

APPENDIX

Can Bent-Core mesogenic molecules exhibit Ferroelectric response in Nematic phase?

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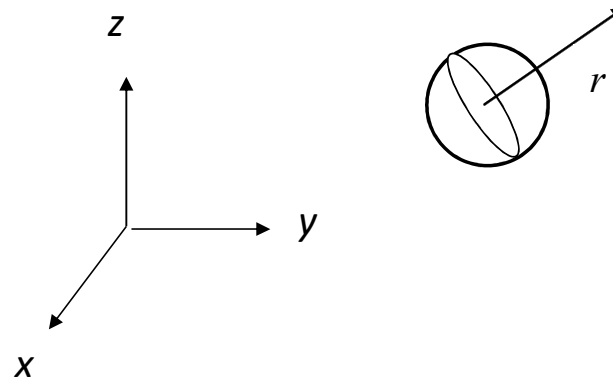
Liquid Crystals (LC) are the 4th state of matter, consisting of a *Mesophase* intermediate between Crystals and Liquid.

We will see that a mesogenic compound is made by elongated molecules (mlc).

On the contrary, 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 mlc) has 3 degrees of freedom* for the center of mass vibration around its equilibrium point (*positional symmetry*).

*Here «degree of freedom» means how many parameters it is necessary to give for defining the average position of an isotropic mlc : in Crystal state, 3 (the mlc centre of mass is free only to vibrate around one point; in Liquid state, zero (the mlc centre of mass can vary without limitations).

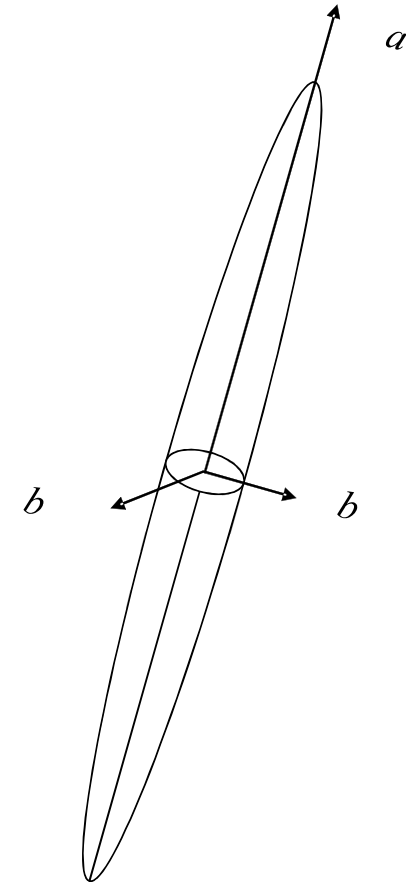
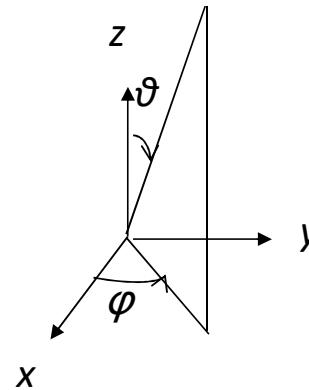


If the molecules are elongated, like in most organic compound, f.i. as rotational ellipsoids, they are **anisotropic** and **uniaxial**.

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

In total, 5 degrees of freedom are locally fixed for molecular equilibrium in **Crystal state**

None in **Liquid state**: the mlc can move each one among the others.



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

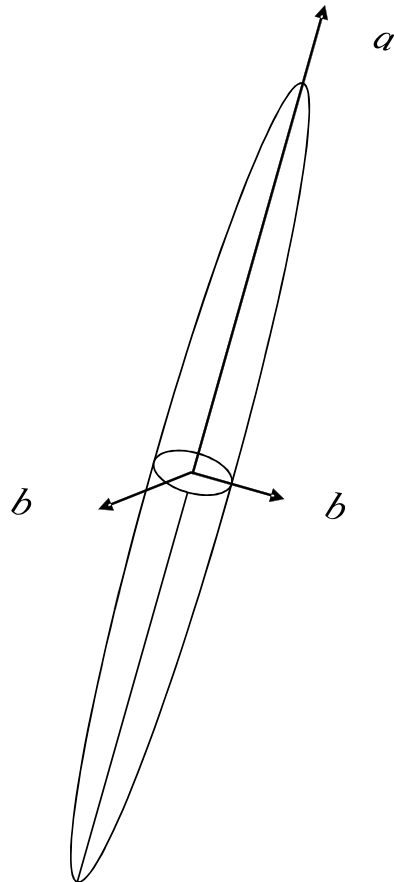
all symmetry disappear overcoming the melting point.

and Liquid Crystals ?

Are not these words a strange *oxymoron*?

