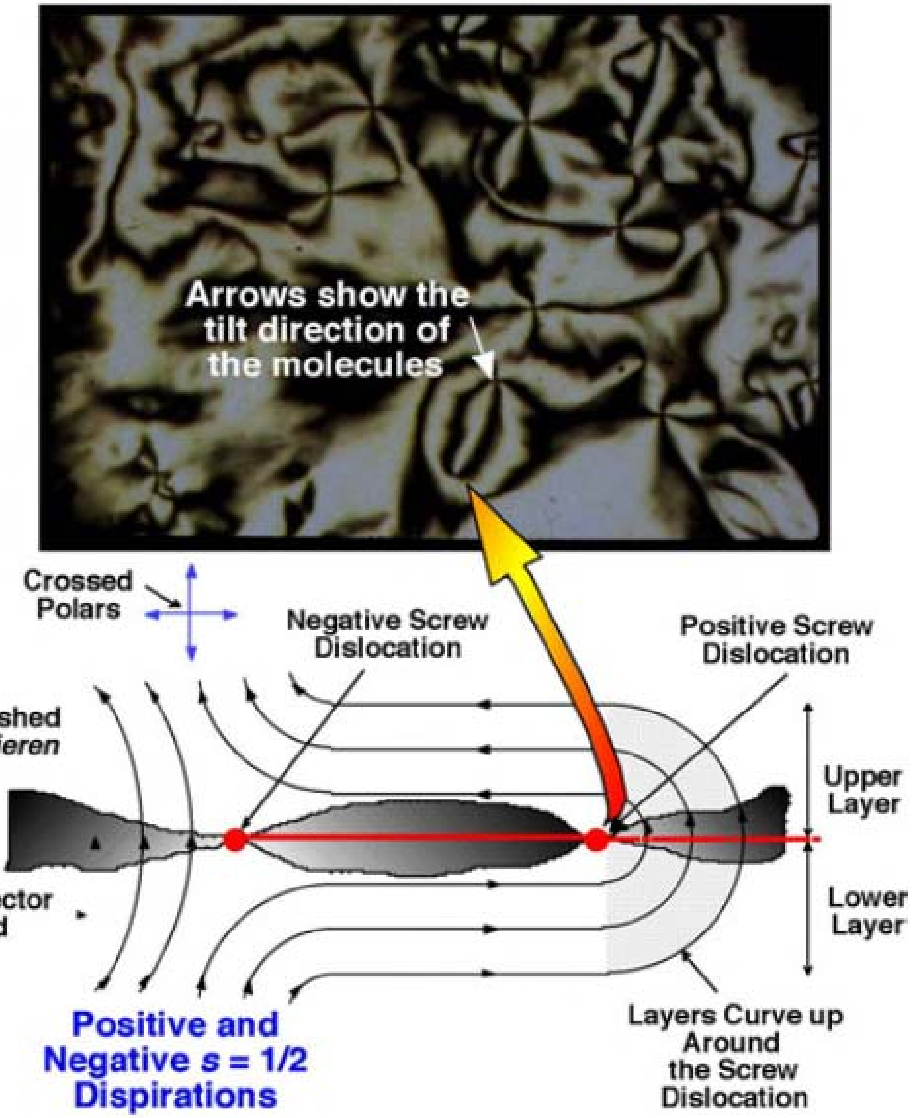
dark brush

Fan shape focal-conic smectic A



Schlieren Defects in Antiferroelectric LCs





Arrows show the tilt direction of the molecules

Positive and Negative $s = 1/2$ Dispirations

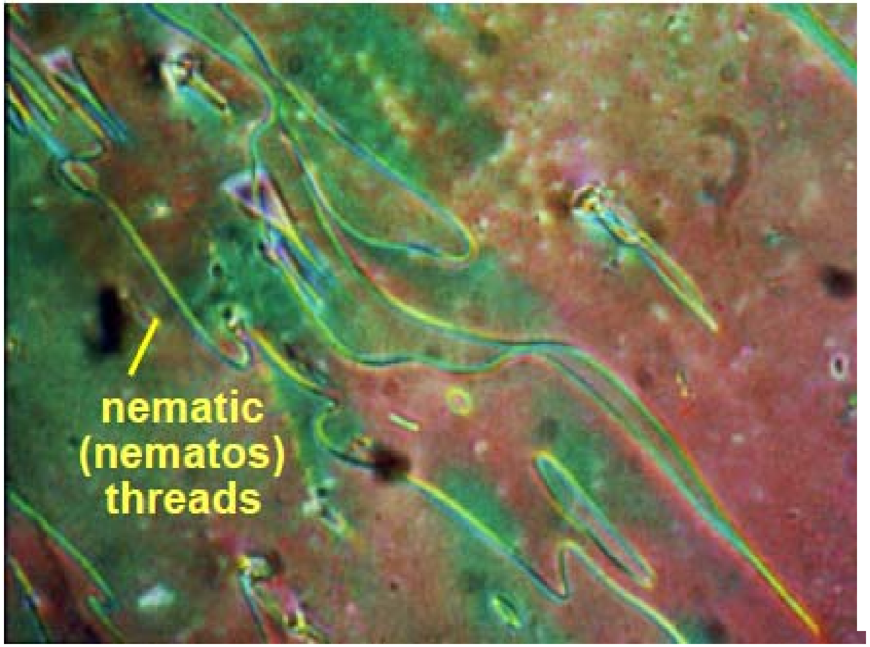
Textures

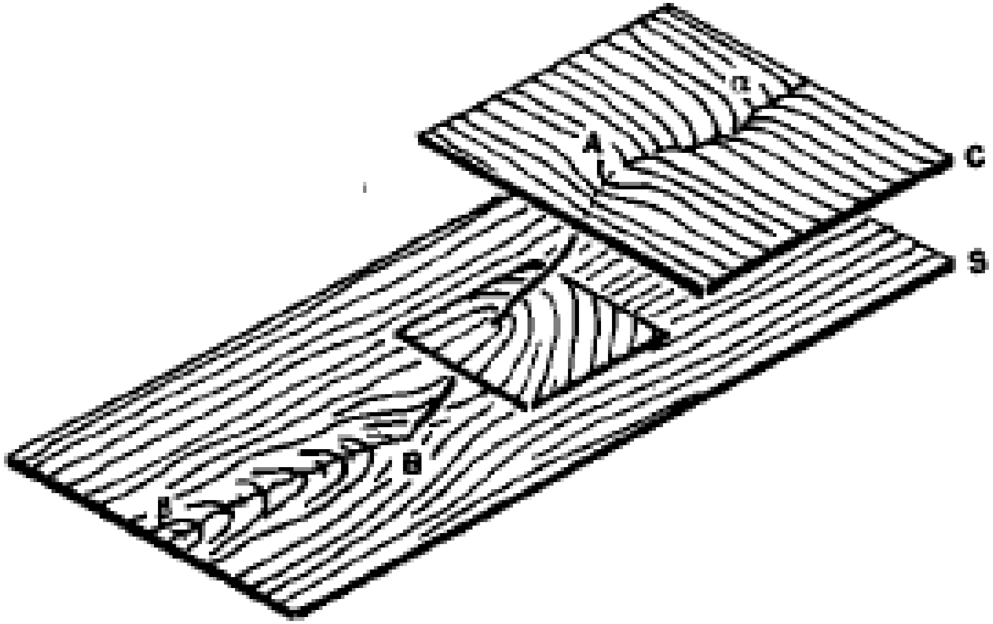
Textures - delocalized topological defects

As the number defects increases the entropy (S) gets larger and free energy (G) decreases

