Study of transparent thin film oxide and they interaction with nematic liquid crystals.

Chapter 1

1.1 Liquid crystals: general properties

With liquid crystalline phase (or "mesophase" or "mosomorphic state") we intend an intermediate phase between the liquid phase and the solid one. This particular thermodynamic state is verifiable in substance constituted by strongly anisotropic molecules, the most common among these are molecules with lengthened shape and cylindrical symmetry respect to their main axes. This kind of compounds can give rice, under opportune temperatures and pressures conditions, to nematic, smectic and cholesteric phases. If the molecules have cylindrical symmetry but they are crushed ("discotic" molecules) they will bee had columnar like phases. They exist, beside, liquid crystal class called polymers formed by fundamental unity (monomer). Two particular kinds of polymers are the linear chains, obtained when the monomers are

rings of the same chain and the comb chains, when the monomers are sideways hooked to the chain. Other important mesophases are the so-called lyotropic phases, formed by the action of a water like solvent on anphyphylic molecules. The amphyphylic molecules are constituted by an hidrophylic head and an hidrophobic tail for which, ander the action of the water like solvent, because of the mutual attraction between the hidrophobic tails and the attraction between the hidrophylic head and the solvent, the amphyphylic molecules tend to join itself forming some agglomerate called micells. These aggregate can give rice to liquid crystalline phases whose structure is mainly determined by polar head interactions. The idrophobic chains, very flexible and messy, are instead responsible of the liquid aspect of the system. In figure (1.1.2) some example of these aggregate are shown. If the transition solid – liquid crystal and liquid crystal – isotropic liquid happen through temperature variation of the compound such compound is called termotropic. When a termotropic compound is heated above is fusion point the solid – liquid crystal transition is observed and still increasing the temperature the liquid crystal – isotropic liquid transition happens. This last transition is often accompanied by brightening of the material that passes from a turbid colour, typical of the liquid crystal phases, to complete

optical transparency. For this reason the temperature to which this transition happens has called "clearing point" (Tc). Many materials exist that, inside the temperature range between solid – Liquid crystal transition and Tc, manifest different mesophases with relative transitions that can be also of superior order to the first one. Such material are called "polimorphic material" and they, usually, are formed by molecules of elongate shape with a central rigid body. The various mesophases of polimorphic termotrophic liquid crystal are gathered in three classes: nematic phase, colesteric phase and smectic phase. In the nematic phase there is not any kind of positional order of the molecular mass centers, but just an orientational order therefore nematic phase is the more similar to the isotropic phase. In fact in a nematic liquid crystal (NLC) the molecules tend to get parallelly to a common axes individualised by a unitary vector called "molecular director" and showed with $\vec{n}$. The direction of $\vec{n}$ is arbitrary in the space; in practice it is imposed by minority forces as the drives effect of confining walls of the NLC. Usually the NLC are invariant for inversion of $\vec{n}$, this mean that a complete indistinguishably there is between $\vec{n}$ state and $-\vec{n}$ state.

The smectic phase, besides the orientational order, it possesses a unidimensional positional order: the molecules are therefore bounded between parallel

plain called "smectic plane". Different displacement of the molecules inside the smectic plain give rice to other smectict subphases; the main among them are smecticA, smecticC and smecticB. In the smecticA the molecular director is perpendicular respect to the plains delimiting the molecular position, instead in the smecticC phase a tilt between the molecular director and the normal to the smectic plains is present. The smecticB phase is characterised by the hexagonal symmetry disposition of the molecules inside the smectic plains. The cholesteric phase is characterised by a helical displacement of the molecular director and the helical step it is of the order of greatness of the visible light wavelength. Due to these peculiarity, the cholesteric liquid crystal are often used as light modulator.