Only at the end of 19^o 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 this



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)

If a compound is mesogenic, the melting point (from Crystal to Mesophase) will be different from the clearing point (from Mesophase to Liquid state)

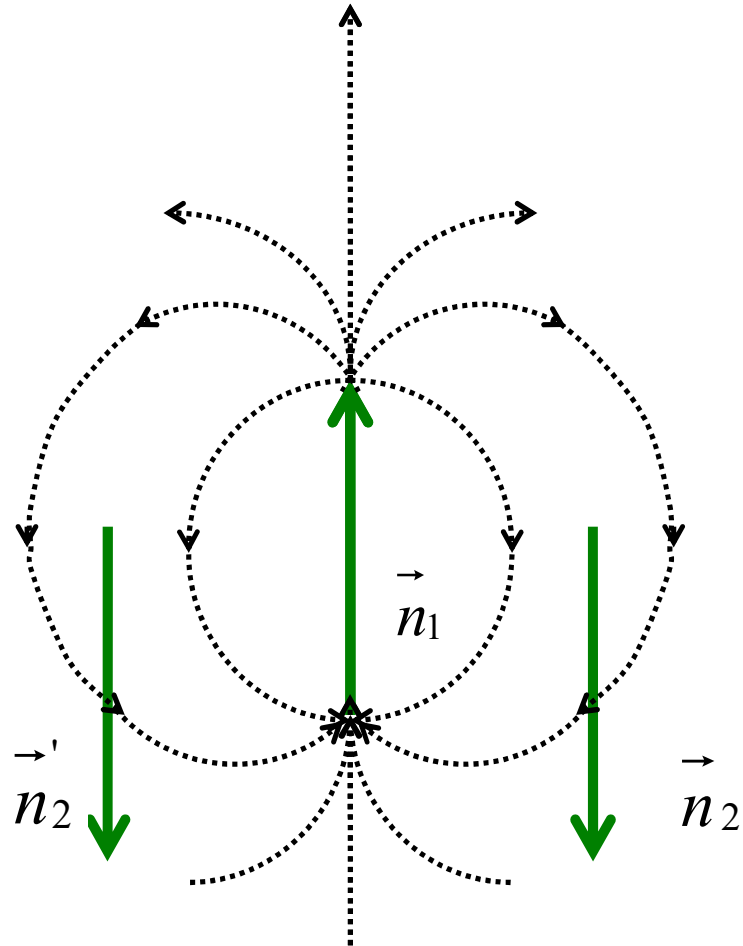
(the clearing point is called like this since usually the Liquid state is more transparent).

A compound in Liquid state is **isotropic**, whereas in Mesophase state it is **anisotropic**, then **birefringent**

Hence it is possible to observe LC textures with polarizing microscope with crossed polarizers

In the simplest case, if the Mesophase range depends only on temperature, we are speaking about Thermotropic LC

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

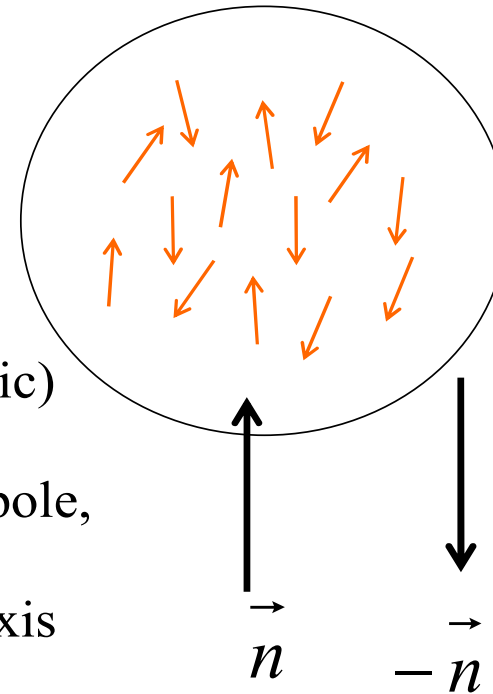
In a certain temperature interval, inside a very small (but not sub-nanosopic) volume, dV the molecules, which are elongated, usually possess an induced dipole, exhibiting a long range interaction.

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**”.