$$G = E - TS$$

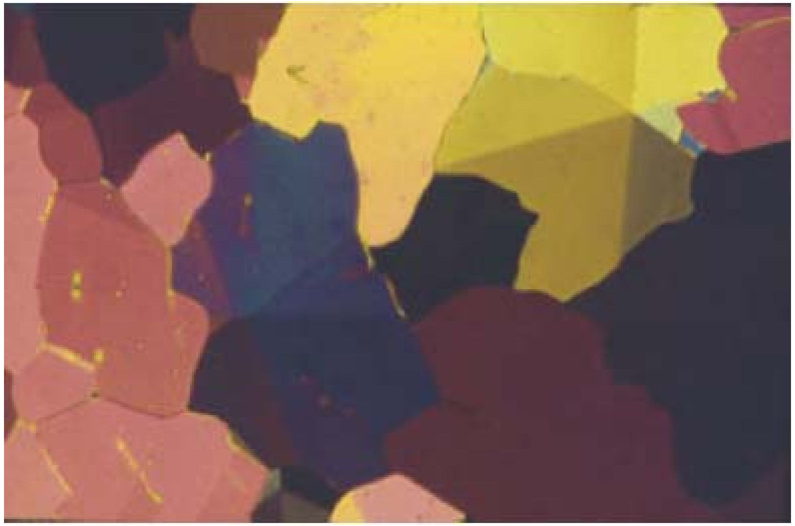
internal energy



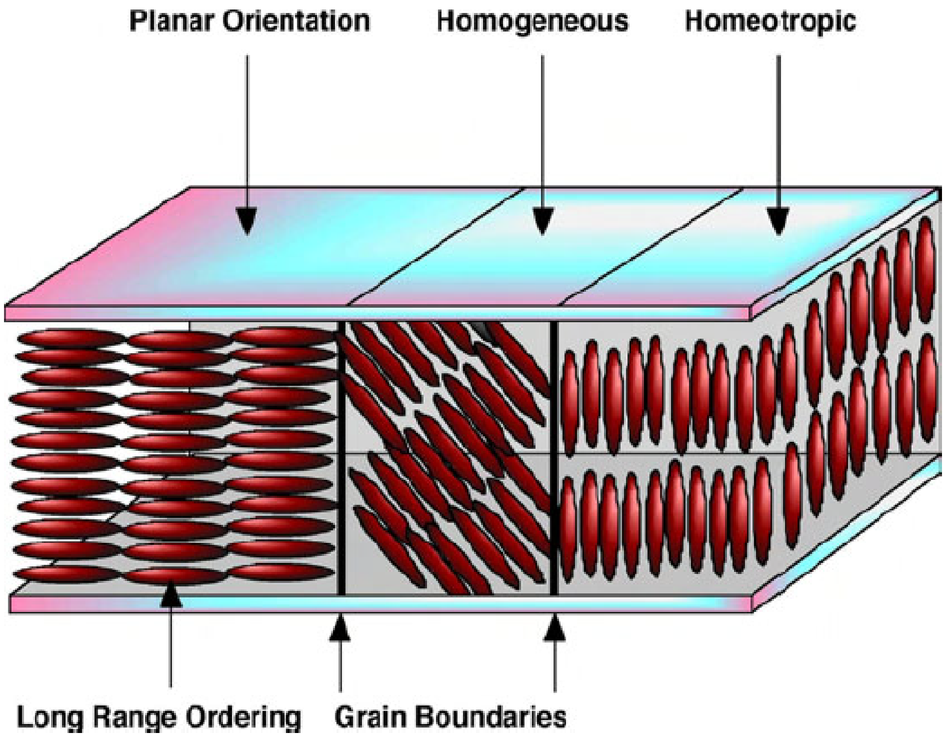


Mosaic textures

Mosaic texture (smectic B)



Mosaic texture (smectic G)



Summary concerning the textures of LC

1. The textures of LC are a „world“ for itself.

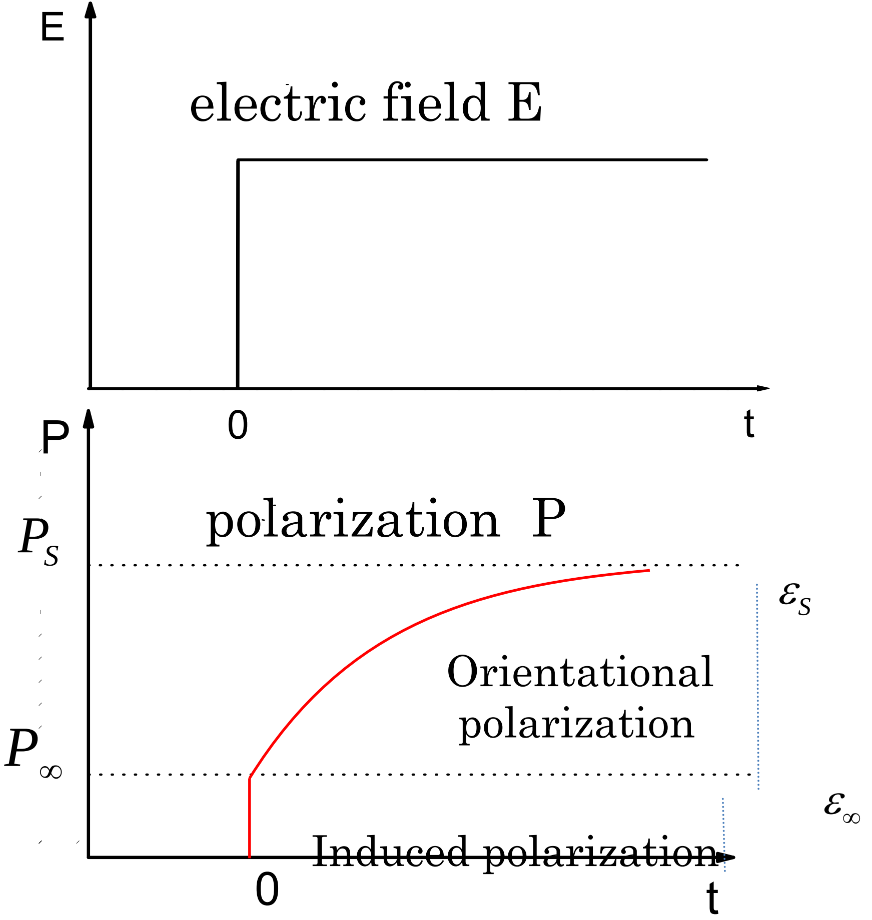
2. Under normal conditions a manifold of defects of different topology can be observed

6. Dynamics of LC

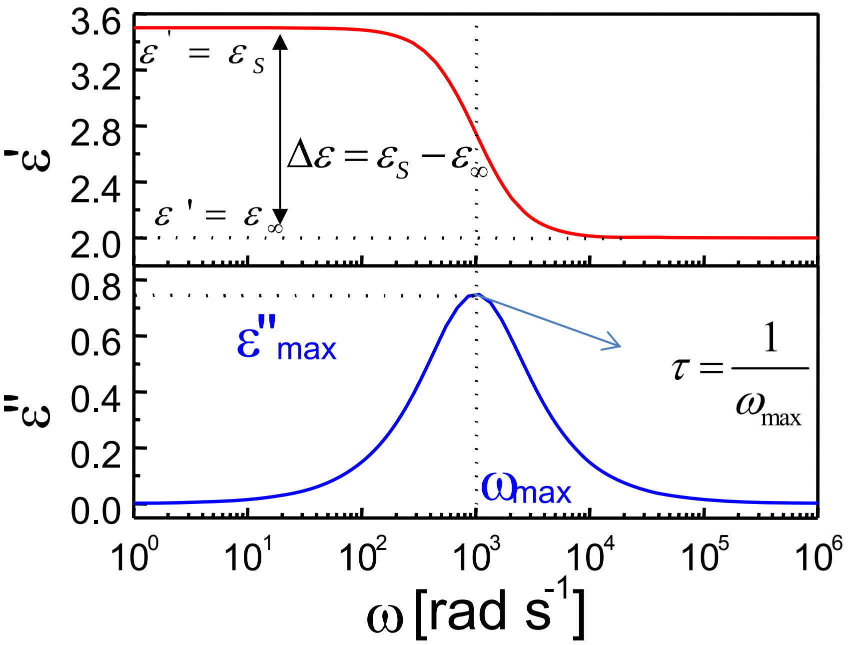
Broadband Dielectric Spectroscopy (BDS)

BDS- measures complex dielectric function in a wide temperature and frequency range.

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$$



Debye relaxation $\varepsilon^* = \varepsilon_\infty + \dfrac{\varepsilon_s - \varepsilon_\infty}{(1 + i\omega\tau)}$



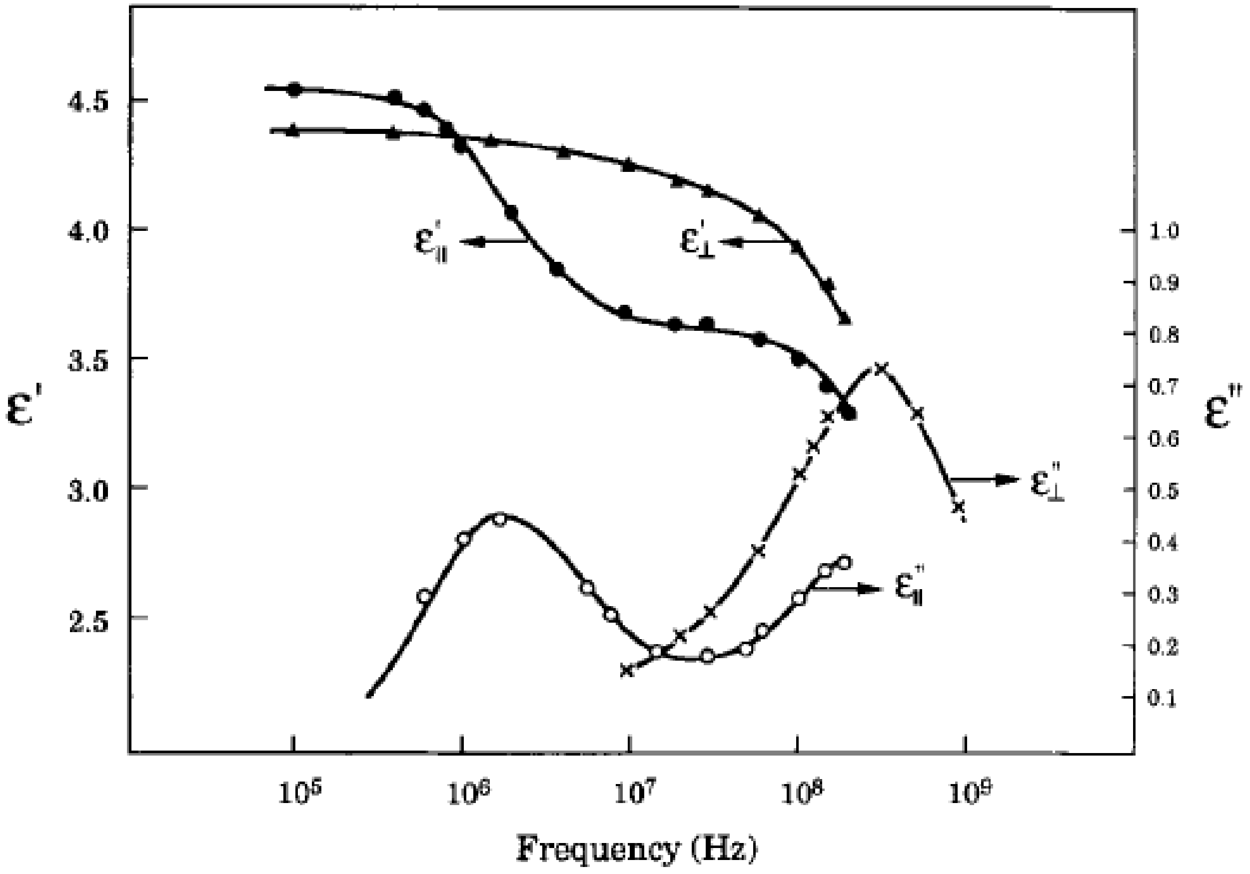
$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (\omega\tau)^2}$$

