

**alfredo.strigazzi@polito.it**

# **INTRODUCTORY TO LIQUID CRYSTALS PHYSICS**

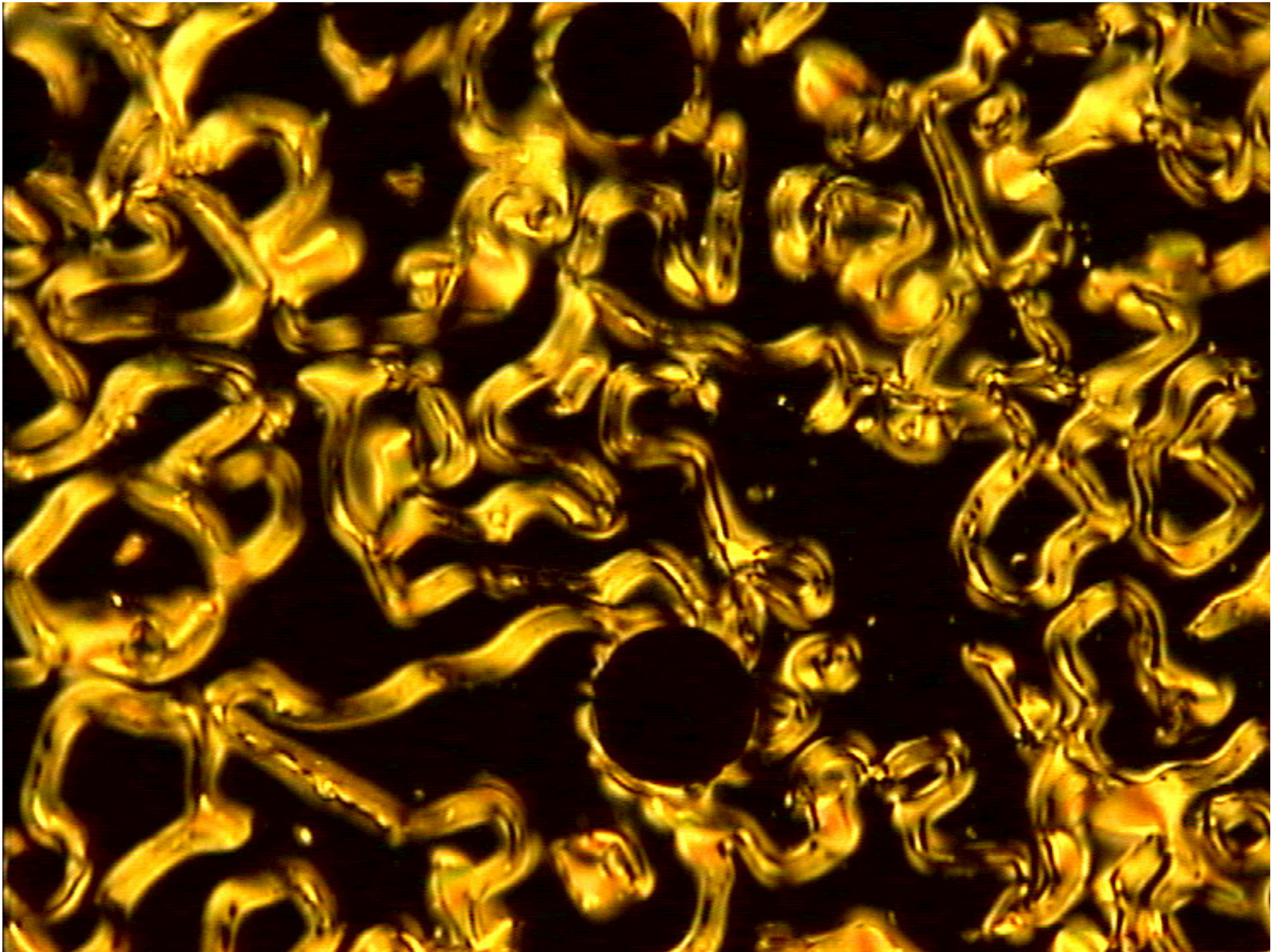
## **1. NOMENCLATURE AND PHENOMENOLOGY OF LIQUID CRYSTAL MESOPHASES**

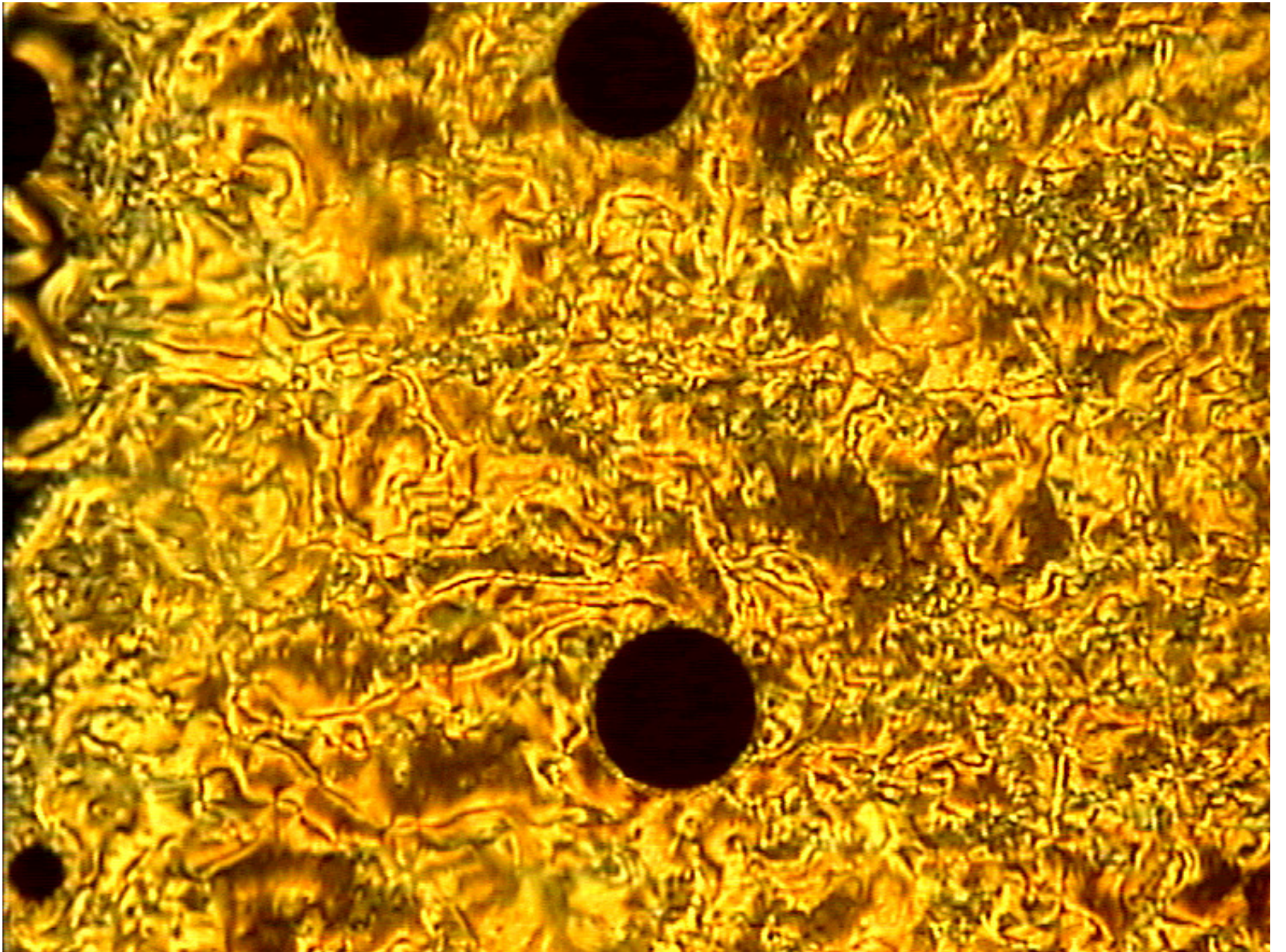
**Alfredo Strigazzi, Senior Professor, Dept of Applied Science  
and Technology (DISAT), Politecnico di Torino, Torino, Italy**

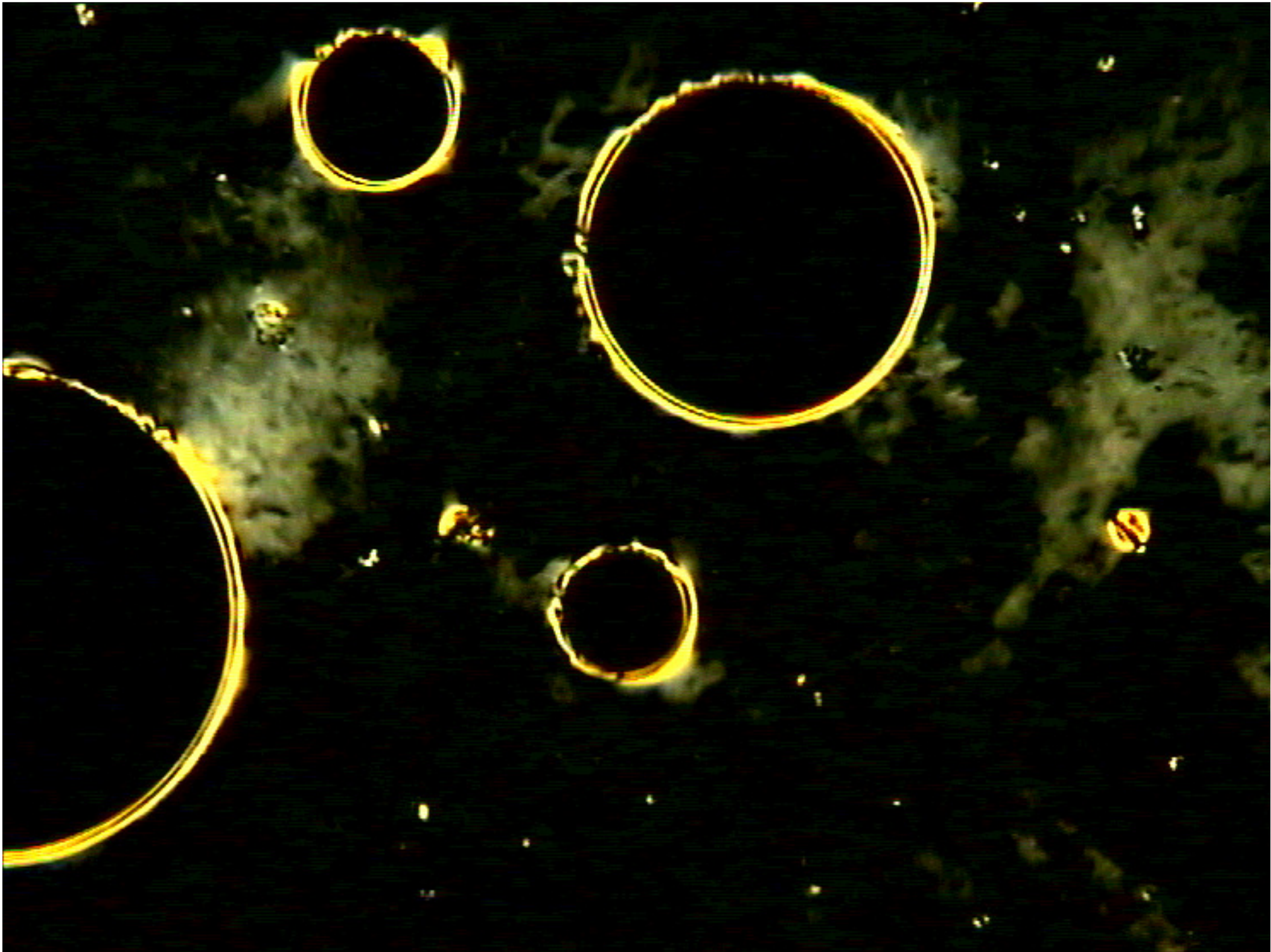
**MEPhI, Moscow, 10 September 2014**

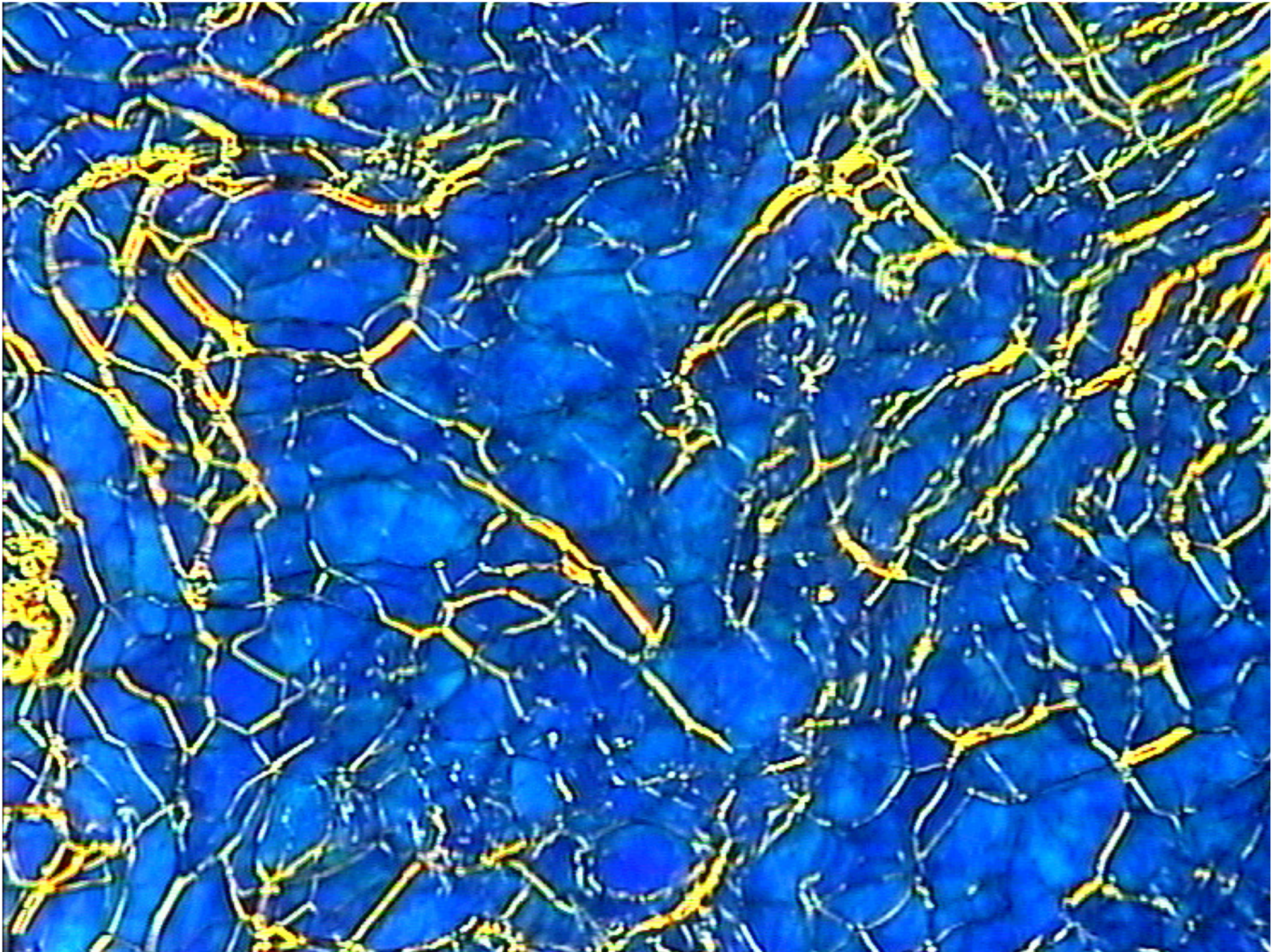
:

## 1.1. Overview









The previous pictures are textures of liquid crystals observed through polarizing microscope, with crossed polarizers.

**Thus they are liquid but birefringent !**

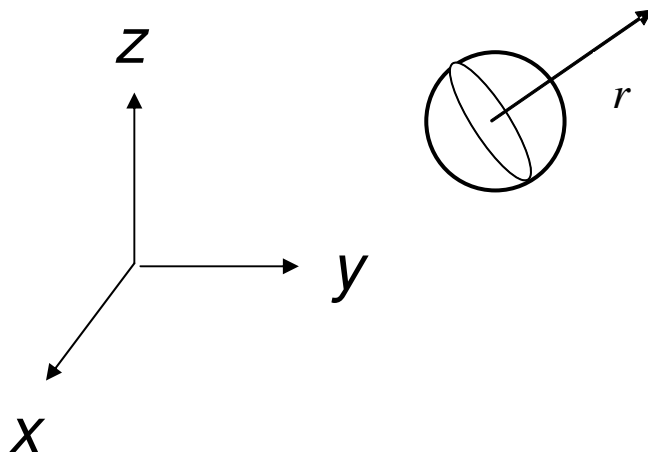
# 1.1.1. Liquid Crystalline State and Birefringence

Inorganic ions and short organic molecules in the most cases are characterized by spherical symmetry: they are **isotropic**.

.

Then, in **crystalline state** every ion (or molecule) has 3 degrees of freedom for the center of mass vibration around its equilibrium point (*positional symmetry*).

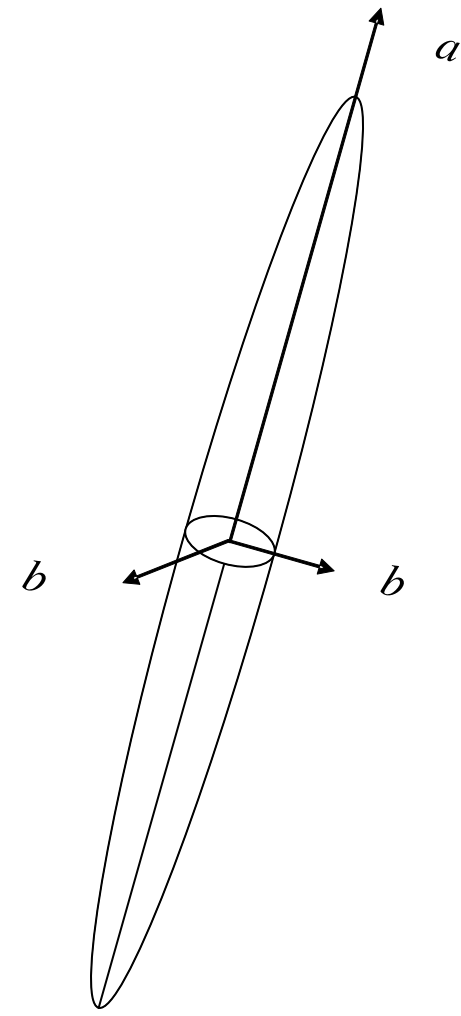
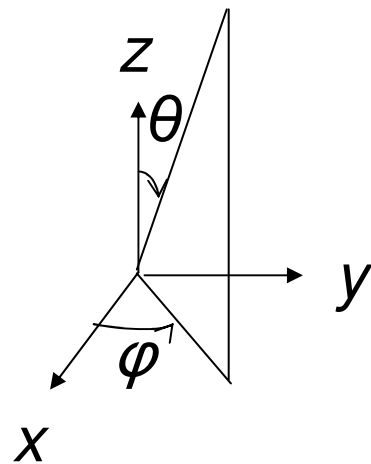
.





If the molecules are elongated, f.i. rotational ellipsoids, they are **anisotropic**.

There are also other 2 degrees of freedom for the angular vibration of the long axis around the equilibrium direction (*orientational symmetry*)



In **liquid state** molecules interact, involving a weaker potential energy, allowing them to have a relative motion, just comprising viscosity:

*all symmetry disappear* overcoming the **melting point**.

Heating at constant pressure, a liquid reach the boiling point, where the interaction field between mlc become very weak, unable to keep the thermal motion of each mlc: it is the **steam (gas) state**.

**Crystal, Liquid and Gas(Steam)** are the 3 main natural phases of matter

and **Liquid Crystals** ?

Are not these words a strange oxymoron?

The words “*liquidi cristalli*” were introduced 1st time in 14° century by the italian poet Francesco Petrarca

*but just in another sense*

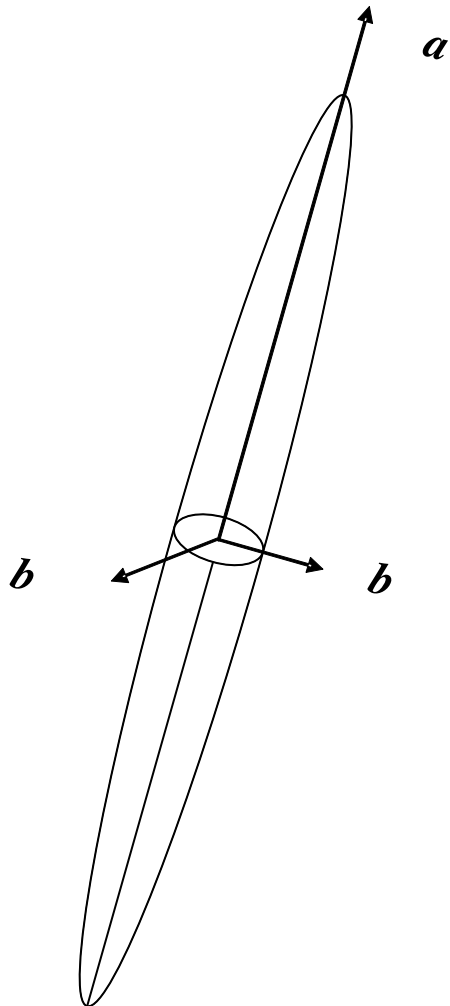
meaning the very pure water jumping from a spring in a small lake.

Later in 16° century the italian literate and polemist Pietro Aretino used these words, but in another context

Only **at the end of 19° century** the debate in science arised: can be something simultaneously *crystal* and *liquid*?!

Around 1910 – 1920 it was proved that yes, the Nature can do

## ***Liquid crystals is the 4th state of matter***



Liquid crystalline state is **intermediate** between Crystal phase and Liquid phase, it is ***a mesophase***: *some symmetries are kept*, in certain temperature ranges.

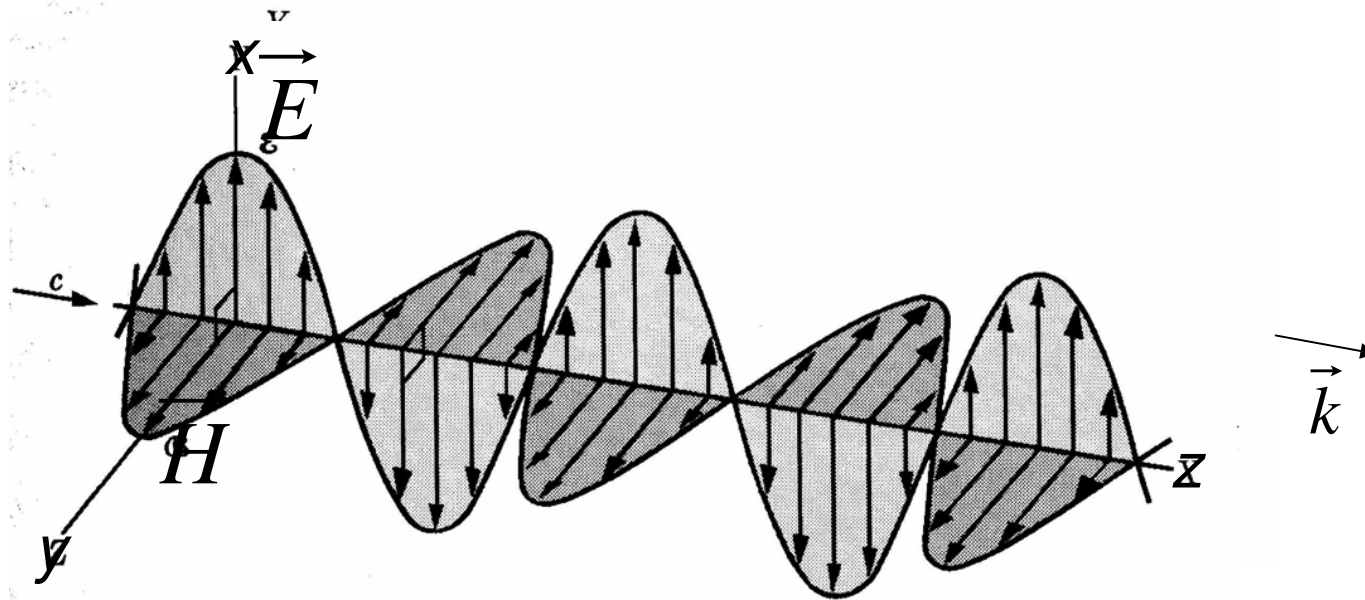
This happens mainly for organic compounds, *if the molecules are long enough* (there is a threshold in the mlc elongation ratio  $a/b$ )

Let us discuss now why it is possible to observe with polarizing microscope the beautiful textures shown before,

speaking about light beam, light polarization, **birefringence** and anisotropy

**Light beam:** transverse electromagnetic wave, traveling in vacuum with fixed speed  $c = 2.998 \cdot 10^8$  m/s

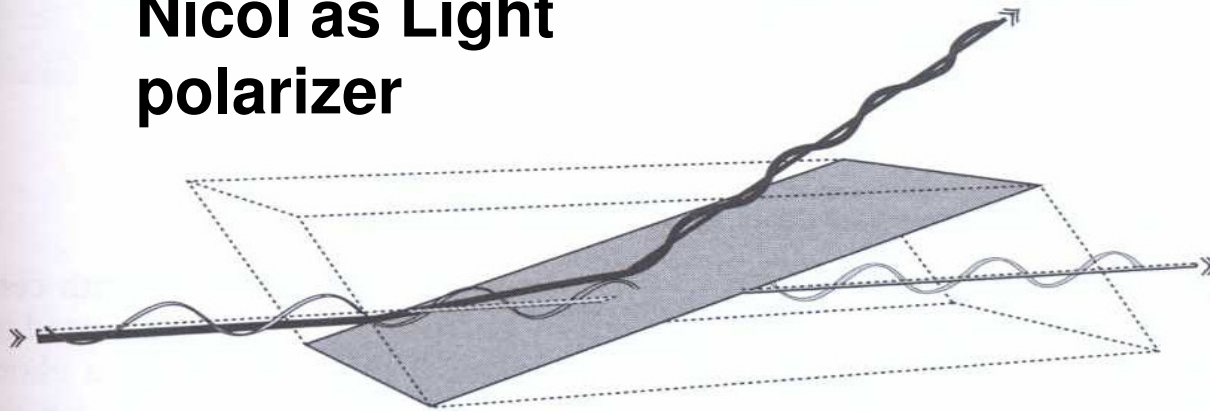
$$\vec{E}_{light} \perp \vec{H}_{light} \perp z - axis$$



Here is represented, traveling in vacuum, a linear polarized beam (the polarization plane  $\vec{k} \times \vec{E}$  does not rotate).

**Birefringence:** double refraction to some crystals i.e. Iceland spar: 2 refracted rays linearly polarized  $\perp$  to each other.

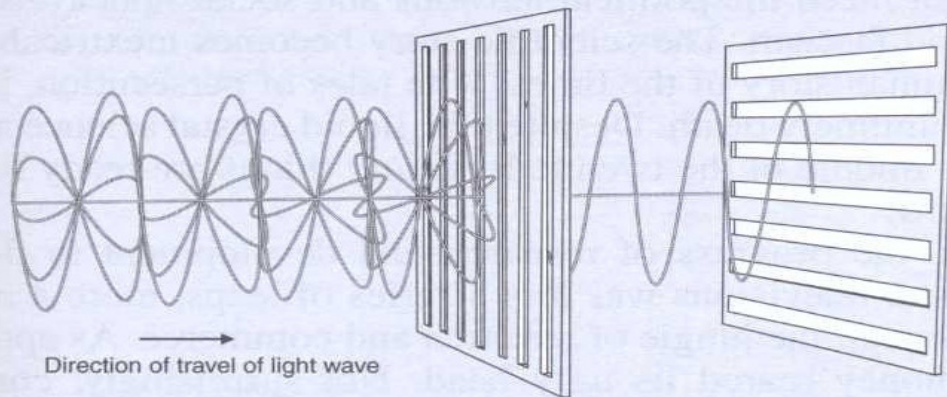
### Nicol as Light polarizer



Ordinary ray follows Snell law, and is pushed away via total reflection; the extraordinary ray emerges vertically polarized

Figure 1.3 The Nicol prism, showing transmission of the extraordinary ray at diversion of the ordinary ray.