It is, otherwise, important to remark that from molecular anisotropy of the liquid crystal they derive macroscopic anisotropy as optical, electrical, magnetic, and mechanic anisotropy. In fig. (1.1.1) are showed the nematic, smectic and colesteric phases.
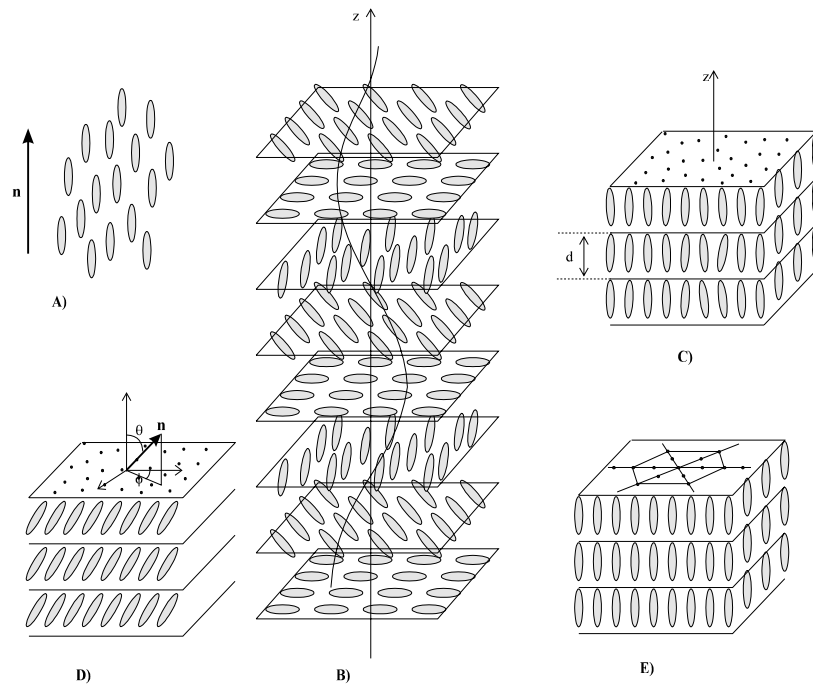
Fig.1.1.1) Nematic (A), colesteric (B), smectic-A (C),   smectic-C (D), smectic-B (E).
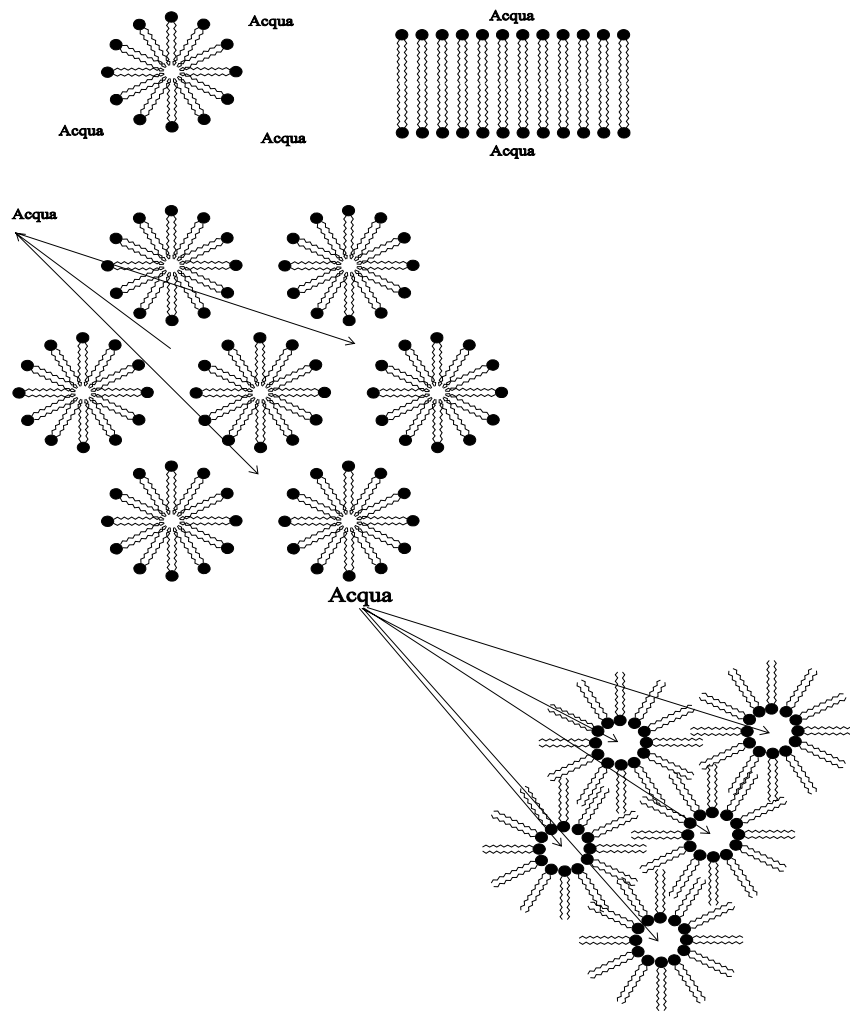
9