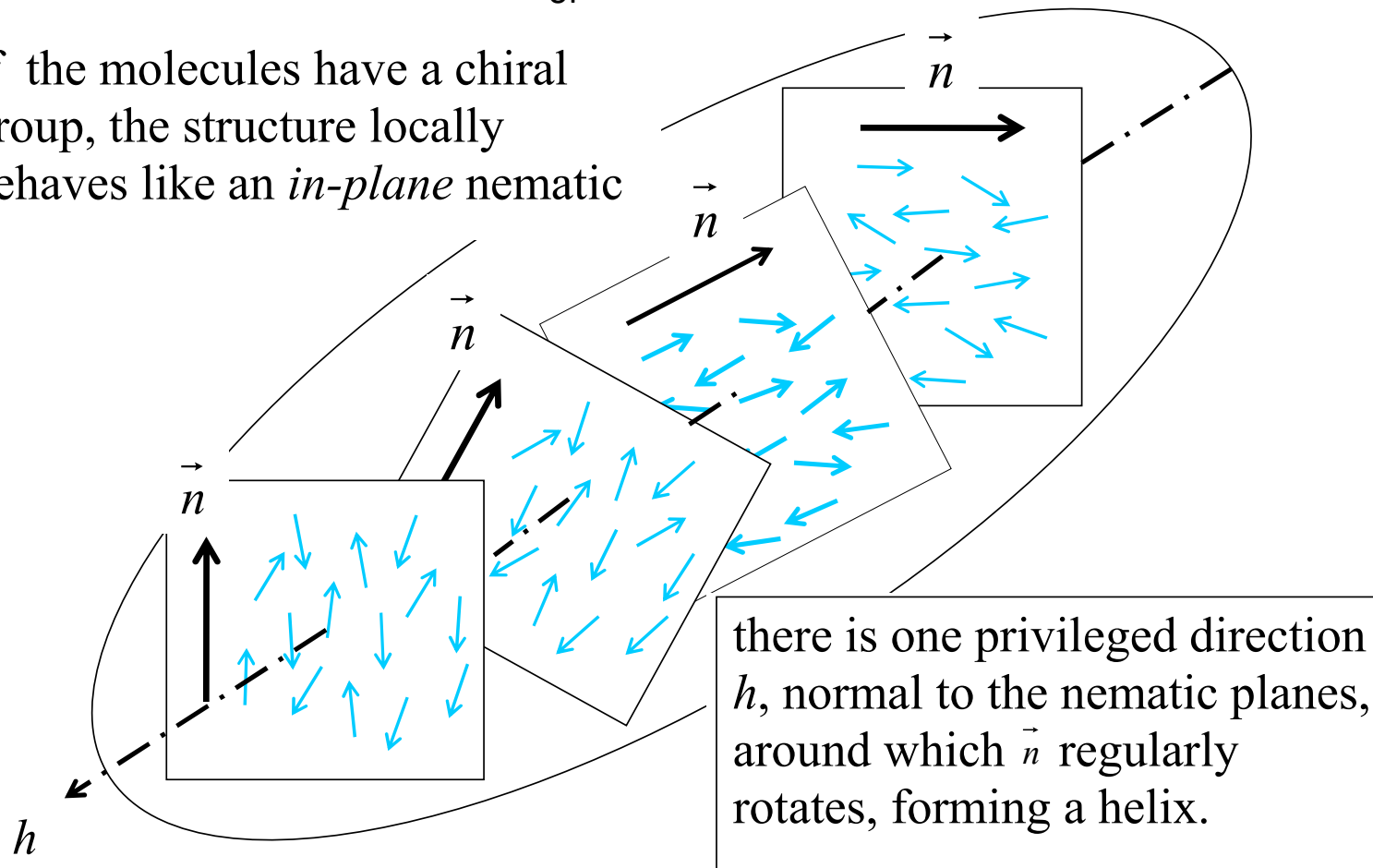
Mark that \vec{n} and $(-\vec{n})$ are equivalent for all physical properties.