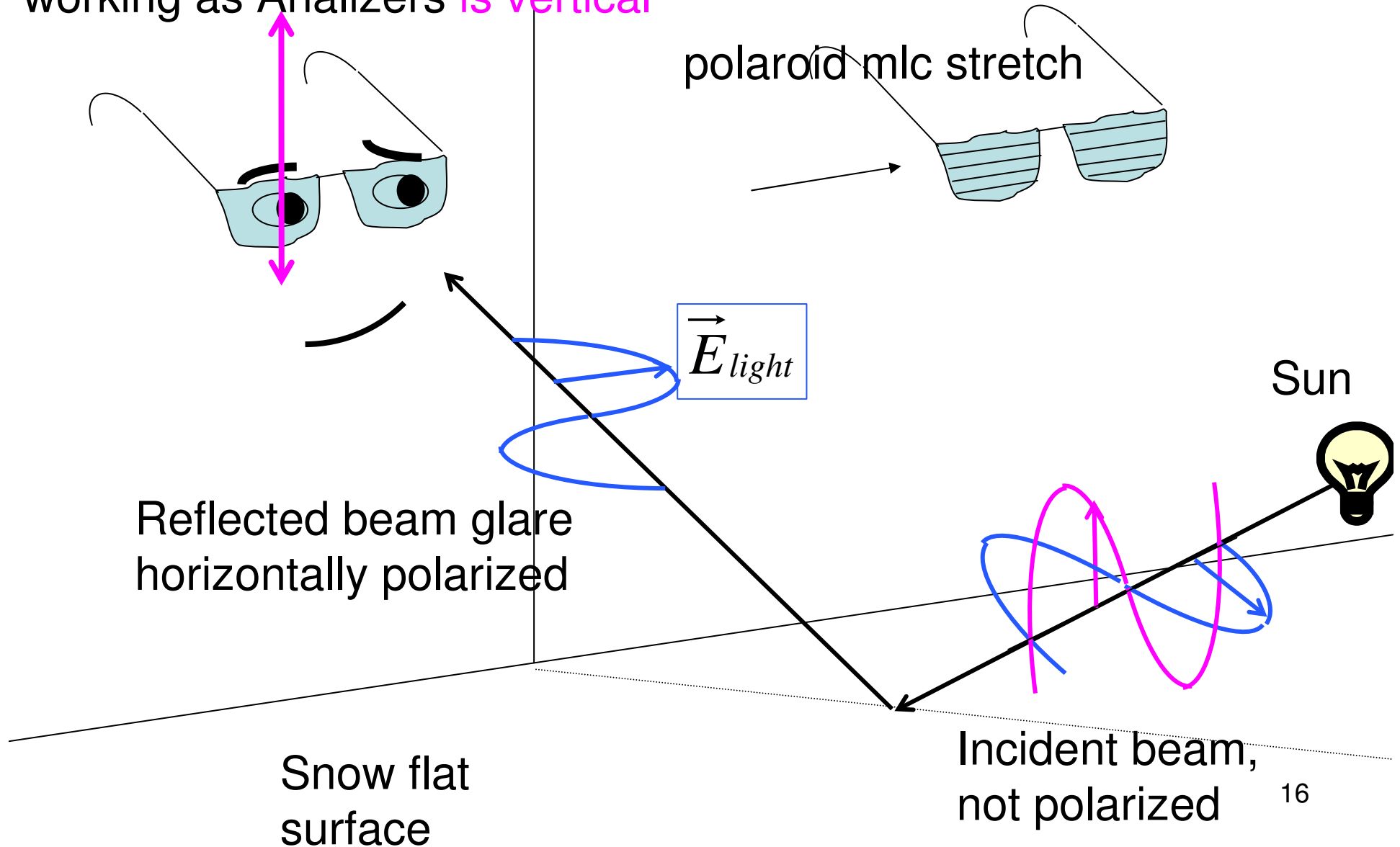
### TECHNICAL BOX 1.4 Polarized light and polarizers



If between crossed polarizers there is nothing, the light beam is not transmitted

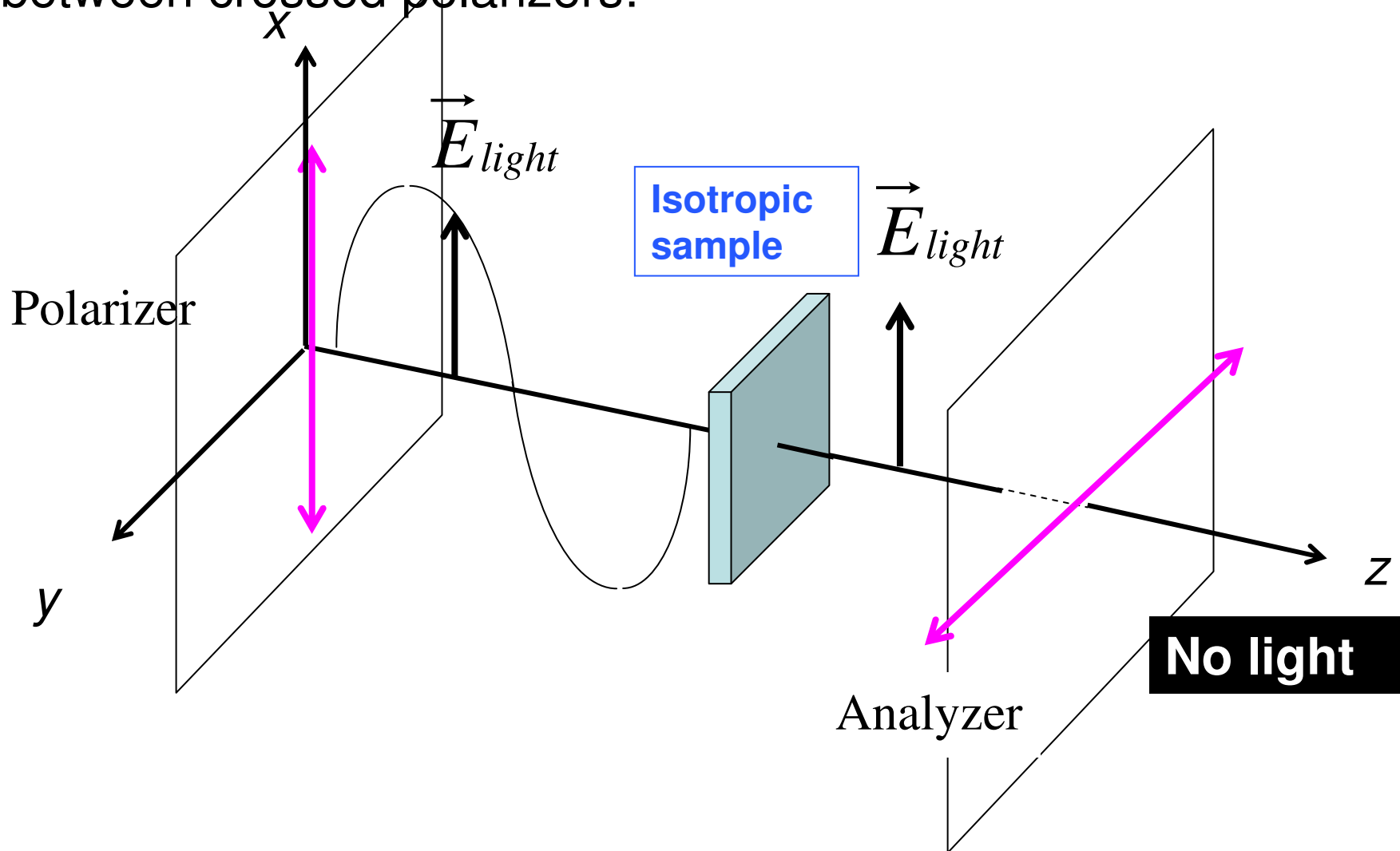
Also polaroids works as Nicols do;

Allowed polarization direction of polaroid spectacles, working as Analyzers is vertical



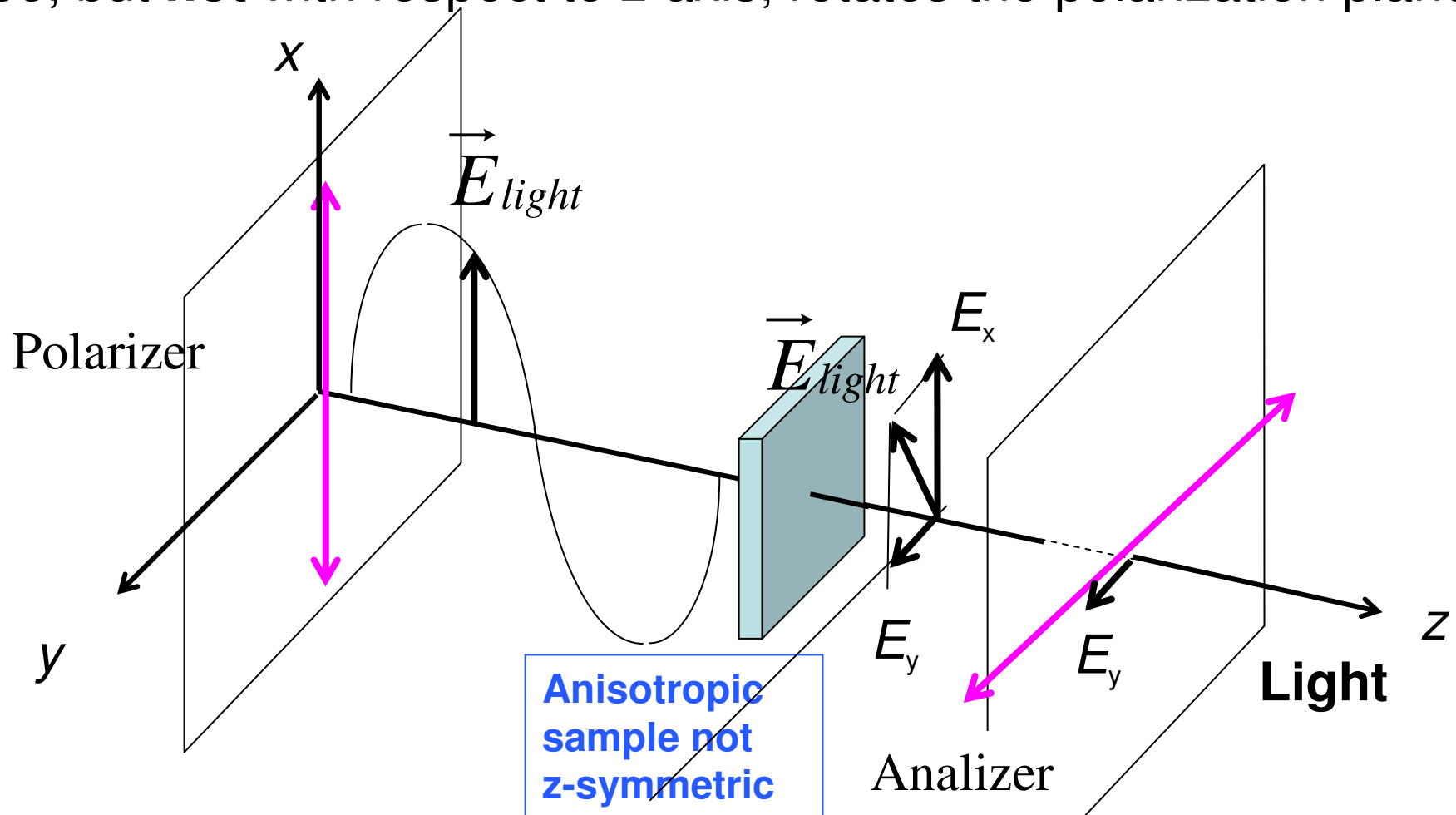


There is also no transmission of light with **isotropic sample** between crossed polarizers:

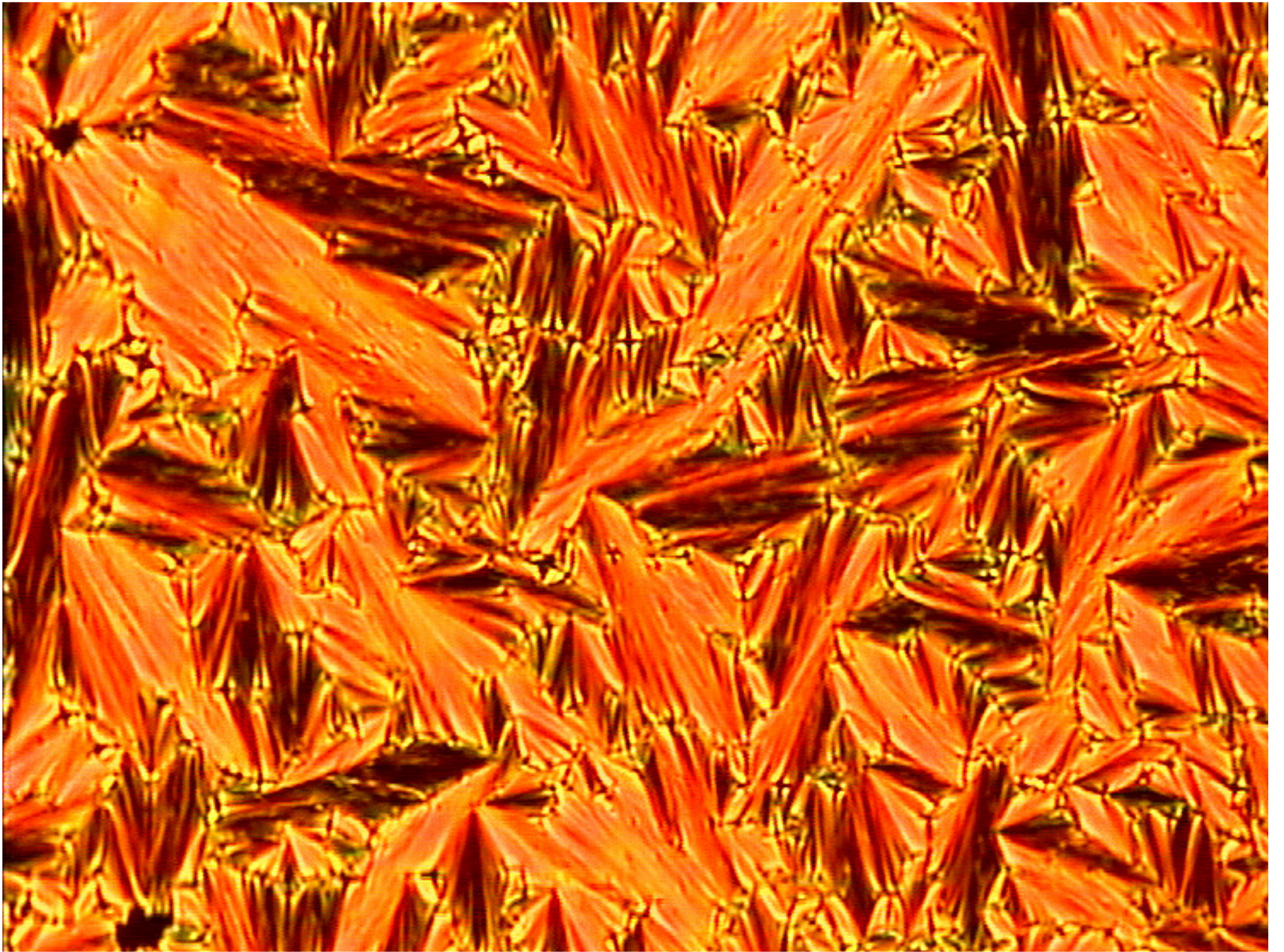


and with **anisotropic sample** as well, but **only** if there is **cylindrical symmetry** with respect to  $z$ -axis

Instead, an **anisotropic sample** *even with cylindrical symmetry too*, but **not** with respect to z-axis, rotates the polarization plane



allowing light to be transmitted as in the “artistic” figures through polarizing microscope, shown in the beginning of the lecture, and now on.



## 1.1.2. Historical sketch

### 1.1.2.1. Prehistory of Liquid Crystals (LC)

Liquid Crystals (LC) were discovered in the second half of 19th Century.

Between 1850 and 1888, researchers in different fields such as chemistry, biology, medicine and physics found that several materials behaved strangely at temperatures near their **melting points**.

It was observed that the optical properties of these materials changed discontinuously with increasing temperatures.

**W. Heintz** 1st reported in 1850 *that **stearin** melted from a solid to a cloudy liquid at 52 °C, changed at 58 °C to an opaque one and at 62.5 °C to a clear liquid.*



**Figure 2.1** Friedrich Richard Kornelius Reinitzer (1857–1927).

In 1888, an Austrian botanist named **Friedrich Reinitzer**, interested in the biological function of cholesterol in plants, was looking at the melting behaviour of cholesteryl benzoate. *He studied carrot juice!*

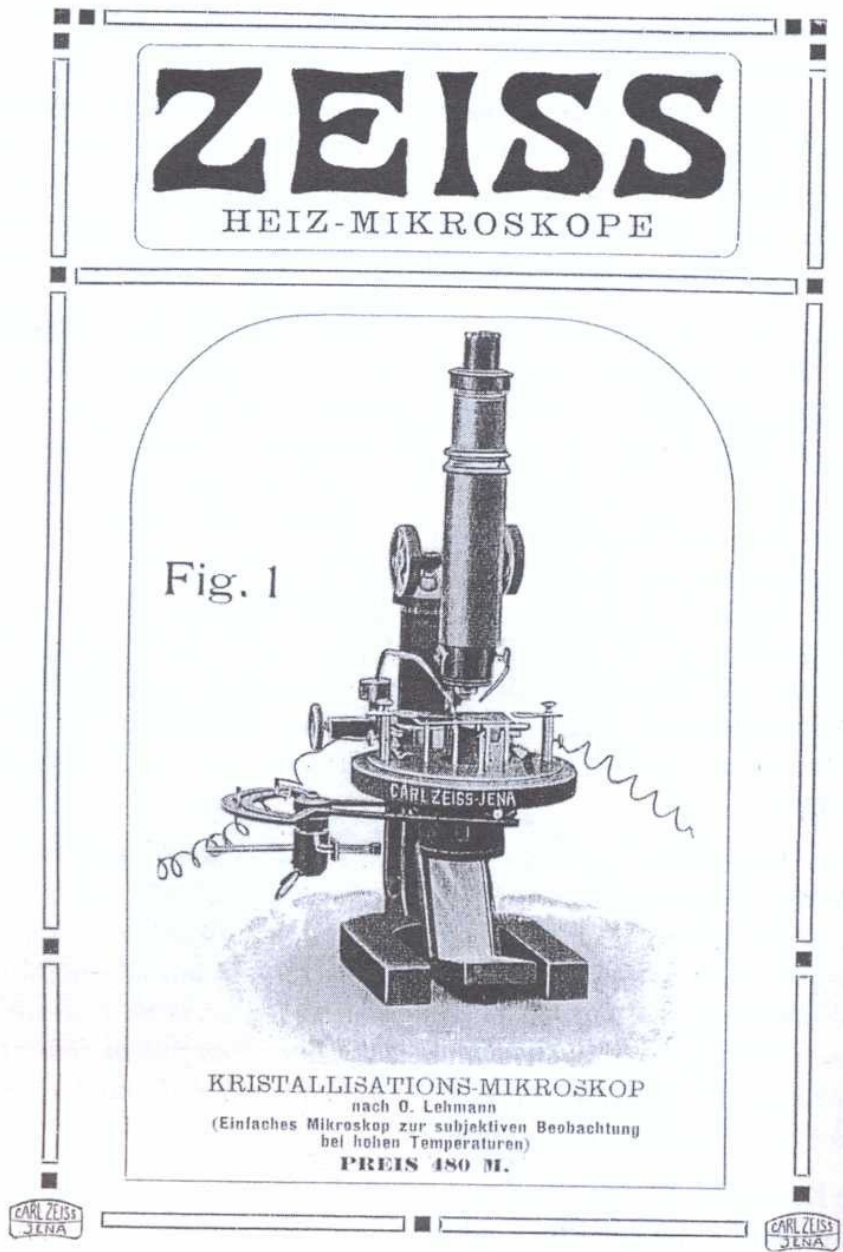
He observed, as W. Heintz did with stearin 38 years before, that the substance *melted to a cloudy liquid at 145.5 °C and became a clear liquid at 178.5 °C.*

But the problem was: **these materials, are they simply emulsions, or they really provide a new phase?**

**Figure 2.3** Otto Lehmann  
(1855–1922).



An important invention of the time was the heating stage microscope by **Otto Lehmann**, a physicist from Karlsruhe, Germany.



**Figure 3.5** Advertisement from the well-known Zeiss company in Jena, Germany, for a hot-stage crystallization microscope designed by Otto Lehmann, dating from about 1906.

Such a microscope was fundamental for studying the arising of the mesophase, on heating and cooling

Alessandro Amerio (1876-1965) wrote in 1902 a report (*in italian*) on Lehmann samples, showing that the transition LC-Liquid (clearing point) involves a *latent heat*, and then it is a *real transition*.



**Discussion, some times hard and not friendly, among Lehmann and other main scientists (f.i. Friedel, from Strasbourg) led finally to the identification of the *liquid crystal phase* as a real new phase of matter.**

It appears soon that there is more than 1 mesophase. Since the parameter governing the new mesophases is the temperature, the LC were called ***Thermotropic***.

Figure 4.1 Georges Friedel (1865–1933).



In 1922 in Paris, France, ***Georges Friedel*** suggested the classification scheme which is used today with the different phases of liquid crystals

**NEMATIC** is the state with texture characterized by defects with shape of threads (Greek: νημα);

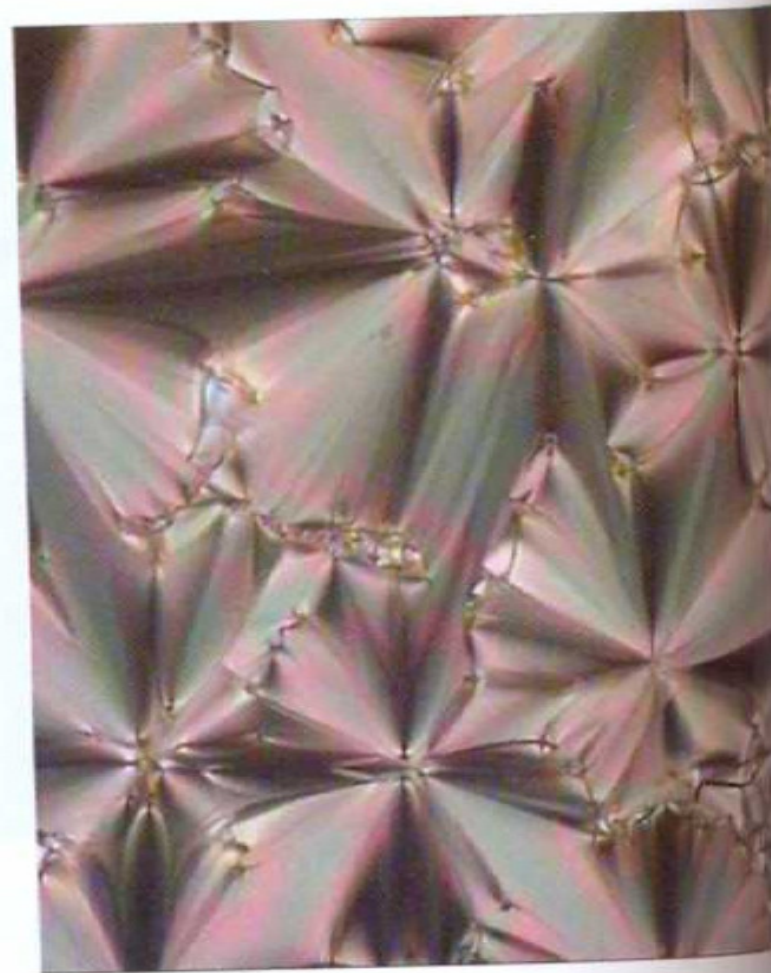
**CHOLESTERIC** the optical active state reached by some of samples, f.i. benzoate of cholesterol;

**SMECTIC** the most viscous mesophase, LC state similar to soap (Greek: σμηγμα).

## Nematic texture



## Smectic texture



**Plate 4** The schlieren texture. This is an optical pattern seen in a polarizing microscope, characteristic of Lehmann's liquid crystals. (See Figure 2.4, p.25)

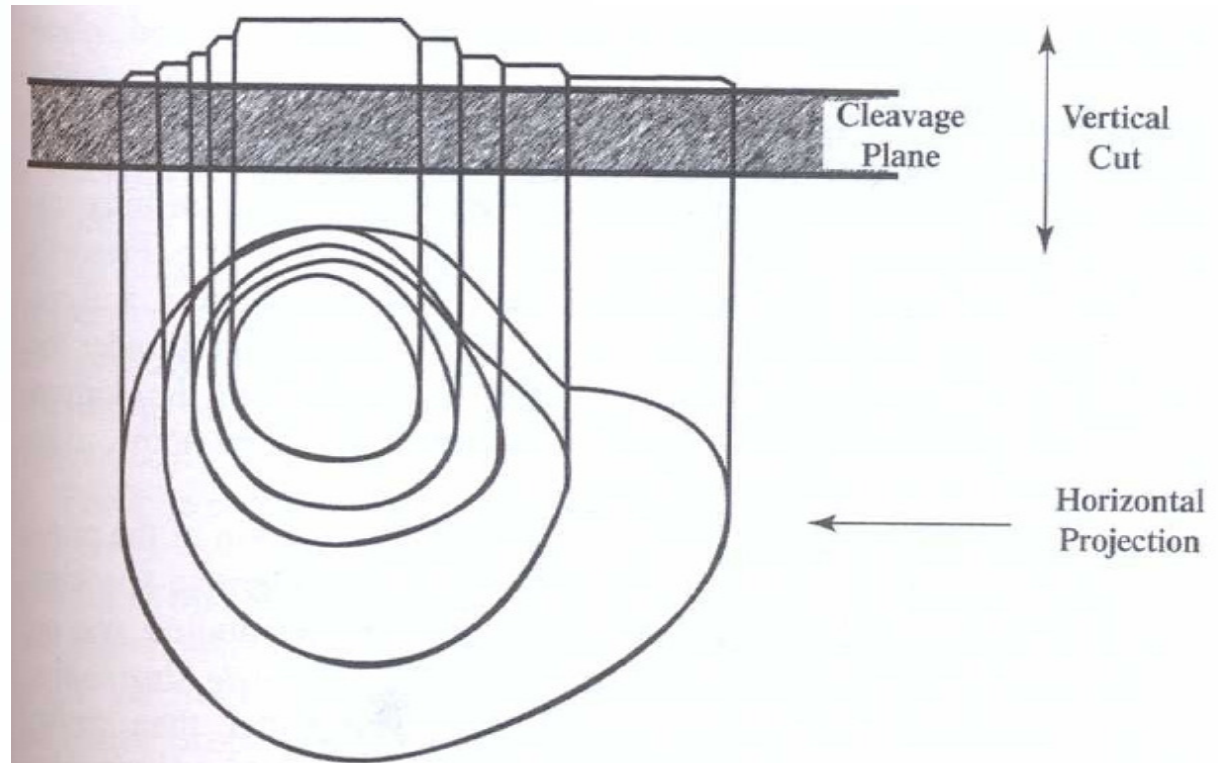
**Plate 5** The fan texture of a smectic liquid crystal © I. Dierking. (See Figure 4.4, p.83)



**Figure 4.2** François Grandjean (1882–1975).

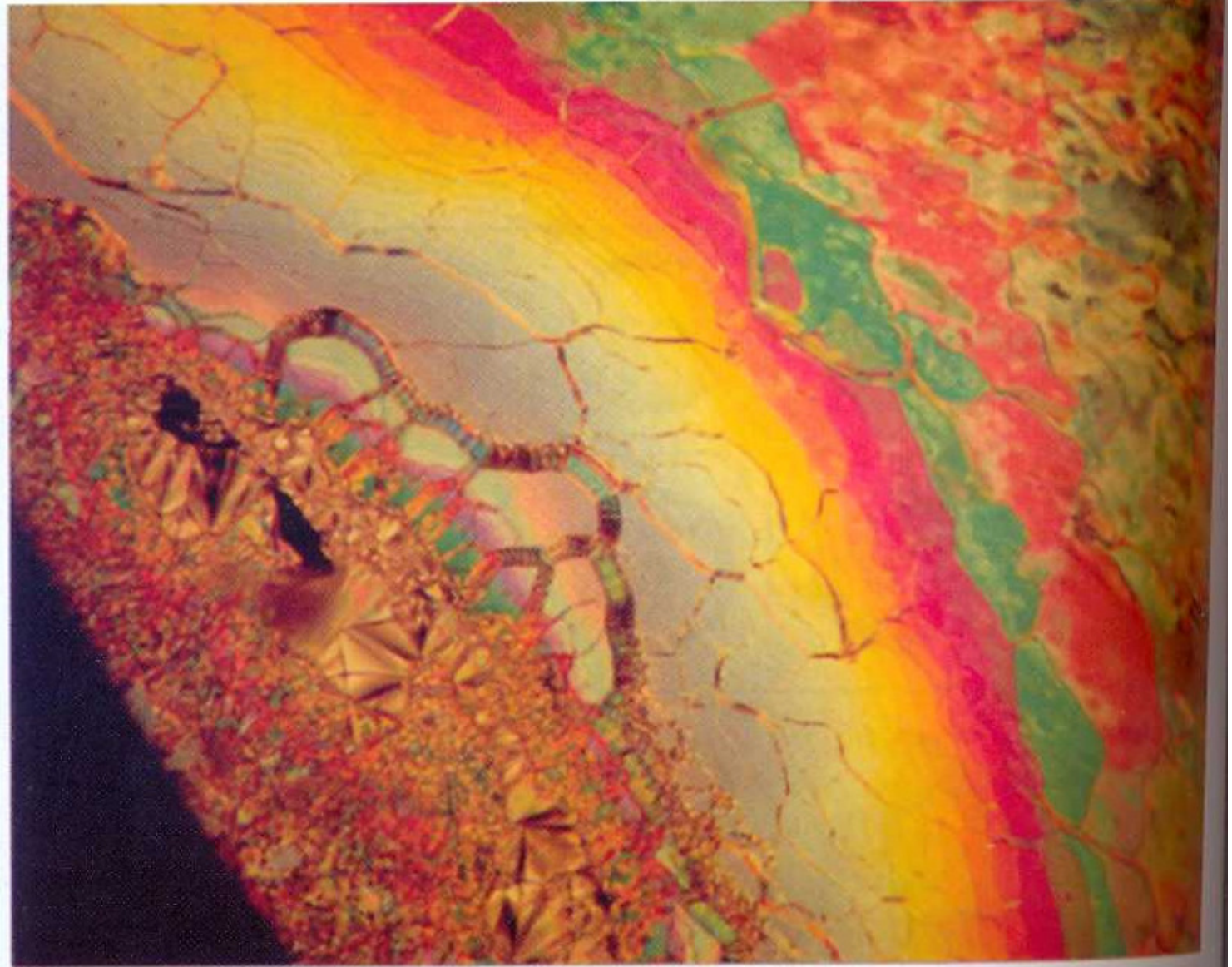
Experimentalist & theoretician, discovered in LC textures with steps and made a pioneer work in mean field theory

After 1921 became an important biologist



**Figure 4.3** Grandjean terraces. Diagram redrawn from Grandjean's 1916 paper with the French legend replaced by English.