Fig 1.1.2) Some possible kind of liotrophic liquid crystal

1.2 Order parameter in NLC

Has been said that NLC have not any positional order but they have an orientational order. It is therefore necessary to define an order parameter giving a quantitative idea of the molecular alignment. In the nematic phase the choice of such parameters is less banal respect to the other phases and to define it needs to proceed step by step. First of all, we image the NLC molecules as a rigid rod. The axes of every molecules is represented by a unitary vector $\vec{a}$. We choose as reference a Cartesian system (x, y, z) so that $\vec{n}$ is on the z direction. Now we can write the polar $\vec{a}$ component as:

$$a_x = \text{sen}\,\vartheta \cos\phi$$

$$a_y = \text{sen}\,\vartheta \, \text{sen}\,\phi$$

$$a_z = \cos\vartheta$$

11

the alignment level of the molecules can bee described by a distribution function

$$f(\vartheta,\phi)d\Omega \qquad 1.2.1)$$

that represent the probability to find molecules aligned with a certain angle θ between the director and the molecular axes into a solid angle $d\Omega = \sin\vartheta\, d\vartheta\, d\phi$. Due to the symmetry of the molecular system respect to the inversion of the director and to the complete cylindrical symmetry of the nematic phase respect to $\vec{n}$ it must bee

$$f(\vartheta) \equiv f(\pi - \vartheta) \qquad 1.2.2)$$

Now we want to characterise the alignment no more by the function $f(\vartheta)$ but by a numeric parameter correlate to it. To do this we define

$$S = \frac{1}{2}\langle 3\cos^2\vartheta - 1 \rangle = \int \frac{1}{2}(3\cos^2\vartheta - 1)f(\vartheta)d\Omega \quad 1.2.3)$$

so that if $f(\vartheta)$ has maximum for $\vartheta = 0$ and $\vartheta = \pi$ we have $\cos\vartheta \cong \pm 1$ so S = 1. If $f(\vartheta)$ is uniform, that mean that θ is randomly distributed, we obtain $\langle \cos^2\vartheta \rangle = \frac{1}{3}$ so S = 0. S is called order parameter and he represent a quantitative value of molecular alignment.[1-2]

1.3 Electric field effects on NLC

A static electric field acting on a NLC produce various effects, some of them are quite complex. In this section our attention will bee oriented exclusively to a like perfect insulator NLC. In this ideal situation the most relevant effect of the coupling between NLC and an external electric field is the anisotropy of the dielectric constant.

The dielectric constant measured parallelly ($\varepsilon_{//}$) or normally ($\varepsilon_{\perp}$) to the molecular axes is different. For a generic direction of the electric field $\vec{E}$, the relation between the electric shift vector $\vec{D}$ and $\vec{E}$ has the form

$$\vec{D} = \varepsilon_\perp \vec{E} + \left(\varepsilon_{//} - \varepsilon_\perp\right)\left(\vec{n} \cdot \vec{E}\right)\vec{n} \qquad 1.3.1)$$

the difference $\varepsilon_a = \varepsilon_{//} - \varepsilon_\perp$ can bee positive or negative according to the chemical structure of the molecules.

If every molecule posses a permanent dipole moment parallel (or almost parallel) to the molecular axes, the molecules can bee easily oriented along the nematic axes by the field, so, in this case we have $\varepsilon_a > 0$. In practice a useful way to obtain a large value of ε_a is to connect a quite strong polar group on one extremity of the molecule.

If, on the contrary, we have a polar moment perpendicular to the molecular axes, the situation is inverted respect to the previous one.

The dielectric anisotropy can bee mainly exploited to align the NLC by an electric field.