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

CHIRAL NEMATIC STATE or CHOLESTERIC STATE

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

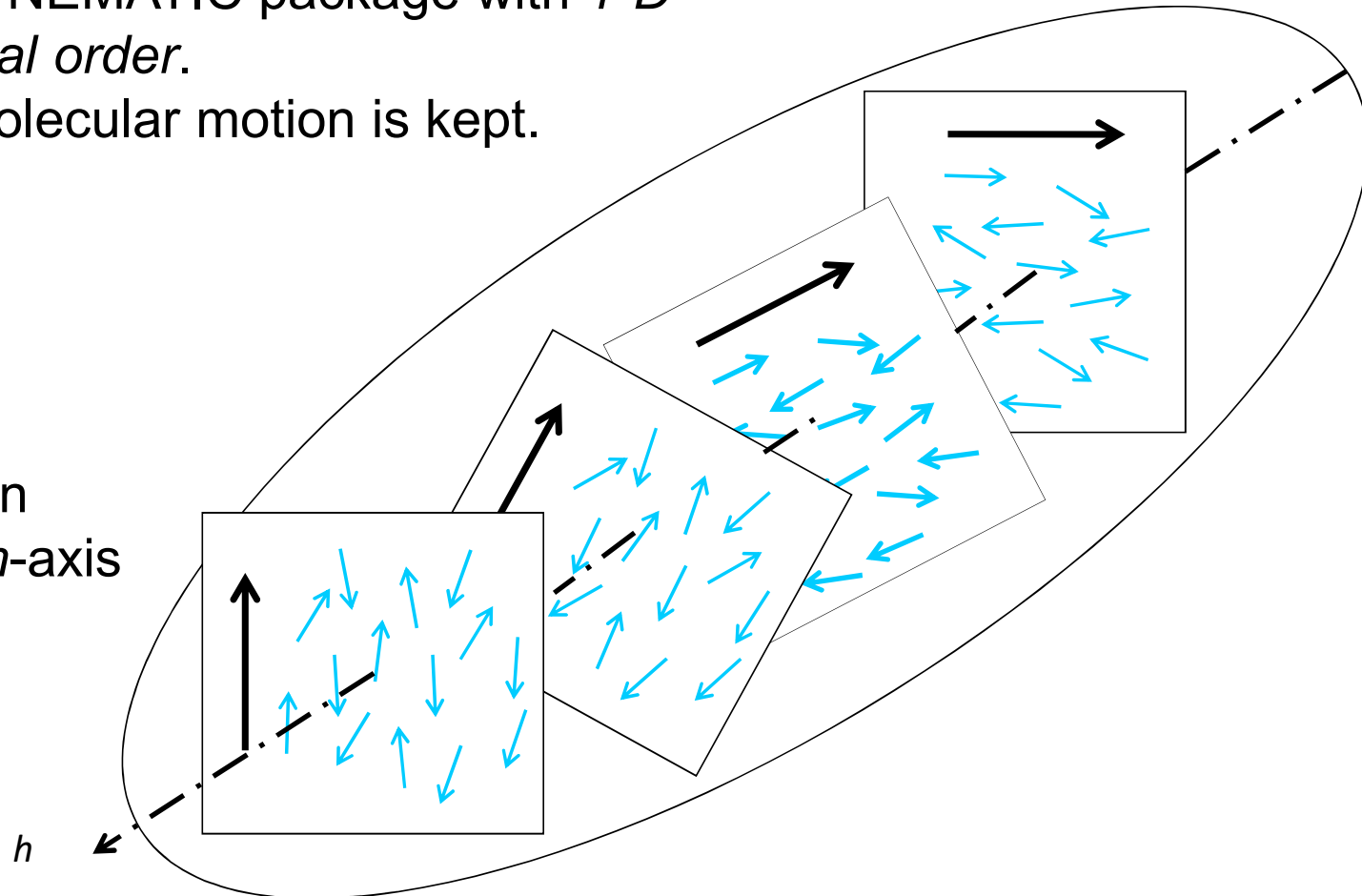


Remember that the helix is *ideal*!

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.

In each plane the average director (in black) is \perp to the h -axis



SMECTIC_A STATE

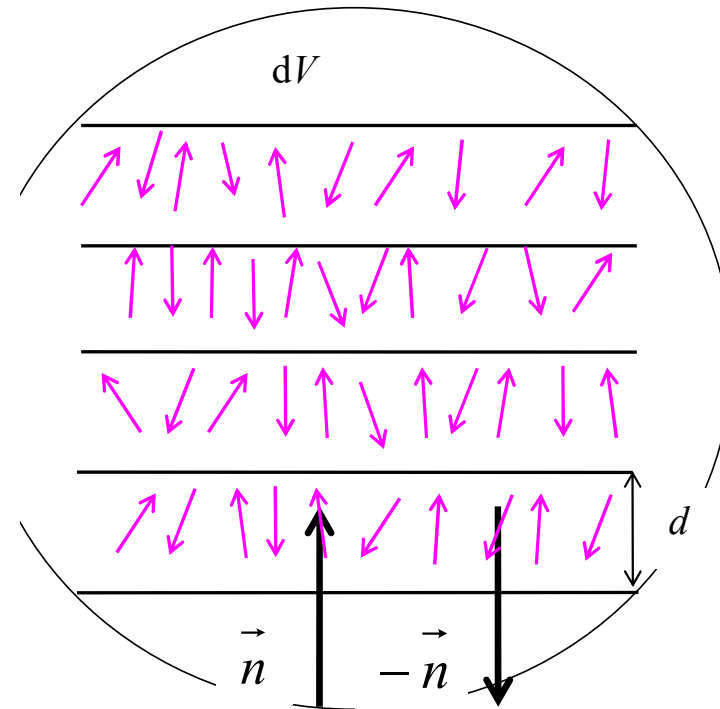
The smectic structure is closer to crystal state than the previous ones.

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

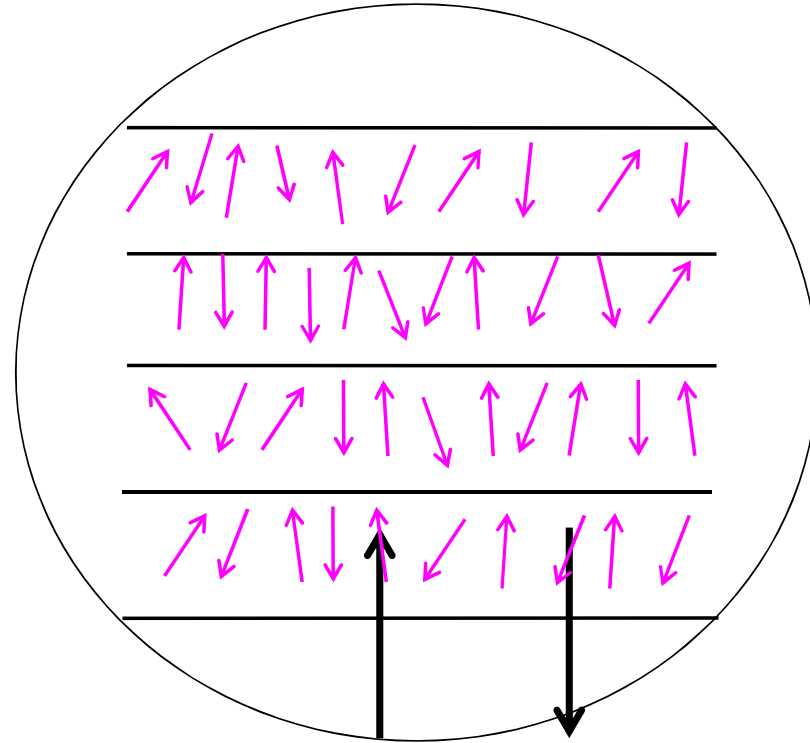
There are many Smectic ordering!