Cholesteric  
texture



**Plate 6** A microscope image of a cholesteric phase. A variety of characteristic optical textures is shown, including fans (left), Grandjean planes (centre) and schlieren (right).  
© D. Dunmur. (See Figure 4.5, p.84)

In 20-ies and 30-ies: theoretical work on elastic continuum theory of distortions by **Oseen, Zocher, Frederiks, Frank**



**Figure 7.1** Hans Zocher (1893–1969).  
Image from citation in *Proceedings of the  
3rd International Liquid Crystal  
Conference, Berlin 1970.*

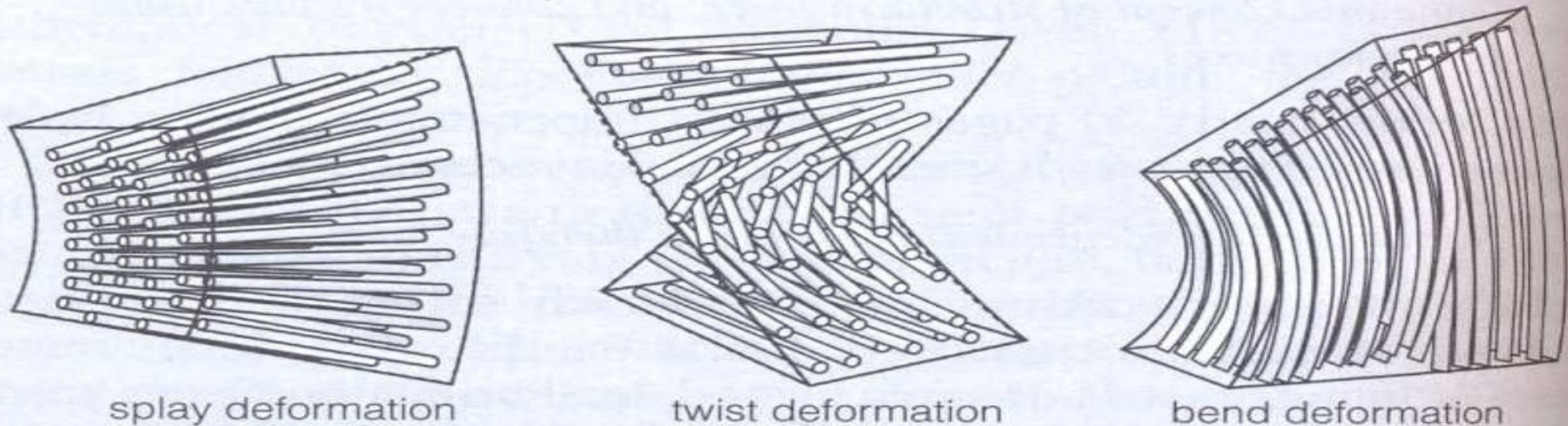
Oseen from Uppsala Univ  
made the pioneering work

Zocher established the fundamentals  
of elastic continuum theory for LC,  
working in Univ of Prag

Frederiks in Leningrad (and in  
Stalin camps) investigated the  
interaction NLC-applied electric  
and magnetic field

Frank in Cambridge, 1958, made  
a reworking of the papers by  
Oseen and Zocher

The great triumph of the theory of Oseen was to formulate this, if not in an easily understandable fashion, at least in a way that made some predictions. The great conclusion of his work was that four parameters were required to define the elasticity of a liquid crystal. Actually we now know that for most purposes three elastic constants are enough, and these determine the ease with which a liquid crystal, or more properly the director of a liquid crystal, can be distorted. These are known as elastic constants for splay, twist, and bend, and a representation of these deformations is given below.



In an unaligned liquid crystal the director will wander around in the liquid crystal, and so there will be a combination of splay, twist and bend deformations. If the liquid crystal is aligned, then these deformations can be forced out and the director lines are everywhere parallel to each other.

Nematic liquid crystals can support splay, twist, and bend deformations, but if layers form, as in smectic phases, then only a splay deformation is possible. For tilted smectic phases (see later) the situation is more complicated since there are now two directors.



## 1.1.2.2. Renaissance after II World War

In 1958 **Glenn Brown**, an American chemist, published an article in *Chemical Reviews* on the liquid crystal phase

He founded the **Liquid Crystal Institute**, in Kent State Univ, Kent, Ohio, which became attractive centre for scientists working in LC field worldwide.



Figure 8.5 Glenn H Brown (1915–1995).

In the same year, 1958, **Alfred Saupe** (just PhD graduate) and **Wilhelm Maier** (responsible of his PhD) published the *mean field theory, describing the order in NLC phase*: subsequently it was the international resurgence in liquid crystal research.

Figure 8.4 Alfred Saupe (1925–2008).  
© Peter Palffy-Muhoray.

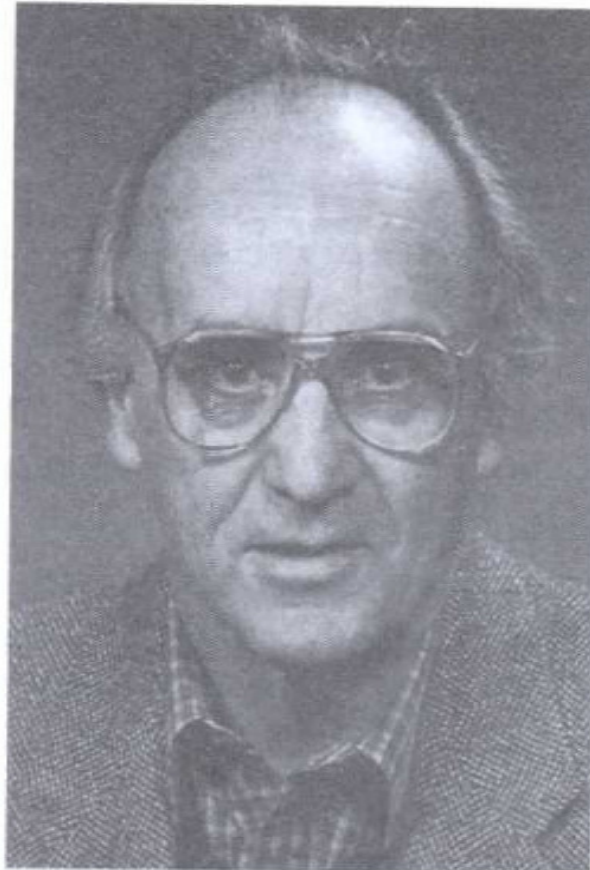
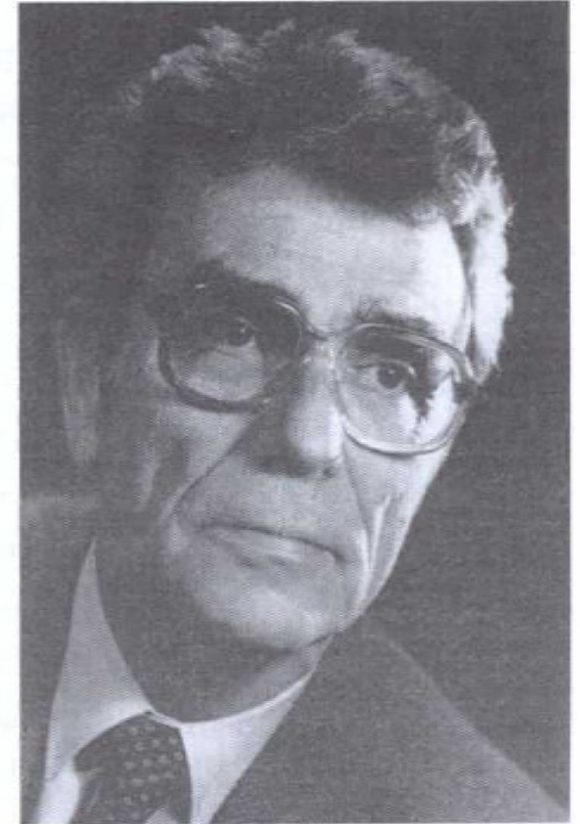
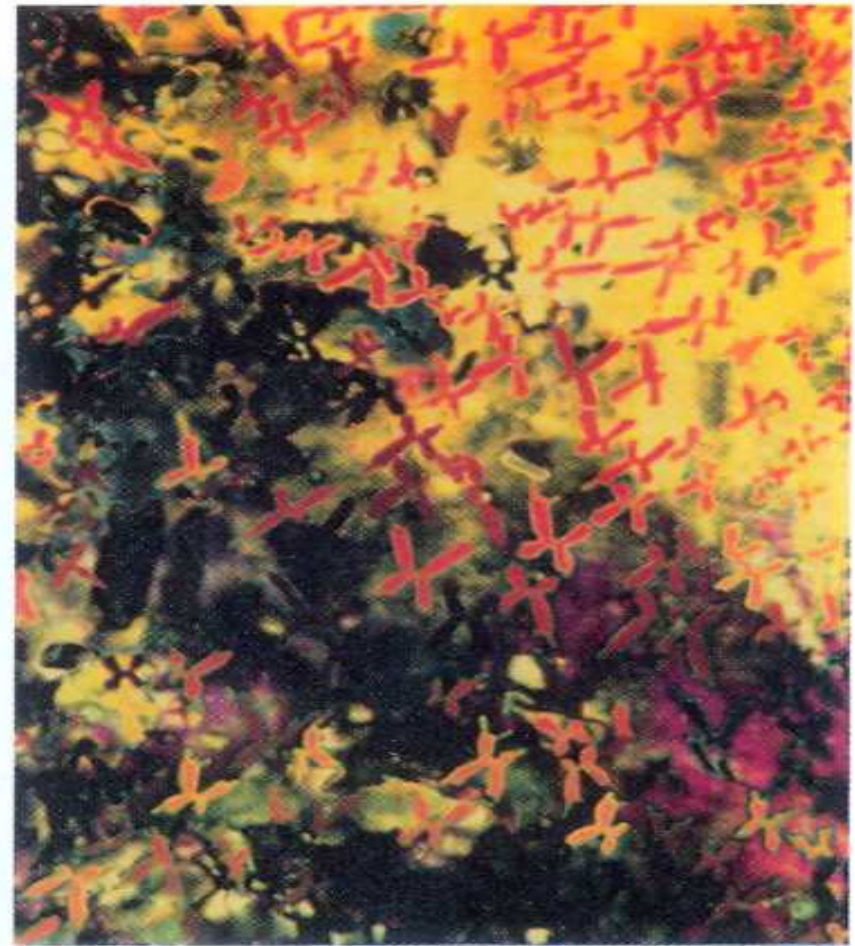
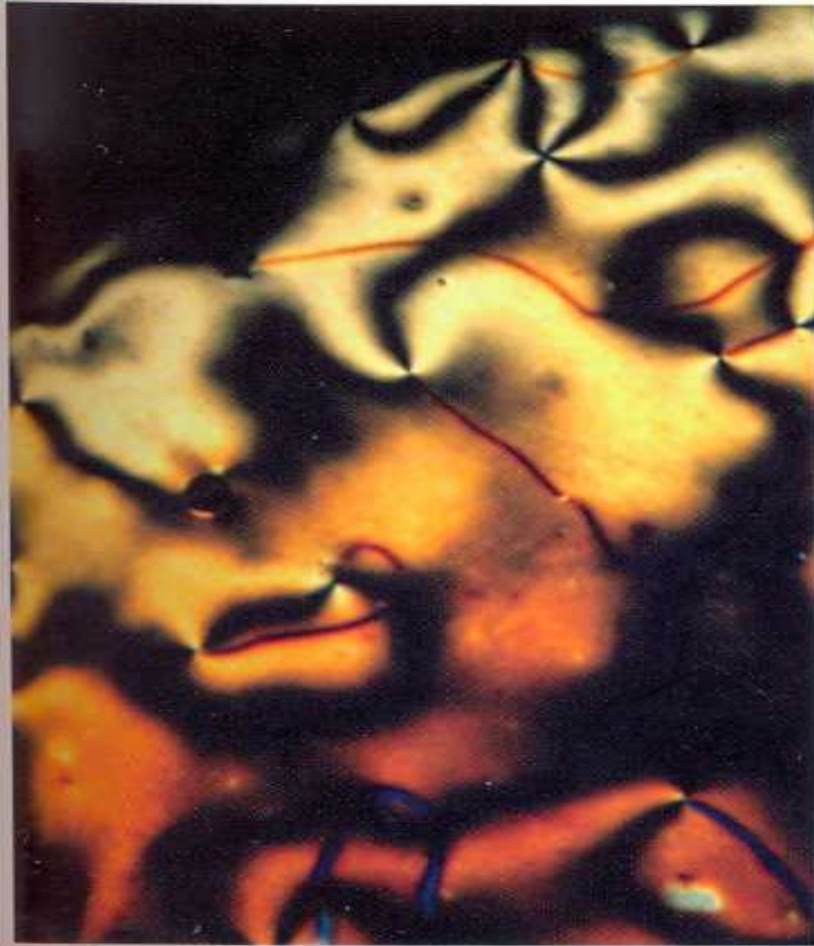


Figure 8.2 Horst Sackmann (1921–1993).

Chemist, after the II World War Director of LC Lab in Univ of Halle, important synthesizer of new material and experimental investigator, with the aim of classifying mesophases.





**Plate 8** Dark threads, appearing as coloured lines, marking fluid defects (known as disclination lines) in a nematic liquid crystal. The black areas emanating from points are known as brushes. They are areas of optical interference which connect through points on the surfaces marking the end of defect lines. © D. Dunmur. (See Technical Box 4.2, p.82)

**Plate 9** A characteristic optical texture of a smectic B phase forming from a nematic phase. The low temperature smectic B phase appears as butterfly shapes in the nematic fluid. There is no way of knowing if Sackmann observed this particular texture. (See Figure 8.3, p.171)

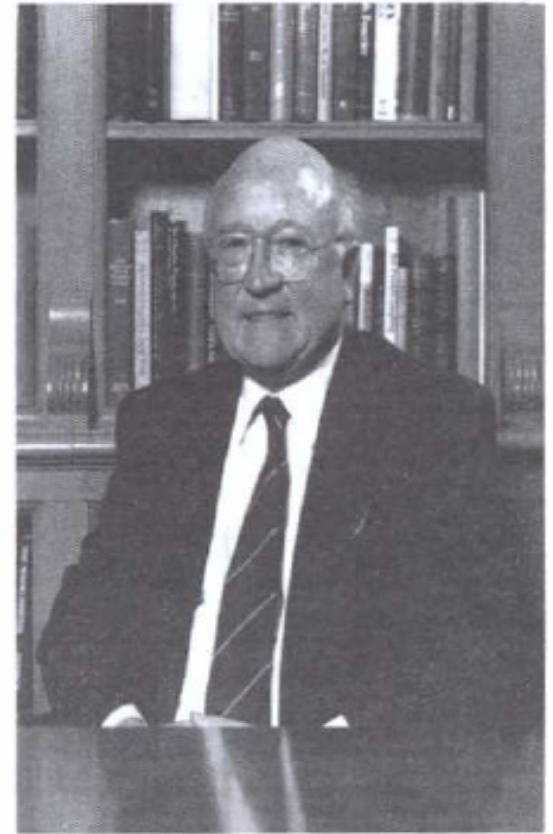
**Chemist, Director of NIOPIK, Moscow; as manager of NIOPIK and President of LC Society of former Soviet Union improved the national and international collaboration in LC as applied science**

Figure 10.8 Victor Titov (1935–1996).



He organized the synthesis of new LC important for application (f.i., to display)

Figure 8.8 Frank Leslie (1935–2000).



Theoretical physicist,  
from Glasgow, Scotland.

1st to establish a  
complete theory of  
**viscosity** in LC

## 1.1.3. Thermotropics and Lyotropics

It was soon recognized that there are two families of LC: **THERMOTROPICS** and **LYOTROPICS**

In ***THERMOTROPICS*** the only leading parameter determining the range of existence of the phase is the **temperature**;

in ***LYOTROPICS*** (greek: λυο, to dissolve), which are mixtures of 2 or 3 (or more) compounds, also the **relative concentration(s)** is (-are) leading parameter(s) together with the **temperature**.

Typical thermotropics are the **Nematic** LC (NLC) used for *watches, computer and TV monitors*, the Chiral **Smectic** LC (S\*LC) today very promising for new HD TV monitors, the **Cholesteric** LC (CLC) *salts of cholesterol* (dangerous when present in the blood arteries in crystalline state – the melting point is increasing by aging).

Typical lyotropics are the *sperm*, the bilayer *cellular membrane*, some *glues*, some *oil-vinegar mixtures* for preparing vinaigrette, and the *mayonnaise*, eatable only in LC phase, and not as separate biphasic system (*if like this, in italian we tell that “la maionese è impazzita = the mayonnaise became crazy”*).



Early in the 30th Vorländer (Halle) reported that can exist liquid crystalline order in synthesized **polymers**

Chemist, he synthesized many new LC,



Figure 3.1 Daniel Vorländer (1867–1941).

which he put in flasks stored in Havana cigar boxes.

The buildings of Halle University survived to the last battle in April 1945



Plate 7 The collection of cigar boxes in which Daniel Vorländer stored his liquid crystal samples. Courtesy of the University of Halle. (See Figure 3.3, p.49)

## 1.1.4. Do LC be alive ?

or do they have something to do with life?

This idea came 1st time to Lehmann due to Virchow, Prussian doctor-pathologist-anthropologist-biologist (against Evolution theory)-politician (against Bismark)

Figure 6.1 Rudolf Virchow.

(1821-1902)



[To know the man temper: Virchow argued that to introduce social structures among poor people could help prevent disease; but also misidentified Neanderthal man as an ill Cossack (1856)] 43

Virchow discovered and created the name “myelin” (from Greek μυελού = marrow)



Figure 6.2 Reproduction of line drawing of Virchow’s nerve fibres.<sup>12</sup>

Lehmann’s fibers later identified as lyotropic structures

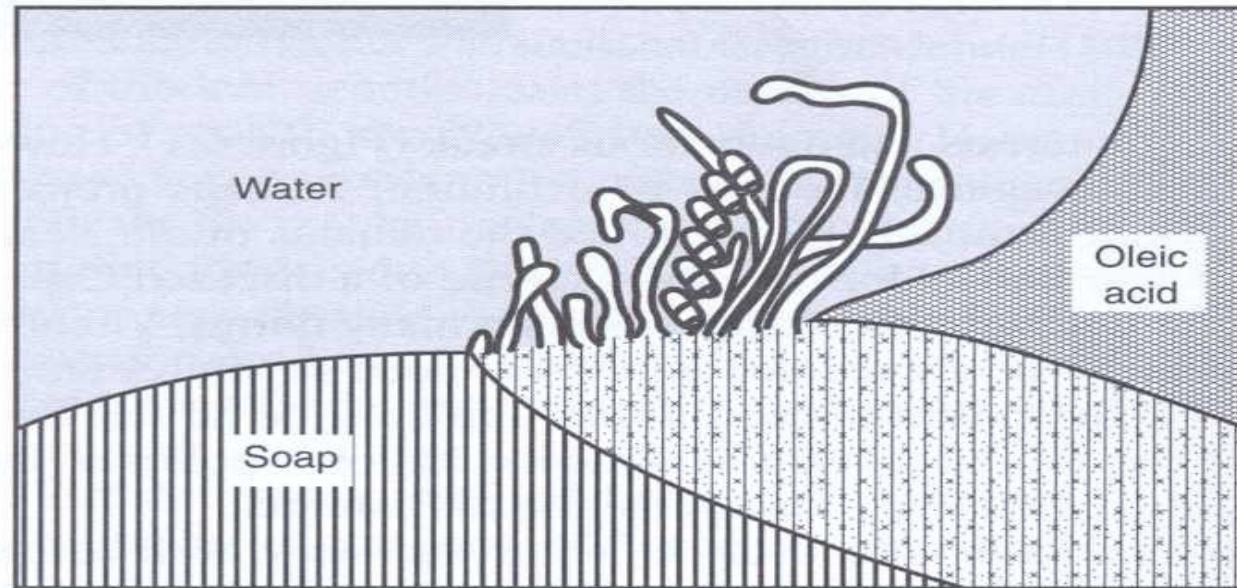
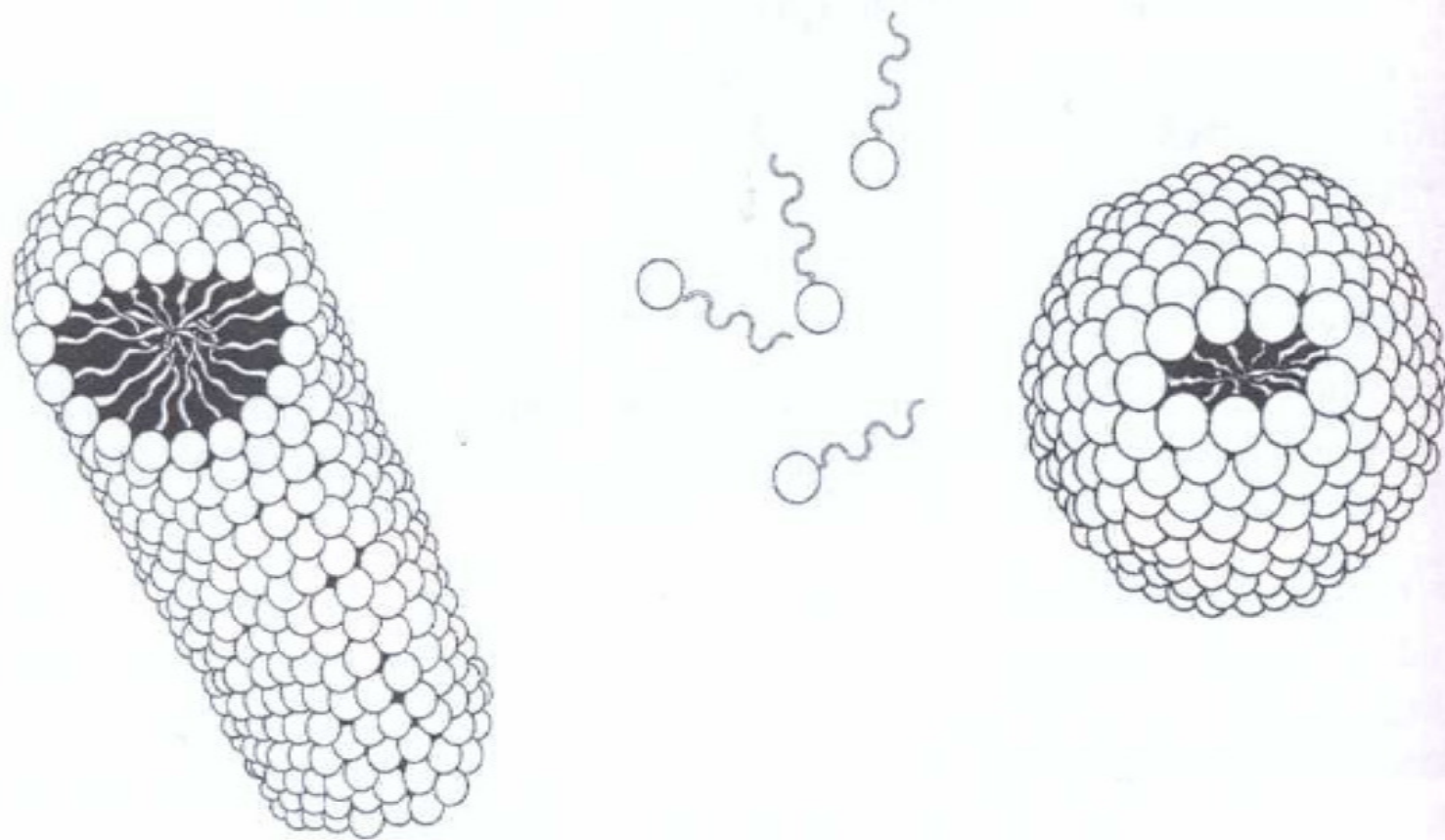


Figure 6.3 Redrawn from Lehmann’s Woodcut<sup>13</sup> showing artificial fibres grown from soap solutions.

## SOAP AND WATER: LYOTROPICS



**Figure 6.4** Spherical and cylindrical micelles formed by clustering of soap molecules in water solution.

Mesophases  
with different  
water soap  
concentration

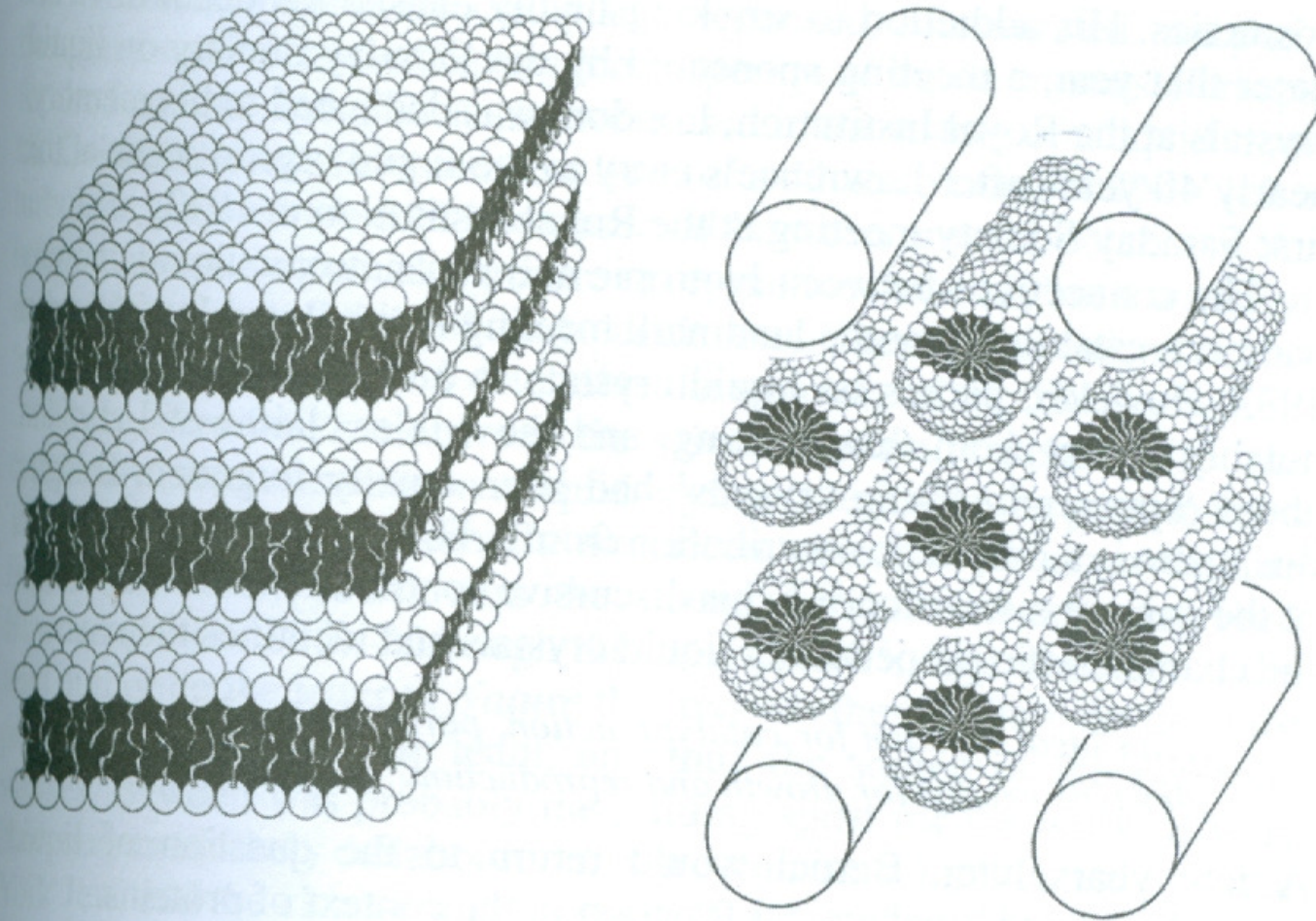
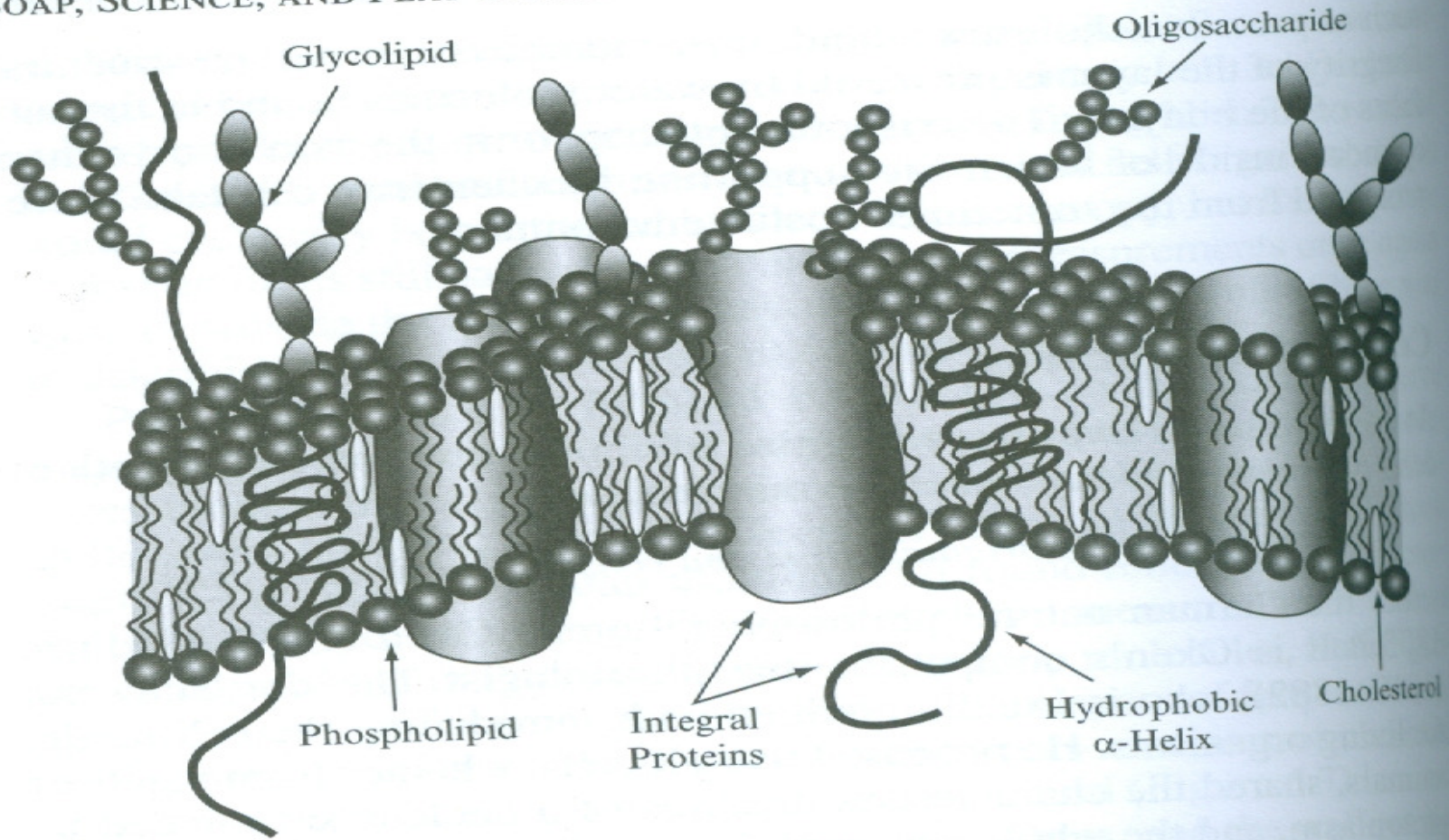
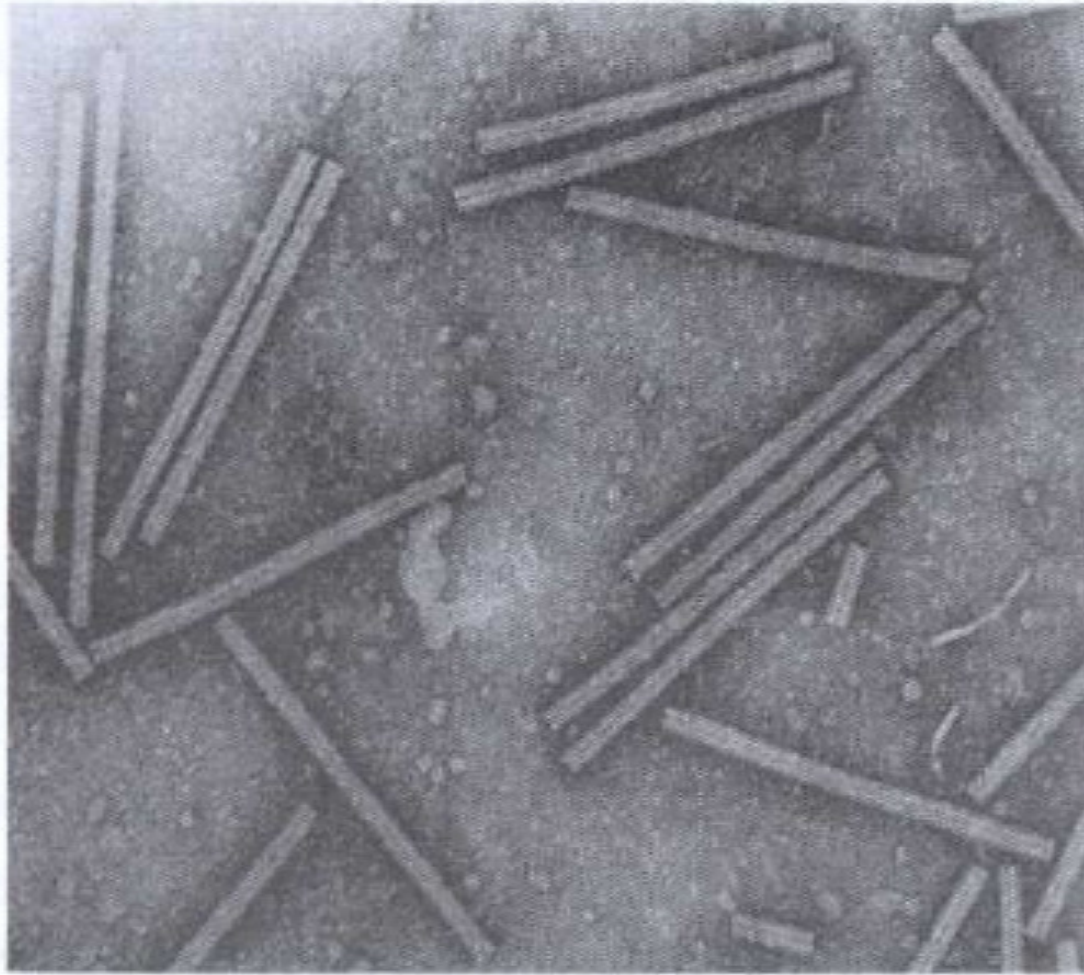