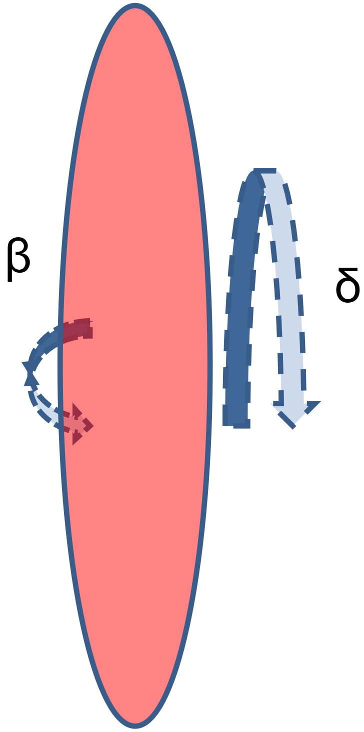
$$\varepsilon''(\omega) = \frac{\varepsilon_s - \varepsilon_\infty}{1 + (\omega\tau)^2}\omega\tau$$

complex dielectric function $\epsilon^*(\omega, T)$

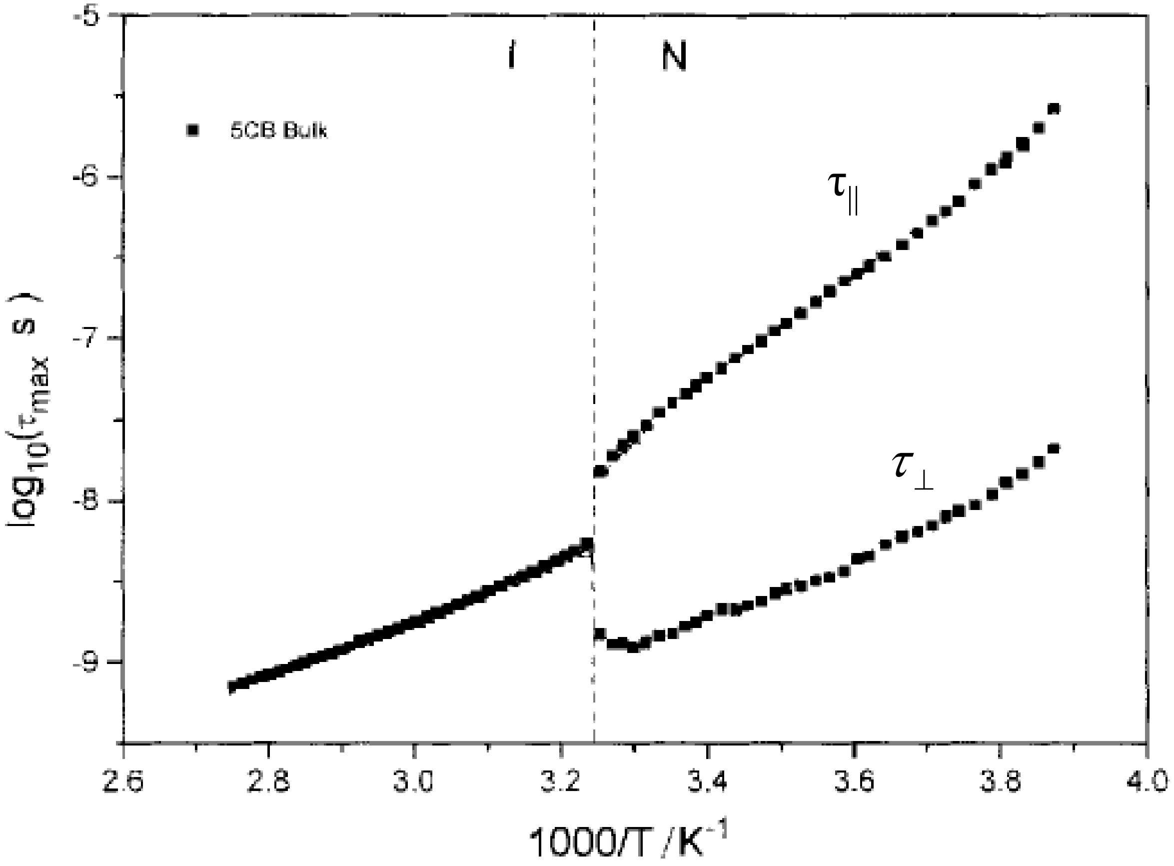
$$P(\omega, T) = (\epsilon^*(\omega, T) - 1)\, E(\omega)$$

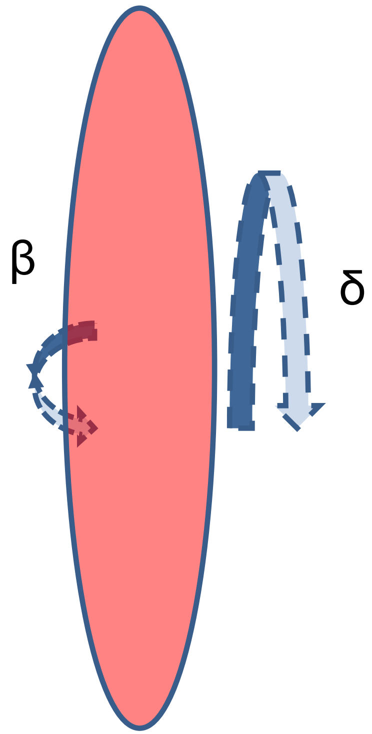
Molecular dynamics in the nematic phase





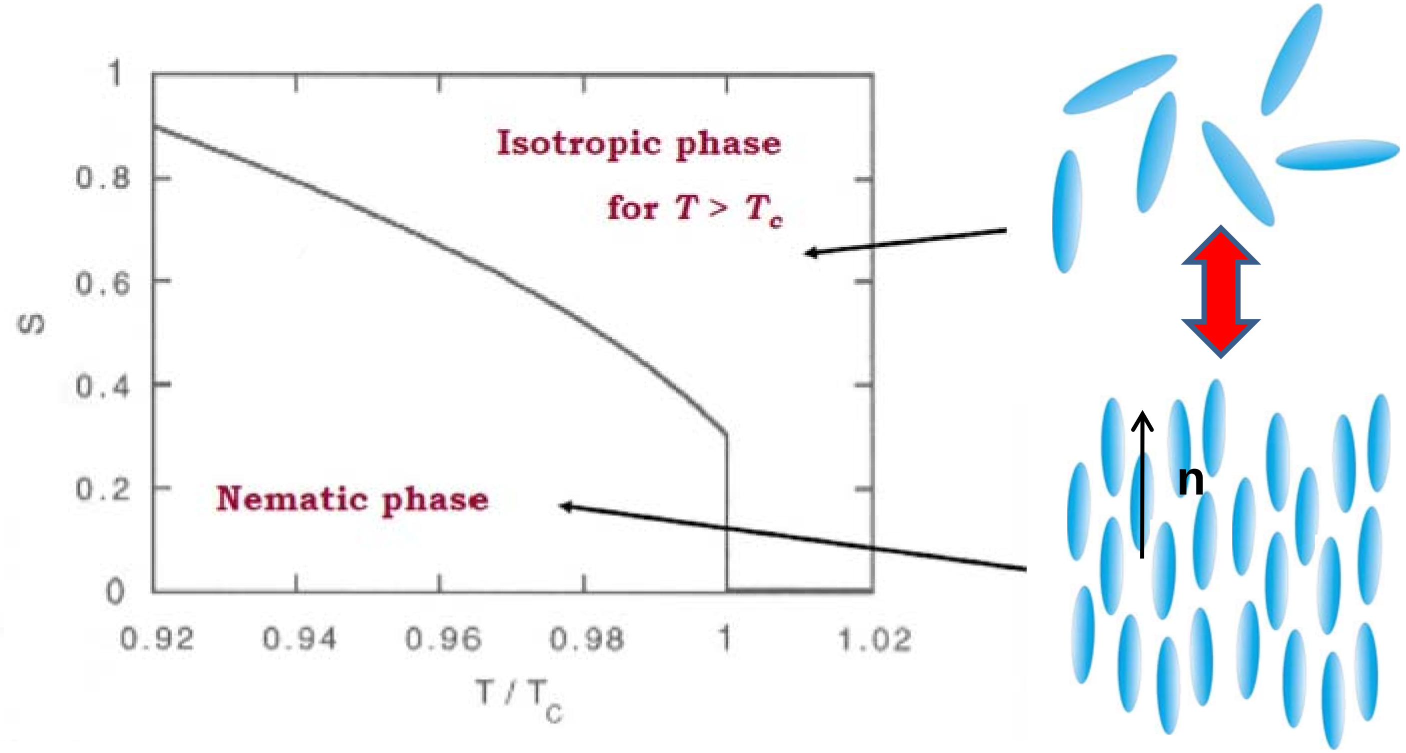
Molecular dynamics in the nematic phase





Nematic to isotropic transition

$$S = \frac{\int f(\theta)\left[\frac{3}{2}\cos^2\theta - \frac{1}{2}\right] d\Omega}{\int f(\theta) d\Omega} \equiv \frac{3}{2}\langle\cos^2\theta\rangle - \frac{1}{2}$$