Smectic A is the simplest .

In a certain temperature interval, inside a very small (but not sub-nanosopic) 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.

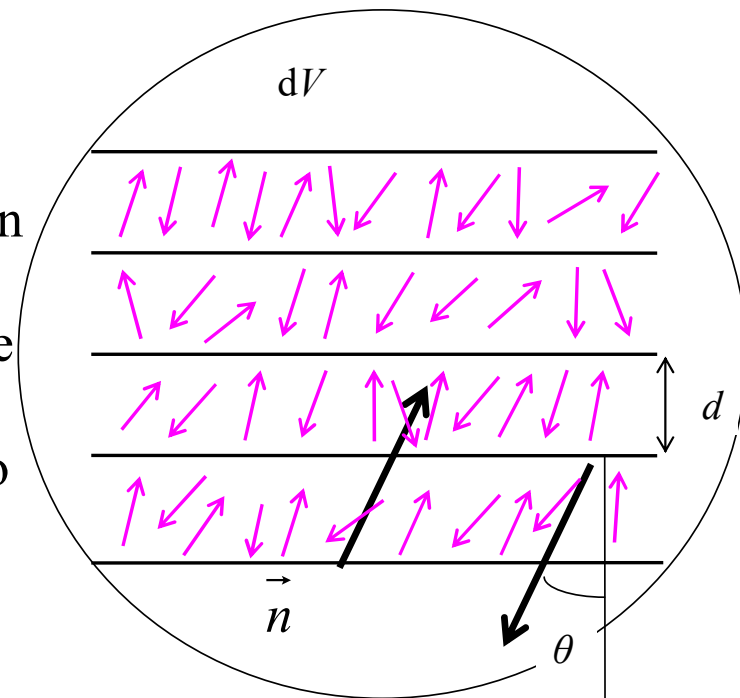
SMECTIC_C STATE

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 θ with respect to the normal to the smectic layers.

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

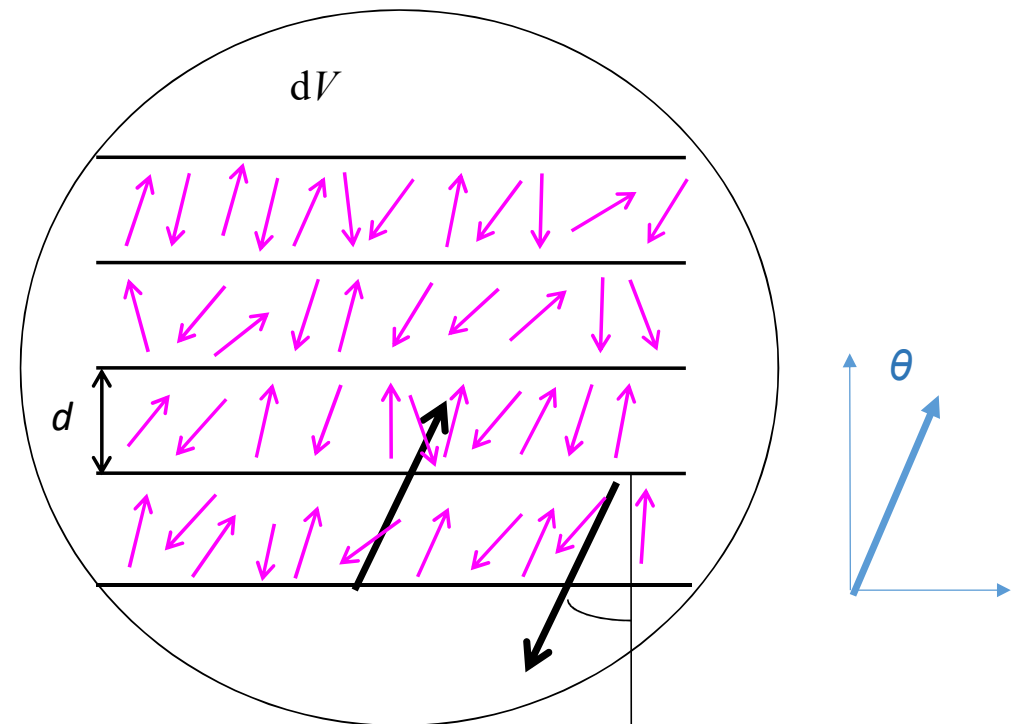


The layer thickness d is of the same order as the molecular length. The molecule centers of mass are relatively free to move inside each layer, as in an usual viscous liquid: but viscosity generally is higher than in nematics and cholesterics.