Figure 6.5 Liquid crystal phases of soap formed from micellar clusters as the water content decreases. On the left is the layered phase of neat soap, with water between the layers. On the right is the phase known as middle soap, in which water occupies the spaces between the cylindrical micelles. Both pictures show schematically the imagined internal structures of the layers and micelles.



**Figure 6.8** Schematic of a cell membrane with embedded proteins and other biomolecules. Courtesy of John Goodby.<sup>29</sup>

Then, LC are not alive, but the life uses LC as active brick<sub>47</sub> and tiles



**Figure 6.6** A modern electron microscope image of tobacco mosaic rods in water, showing their parallel organization. Courtesy of Seth Fraden.

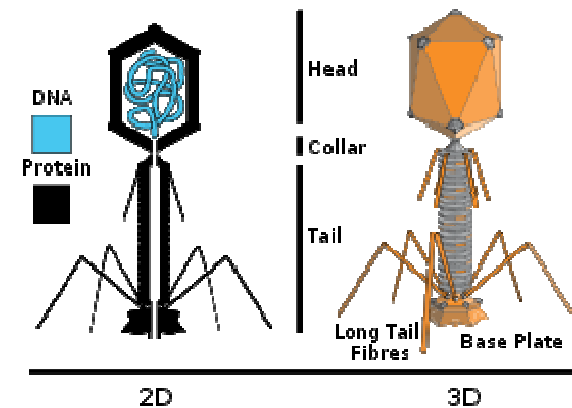
† Tobacco mosaic virus is a complex between a protein and a nucleic acid (RNA).



In the last 50 years it was recognized that in Nature do exist ***liquid crystal polymers***

f.i. the RNA or DNA of some viruses bacteriophages (killing bacteria after penetrating into their cells, from Greek φαγεῖν, to devoure )

Diagram of a typical tailed bacteriophage structure  
“moon landing”



***Phage average concentration in sea water:  $10^8$  phages/cm<sup>3</sup>***

Note that phages were discovered to be antibacterial agents and were used in Georgia and the USA during the 1920s and 1930s for treating bacterial infections. They had widespread use in Soviet Union, including treatment of soldiers in the Red Army.

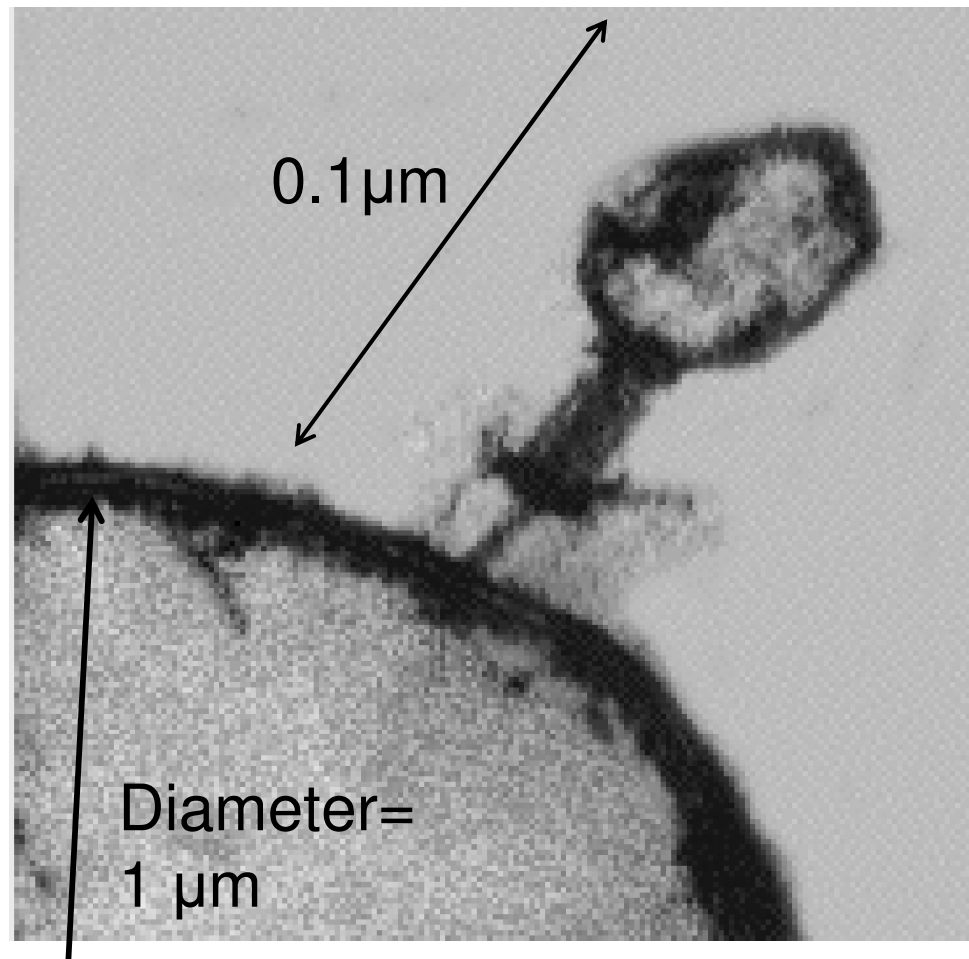
The superbug deaths relentlessly advance causing 40,000 U.S. and 8,000 Canadian deaths annually.

### NEW PHAGE IN MEDICINE:

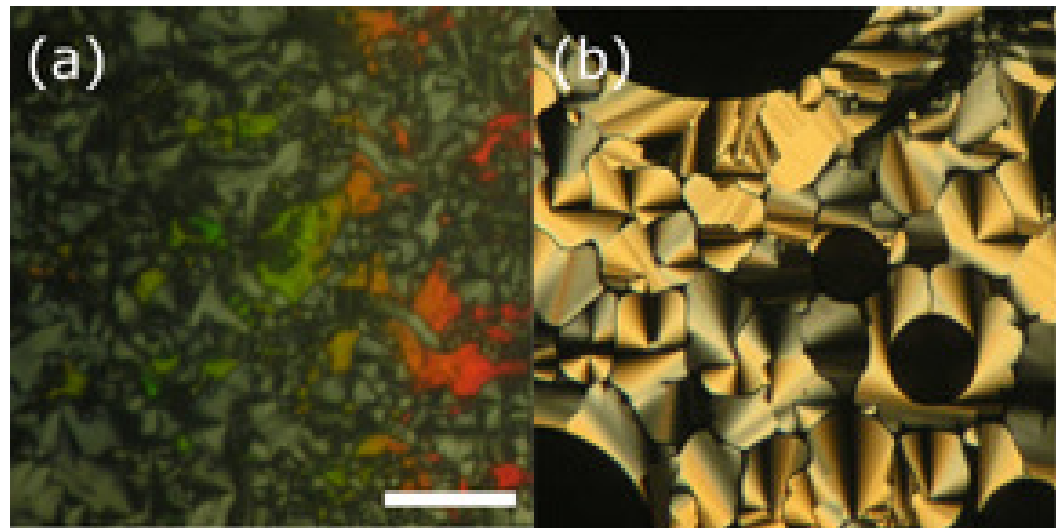
A phage “moon landing” on a superbug (antibiotic resistant microbe) into which it injects phage proteins which become more phages to eliminate superbugs which cause infections and disease.

Dr. Elizabeth Kutter, 2005

Speed of injection=1mm/s



The ability of long, hydrated, double-stranded DNA to form liquid crystal phases has been known for more than 50 years and played a key role in the initial deciphering of its structure.



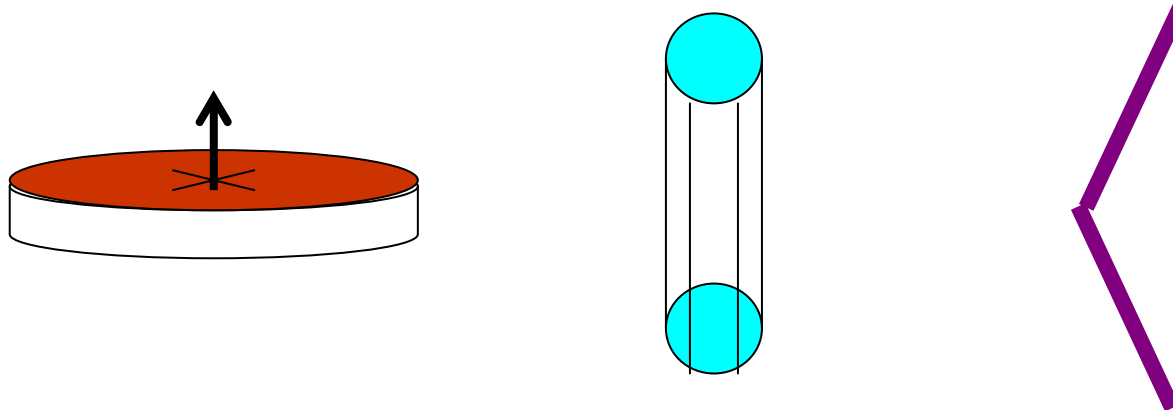
**Figure 1.** Polarized microscopy images of LC phases of ultra-short DNA strands. (a) Chiral nematic phase of CGCAATTGCG: the colored textures reveal a sub-micrometer pitch, increasing from left to right along the concentration gradient. (b) Domains of hexagonal columnar phase. Scale bar is 50  $\mu\text{m}$ .

## 1.1.5. Discotics, Calamitics, Banana-like

Mark that LC can have as elementary unit not only one molecule, but **a package of molecules!**

Then we have to consider another type of LC classification, based on the shape of the unit :

**DISCOTICS** , **CALAMITICS** , and **BANANA-LIKE**



Discotics and Calamitics can be not only a molecule, but also a **supramolecular system**.

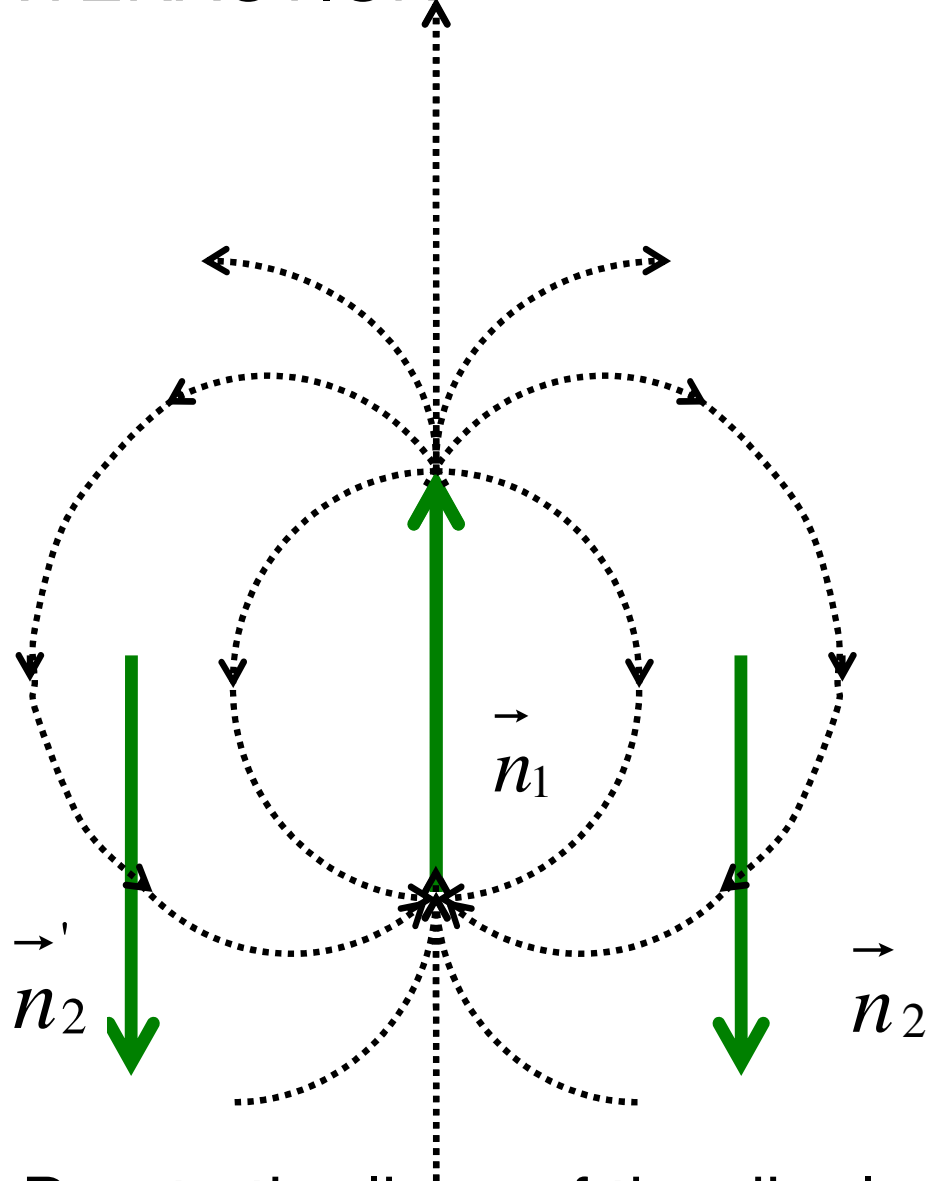
## **1.2. Classification**

### **1.2.1. Thermotropics: structure and simple properties**

**Alfredo Strigazzi, Senior Professor, Dept of Applied Science and Technology (DISAT), Politecnico di Torino, Torino, Italy**

**MEPhI, Moscow, 10 September 2014**

# THE MOLECULAR INTERACTION IS MAINLY DIPOLE-DIPOLE INTERACTION



Let us consider a liquid crystal molecule with cylindrical symmetry, with its electric dipole (either induced or permanent) parallel to the molecular long axis. The long axis average alignment of molecule 1 is defined by the unit vector  $\vec{n}_1$ .

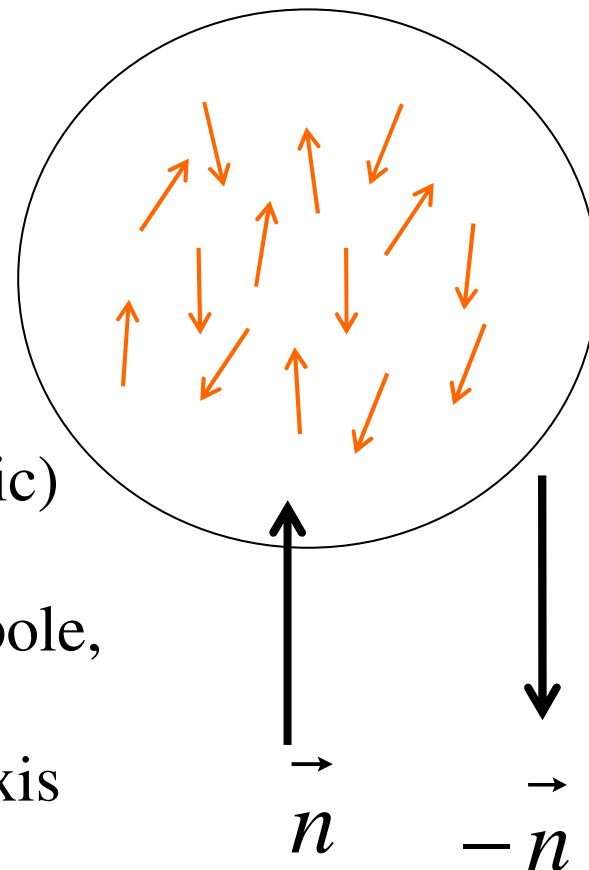
Due to the lines of the dipole field, the energetically favored orientation of the adjacent lateral molecules 2, 2' is the **antiparallel** one.

## NEMATIC STATE

In a certain temperature interval, inside a very small (but not sub-nanoscopic) volume,  $dV$  the molecules, which are elongated, usually possess an induced dipole, exhibiting a long range interaction. Due to this, the orientation of their long axis (here represented by orange arrows) is distributed around a common direction, defined

by a unit vector  $\vec{n}$  called “**director**”.

Mark that  $\vec{n}$  and  $(-\vec{n})$  are equivalent for all physical properties.

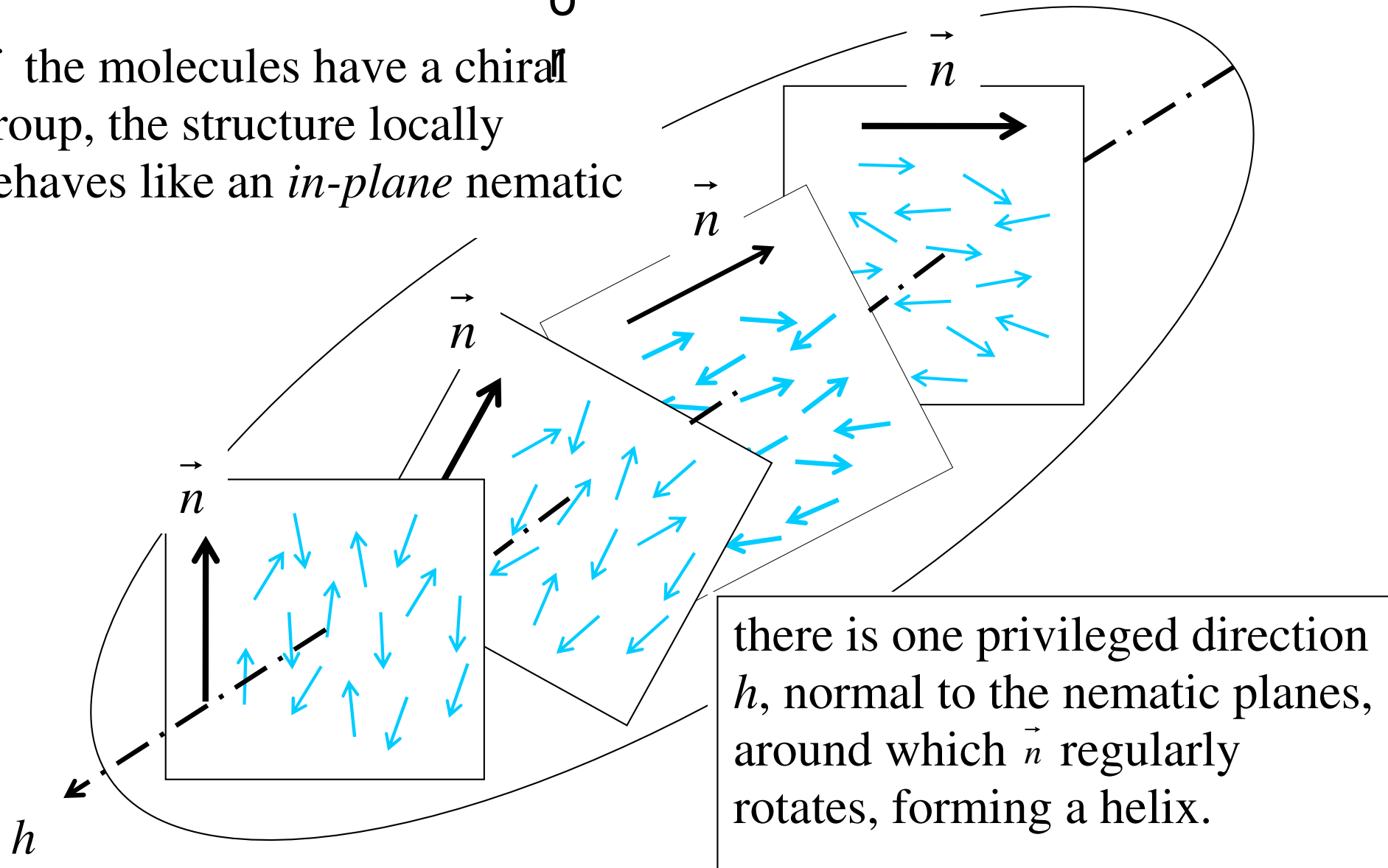


The mic motion is 3D liquid-like, with *orientational order*

# CHIRAL NEMATIC STATE or CHOLESTERIC STATE

0

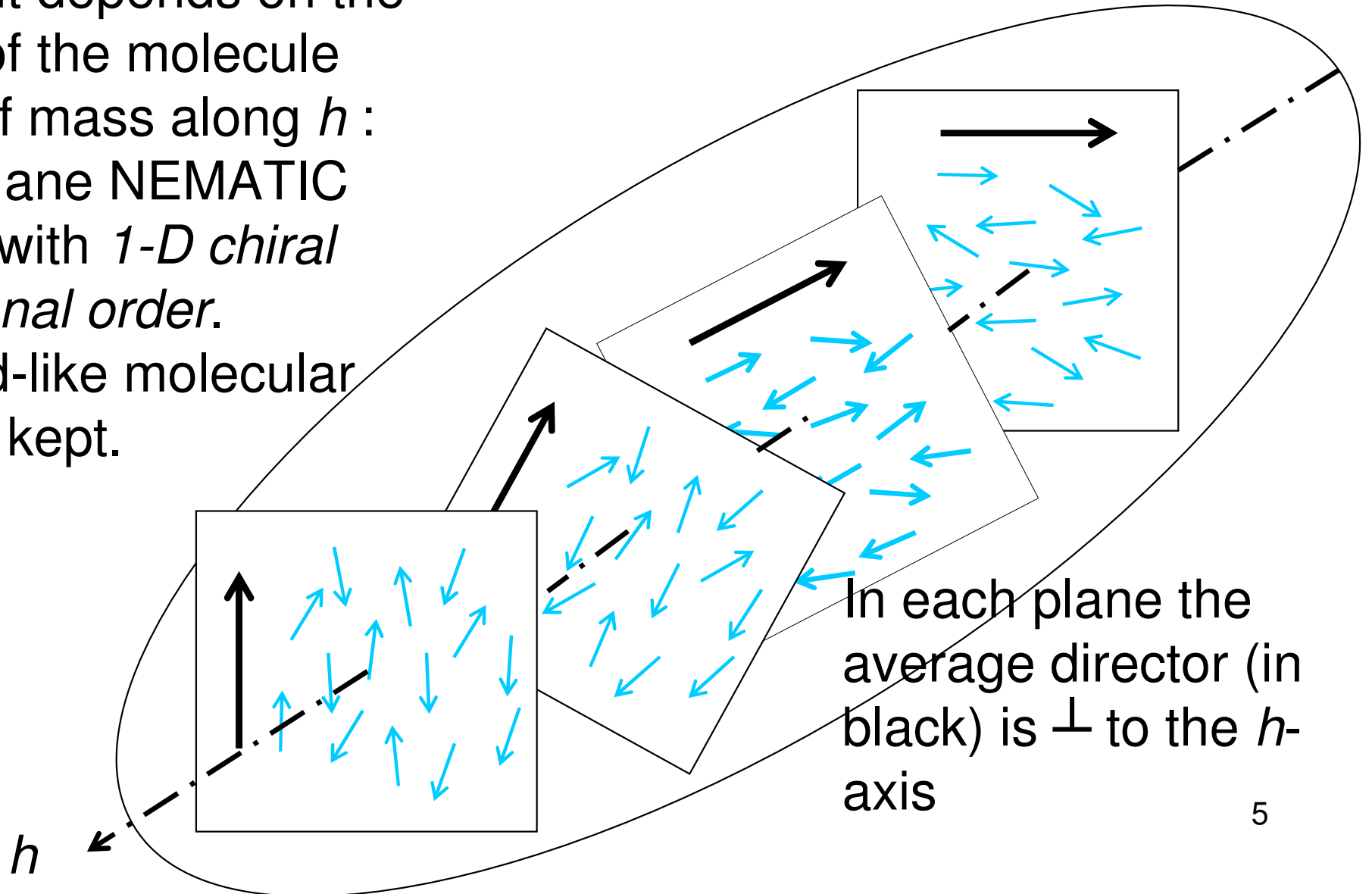
If the molecules have a chiral group, the structure locally behaves like an *in-plane* nematic



Remember that the helix is *imaginary*!



The molecules here are represented by blue arrows. There is not a uniform *orientational order in the bulk*, but it depends on the position of the molecule centers of mass along  $h$ : it's a in-plane NEMATIC package with *1-D chiral orientational order*. The liquid-like molecular motion is kept.