for a typical liquid crystal sample, S is on the order of 0.3 to 0.8

Theoretical Considerations of the dielectric properties of LCs

The nematic potential Ui in a mean field approximation (Meier and Saupe):

$$U_i \sim S\left(\frac{3\cos\theta_i - 1}{2}\right)$$

S - the order parameter

θ_I - is the angle between the long Molecular axis and the director

The mean square dipole moments parallel $\langle \mu_{II}^2 \rangle$ and perpendicular $\langle \mu_{\perp}^2 \rangle$ to the director:

$$\langle \mu_{II}^2 \rangle = \frac{\mu^2}{3k_B T}\left[1 - (1 - 3\cos^2\Psi)S\right]E$$

$$\langle \mu_{\perp}^2 \rangle = \frac{\mu^2}{3k_B T}\left[1 + \frac{1}{2}(1 - 3\cos^2\Psi)S\right]E$$

k_B – Boltzman constant

ψ- the angel between the dipole moment and the long molecular axis

Summary concerning the dynamics of LC

1. **LC have a dynamics which reflects the shape of the molecule. In nematics one has two relaxations corresponding to fluctuations around the short (δ-relaxation) and long (β-relaxation) molecular axis**

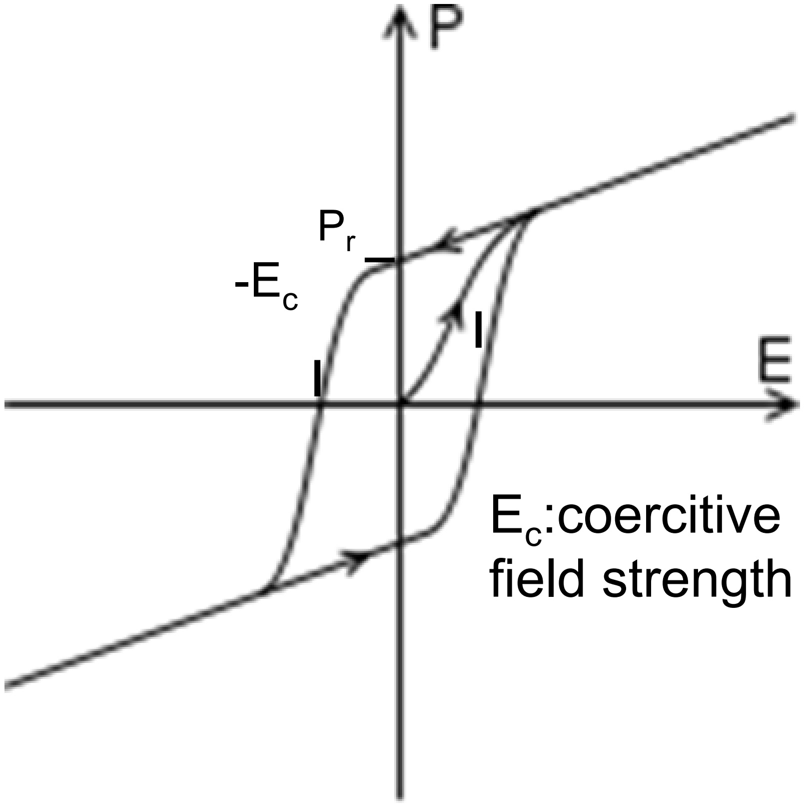
2. **If the LC has a glassy state a dynamic glass transition is observed as well (α-relaxation)**

3. **The Meier-Saupe theory is able to show that the transition from the nematic to the isotropic state has the character of a first-order phase transition**

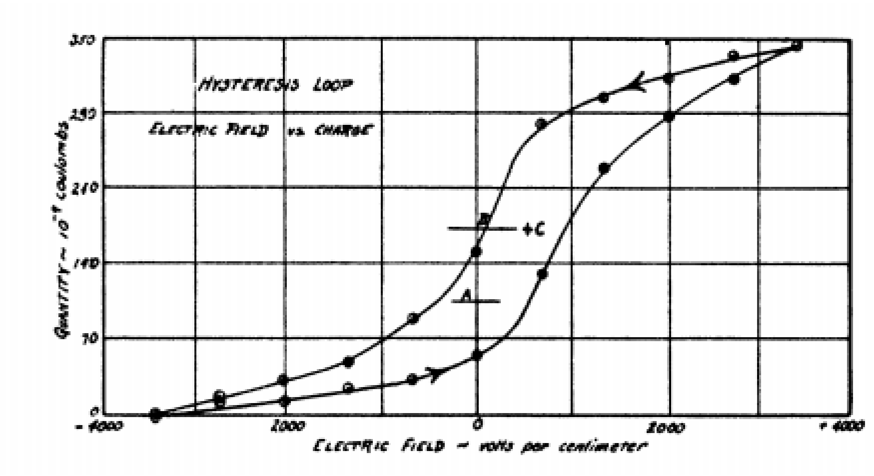
7. Ferroelectric LC

Ferroelectricity in solids

Rochelle salt in *P* analogous to the magnetic hysteresis (*Phys. Rev. (1921))* 1921 - J. Valasek, Rochelle Salt (NaK($C_4H_4O_6$)$4H_2O$) : an electric hysteresis of



E_c:coercitive field strength



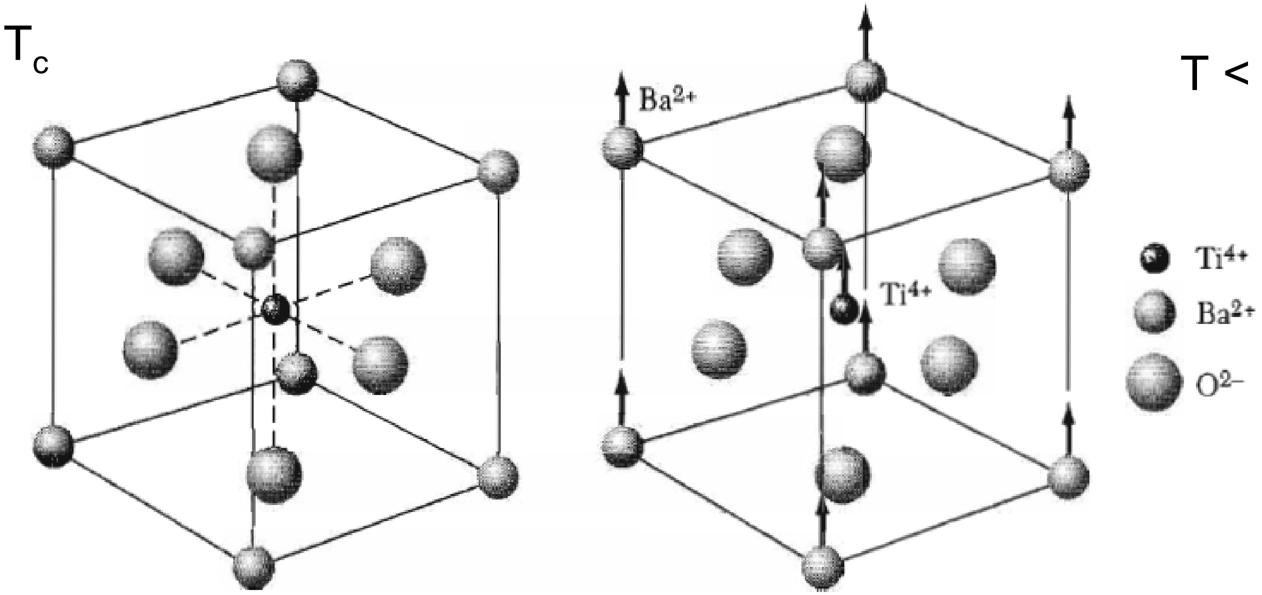
J. Valasek (*Phys. Rev. (1921)*)