The electric contribution to the thermodynamic potential (per cm^2) is

$$-\frac{1}{4\pi}\int \vec{D} \cdot d\vec{E} = -\frac{\varepsilon_\perp}{8\pi}\left(\vec{n} \cdot \vec{E}\right)^2 \qquad 1.3.2)$$

the first term is orientational indipendent. The second term determine the alignment of the NLC respect to the electric field.[1]

1.4 Continuum theory and elasticity in nematic

Due to the tendency of NLC to have a well determined orientational order, when external forces shift out the molecules from their equilibrium position, they react so that to restore the initial state. Those, a contribution to the nematic free energy can bee ascribed to the distortion that external forces could induce on the system. Such contribution has been described by Oseen in the form

$$f_d = \frac{1}{2}K_{11}(div\,\vec{n})^2 + \frac{1}{2}K_{22}(\vec{n}\cdot rot\,\vec{n})^2 + \frac{1}{2}K_{33}(\vec{n}\times rot\,\vec{n})^2 \quad 1.4.1)$$

K_{11}, K_{22} and K_{33} are the Frank elastic constant corresponding to the three fundamental type of distortion, respectively: splay, twist and bend (see fig. 1.4.1)
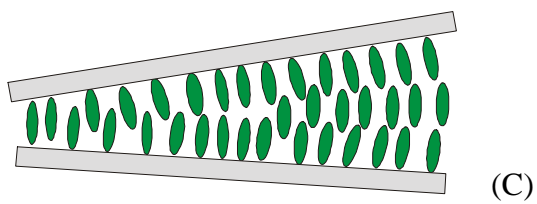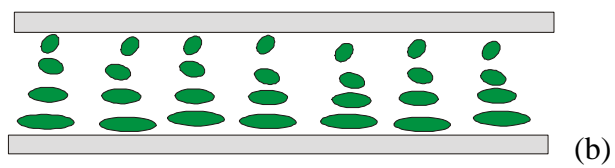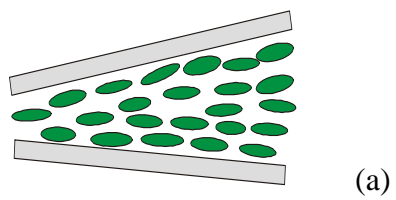
Fig. 1.4.1) Fundamental distortion. Splay (a), twist (b) and bend (c)

It need to remark that this theory is valid only in the case in witch the distortion are propagating on the system for long distance respect to the molecular dimensions, that mean: the director $\vec{n}$ change very slowly in function of the position.[1]

1.5   Frederiks effect

We take back in consideration the dielectric anisotropy of the NLC that had expressed as $\varepsilon_a = \varepsilon_{//} - \varepsilon_{\perp}$ where $\varepsilon_{//}$ and $\varepsilon_{\perp}$ are, respectively, the parallel and perpendicular dielectric constant.
As we have already seen in section 1.3, when an electric field is acting on NLC, the molecules will orient itself so that to dispose the greatest of the two suscettivity parallelly to the applied field, therefore, there will bee a further contribution to the free energy given by equation 1.3.2

$$f_e = -\frac{\varepsilon_a}{8\pi}\left(\overline{n}\cdot\overline{E}\right)^2$$

Now we suppose to have a thin NLC layer contained between two surfaces treated to impose to the molecules to get parallelly to them (planar

alignment). If an electric field is applied perpendicularly to the surfaces, in the case $\varepsilon_a \geq 0$, such system will minimizes the free energy varying the molecular orientation compatibly with the external field and the surfaces induced orientation.

What is experimentally observed in these cases is that the molecular reorientation happens only when the electric field reaches a determined threshold value. In order to obtain a mathematical expression of the threshold field we can start from the complete expression of the free energy for the considered problem.

$$F = \frac{1}{2} \int_0^d \left[K_{11} (div\,\vec{n})^2 + K_{22} (\vec{n} \cdot rot\,\vec{n})^2 + K_{33} (\vec{n} \times rot\,\vec{n})^2 - \frac{\Delta\varepsilon}{4\pi} (\vec{n} \cdot \vec{E}) \right] dz$$