# SMECTIC\_A STATE

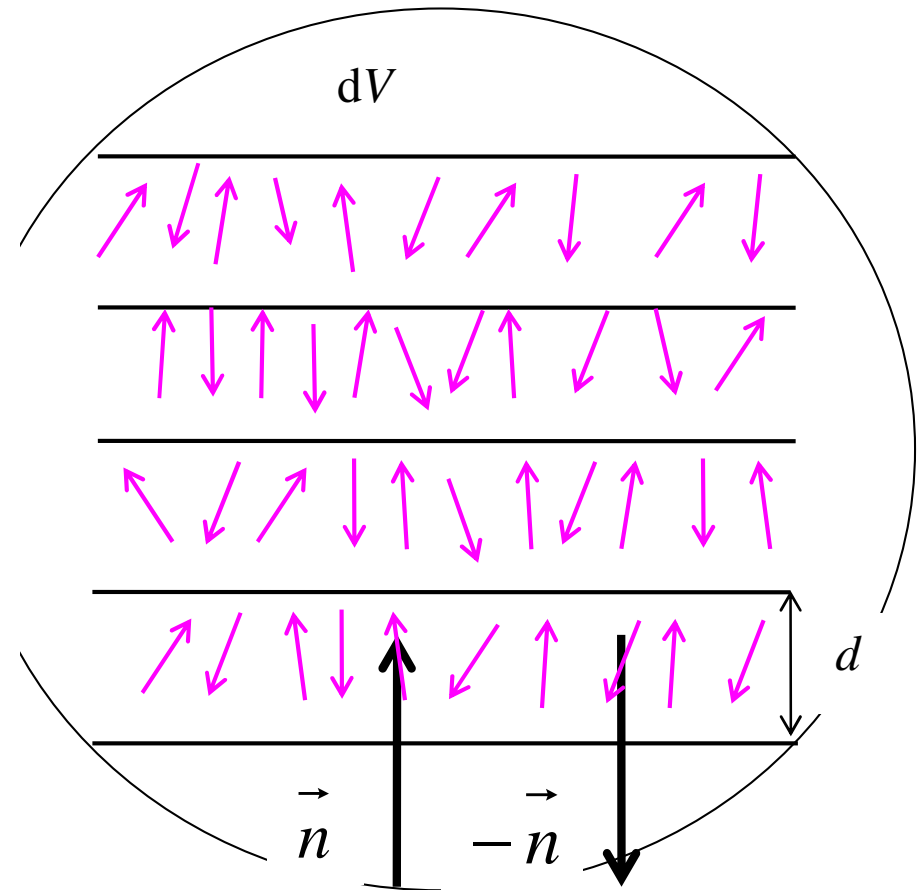
The smectic structure is closer to crystal state than the previous ones.

There is not only an *orientational symmetry*, but also a *positional symmetry* with various degrees, which distinguish different kinds of smectic states.

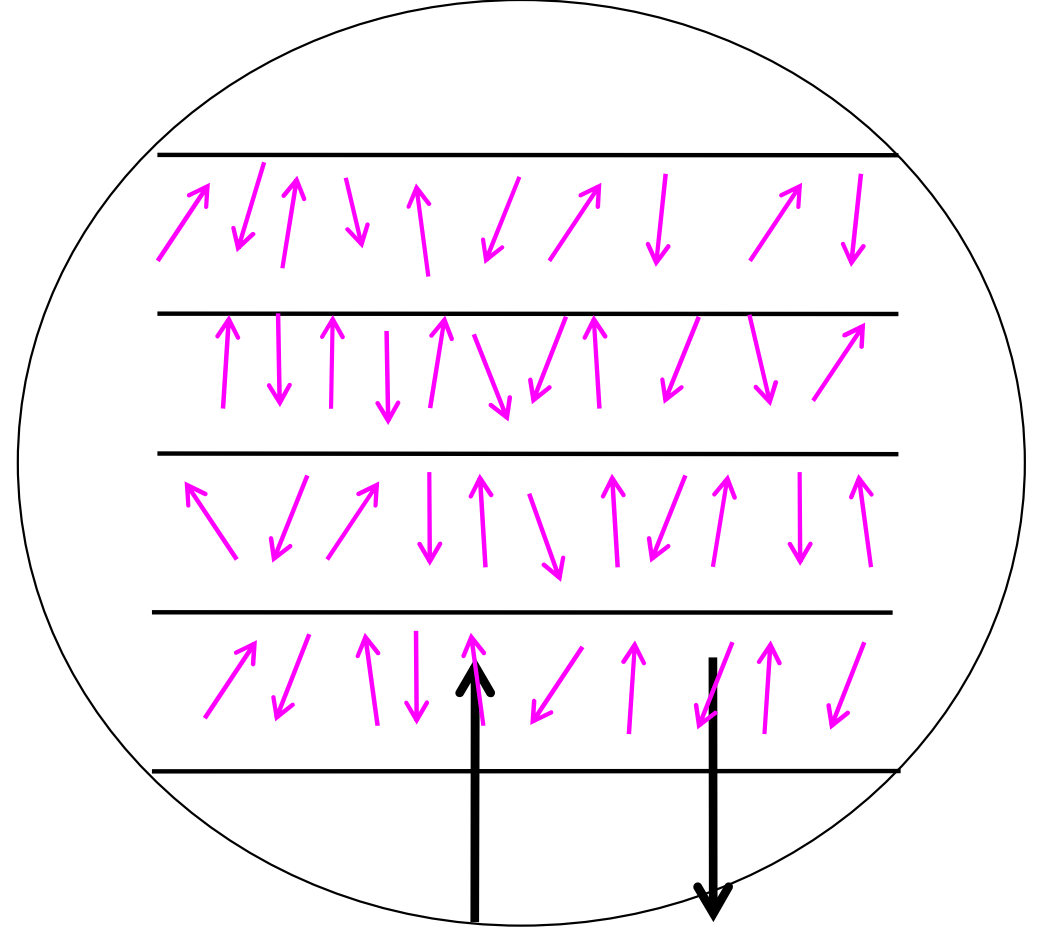
***There are many Smectic ordering!***

Smectic A is the simplest .

In a certain temperature interval, inside a very small (but not sub-nanoscopic) volume  $dV$ , the molecules self-assemble in plane layered structure. The layer thickness  $d$  is a little bit greater than the molecular length.



Inside each layer, the molecule orientation (here represented by pink arrows) is distributed around an average director normal to the smectic layer.



The molecule centers of mass are relatively free to move inside each layer, as in an usual viscous liquid: but viscosity generally is higher than in nematics and cholesterics.

Smectic A behaves as a package of 2D-nematics with fixed average molecular alignment, normal to smectic layers.

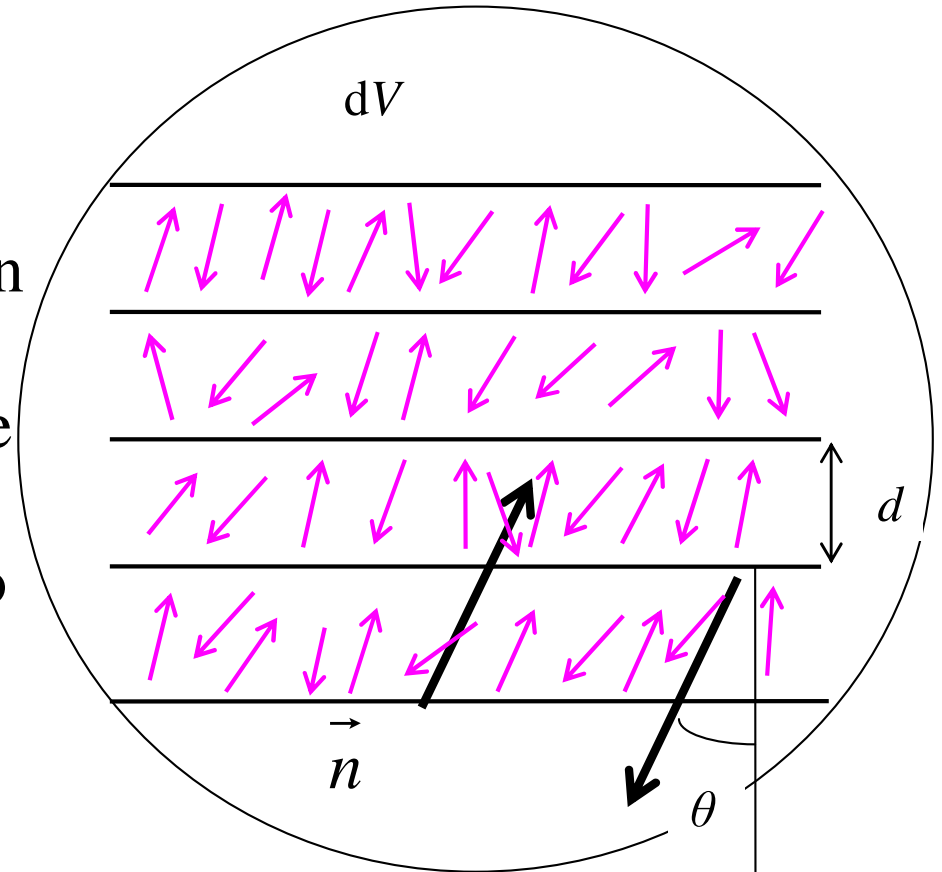
## SMECTIC\_C STATE

Smectic C is a tilted uniform smectic structure.

The molecules have no longer cylindrical symmetry, but do not contain chiral groups. The *positional symmetry* is the same as in smectic A; whereas the *orientational symmetry* has one privileged axis inclined with respect to the layers, and uniform in the small volume  $dV$ .

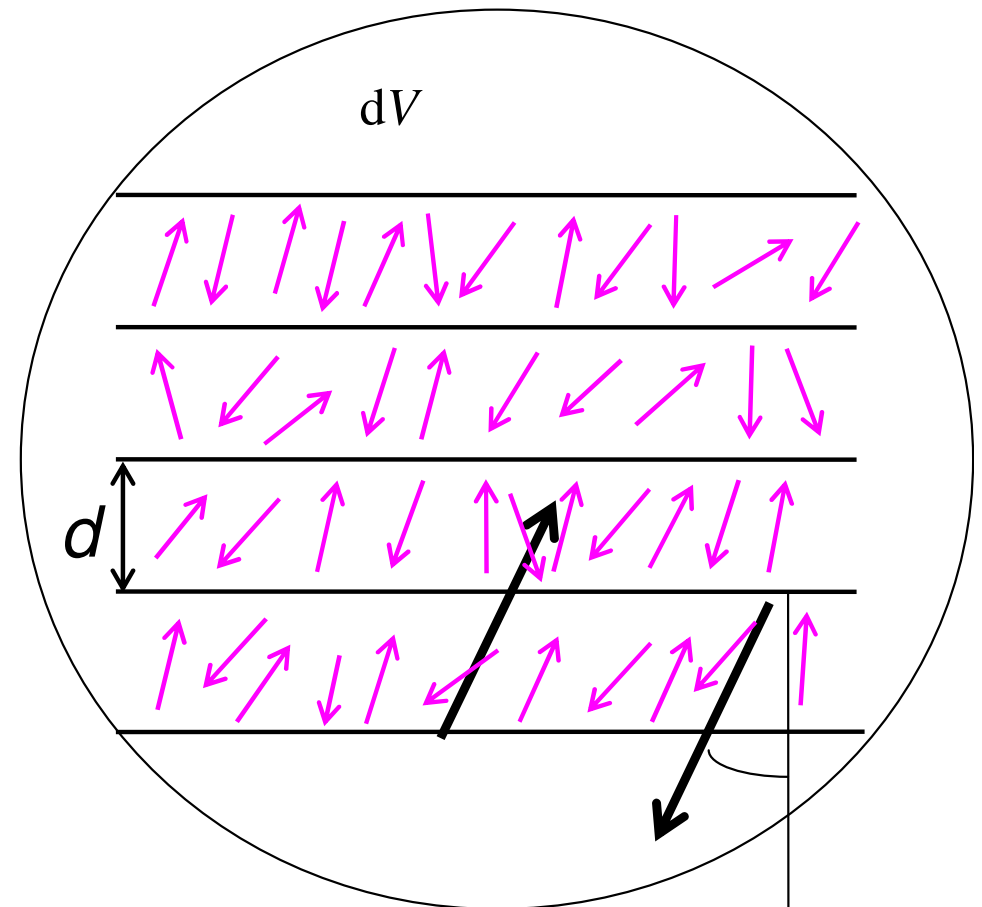
The director  $\vec{n}$  is tilted by a polar angle  $\theta$  with respect to the normal to the smectic layers.

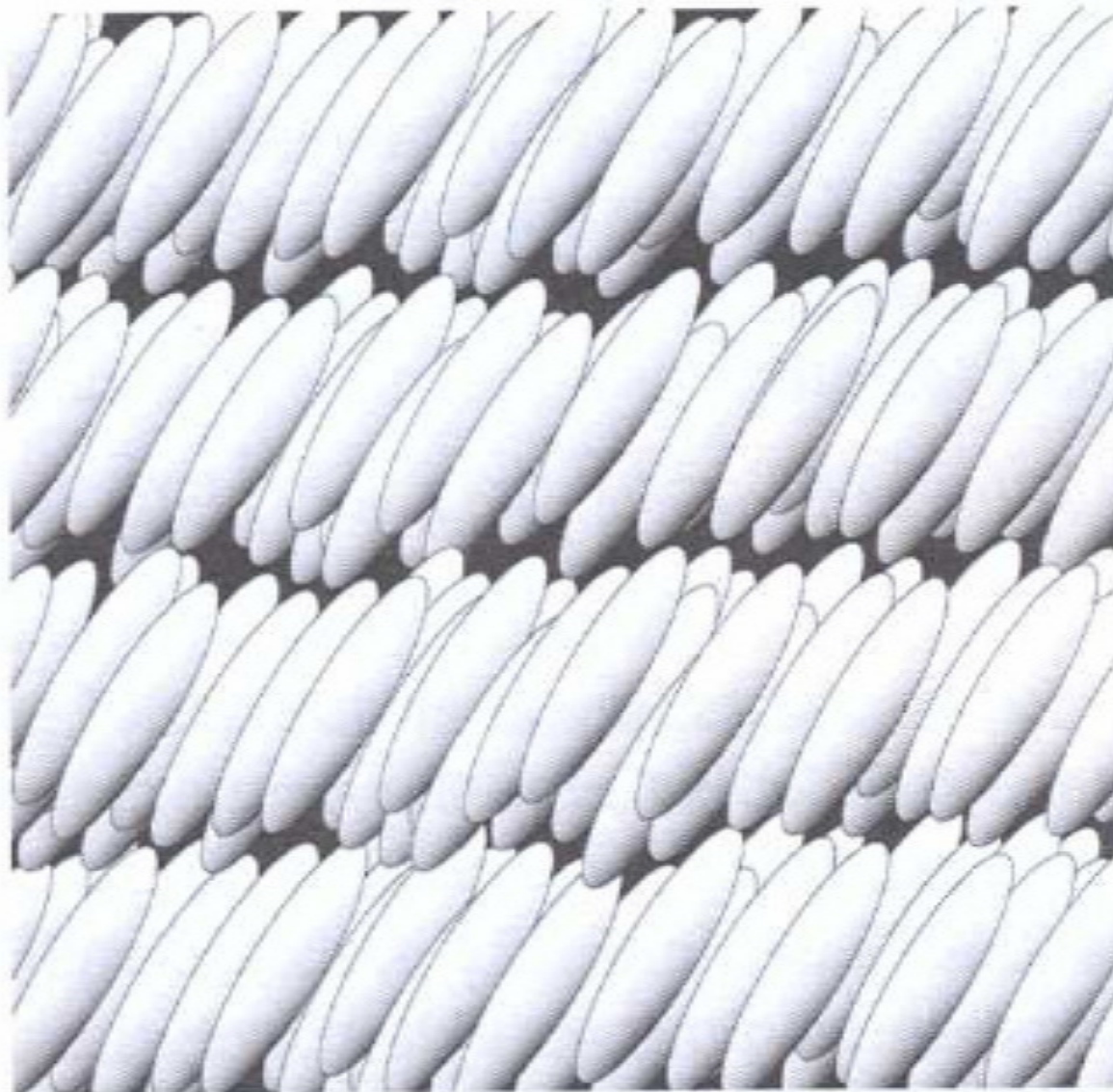
$\vec{n}$  in average is the same in all the sample.



The layer thickness  $d$  is of the same order as the molecular length. The molecule centers of mass are relatively free to move inside each layer, as in an usual viscous liquid: but viscosity generally is higher than in nematics and cholesterics.

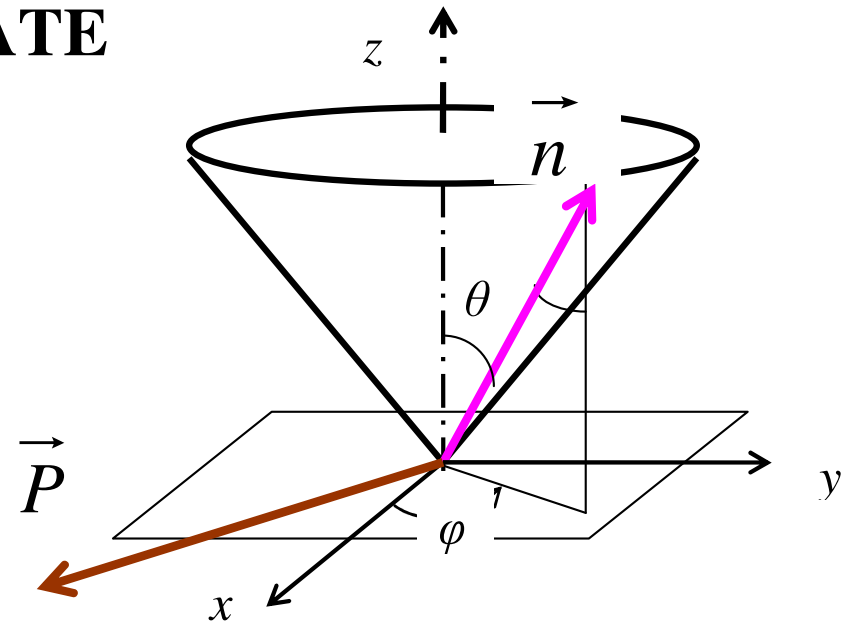
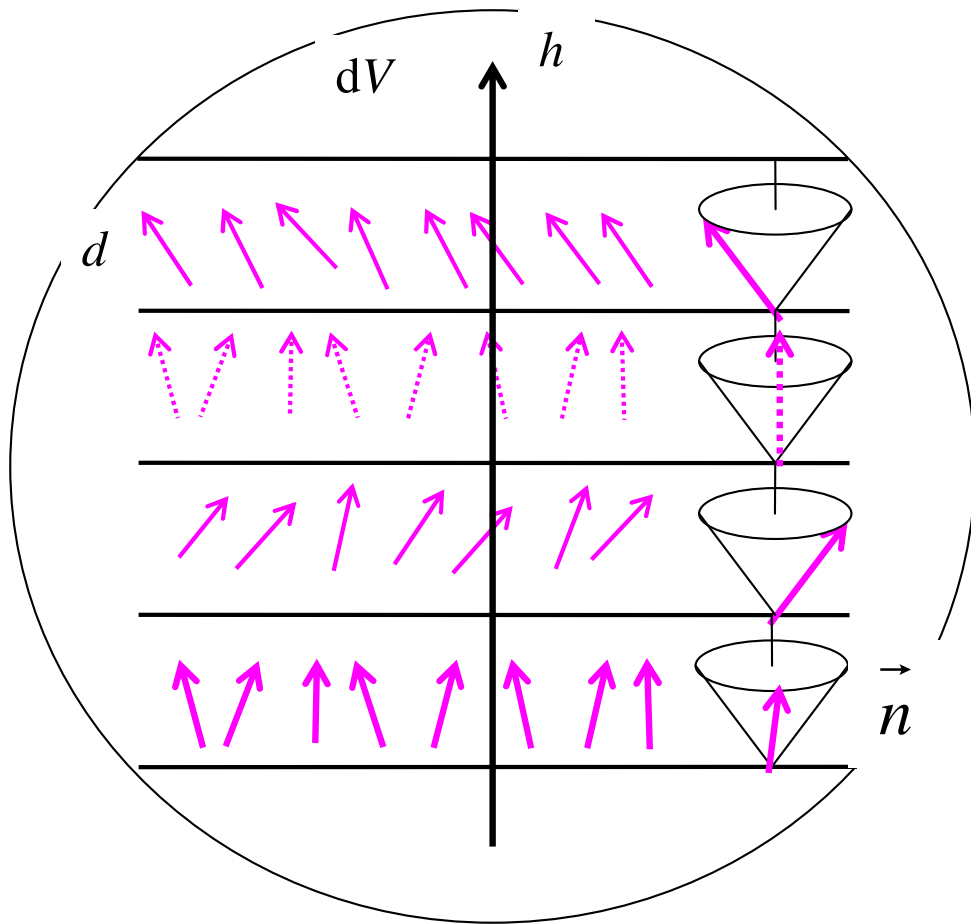
Smectic C behaves as a 2D-nematic with average molecular alignment uniformly inclined with respect to the layers.



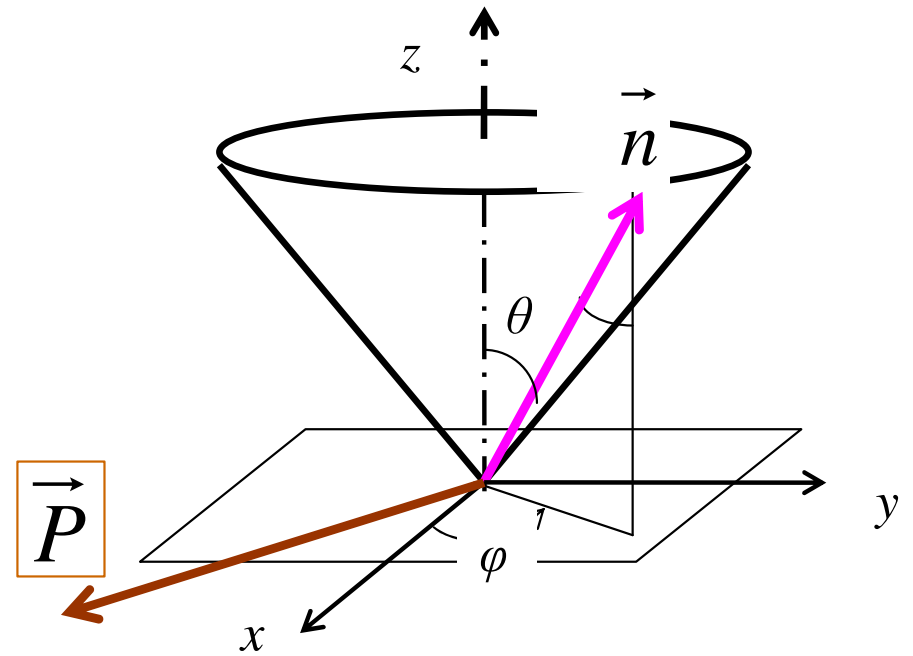
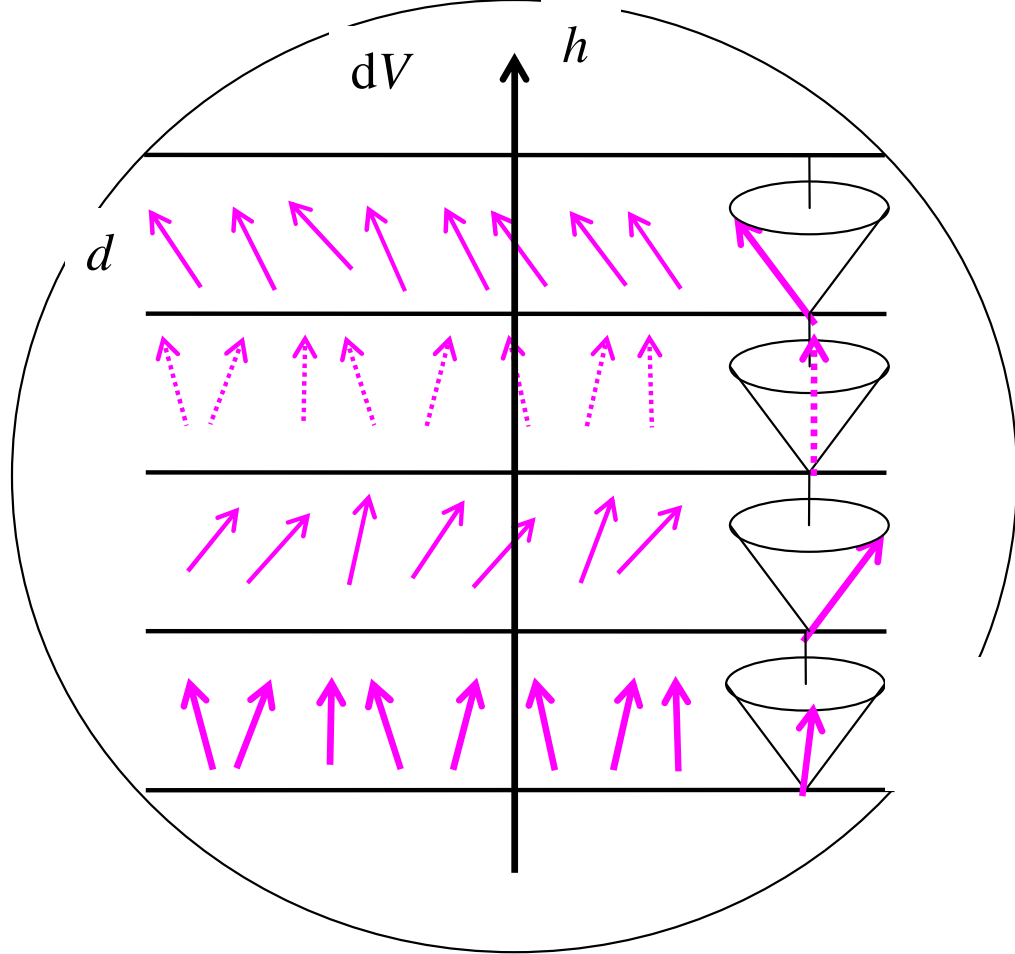


**Figure 8.6** A representation of the molecular structure of a tilted smectic C phase. Compare this figure with the untilted structure of a smectic A phase in Technical Box 4.3.

# SMECTIC\_C\_CHIRAL (or C\*) STATE



Smectic C\* is a tilted but nonuniform smectic structure. As for smectic C, the molecules have no longer cylindrical symmetry, but in smectic C\* they contain chiral groups.

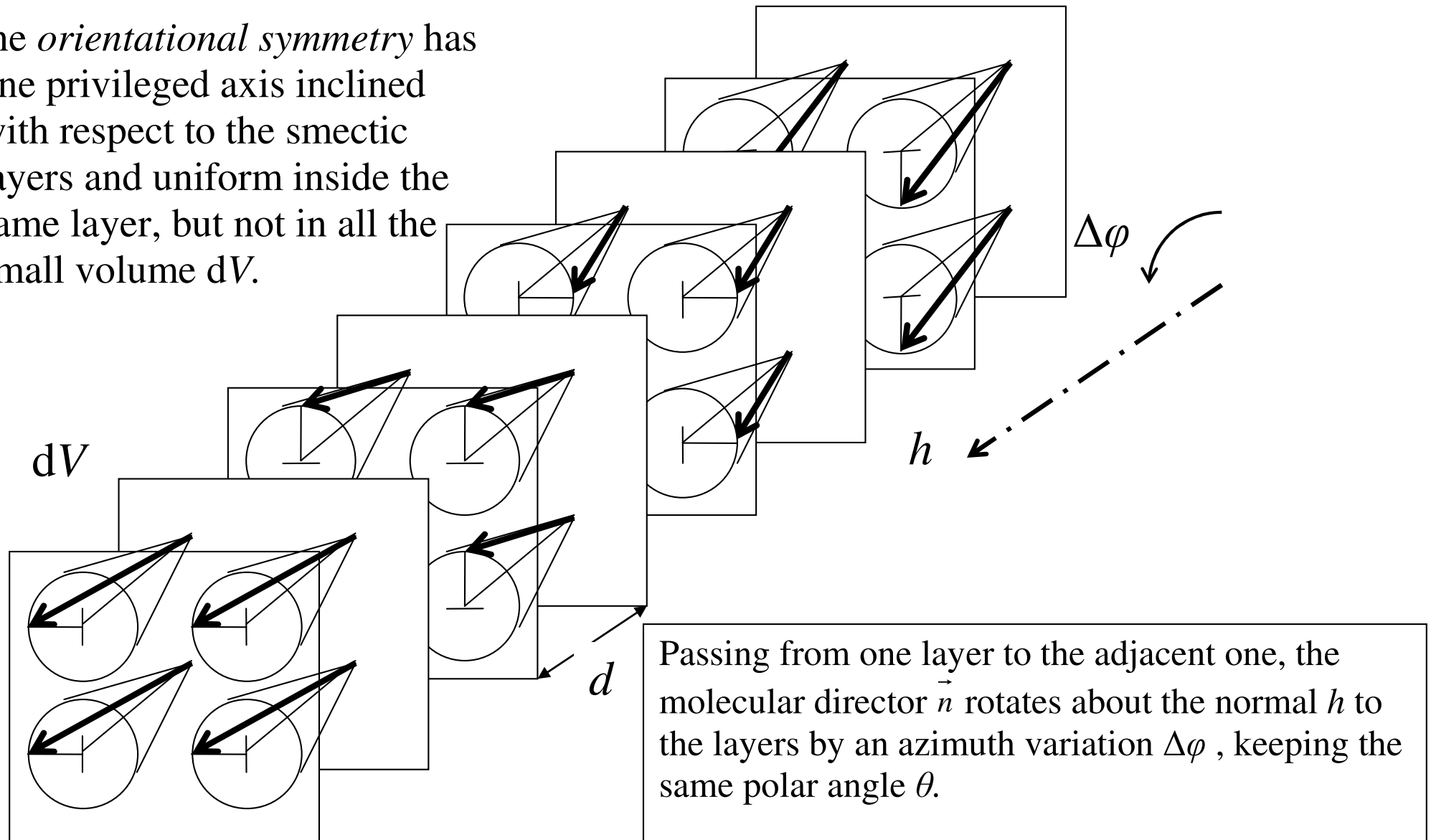


The short range interaction between molecules favors the direct parallelism among them: thus  $\vec{n}$  and  $(-\vec{n})$  are no longer equivalent, and each layer has a transverse polarization, being the polarization normal to  $\vec{h}$  and to  $z$ : **FERROELECTRIC ORDER.**

The *positional symmetry* is the same as in smectic A & C, whereas



the *orientational symmetry* has one privileged axis inclined with respect to the smectic layers and uniform inside the same layer, but not in all the small volume  $dV$ .