Ferroelectricity in solids

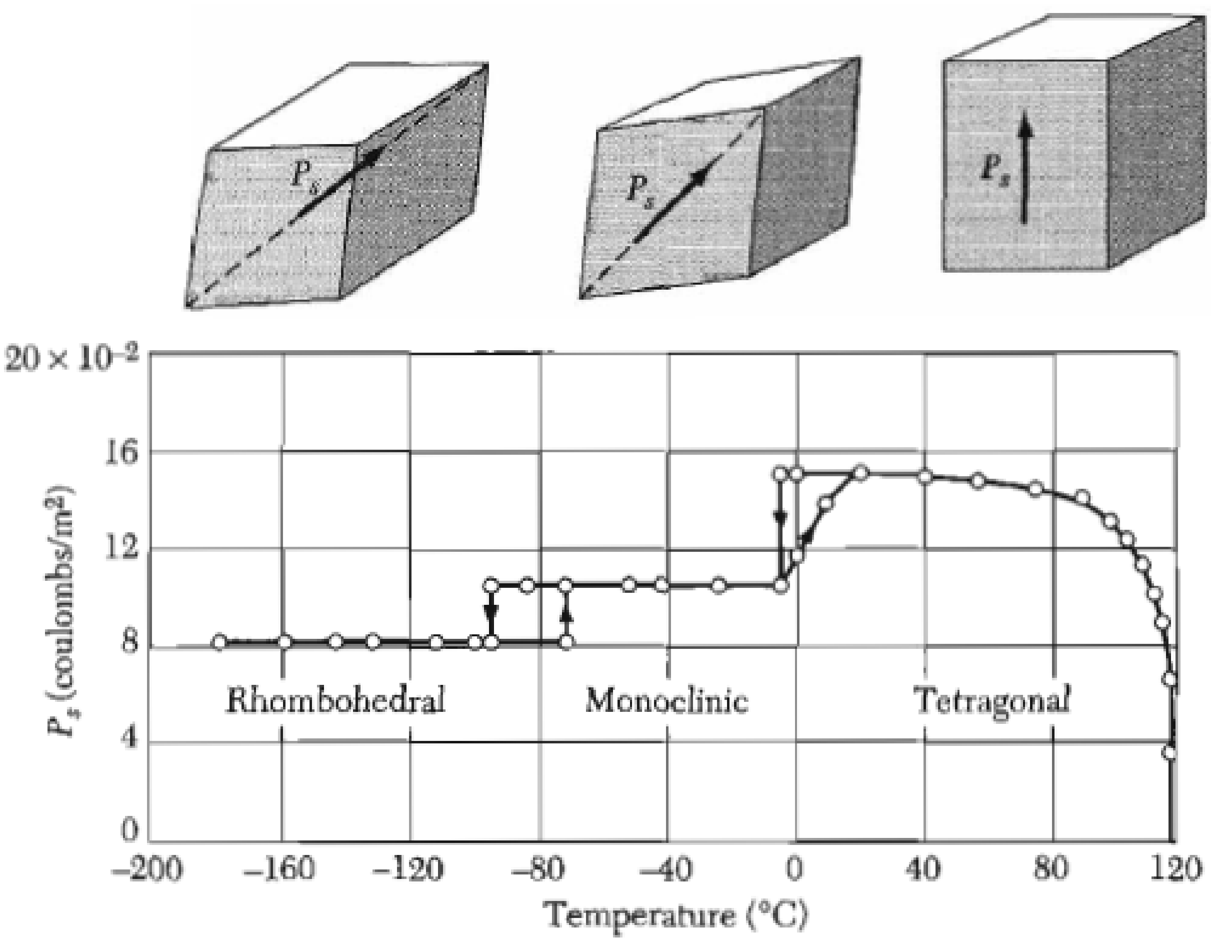
1945 - $BaTiO_3$ perovskite-structure (Tc = 408 K)

T > T_c

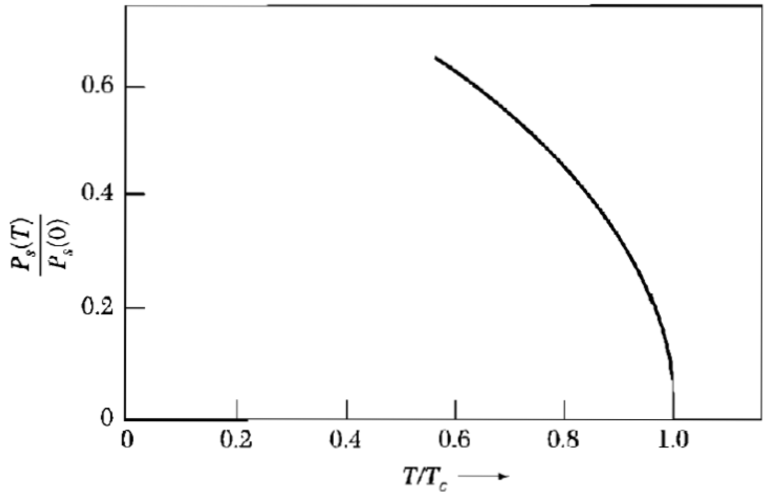
T < T_c



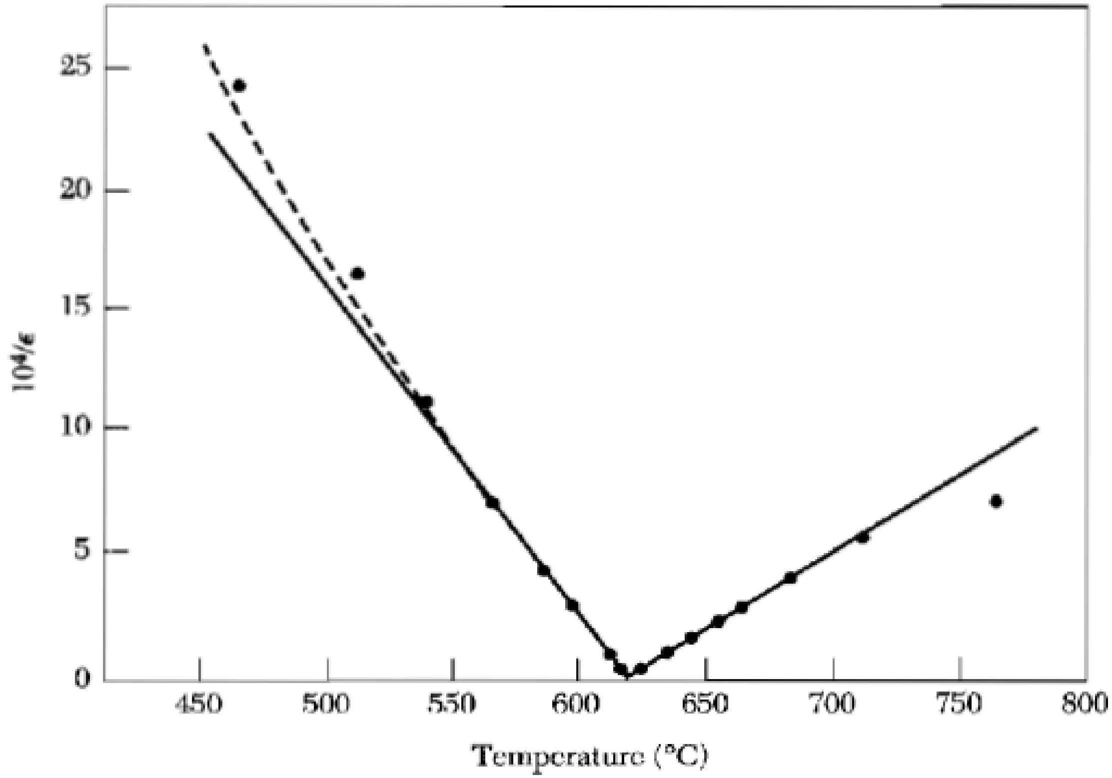
The crystal structure of barium titanate.



Spontaneous polarization projected on cube edge of barium titanate, as a function of temperature.



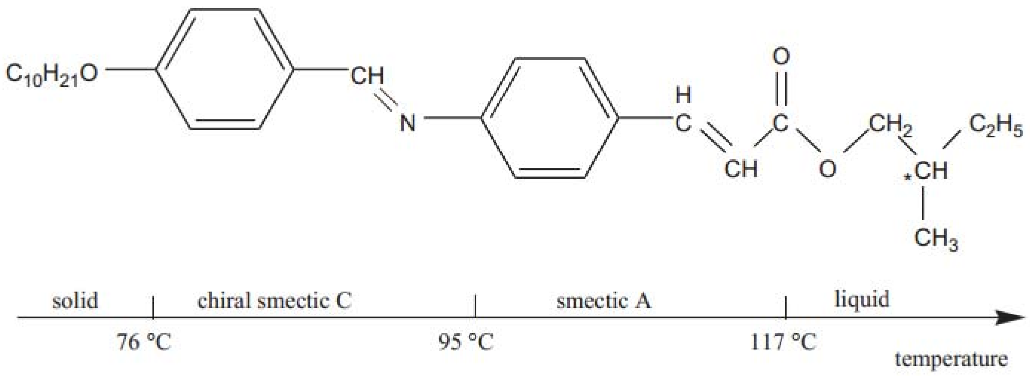
Spontaneous polarization versus temperature, for a second-order phase transition



Temperature variation the polar-axis static dielectric constant of LiTaO,

Ferroelectric Liquid Crystals

ferroelectric liquid crystals (FLC) were predicted (analysis of the symmetry of the molecules) and proved experimentally by Mayer (1975)



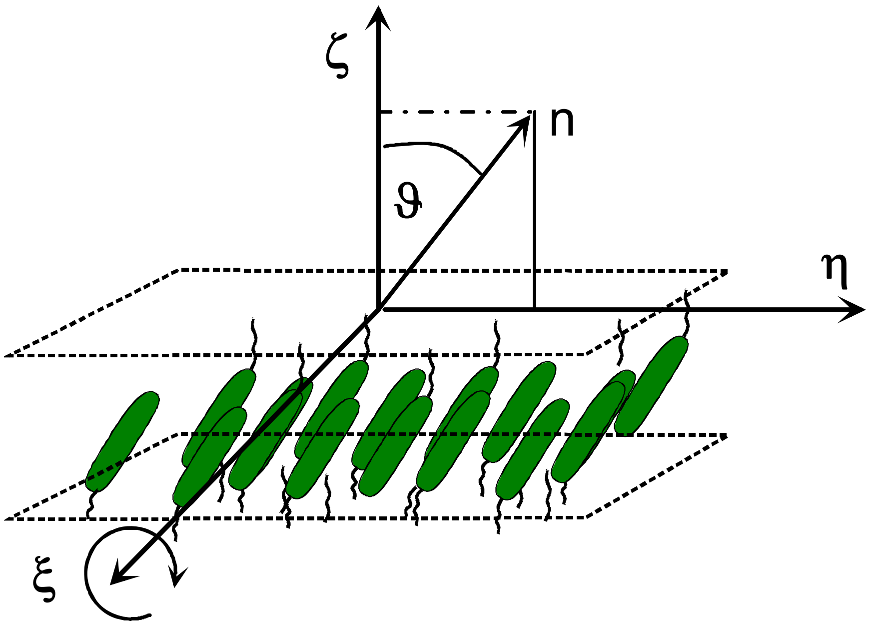
First ferroelectric liquid crystal

molecules are chiral and have a permanent dipole moment transverse to their long axis

Polarization vector must be invariant under all the symmetric operation (Neumann's principle)

The symmetry plane of SmC is absent. The symmetry elements of SmC* : a twofold axis parallel to the layers and a normal to the long molecular axis.