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

The average polar angle θ and azimuth $\varphi = 0$ are constant in all the sample.

If $\theta = 0$ the LC reduces to Sm A



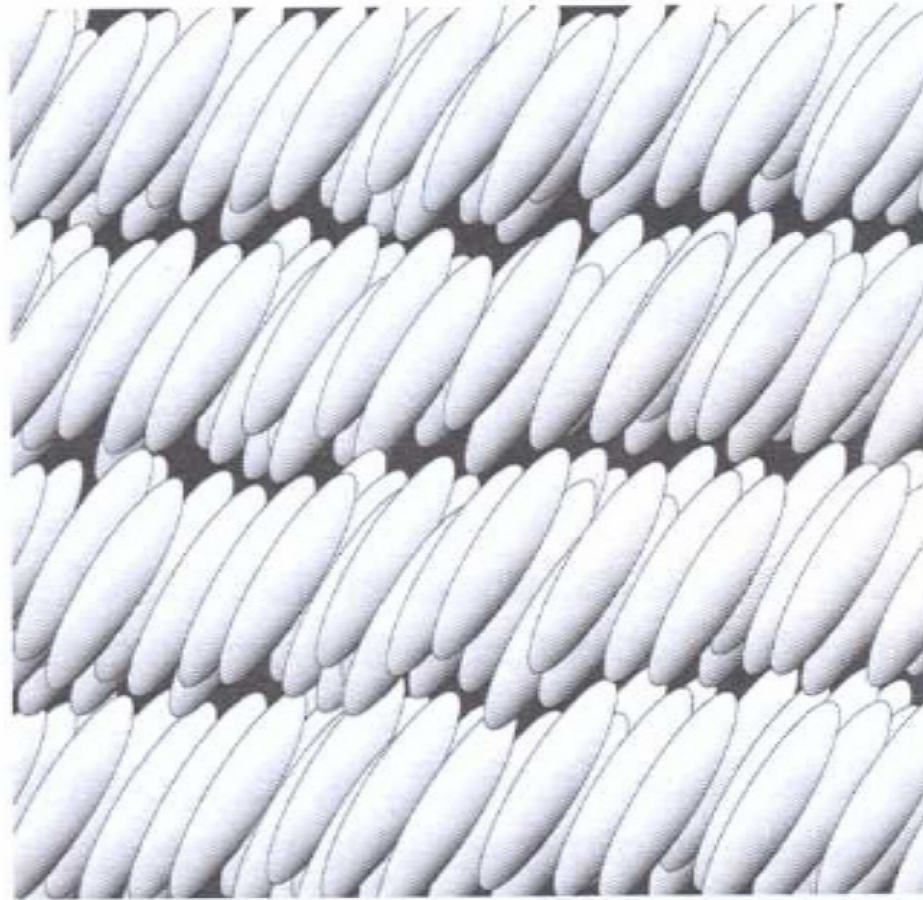


Figure 8.6 A representation of the molecular structure of a tilted smectic C phase. Compare this figure with the untilted structure of a smectic A phase in Technical Box 4.3.

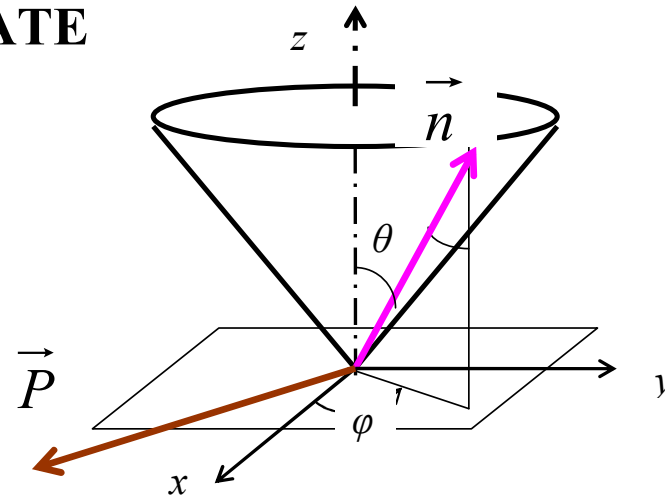
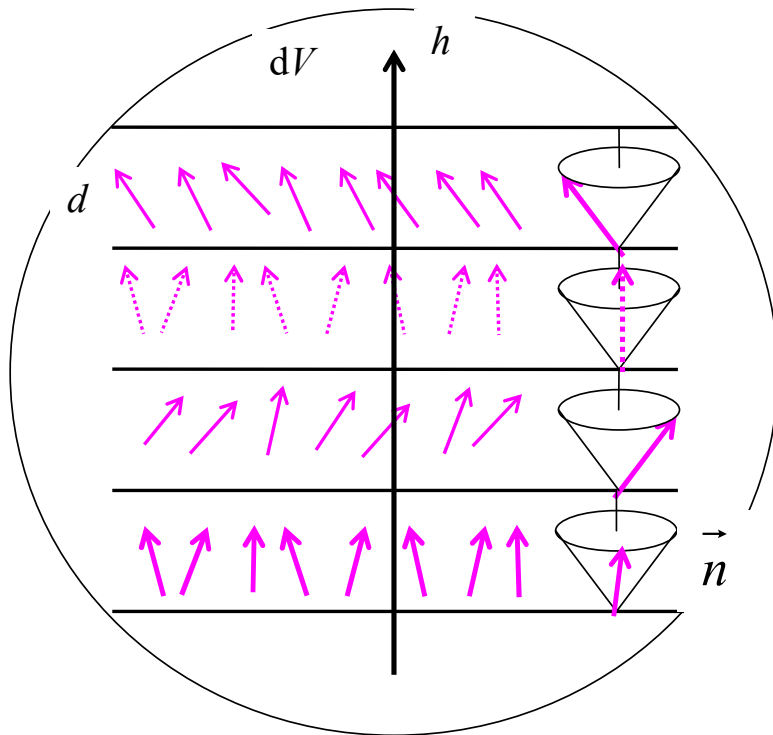
In LC compounds which exhibit as possible Mesophase the Nematic, Smectic A, Smectic C, the director (\mathbf{n}) is indistinguishable by $(-\mathbf{n})$