Remember that the cones are *imaginary*!

Hence a helix with axis  $h$  is defined,  $\Delta\varphi$  comprising the right- and left-handed possibility.

Thus, in every small droplet – but nonsub-nanoscopic -  $dV$ , containing many helical wavelengths, **the resulting polarization naturally vanish.**

Both  $\vec{n}$ - inclination  $\theta$  and azimuth variation  $\Delta\varphi$  depend on the material and on the temperature, but  $\Delta\varphi$  depends also by external constraints (interface conditions, applied electric fields, etc.).

The layer thickness  $d$  and viscosity are of the same order as in the case of smectic C.

Smectic C\* in a natural droplet behaves quite similar to a package of 2D-cholesteric layers.

## 1.2.2. Phase sequence and typical LC compounds

A liquid crystal state is generally called **mesophase**: the transition temperature from crystal is called ***melting point***; the transition temperature to isotropic liquid is called ***clearing point*** (since usually the liquid state is more transparent).

This temperature range is the interval of existence of liquid crystallinity, which can be simple, exhibiting only one state, like f.i. nematic, or multiple, exhibiting more states, like smectic A and nematic.

In the latter case the liquid crystal range is shared in sub-ranges, and there is (are) other intermediate transition(s).

Note that:

1. Usually as higher the temperature, as less is the degree of symmetry order kept in the actual phase (f.i. crystal, smectic C, smectic A, nematic, liquid). When this condition fails, there is a "re-entrant phase" (f.i crystal, smectic A, nematic, smectic A, liquid).
2. There is not a transition point between cholesteric and nematic, but a continuous transition.
3. More rigid is the molecule core, more high is the degree of symmetry of the existing mesophase at that temperature.

From Hull Univ,  
Great Britain

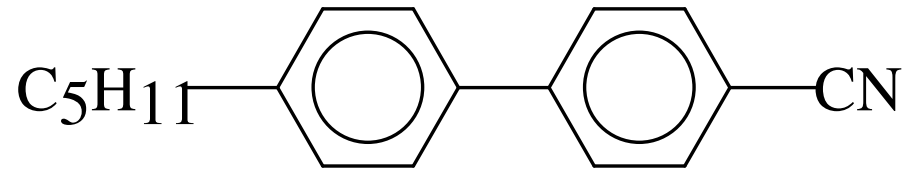
Inventor of nematic  
5CB, and other  
alkyl- and alkoxy-  
cyanobiphenils,  
which allowed the  
development of  
display and monitor  
application



**Figure 10.6** George Gray (b.1926–2013).

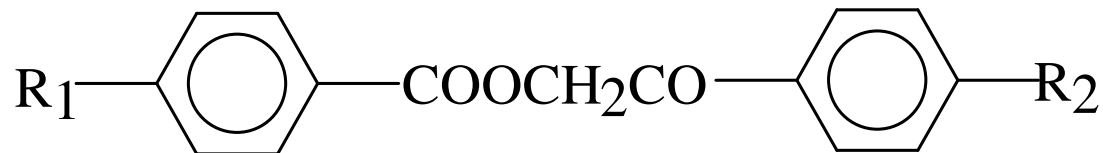
# EXAMPLES OF DIFFERENT LC COMPOUNDS

**Example of nematic compound –5CB: 4'amylycyanobiphenyl**



**This compound exhibit only nematic phase**

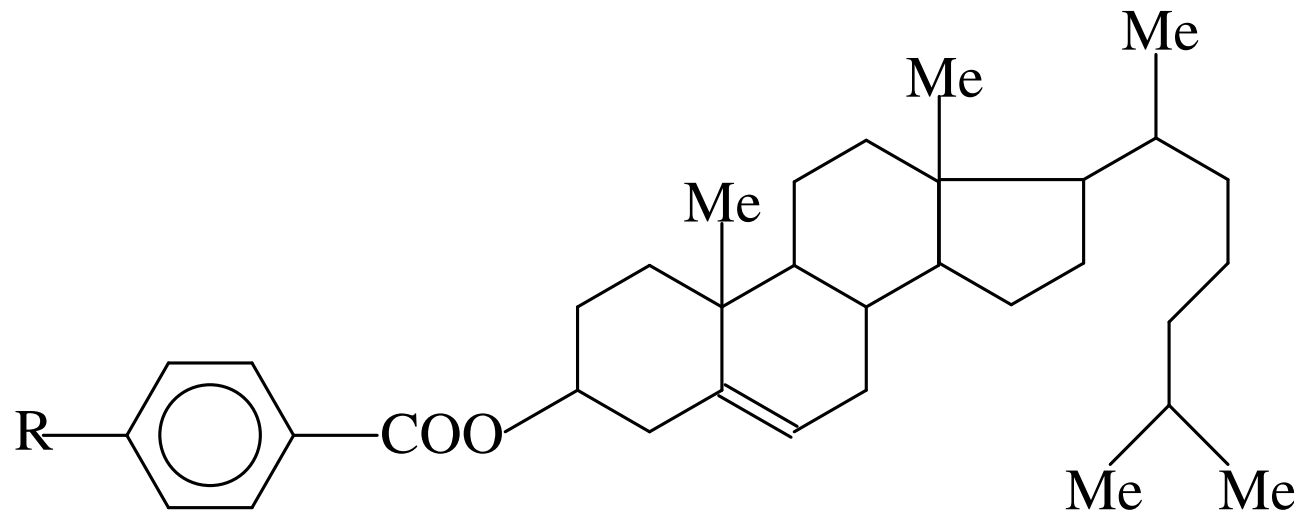
**Example of polymorphic compound – phenacylic esters**



**Compounds of this series have the following phase sequence:**

**C-S<sub>C</sub>-S<sub>A</sub>-N-I**

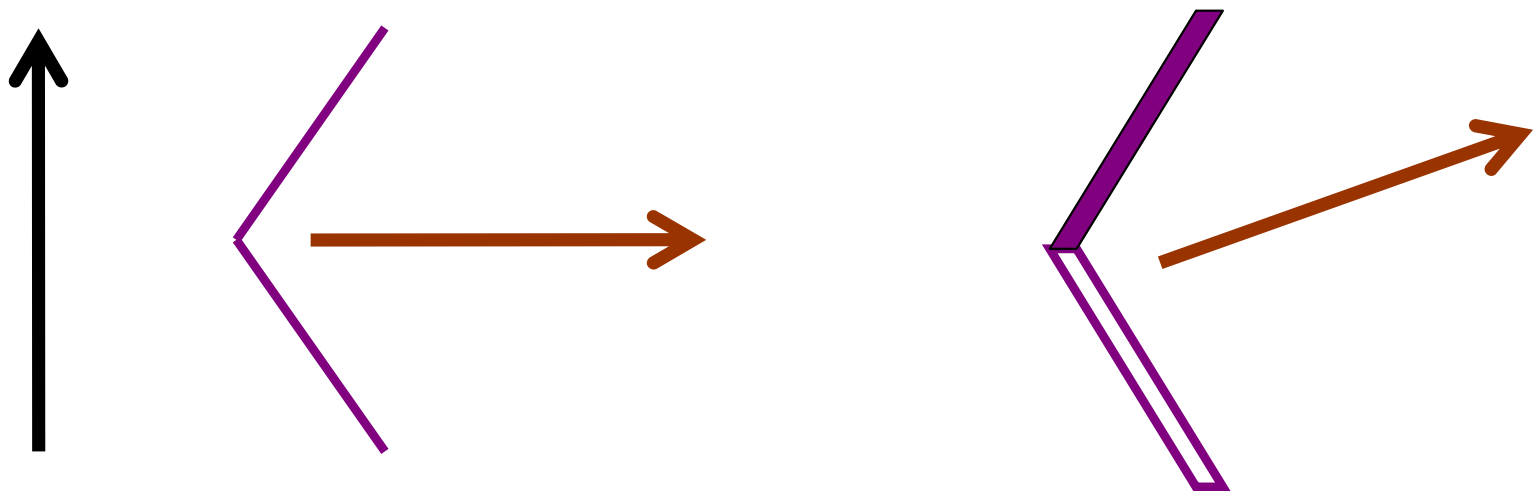
## Example of cholesteric compound - cholesteryl benzoate



Me  $\equiv$  Methyl group: — CH<sub>3</sub>

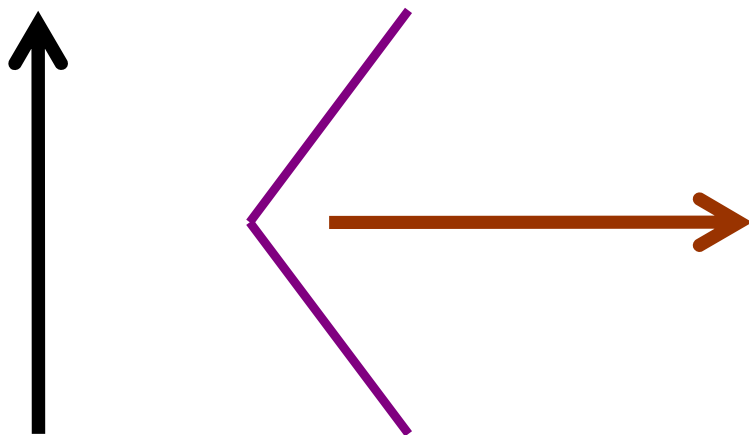
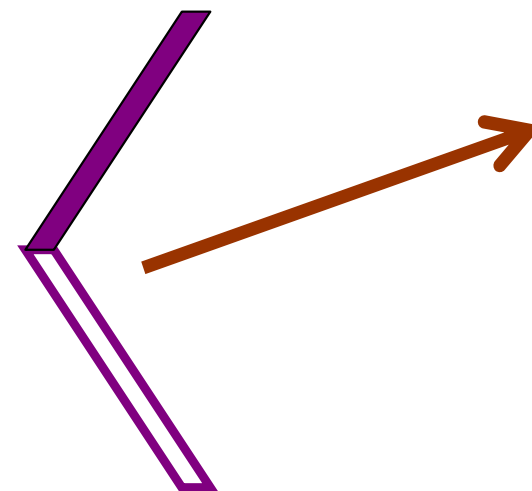
# Banana\_like structures

In late 90-ies it was shown the liquid cristallinity of compounds which molecule has a rigid core forming an angle of  $130^\circ - 150^\circ$ , thus giving to the molecule the shape of a *boomerang*, or of a *banana*. The molecules of such type usually don't have chiral centre, just have **permanent electric dipole**, but nevertheless a small droplet of material can have no spontaneous polarization, if the single dipoles orientation is compensated.



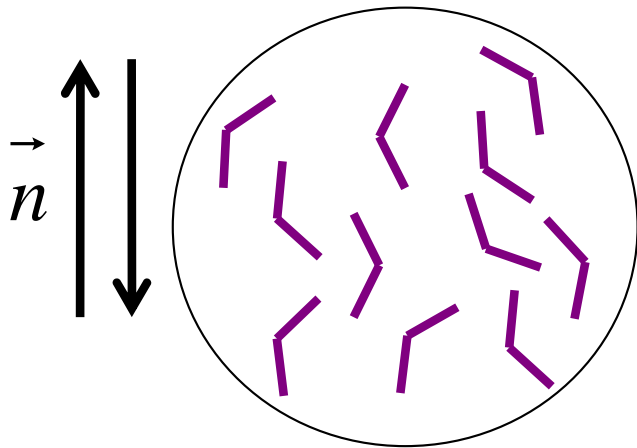


A banana\_like molecule can be symmetric or not, either due to core or to tails



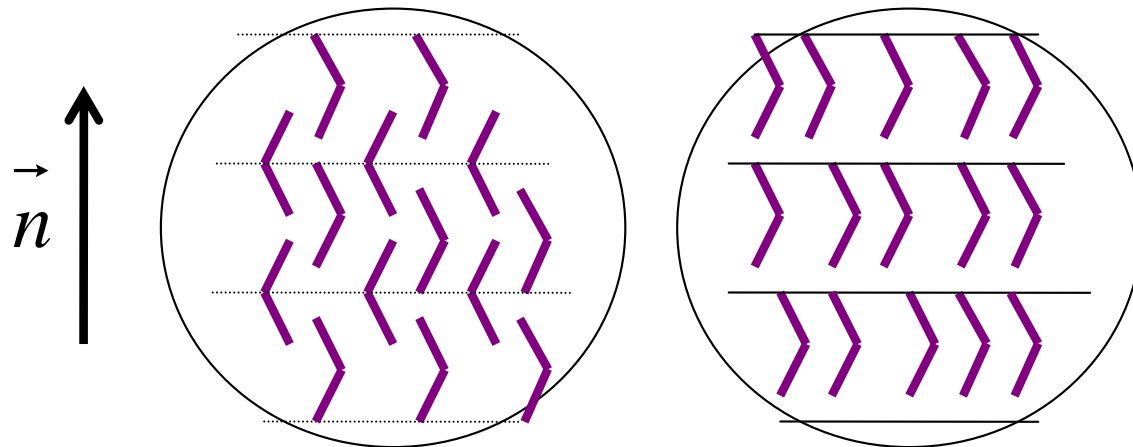
As a consequence the permanent dipole, always being *in-plane*, can be symmetric or not

A mesomorphic banana\_like compound can exhibit **nematic** phase



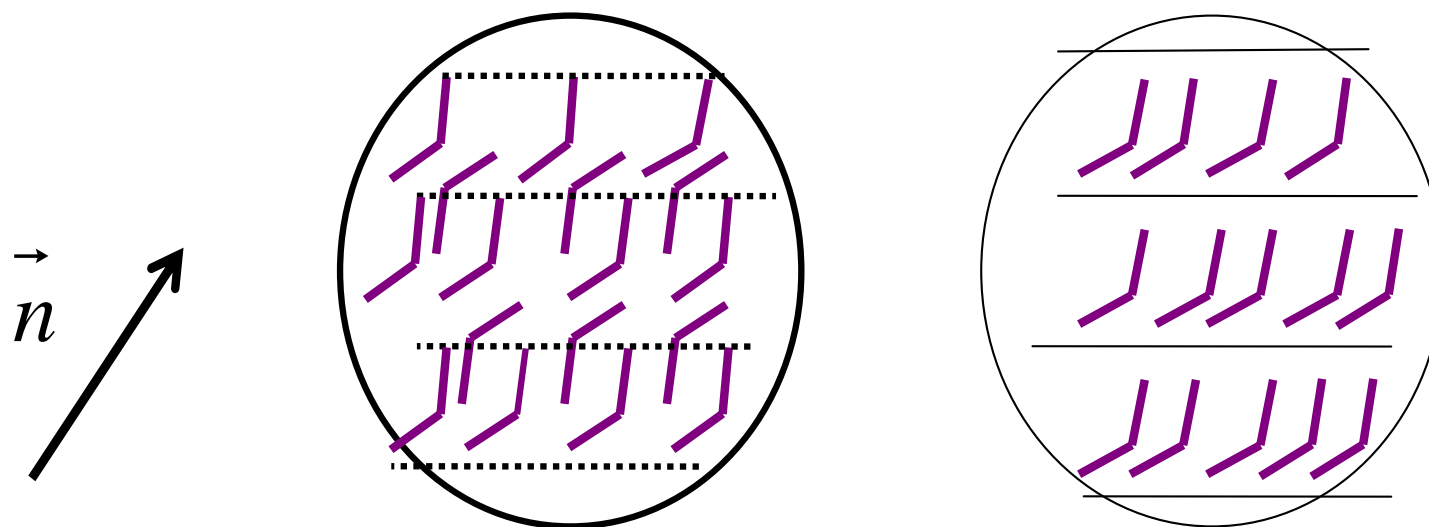
and/or **smectic A** phase,  
either interdigitated

or not



and/or **smectic C** phase, either  
interdigitated

or not



The most common mesomorphic compounds having banana-shaped molecules exhibit smectic phase(s): some of them, nematic phase too, and others, only nematic phase.

# 1.2.3. Interaction of applied electric fields with NLC & SC\*LC

Thermotropic nematics and smectics C\* are mainly used in the application as signal transducers, due to their response to an applied electric field.

## NEMATICS

They are materials with molecules characterized only by *induced dipoles*

.

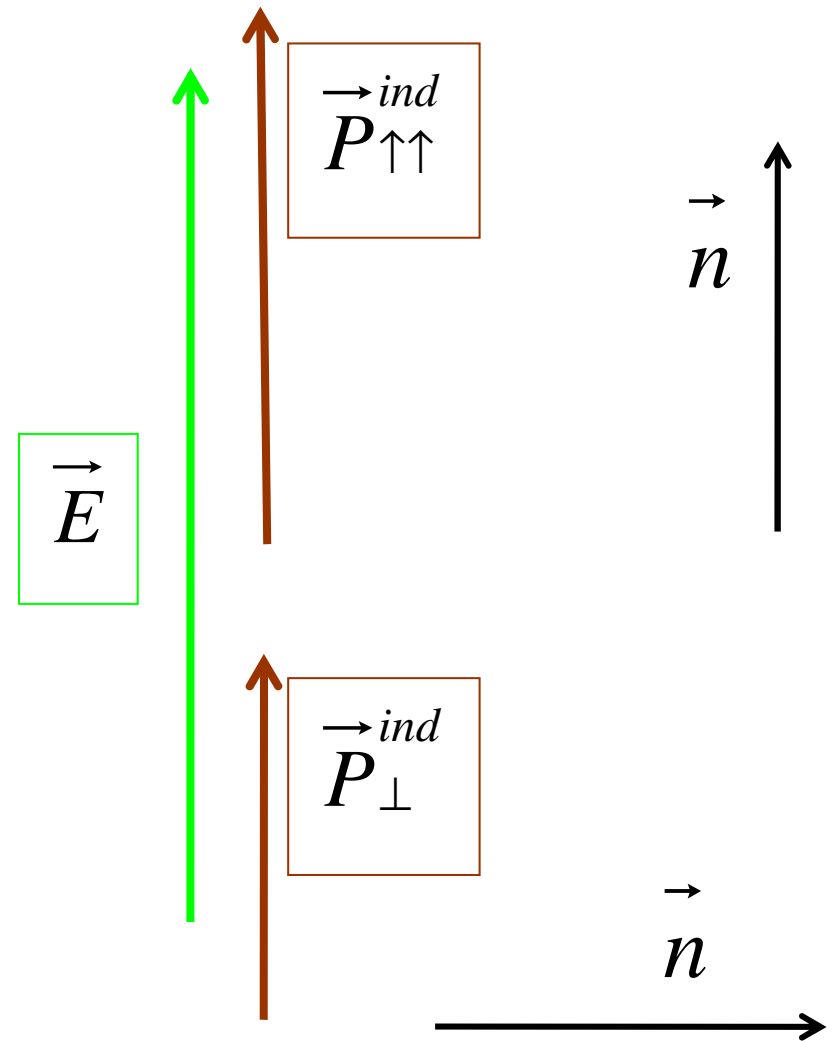
Then the interaction is **quadratic** with field (independent of the field **sense**):

the field can be produced by an alternate voltage.

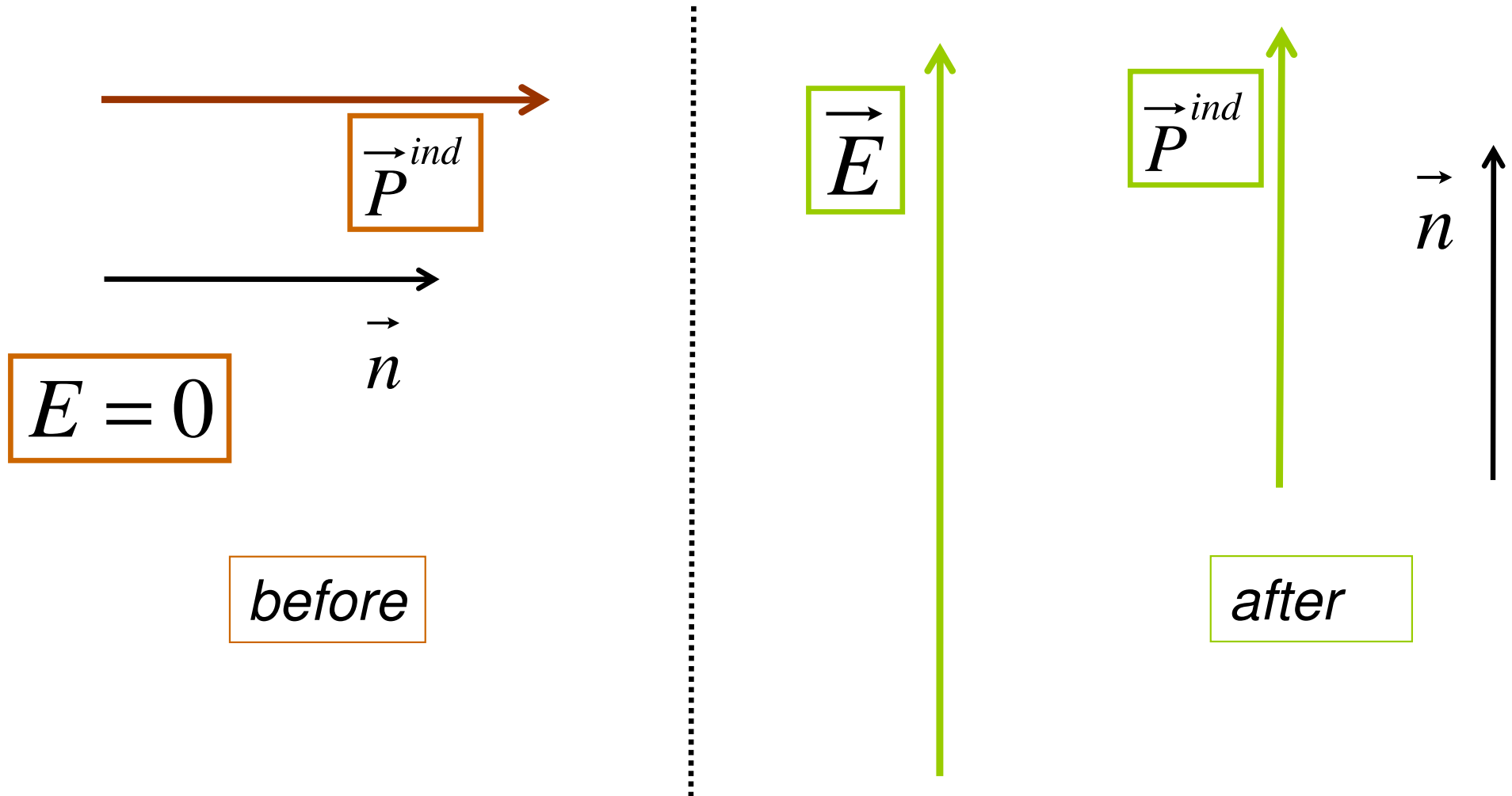
*Induced dipole* can be parallel or perpendicular to the molecule long axis:  
 then a drop of well aligned NLC has positive or negative permittivity anisotropy.

$$\epsilon_a \equiv \epsilon_{\uparrow\uparrow} - \epsilon_{\perp}, \text{ respectively,}$$

Hence the equilibrium condition of the director  $\vec{n}$  alignment is reached for  $n$  parallel or perpendicular to the field, respectively.



This means that in the 1st case (induced dipole parallel  $\parallel$ ) a nematic director kept horizontal by some reason

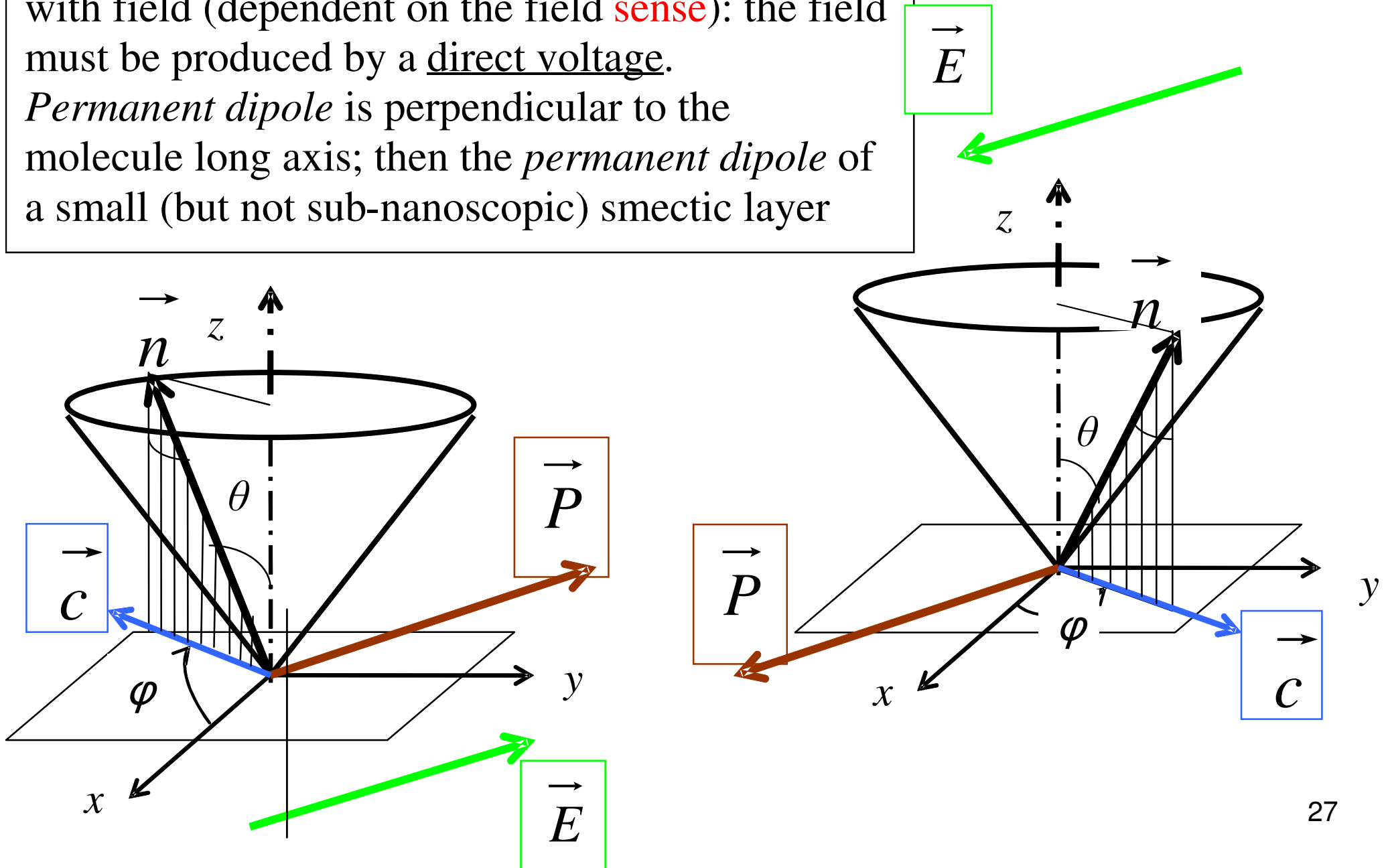


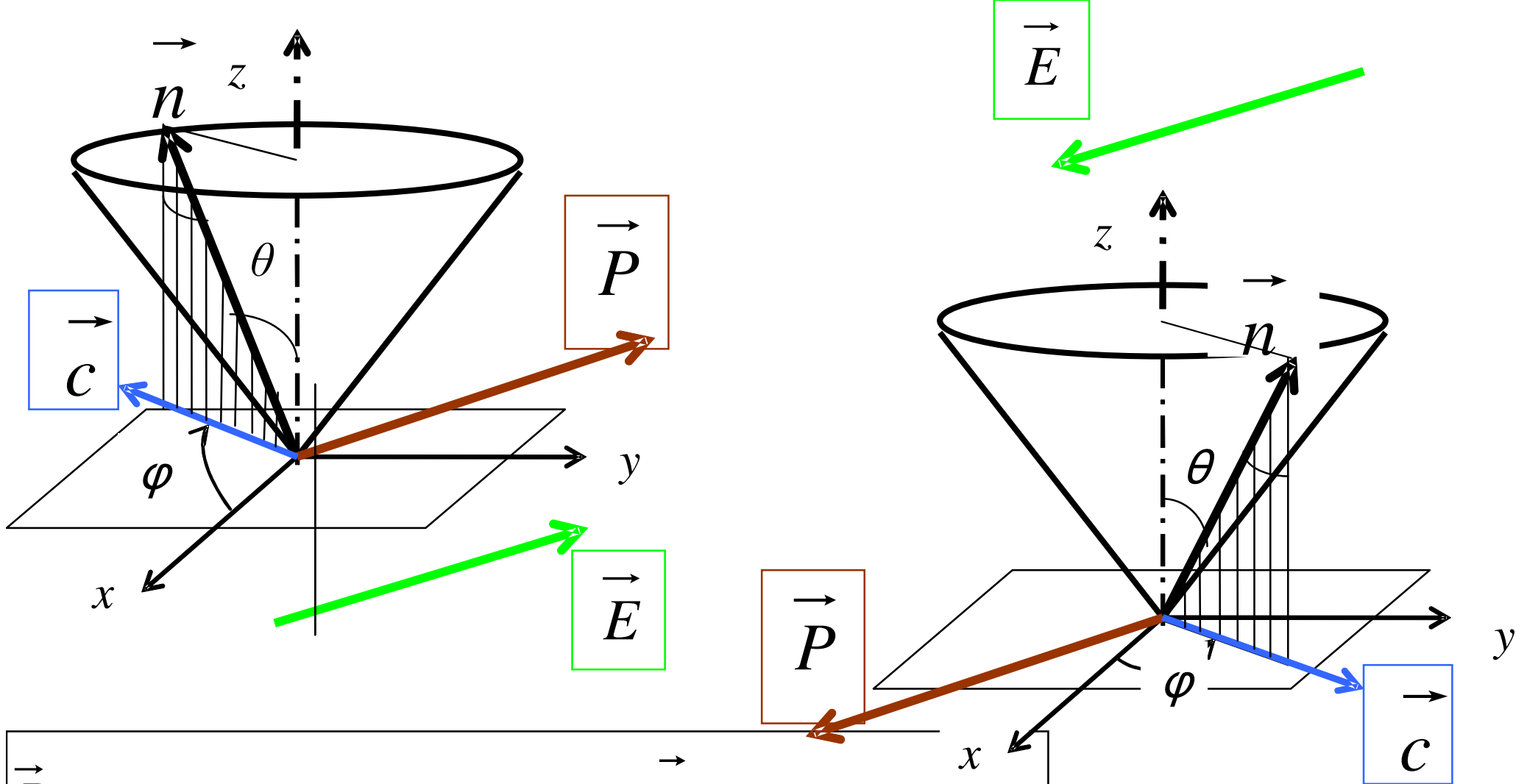
can be turned by the application of a convenient electric field  $\vec{E}$

# SMECTIC C\*FERROELECTRIC LC

Materials with molecules exhibiting *permanent dipoles* are used. Then the interaction is **linear** with field (dependent on the field **sense**): the field must be produced by a direct voltage.