Feroelectricity in Liquid Crystals (FLC)



Symmetric molecules:

C_2 and $\sigma_{\eta\zeta}$ transformation are allowed

$$\begin{pmatrix} p_\xi \\ p_\eta \\ p_\varsigma \end{pmatrix} \xrightarrow{C_2} \begin{pmatrix} p_\xi \\ -p_\eta \\ -p_\varsigma \end{pmatrix} \qquad \begin{pmatrix} p_\xi \\ p_\eta \\ p_\varsigma \end{pmatrix} \xrightarrow{\sigma_{\eta\,\varsigma}} \begin{pmatrix} -p_\xi \\ p_\eta \\ p_\varsigma \end{pmatrix}$$

$$\vec{P} = 0$$

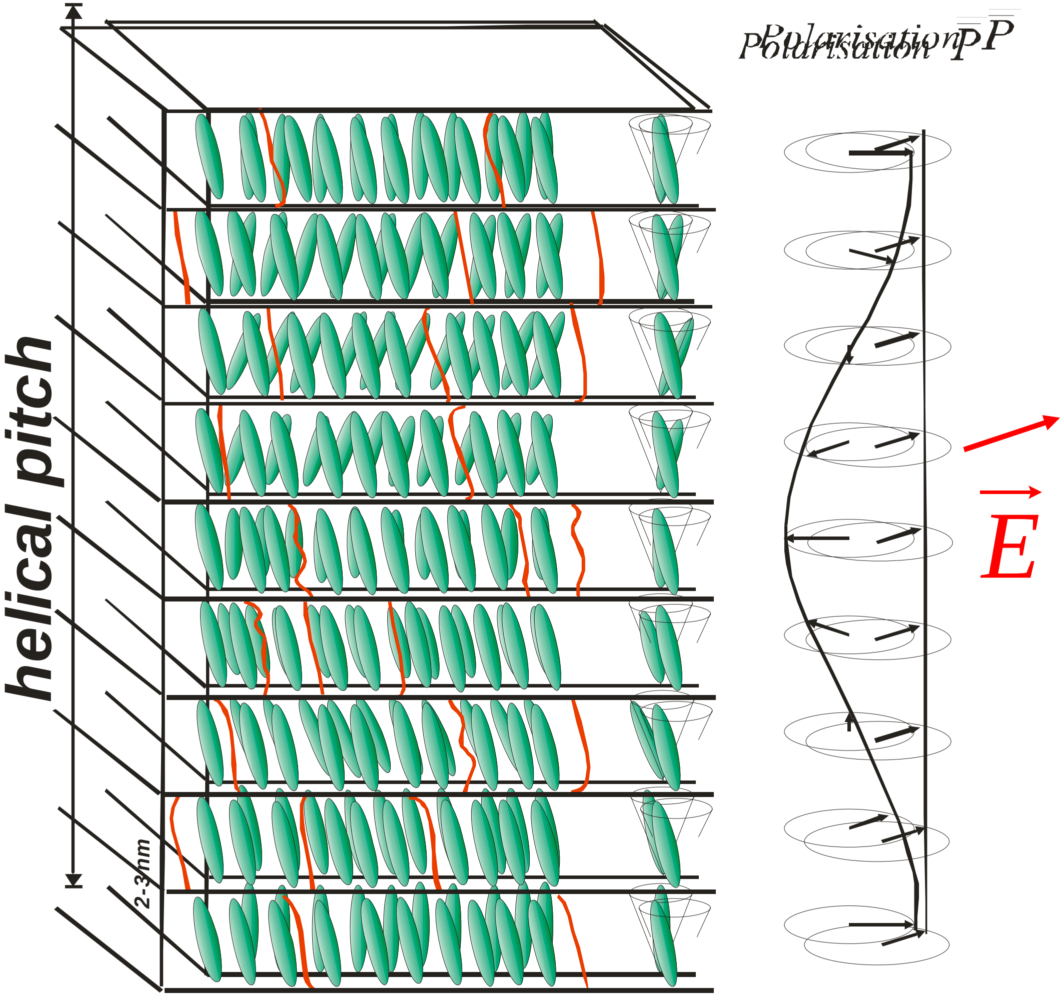
Asymmetric molecules:

$\sigma_{\eta\zeta}$ is forbidden

$$\begin{pmatrix} p_\xi \\ p_\eta \\ p_\varsigma \end{pmatrix} \xrightarrow{C_2} \begin{pmatrix} p_\xi \\ -p_\eta \\ -p_\varsigma \end{pmatrix} \dashrightarrow \vec{P} = \begin{pmatrix} p_\xi \\ 0 \\ 0 \end{pmatrix}$$

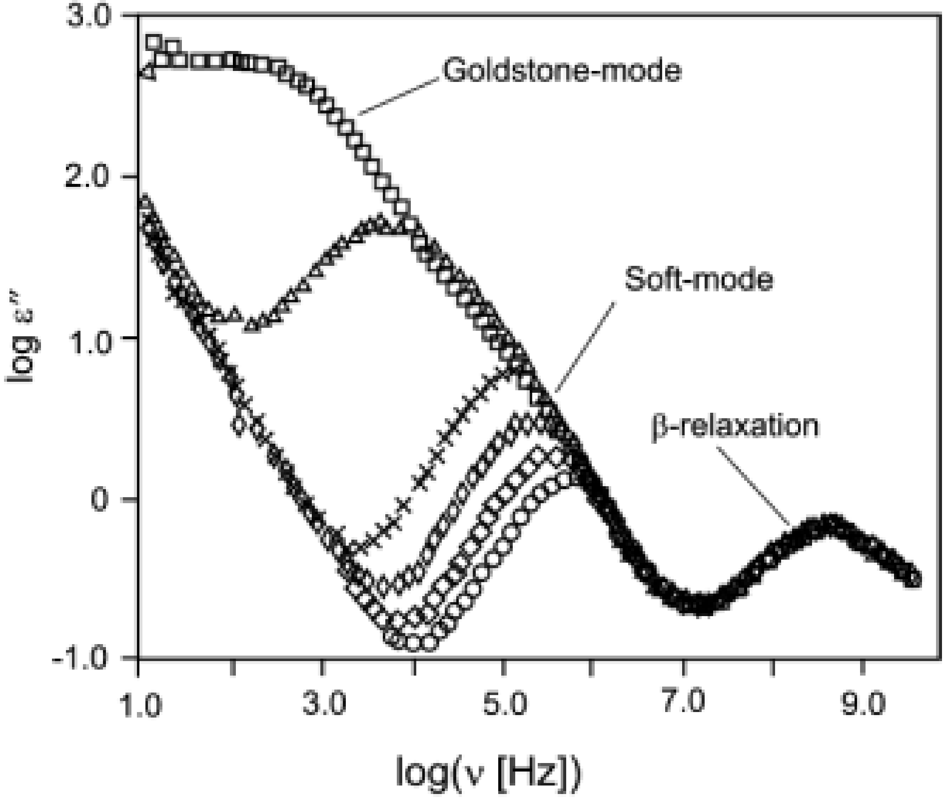
Ferroelectricity in FLC is a local property of the smectic layer

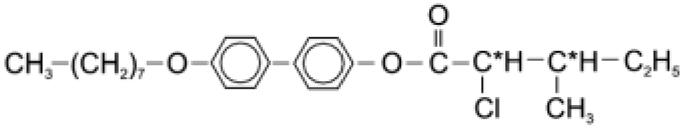
The helical superstructure of ferroelectric liquid crystals

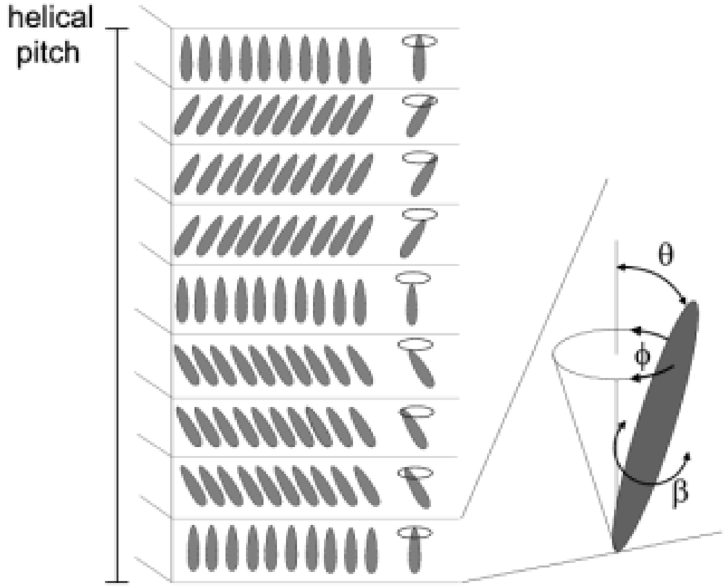


In order to reduce the free energy a helical superstructure is formed which can be unwound by applying an external electrical or mechanical (stress) field and which then can be frozen by a **crosslinking** reaction