1.5.1)

where d is the cell thickness and z is parallel to the direction of applied field. Setting

$$K_{11} = K_{22} = K_{33} \qquad 1.5.2)$$

and assuming that the field is uniform and the surface anchoring is strong

$$\theta|_{z=0} = \theta|_{z=d}=0 \qquad\qquad 1.5.3)$$

the free energy can bee written as follow

$$F = \frac{1}{2}\int_0^d \left[K\left(\frac{\delta\vartheta}{\delta z}\right)^2 - \frac{\Delta\varepsilon}{4\pi}E^2\sin^2\vartheta \right]dz \quad 1.5.4)$$

in the last expression the interaction term between the field and the NLC has been written as

$$\frac{\Delta\varepsilon}{4\pi}\left(\vec{n}\cdot\vec{E}\right)^2 = -\frac{\Delta\varepsilon}{4\pi}E^2\cos^2\psi = -\frac{\Delta\varepsilon}{4\pi}E^2\sin^2\vartheta \quad 1.5.5)$$

where ψ is the inclusive angle between the director and the field and $\vartheta = \pi/2 - \psi$ is the angle between the director and his original direction. From the last equation, using a variational calculus process, we obtain the expression of the threshold field.

$$E_s = \frac{\pi}{d}\left(\frac{4\pi K}{\Delta\varepsilon}\right)^{\frac{1}{2}} \qquad\qquad 1.5.6)$$

A similar process can bee used in the case of a magnetic field.[1-2]

1.6 Electric conductivity in nematic liquid crystals

The electric charge flowing in a medium under the effect of an electric field is described by the Ohm law

$$\vec{J} = \sigma\vec{E}$$

1.6.1)

where $\vec{J}$ is the current density and σ the conductivity of the material. Obviously, in the case of liquid crystal, it is must to bee considered the anisotrpy of the material. In general, in a NLC, the conductivity measured along the direction perpendicular to the molecular axes is bigger than the conductivity measured perpendicularly to the axes. Moreover the termotropic liquid crystal has a dielectric behaviour, for that the charges carriers are in largest number, constituted by ions coming from dissociation of the compound, from impurities

present in the liquid crystal or injected from the electrodes. It is properly to avoid these phenomenon that most of the measurement on liquid crystals are effected using alternate voltage.

In the case of polar molecules there is another contribution to the electric conductivity given by the polarization density

$$\vec{J} = \frac{d\vec{P}}{dt}$$ 1.6.2)

such effect is generated by the dipole shifting ander the effect of an alternate electric field.[1]

1.7 Optical properties of NLC

Among the anisotropies of the liquid crystals, the most evident is the optical anisotropy or birifringens. As it is well known the propagation of light ray through a completely transparent medium can bee macroscopically described by a real adimensional number called "refractive index"(n). The refractive index represent the effect on macroscopic scale and optical frequencies of the microscopic quantity called "molecular electronic

polarizability". In the passage from microscopic to macroscopic scale it is necessary to mediate on a large number of molecules and, in the case of anisotropic molecules, on their orientations. To do this is need to take into account the interactions molecular forces and the thermal motion. When the refractive index of a material is determined we can predict the propagation of a light ray through it. By using the Snel law (equation 1.7.1), for example, is possible to establish how a light ray is refracted or reflected by a certain material.

$$n_1 \sin\vartheta_1 = n_2 \sin\vartheta_2 \qquad 1.7.1)$$

while the propagation speed of the light in the material is given by $v = c/n$ where c is light speed in the vacuum.

This description can bee also extended to the anisotropic materials taking in mind that such materials have two refractive index, one of which is function of the propagation direction of the ray. Then, for a single incident angle θ_1, they are two refraction angles given by

$$n_1 \sin\vartheta_1 = n_o \sin\vartheta_2$$

$$n_1 \sin\vartheta_1 = n_e\left(\vartheta_3\right)\sin\vartheta_3 \qquad 1.7.2)$$

where n_e and n_o are called, respectively, "extraordinary" and "ordinary" refractive index. Then, due to the birifrengens phenomenon, a light beam is divided in two beam that are propagating through the material along different directions with different velocity. The beam for which the refractive index doesn't depend by the propagation direction is called "ordinary ray" and its propagation speed is c/n_o, the other one is called "extraordinary ray" and its speed is c/n_e that is function of the propagation direction. However, for a complete description of the phenomenon it is necessary to take in mind the undulated nature of the light and its polarisation. The birifrengens medium are, optically, classified in "uniaxial medium" and "biaxial medium". The firsts ones are of great interest from the application point of view, because the greatest part of electro-optics devices needs of uniaxials systems to work correctly, therefore we will restrict our attention to the uniaxials liquid crystals. The uniaxials medium can have $n_e > n_o$ (positive uniaxial medium) or $n_o > n_e$ (negative uniaxial medium). The greatest part of thermotropic uniaxials mesophases shown a

positive birifrengens and, among these, the nematic phase shown exclusively the positive birifrengens.