Then even if each mlc should have an induced or a permanent dipole, the dielectric polarization of a small but not nanoscopic volume dV is zero, since it contains a huge number of mlc, which compensate each other

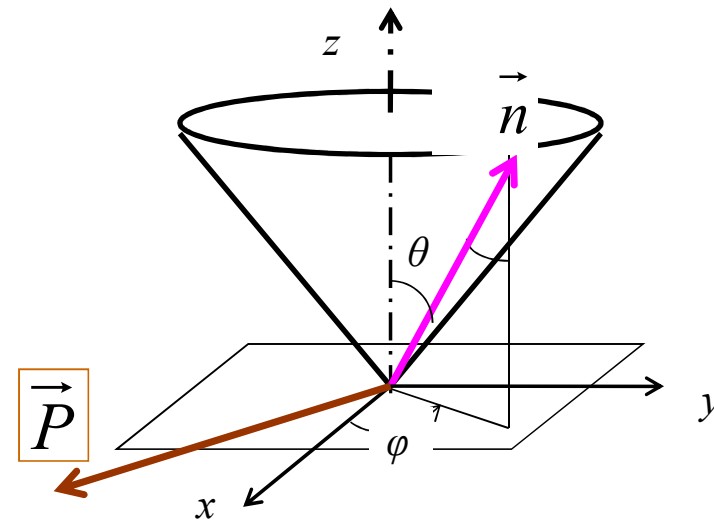
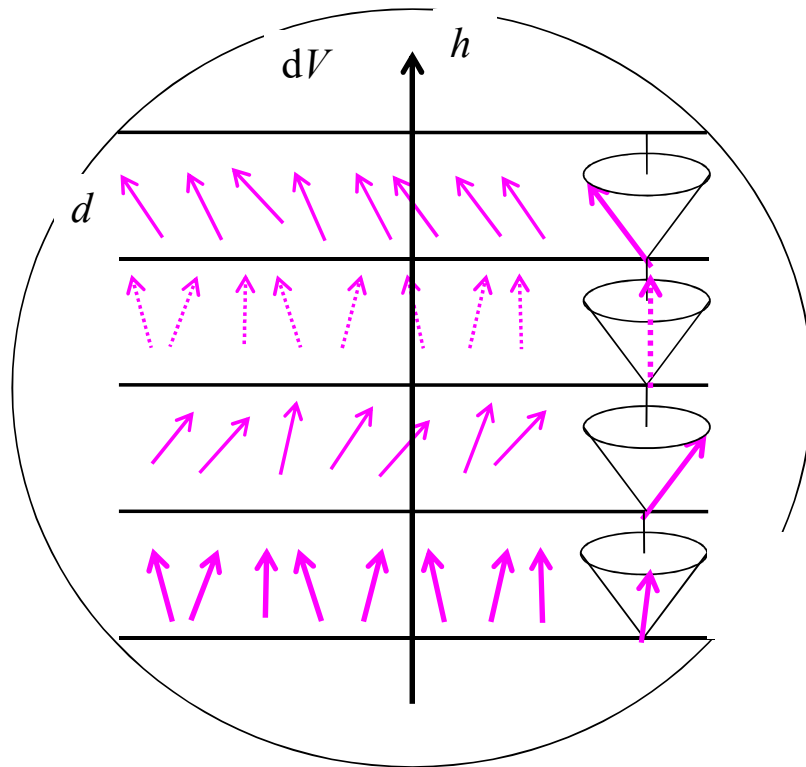
But...