*Permanent dipole* is perpendicular to the molecule long axis; then the *permanent dipole* of a small (but not sub-nanoscopic) smectic layer





$\vec{P}$  is perpendicular to the director  $\vec{n}$  and to the azimuthal director  $\vec{C}$ . By changing the **sense** of  $\vec{E}$ ,  $\vec{n}$  turns around the  $\theta$ -cone, and  $\vec{C}$  turns as well. In the absence of constraints,  $\Delta\varphi = \pi$ .



# **1.3. Surface-Field Competition**

**Alfredo Strigazzi, Senior Professor, Dept of Applied Science and Technology (DISAT), Politecnico di Torino, Torino, Italy**

**MEPhI, Moscow, 10 September 2014**

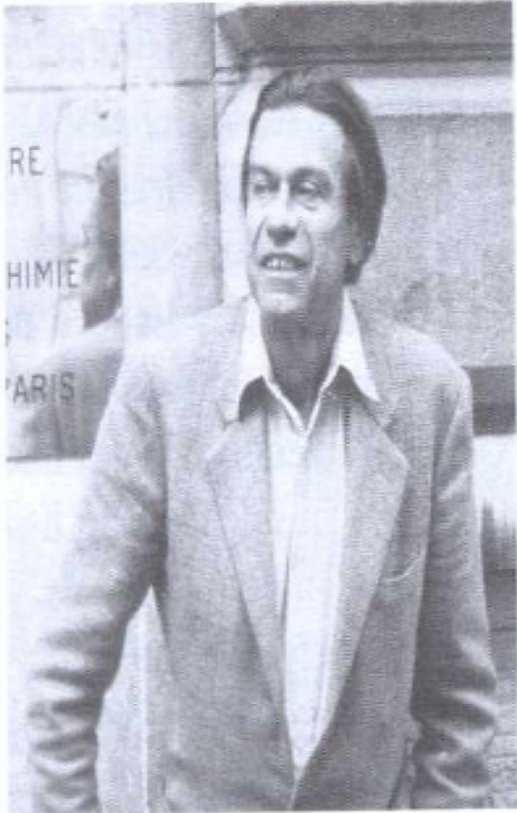


Figure 8.7 Pierre-Gilles de Gennes (1932–2007).

College de France, and Orsay group, worldwide animator of modern LC research.

Nobel Prize in Physics, 1991, due to his work in LC, Polymers, and complex liquids

It was established Landau-de Gennes theory of LC

## 1.3.1. LC-Surface interaction: anchoring

For application as signal transducers, LC must be organized in *macroscopic* (front size = 0.25 - 100 mm<sup>2</sup>, thickness = 2 – 10 μm) “*monocrystals*”, i.e. homogeneous samples.

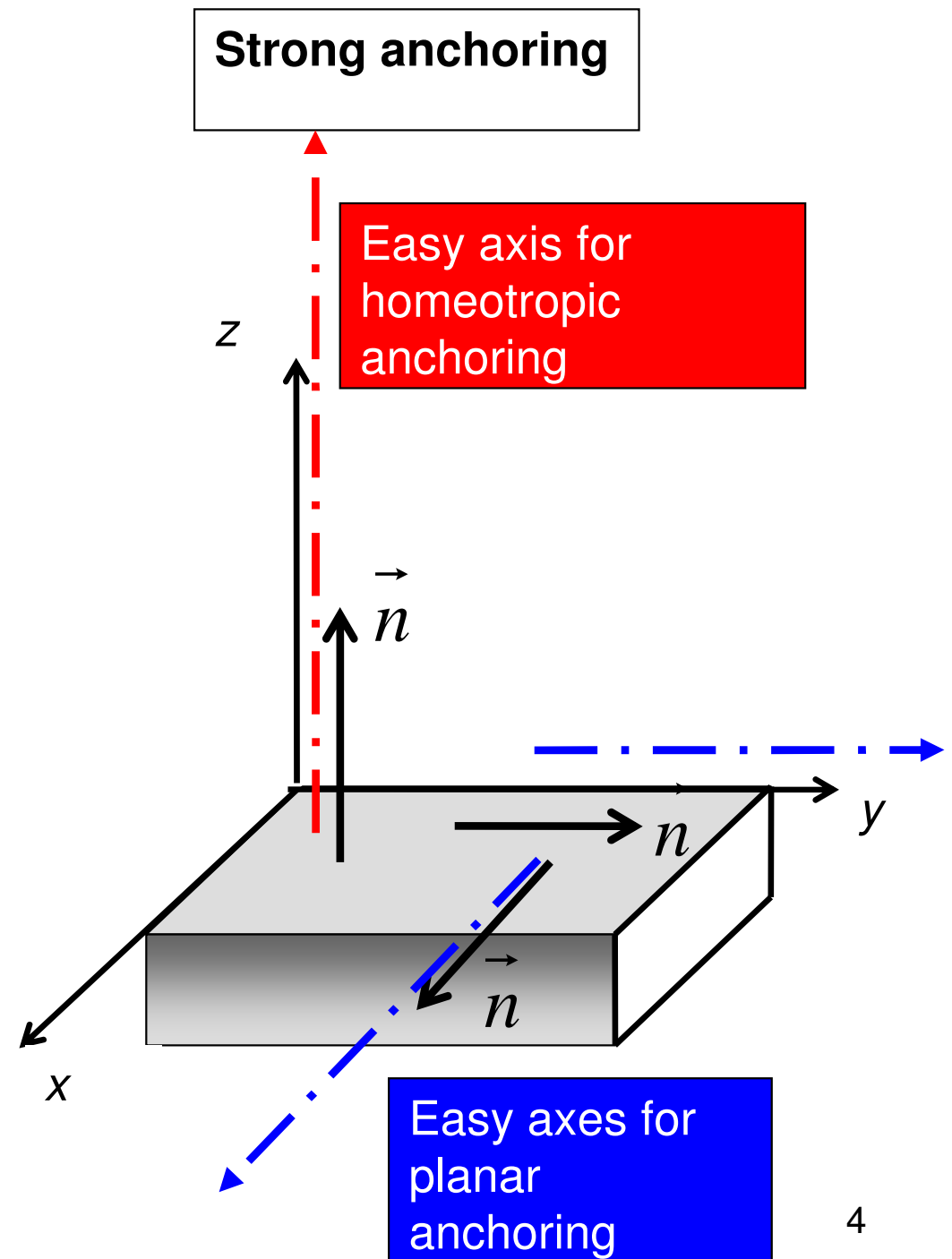
This is possible to obtain via surface interaction.

A LC-cell is a sandwich made by 2 glass plates treated in order to ensure both transparency and applicability of a voltage, taking care to avoid charge injection, using an insulating layer in contact with LC.

Through H-bonds LC molecules are attached to the internal surface layer of the glass plates, by means of either rubbing, or carving, or surfactant deposition.

2 are the anchoring modes, **homeotropic** and **planar**.  
Also the anchoring strengths are 2: **strong-** and **weak**.

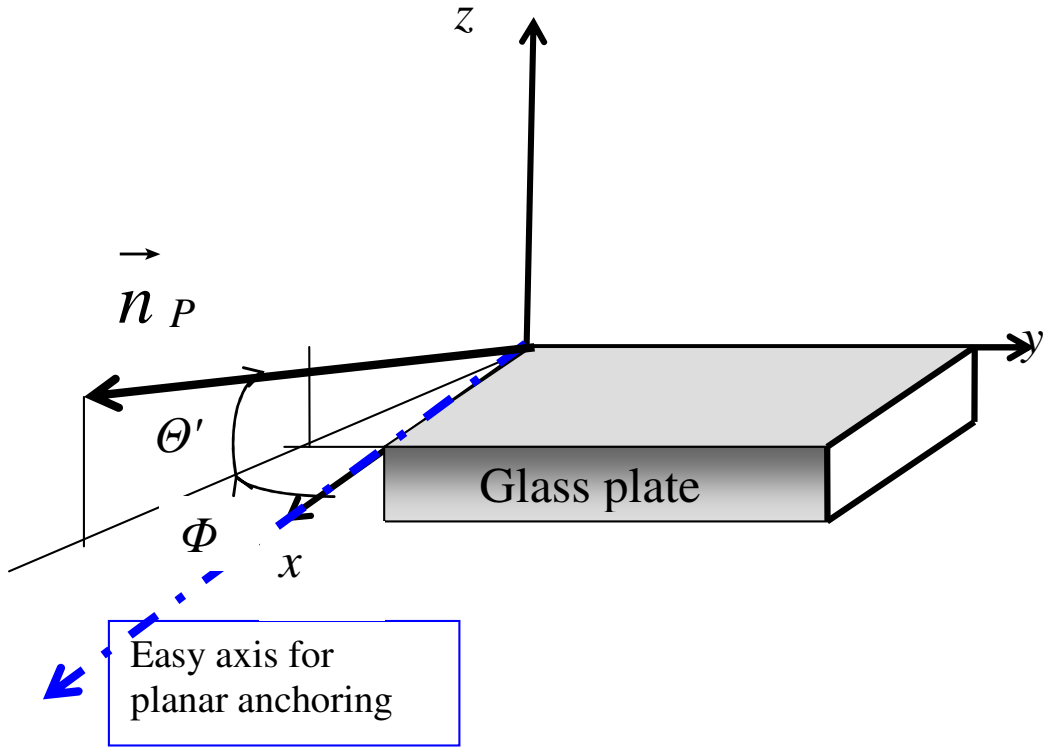
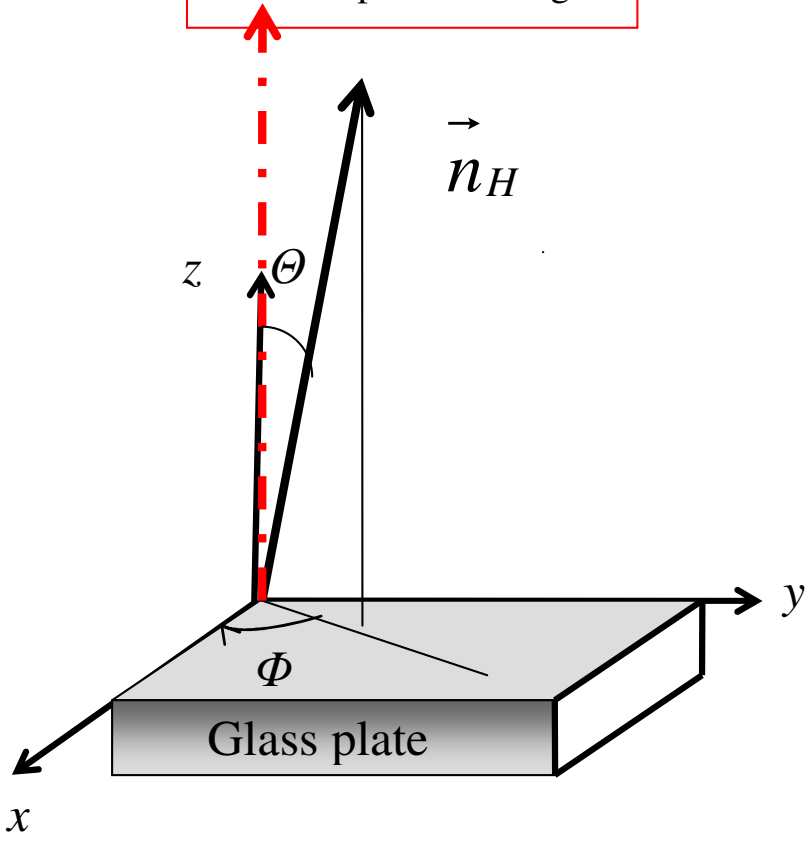
For strong anchoring the surface energy is much larger than any other energy involved, and can be considered as infinite.



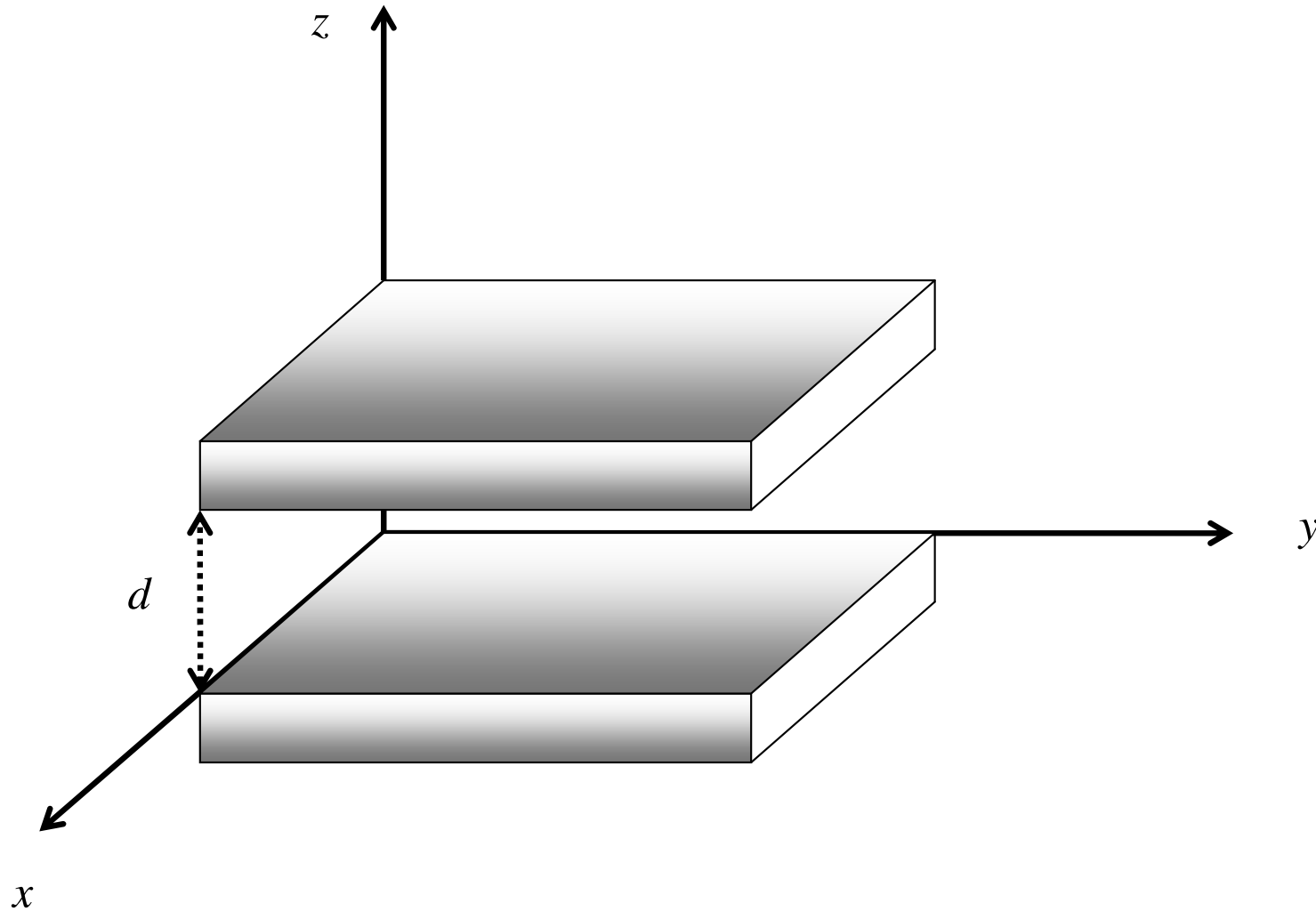
For **weak anchoring** the surface energy is comparable with others: then the actual surface alignment can be different than the one requested by the anchoring.

**Weak anchoring**

Easy axis for homeotropic anchoring



By establishing a proper anchoring on both glass plates a “*monocrystal*” cell can be constructed



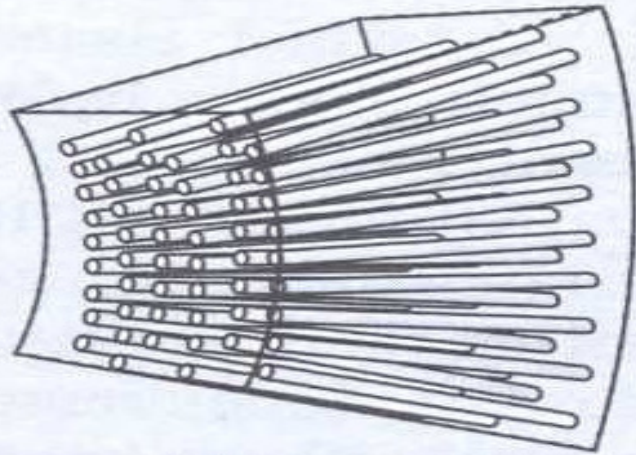
*Pixels* are “monocrystal” cells

# 1.3.2. Main Elastic Distortion Modes

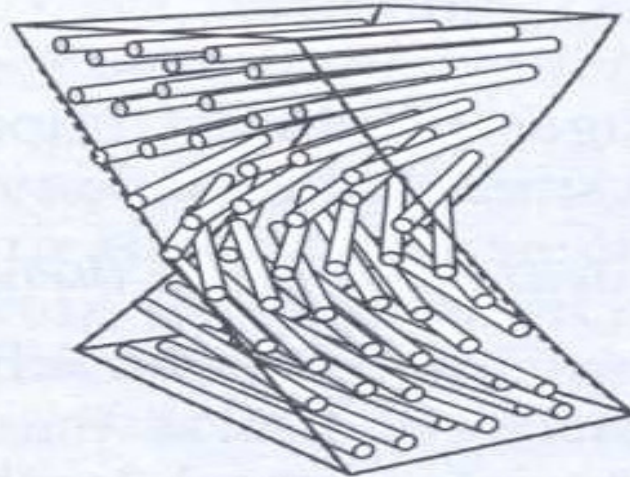
as presented in the elastic continuum theory  
(pioneers **Oseen** and **Zocher**)



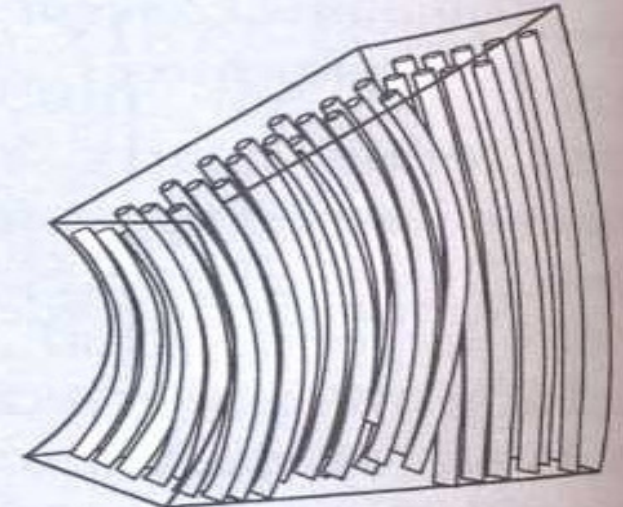
The great triumph of the theory of Oseen was to formulate this, if not in an easily understandable fashion, at least in a way that made some predictions. The great conclusion of his work was that four parameters were required to define the elasticity of a liquid crystal. Actually we now know that for most purposes three elastic constants are enough, and these determine the ease with which a liquid crystal, or more properly the director of a liquid crystal, can be distorted. These are known as elastic constants for splay, twist, and bend, and a representation of these deformations is given below.



splay deformation



twist deformation

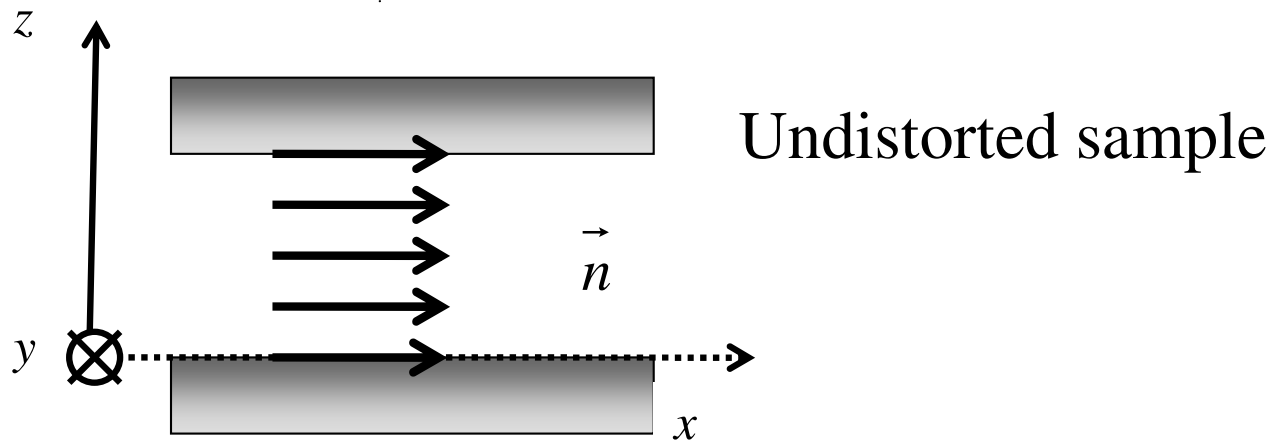


bend deformation

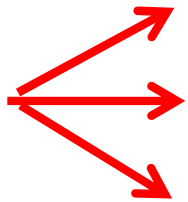
In an unaligned liquid crystal the director will wander around in the liquid crystal, and so there will be a combination of splay, twist and bend deformations. If the liquid crystal is aligned, then these deformations can be forced out and the director lines are everywhere parallel to each other.

Nematic liquid crystals can support splay, twist, and bend deformations, but if layers form, as in smectic phases, then only a splay deformation is possible. For tilted smectic phases (see later) the situation is more complicated since there are now two directors.

# Bulk distortion modes

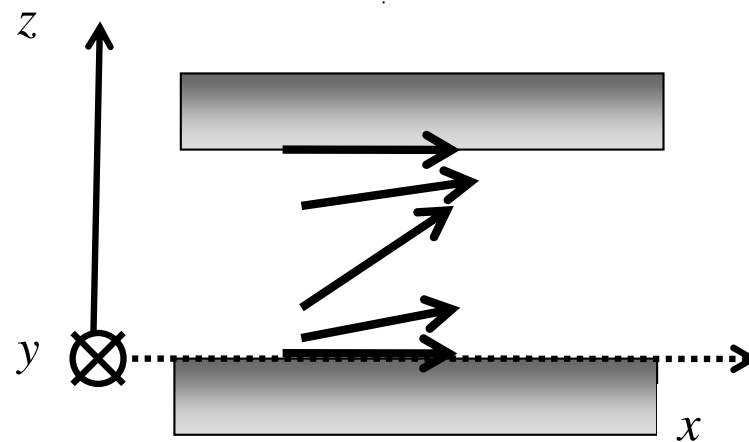


1<sup>st</sup> mode: radial distortion = splay



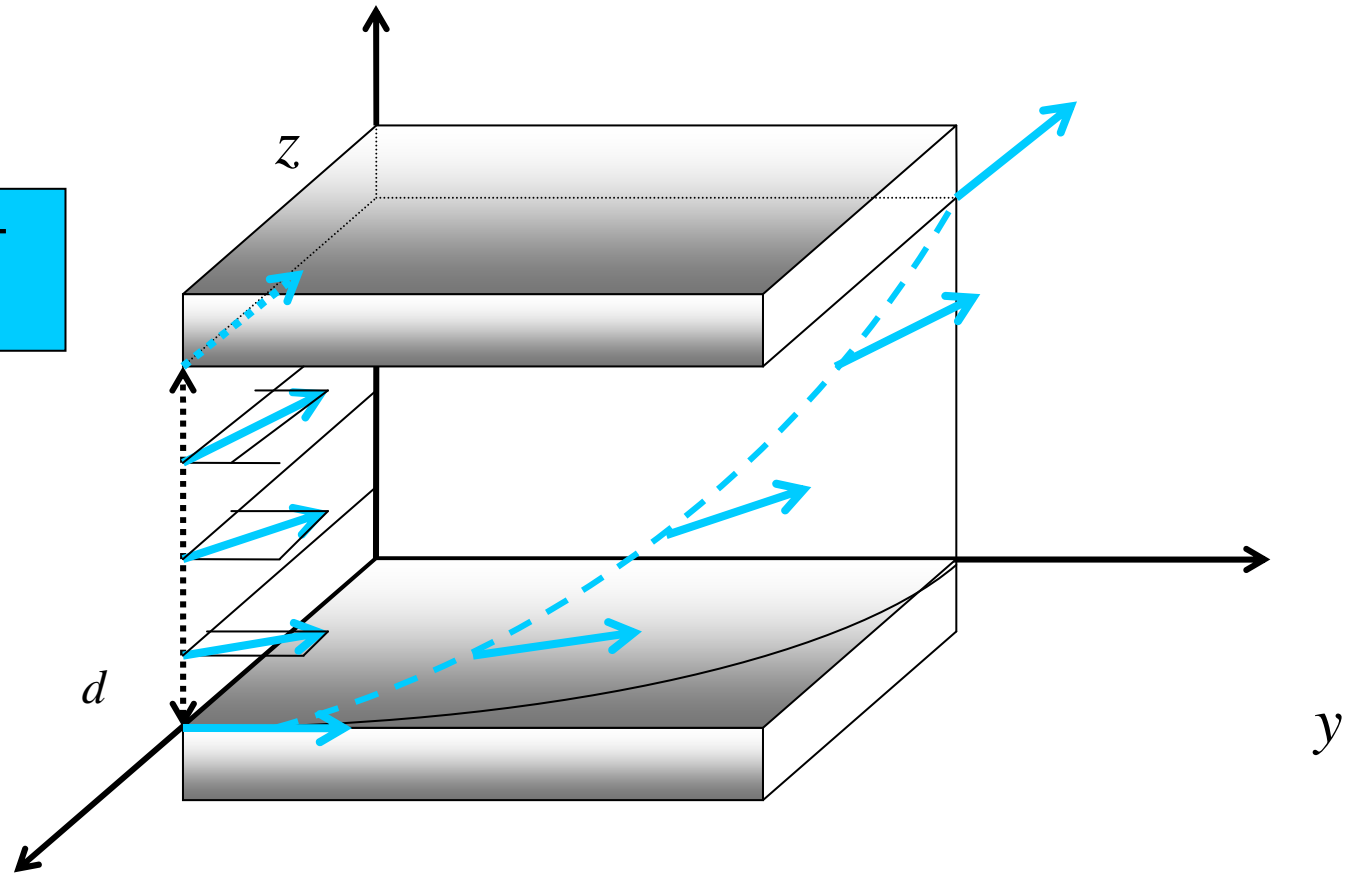
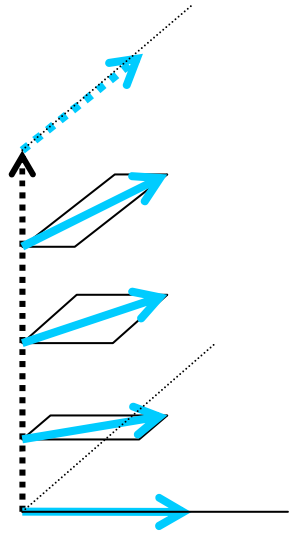
**SPLAY**

$$f_S = \frac{1}{2} K_{11} (\text{div} \vec{n})^2$$



2<sup>nd</sup> mode: screw = twist

TWIST

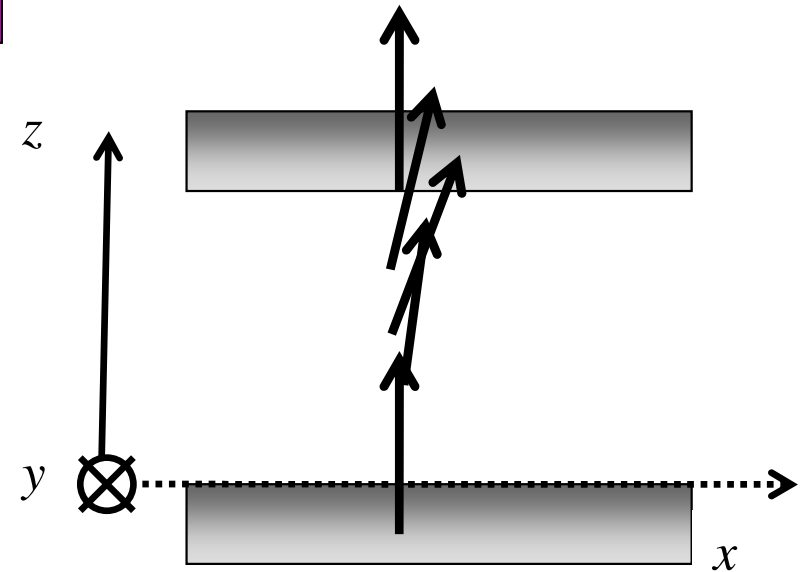
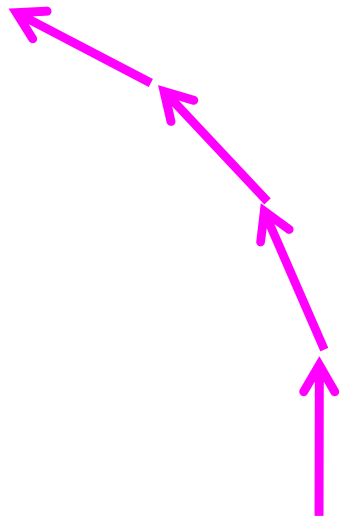


$$f_T = \frac{1}{2} K_{22} (\vec{n} \cdot \text{rot} \vec{n})^2 \quad x$$

### 3<sup>rd</sup> mode: **tangential = bend**

**BEND**

$$f_B = \frac{1}{2} K_{33} (\vec{n} \times \text{rot} \vec{n})^2$$



## 1.3.3. Basic transitions driven by Electric field

V. Frederiks  
(1885-1944)

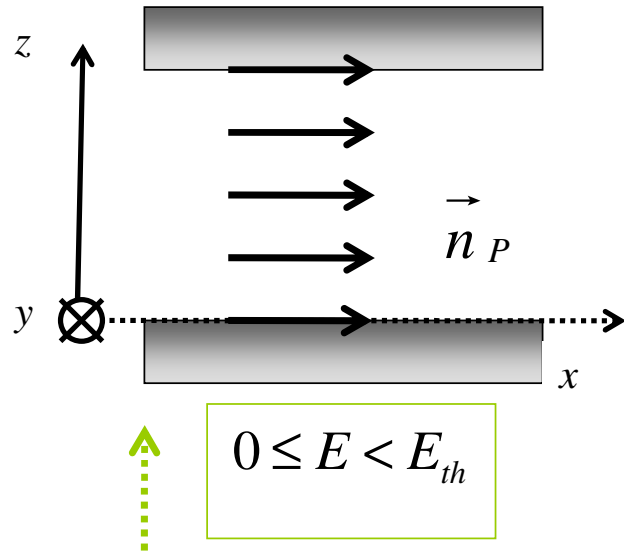


*А.С. Солин, В.Я. Френкель*

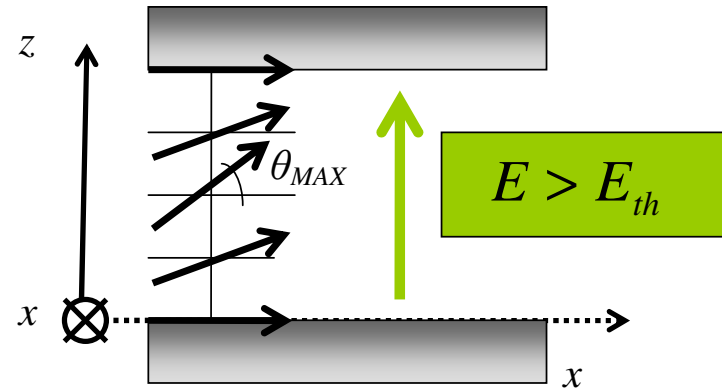
**Всеволод  
Константинович  
ФРЕДЕРИКС**