Let's now to describe the behaviour of a light beam passing through a NLC cell. Firsts of all we report the equation connecting the light intensity I, coming out from the cell, to the angle ϕ_0 inclusive between the light polarisation vector and the initial orientation of the molecular director.

$$I_0 = sin^2 2\phi_0 \, sin^2\left(\frac{\Delta\phi}{2}\right) \qquad 1.7.3)$$

where I_0 is the intensity of the plain polarised light incident on the cell and $\Delta\phi$ is the phase-displacement induced by the two refractive index on a monochrome light. $\Delta\phi$ and $\Delta n = n_e - n_0$ are correlate by the equation

$$\Delta\phi = \frac{2\pi}{\lambda}\int_0^d \Delta n \, dz = \frac{2\pi d \langle \Delta n(r)\rangle}{\lambda} \qquad 1.7.4)$$

We have previously seen as the application of an external electric field can modify the director orientation, consequently, also Δn and $\Delta\phi$ are

24

varying in function of the applied field. Due to the $\Delta\phi$ variation an amplitude oscillation of the signal coming out from the cell arises. When $\varphi_0 = 45°$ the maximum amplitude of these oscillations is obtained and the oscillation number is $\Delta nd/\lambda$.[2]

1.8 Ferroelectricity in liquid crystals

Most liquid crystalline phases have too high symmetry to allow spontaneous polarisation, which is the main characteristic of a ferroelectric. As the medium must not bee more symmetric than any of its macroscopic physical properties (it may bee less symmetric), the highest symmetry allowed for the ferroelectric phase is C_∞, which is the symmetry of a polar vector. Specifically, known nematics are symmetric when we change the sign of the director $\vec{n}$ and, till now, they are not any evidence of nematic with ferroelectric properties. With the help of the symmetry condition

$$\vec{n} \rightarrow -\vec{n} \qquad\qquad 1.8.1)$$

it is possible to deduce the first basic property of the polarisation in a ferroelectric liquid crystal: it

may not have any component along the director, because this would violate the $\vec{n} \to -\vec{n}$ invariance. Thus

$$\vec{P} \perp \vec{n} \ \text{ or } \ \vec{P} \cdot \vec{n} = 0 \qquad 1.8.2)$$

The ferroelectric liquid crystals (FLCs) are the most recent members of the already rich family of ferroelectric materials, the first one with fluid properties. In many aspect they are quite similar to ferroelectric solids. Like these they have a Curie point and their macroscopic polarisation vanishes in a closely similar way when the system approaches this point. A Curie-Weiss law is also often obeyed by the electric permittivity. In other respect, however, they are rather different from the solid-state ferroelectrics, and the origin of ferroelectricity in their molecular-chiral asymmetry is unique, till now well-known, among ferroelectrics.

In ferroelectrics crystals the polarisation is most often the primary order parameter of ferroelectric phase, whereas in FLCs it is a structural byproduct of the symmetry of tilted chiral smectics. The electrooptic properties are also quite different. Whereas crystalline ferroelectrics generally exhibit fast ($\approx 10\,\text{ns}$) switching with low refractive index

changes ($\Delta n \approx 10^{-3}$), FLCs switching is slower ($\approx 1\,\mu\text{s}$) but with a much larger refractive index change ($\Delta n \approx 0.1$). The microsecond response speeds of FLCs are, however, very fast compared to the conventional liquid crystals.[3]

References.

[1]   L. M. Blinov and V. G. Chigrinov: *Electrooptic Effects in Liquid Crystal Materials* (Springer-Verlag, New York, 1994).

[2]   P. G. De Gennes and J. Prost: *The fhysics of Liquid Crystal* (Oxford University Press, London, 1993).

[3]   J.W. Goodby, Robert Blinc, Noel A: Clark, Sven T. Lagerwall, M.A. Osipov, S.A. Pikin,Takao Sakurai, Katsumi Yoshino, Bostjan Zeks: *Ferroelectric liquid Crystals.*