Collective and molecular dynamics in FLCs

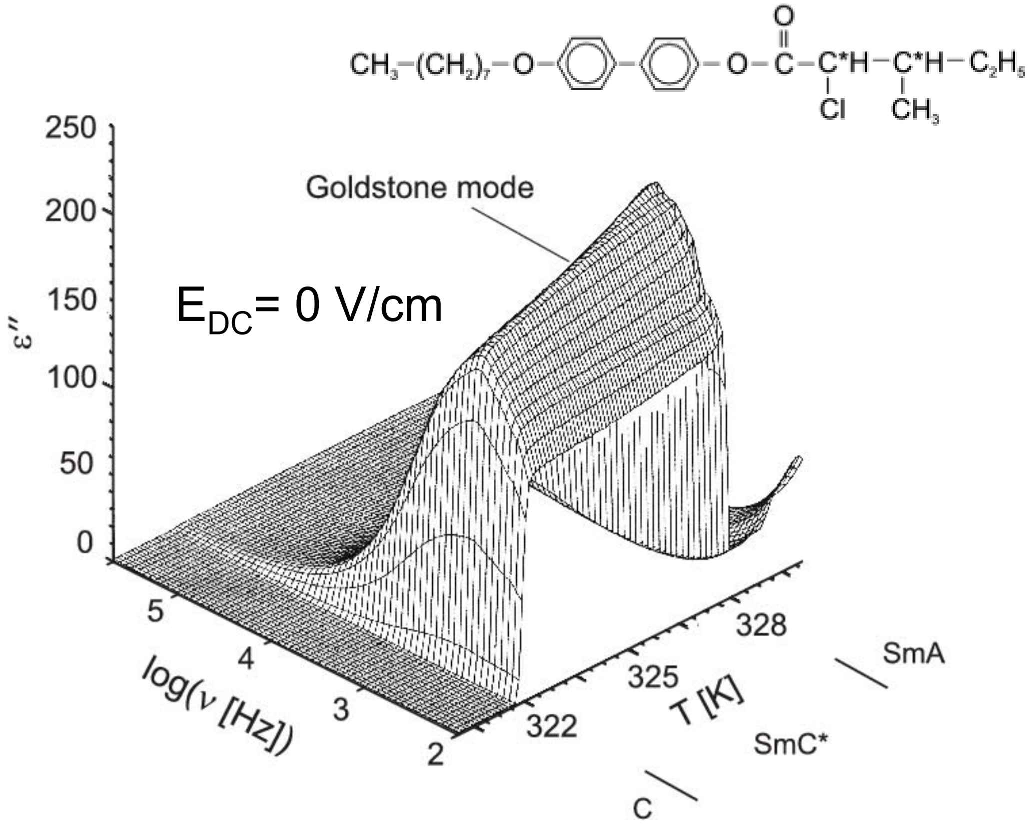




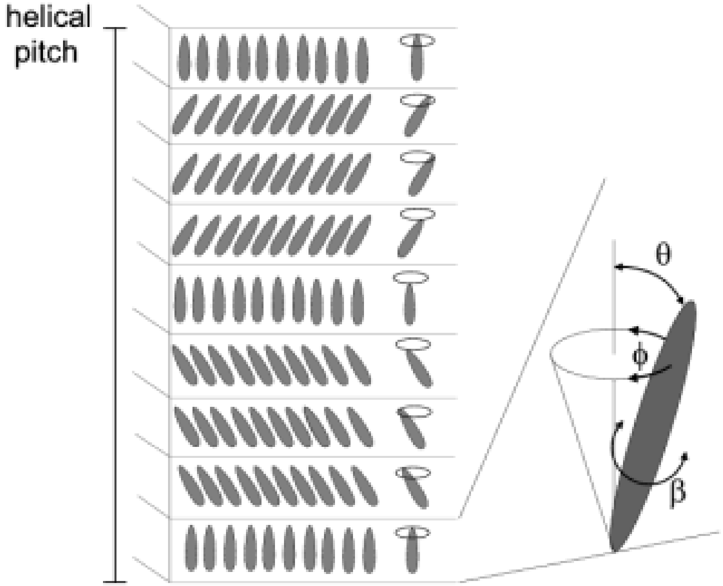


- the Goldstone-mode - fluctuations of the phase Φ (phason)
- the soft mode motions of the amplitude of the helical superstructure (amplitudon)
- β-relaxation - librations of the mesogen around its long molecular axis

The Goldstone-mode

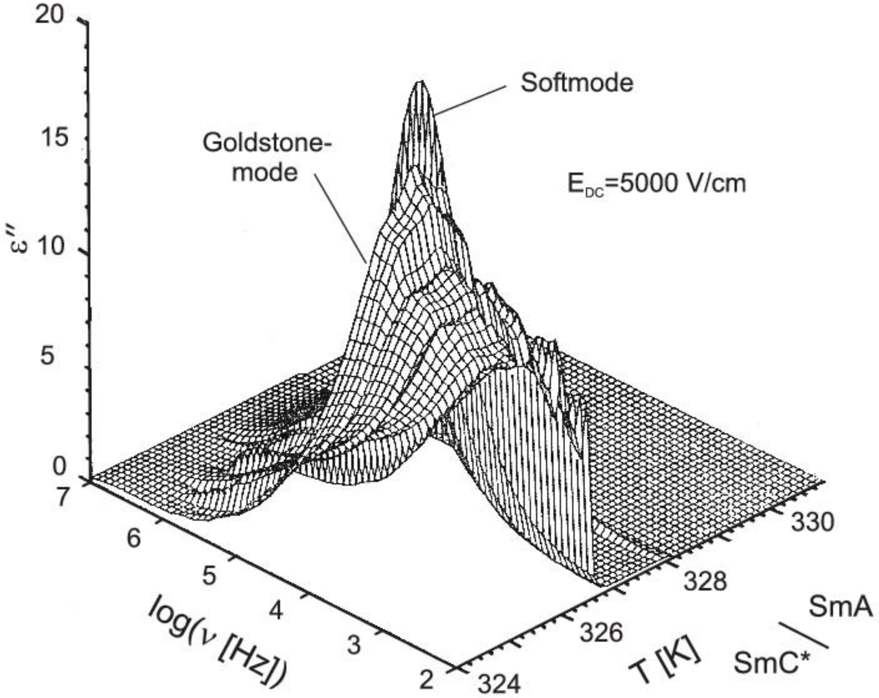


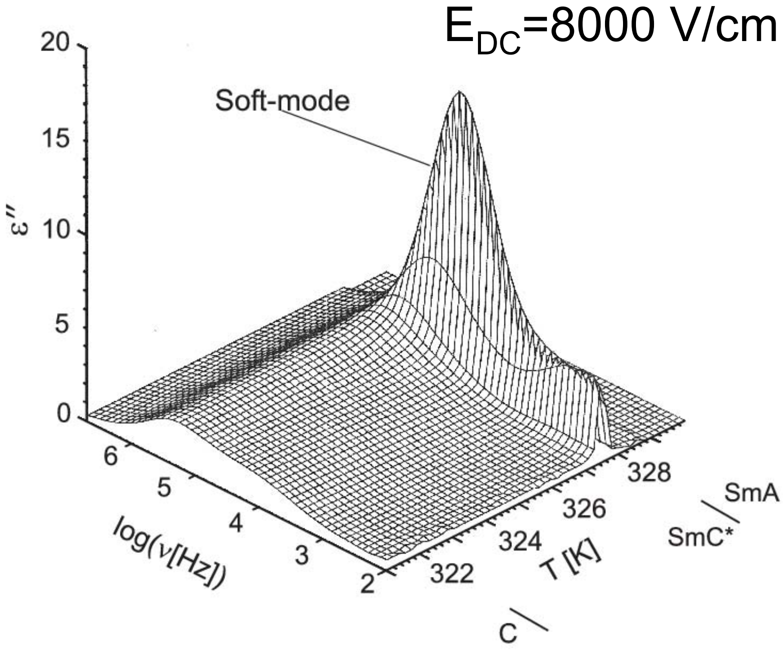
E_{DC}= 0 V/cm



- **The Goldstonemode exists only in the ferroelectric phase**
- **It has a negligible temperature dependence**

Collective processes in FLCs (effect of a d.c.-bias field)