# Interaction of unidirectional planar NEMATICS with electric field

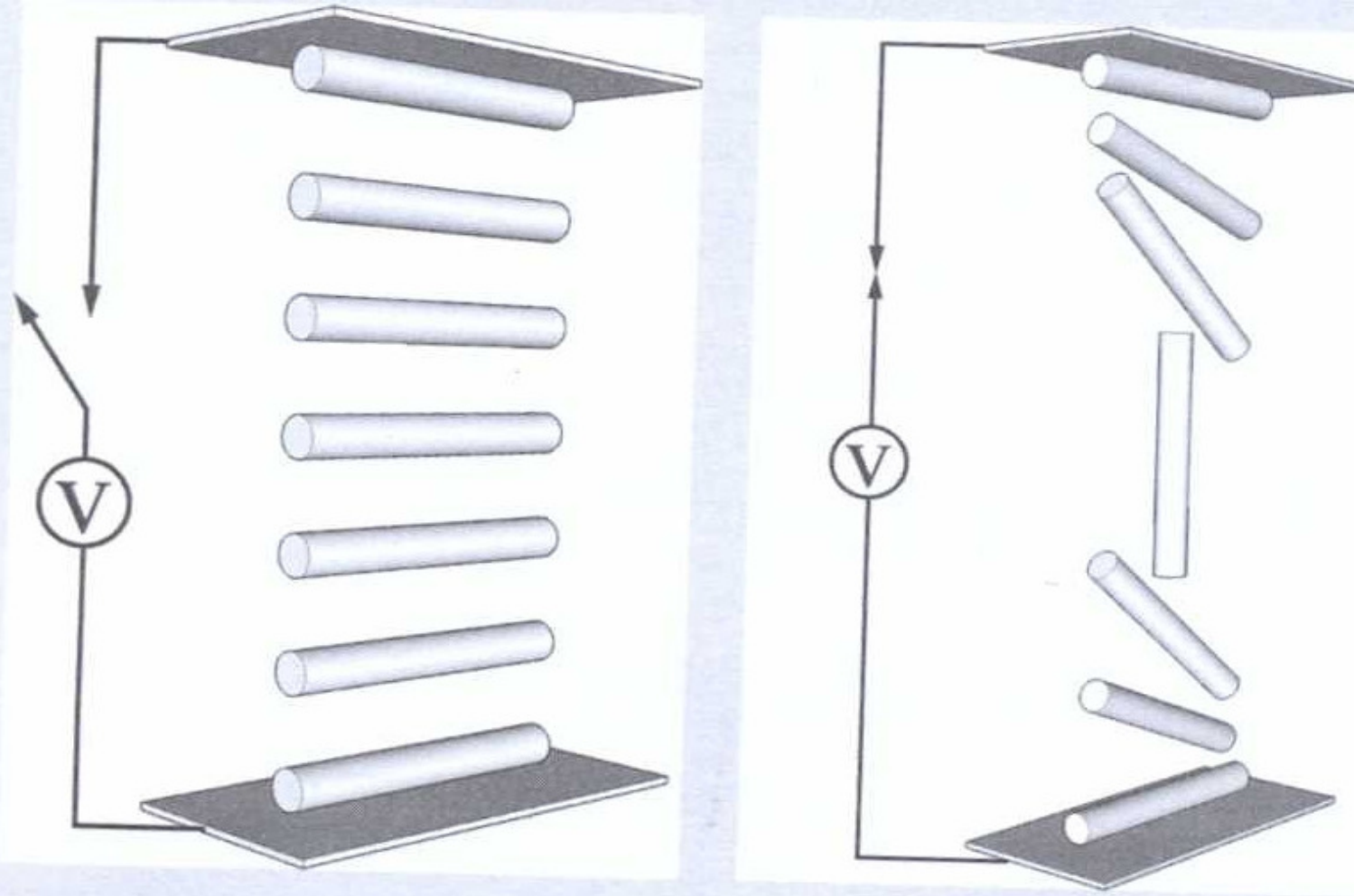
**Frederiks transition** in the conditions: NLC with  $\epsilon_a > 0$ , NLC-cell with unidirectional planar alignment and **strong anchoring**: *elastic distortion above a threshold.*



$$E_{th} = \frac{\pi}{d} \sqrt{\frac{K_{11}}{\epsilon_o \epsilon_a}}$$

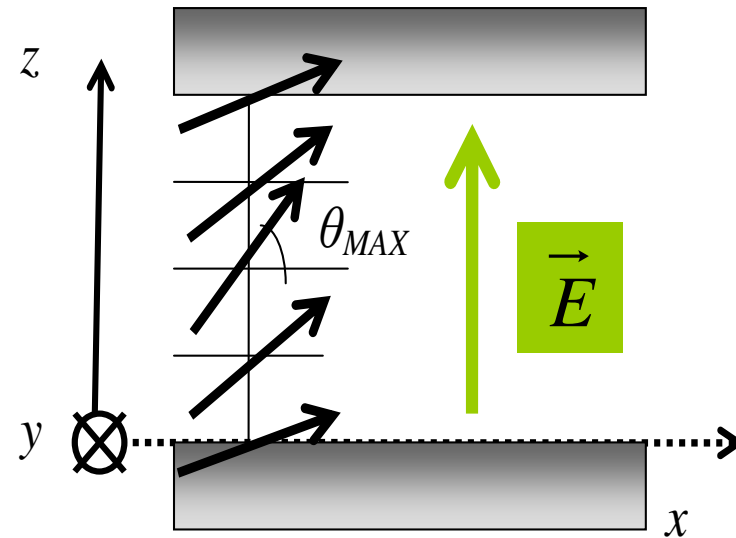
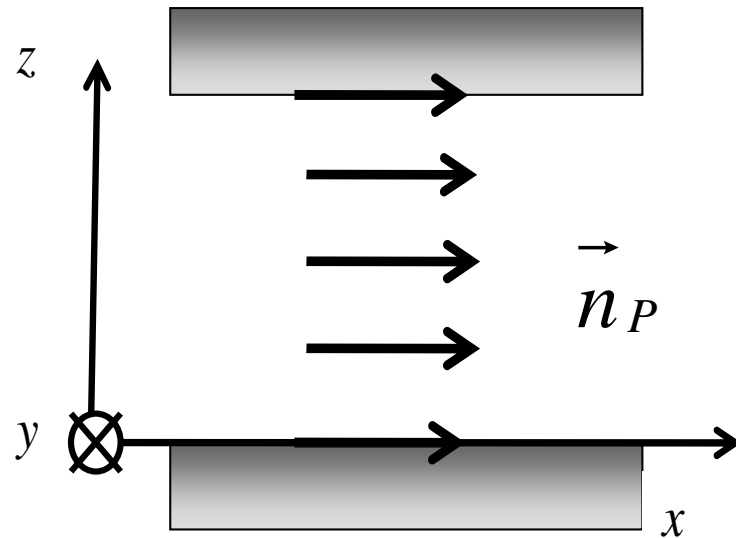


Strong anchoring implies planar alignment at the surfaces also in the presence of field



In the figures above, the Frederiks effect induced by an electric field is depicted. In the *off state* (left) the director is aligned by the surfaces of the top and bottom plates. When a voltage exceeding the threshold is applied between the plates the director realigns with the electric field between the plates to create the *on state* (right). The alignment of the director parallel to the electric field depends on the liquid crystal having the correct electric properties (positive dielectric anisotropy). These properties are determined by the chemical structure of the liquid crystal. It is possible to make liquid crystals with negative dielectric anisotropy, in which case they align perpendicular to an electric field.

**Frederiks transition** for unidirectional planar alignment in the case of **weak anchoring**:  
*elastic distortion with lower threshold*



$$E_{th}^w = \frac{\pi}{d + 2L} \sqrt{\frac{K_{11}}{\epsilon_o \epsilon_a}}$$

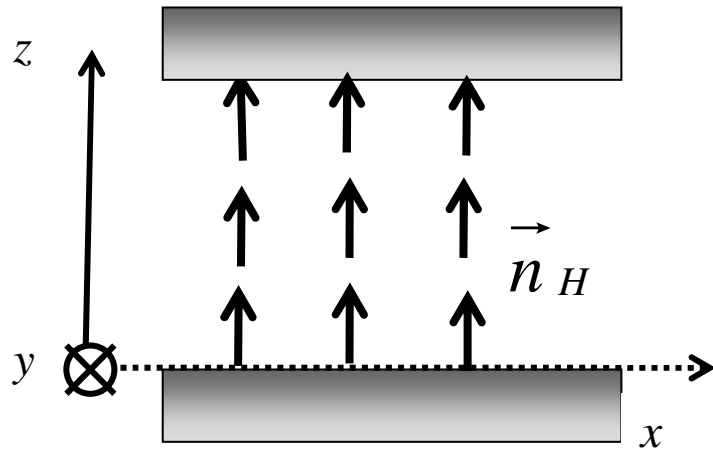
L= surface extrapolation length

1. The threshold field is lower;
2. The angle at the surface is small but positive



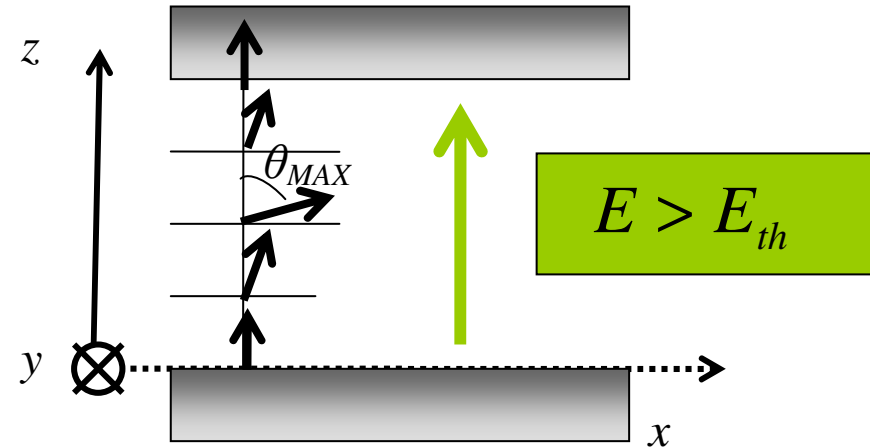
## Interaction of homeotropic NEMATICS with electric field

**Frederiks transition** in the dual conditions: NLC with  $\epsilon_a < 0$ , NLC-cell with homeotropic alignment and **strong anchoring**: *elastic distortion above a threshold.*



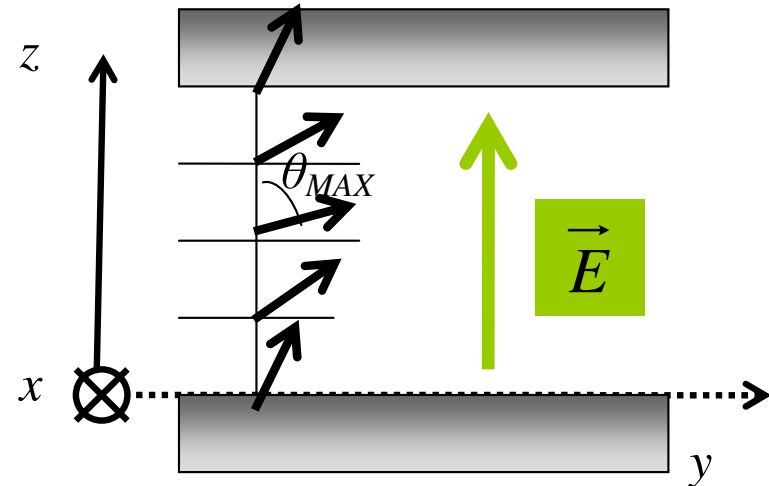
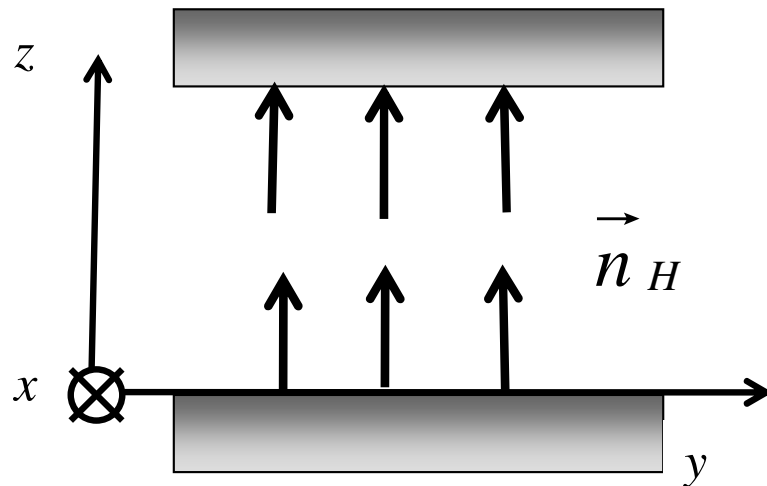
$$0 \leq E < E_{th}$$

$$E_{th} = \frac{\pi}{d} \sqrt{\frac{K_{33}}{\epsilon_o |\epsilon_a|}}$$



Strong anchoring implies homeotropic alignment at the surfaces also in the presence of field

**Frederiks transition** for homeotropic alignment  
in the case of **weak anchoring**:  
*elastic distortion with lower threshold*

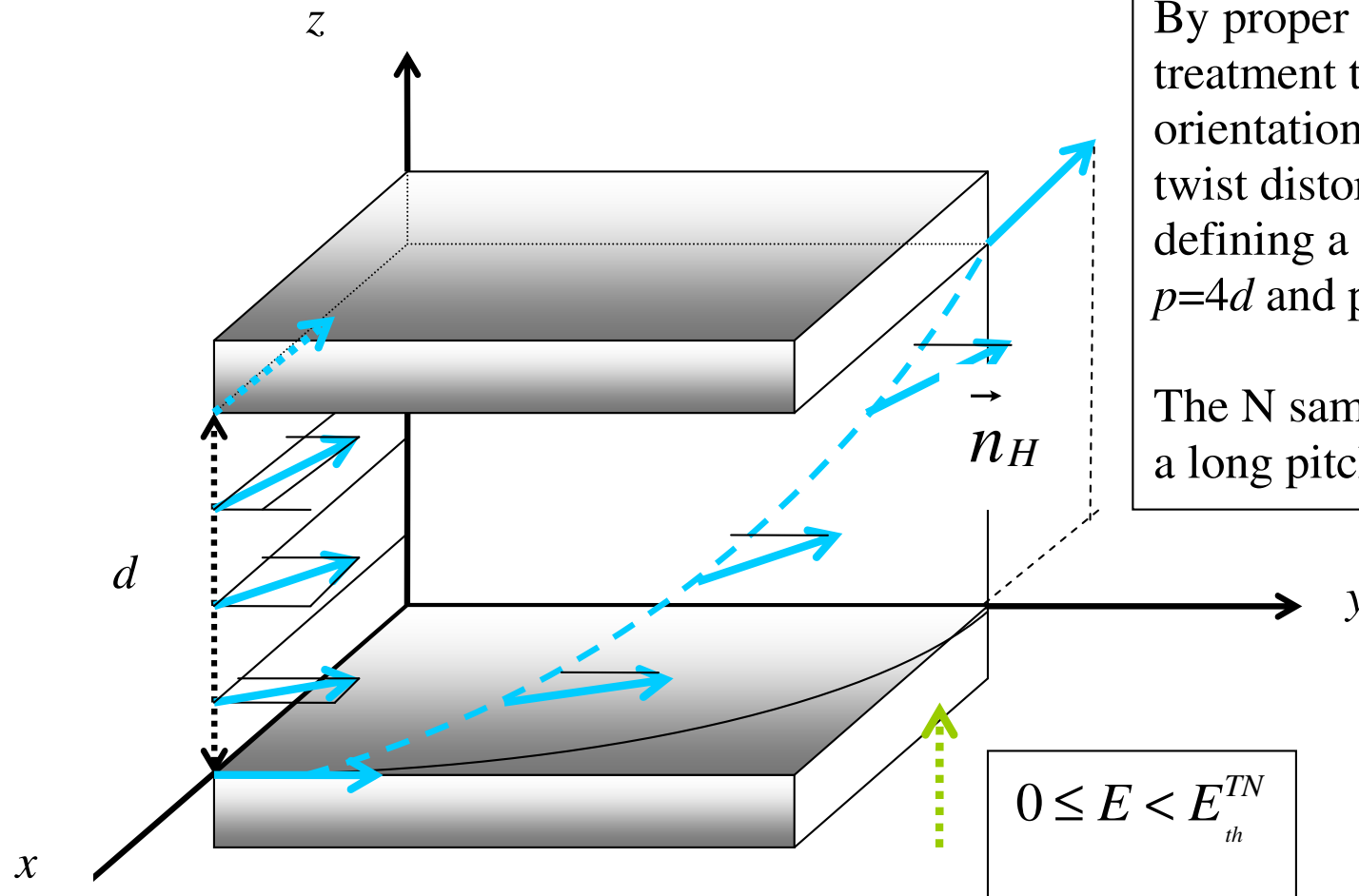


$$E_{th}^w = \frac{\pi}{d + 2L} \sqrt{\frac{K_{33}}{\epsilon_o |\epsilon_a|}}$$

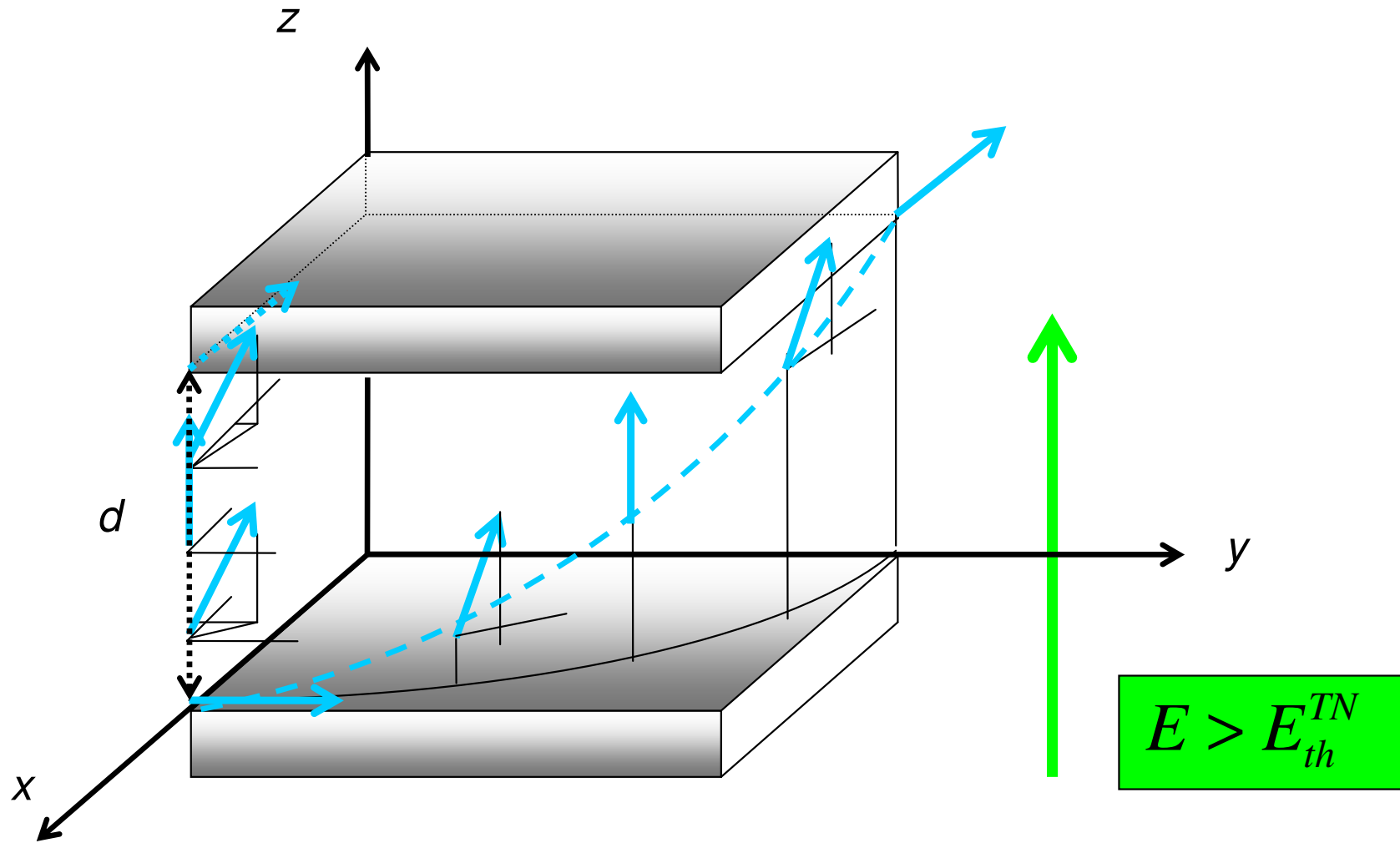
1. The threshold field is lower;
2. The angle at the surface is small but positive

## Twisted nematic (TN)-cell

The cell exhibits a simple distortion in the OFF-state. NLC has  $\varepsilon_a > 0$ , the NLC-cell is with planar  $90^\circ$ -twisted alignment and **strong anchoring**: getting a more complex *elastic distortion above a threshold*.

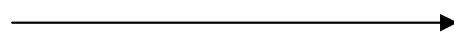
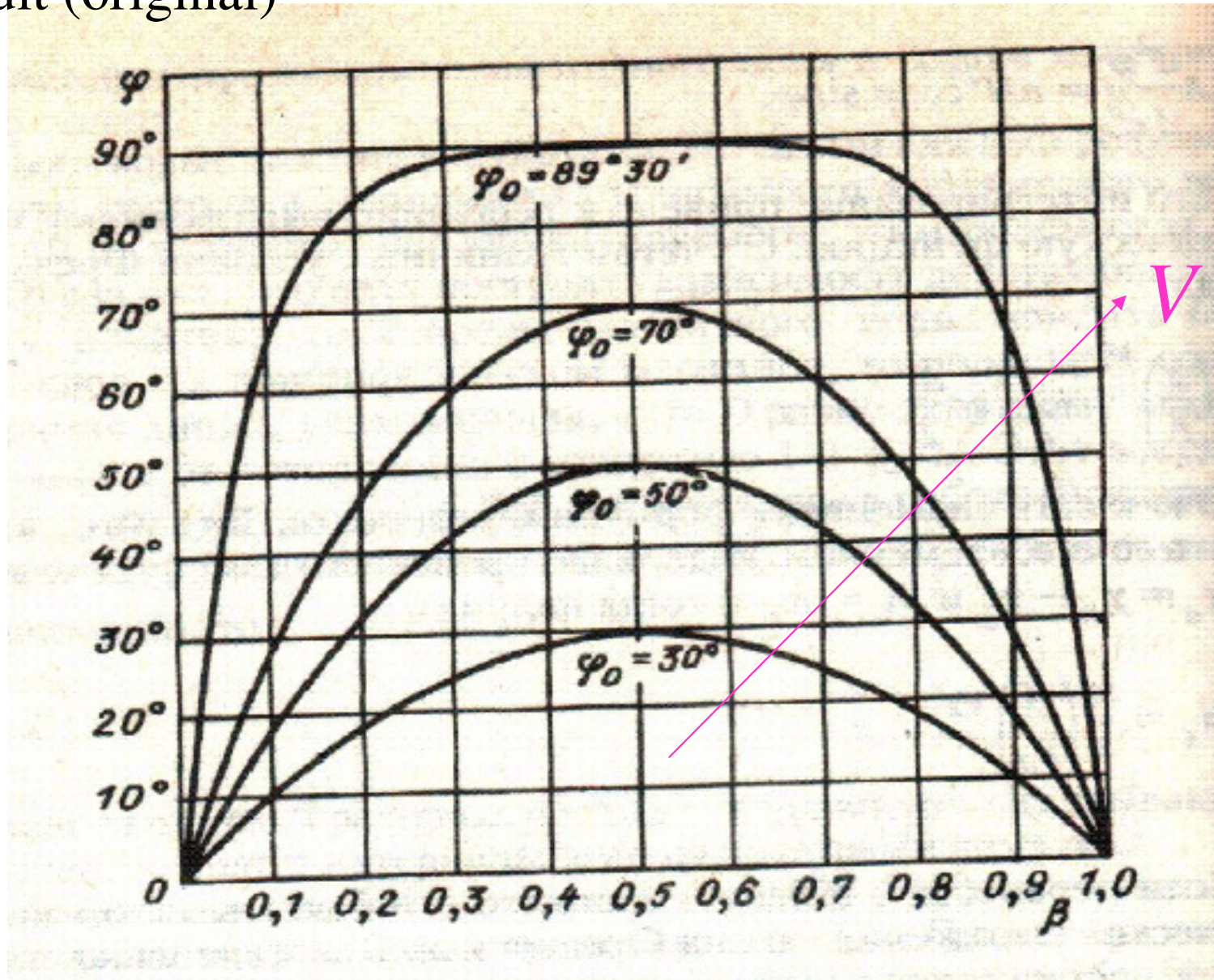


By applying an electric field above the threshold normal to the cell plates, the directors rotate about an angle as greater as higher is the distance from the closer surface.



# Frederiks result (original)

$\varphi$



$$\beta \equiv z/d$$

# 1.1. Conclusions

- LC are mesomorphic materials i.e. able to form mesophases, intermediate between crystal- and liquid state
- Due to their anisotropy, LC form textures
- LC are THERMOTROPICS (Nematics, Cholesterics, Smectis) or LYOTROPICS
- LC can be used as bricks and tiles by Life
- Due to the unit shape, LC can be DISCOTICS, CALAMITICS, and BANANA-like

## 1.2. Conclusions

- **Nematics** are 3D liquids with 1D orientational order
- **Cholesterics** are 3D liquids with 1D orientational chiral order
- **Smectics A, C, C\*, ... (B, ...)** are 2D (or 1D) liquids with 1D orientational achiral or chiral order
- **LC** can interact with **applied electric field**

# 1.3. CONCLUSIONS

- NLC distortion modes are: *splay, twist, bend*
- LC are sensitive to surface effect, and to applied fields, due to their anisotropy
- NLC aligned without distortion undergo Frederiks transition if subjected to normal electric field with intensity high enough



# 1. REFERENCES

1. D. Dunmur, T. Sluckin, “Soap, science, & flat-Screen TVs - A history of LC”, 2014, Oxford University Press, London
2. A.S. Sonin, V.Ya. Frenkel, “Vsevolod Konstantinovich Frederiks (1885-1944)”, 1995, Nauka Publishing House, Moscow (*in Russian*)