If there is a chiral group in the mlc, then

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.

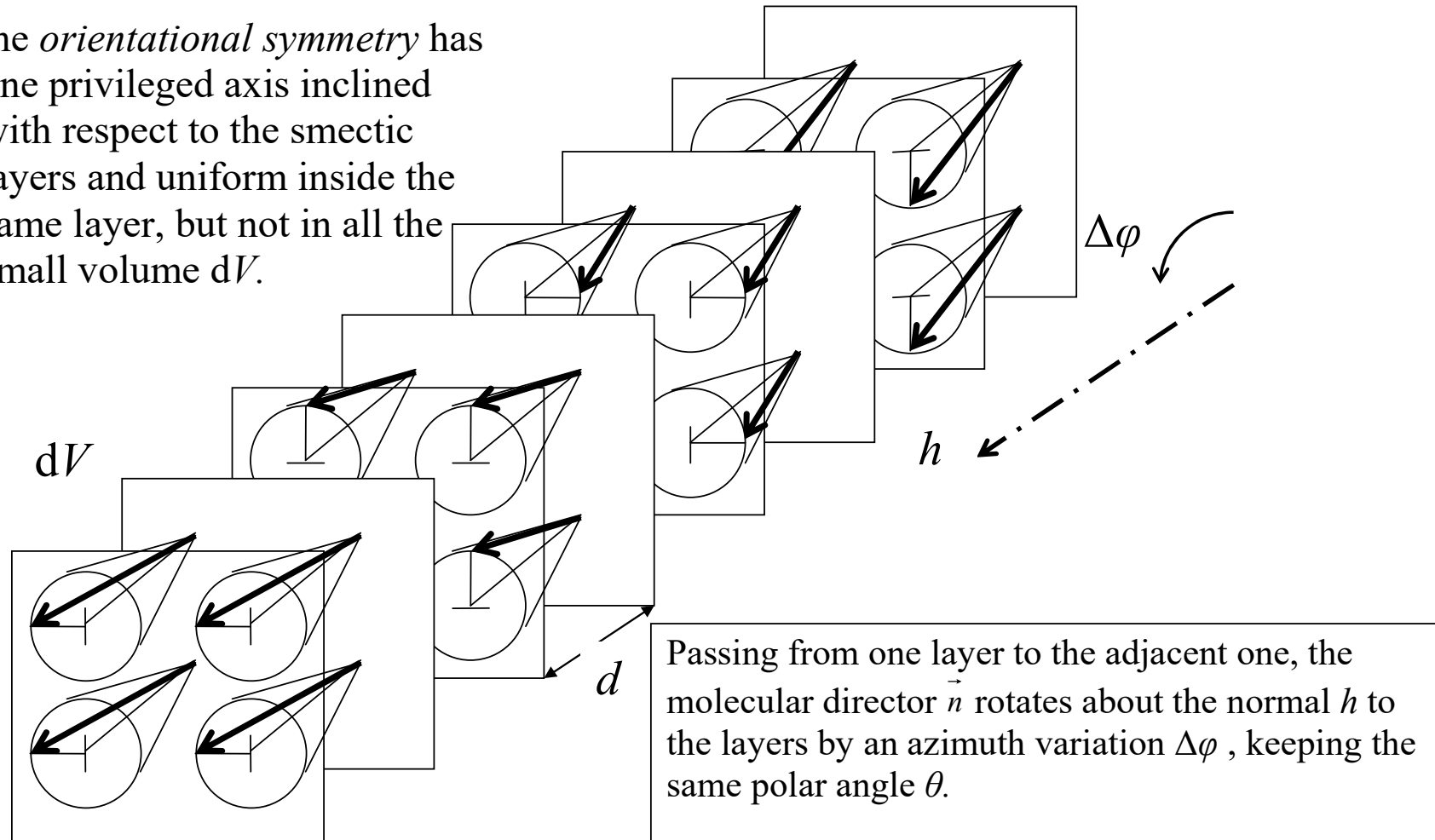


The short range interaction between molecules favors the direct parallelism among them: thus \vec{n} and $(-\vec{n})$ are no longer equivalent, and each layer has a transverse polarization, being the polarization normal to \vec{n} and to h, z : in each Smectic plane there is

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 *ideal!*

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

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

Both \vec{n} - inclination θ 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.). **Then the helix can be unwound and the sample gains a Ferroelectric Polarization P_s**

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.

Phase sequence

Some compounds have a **Mesophase** of one type only, f.i. either:

Nematic (only 1 directional degree of freedom is kept);

Smectic A (2 degrees of freedom, 1 positional and 1 normal directional);

Smectic C (2 degrees of freedom, 1 positional and 1 oblique unidirectional);

Smectic C* (3 degrees of freedom, 1 positional and 1 oblique directional) with 1 helical constraint)

Other compounds inside the temperature range between **melting** and **clearing points** exhibit more than one state of Mesophase, like Smectic C* and Nematic, in temperature sequence.

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 on heating). 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.

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