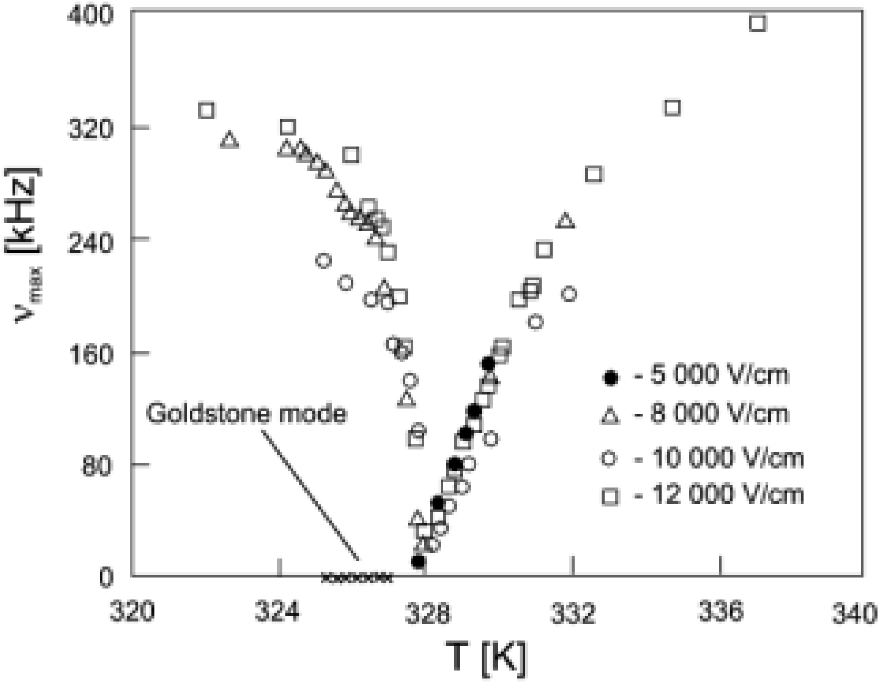


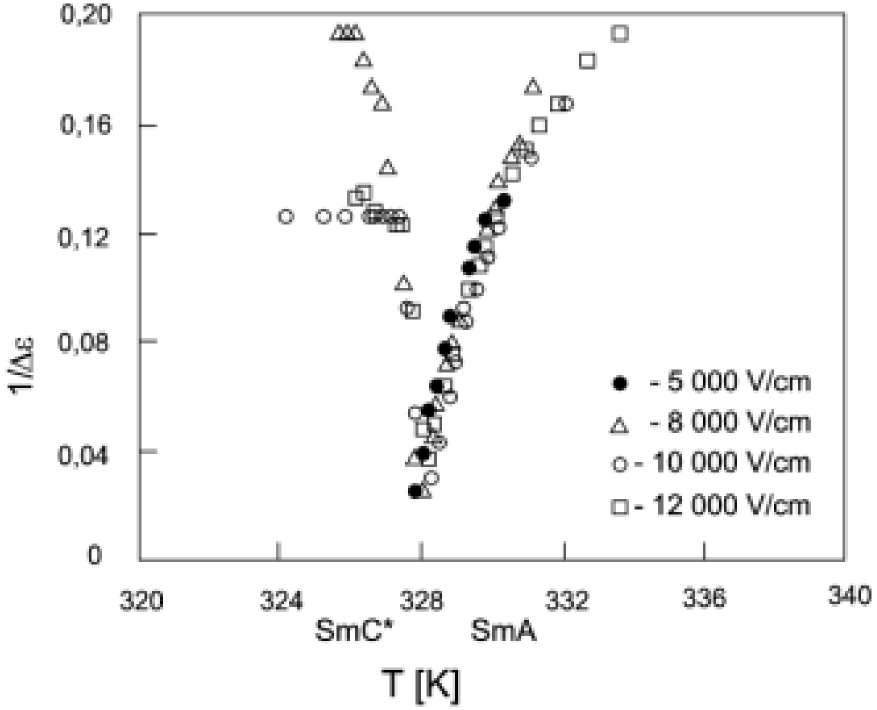


E_{DC}=8000 V/cm

- **the soft mode shows a negligible dc-bias field dependence**

Soft mode : relaxation rate and the inverse of the dielectric strength





Landau Theory

Gibbs free energy per unit volume

$$G(T,S) = G_0 + \frac{1}{2}A(T)S^2 + \frac{1}{3}BS^3 + \frac{1}{4}CS^4$$

Follows the nature of mean field theories!

Main assumptions:

$$A(T) = A_0(T - T^*) \qquad G(T,S) \neq G(T,-S)$$

$$B \neq 0 \qquad A_0 > 0$$

$$C \neq 0$$

Values of the order parameter *S* for given phases?

$$\left(\frac{\partial G}{\partial S}\right)_T = 0$$

Search for local minima...

⇒

$$S = 0$$

In the isotropic phase (constant)

$$S = \frac{-B \pm \sqrt{B^2 - 4AC}}{2C}$$

In the nematic phase, *S* depends on *T*

Find the critical temperature T_c, where $G_{\text{nematic}} = G_{\text{isotropic}}$

$$G - G_0 = S^2 \left[\frac{1}{2} A(T) + \frac{1}{3} BS + \frac{1}{4} CS^2 \right] = 0$$

➡

$$S = \frac{-2B \pm \sqrt{4B^2 - 18AC}}{3C}$$

$$S = \frac{-2B}{3C}$$

(Discontinuous phase transition)

Hence at T_c there are two alternatives:

$$S = 0 \qquad\qquad S = \frac{-B \pm \sqrt{B^2 - 4AC}}{2C}$$

Isotropic phase | **Nematic phase**

Notice the discontinuity at T_c, meaning that here we have a first-order phase transition.

We want a positive solution $S \geq 0$, thus $-\frac{2B}{3C} \geq 0$

On the other hand $C > 0$, because the free energy must have a minimum for a finite *S*

⇒ $$B < 0$$

Next, what is T_c? Find *A*:

$$G - G_0 = \left[-\frac{2B}{3C}\right]^2 \left[\frac{1}{2}A(T) + \frac{1}{3}B\left(-\frac{2B}{3C}\right) + \frac{1}{4}C\left(-\frac{2B}{3C}\right)^2\right] = 0$$

⇒ $$A = \frac{2}{9}\frac{B^2}{C}$$

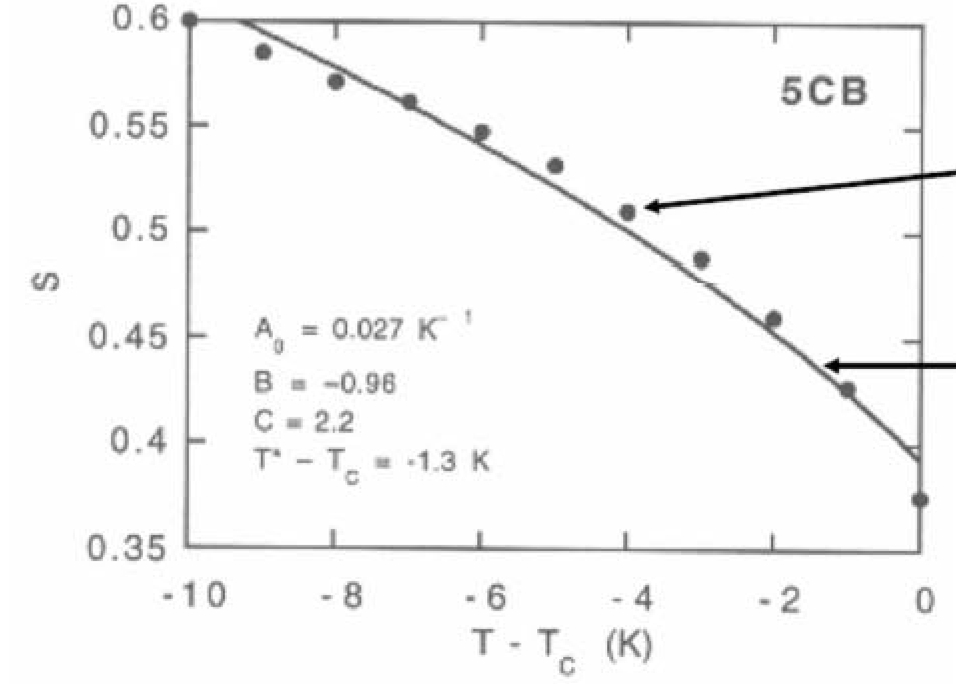
$$A_0(T - T^*)|_{T_c} = A_0(T_c - T^*) = \frac{2}{9}\frac{B^2}{C}$$

$$\boxed{T_c = T^* + \frac{2}{9}\frac{B^2}{A_0 C} > T^*}$$

Finally, we can look how the order parameter profile $S(T)$ looks like

At the critical point $A(T_c) = \frac{2B^2}{9C}$

$$\begin{tikzcd}
 & -\frac{B}{3C} & \\
\Rightarrow \quad S = \frac{-B \pm \sqrt{B^2 - 4A(T)C}}{2C} \arrow[ur] \arrow[rr] & & \boxed{-\frac{2B}{3C}} \arrow[dl] \\
\text{As a general solution we get} & S = \frac{-B - \sqrt{B^2 - 4CA_0(T - T^*)}}{2C} &
\end{tikzcd}$$



Experiments (points)

Theory (full line)

As a final remark, the enthalpy change (latent heat) associated with the transition at the critical temperature

$$\begin{aligned}
\Delta H &= -T_c \Delta \Sigma \\
&= -T_c (\Sigma_{\text{nematic}} - \Sigma_{\text{isotropic}}) \\
&= T_c \left(\frac{\partial [G(S,T) - G_0]}{\partial T} \right)_{\mathrm{S=S_c}} \\
&= \frac{2A_0 B^2 T_c}{9C^2} > 0
\end{aligned}$$

The positive non-zero value implies that this is indeed a first-order phase transition.

Summary concerning ferroelectricity in LC

1. The ferroelctricity in LC is a local property of one smectic layer. It is founded due to symmetry considerations applied for chiral molecules

2. In order to minimize the free energy the directors of the single smectic layers form a helical superstructure

3. The fluctuation of the phase of the helical superstructure has the character of a „Goldstone“ mode; the fluctuation of the amplitude of the superstructure has the character of a „soft mode“

4. The helical superstructure can be „unwound“ by an external electric field and by that the local ferroelectricity becomes macroscopically observable

Final Summary for LC

1. LC form a special class of materials between the solid and the liquid state

2. LC show a manifold of mesophases which is determined by ist chemical structure

3. LC gained tremendous technological impact within the last 2 decades

4. LC con be incorporated into polymeric and elastomeric systems; by that novel materials are designed, e.g. artificial muscels or soft organic lasers