

Optical studies of liquid crystals

A. MARINO^{(1)(2)(*)}

⁽¹⁾ *Institute of Applied Sciences and Intelligent Systems (CNR-ISASI) Via Campi Flegrei 34, I 80078, Pozzuoli (NA), Italy*

⁽²⁾ *Physics Department, University of Naples Federico II Via Cinthia Monte S. Angelo, I-80126, Naples, Italy*

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Summary. — Ellipsometry is well known as an optical technique for investigating the dielectric properties of thin films. Its evolution into spectroscopic and also variable-angle ellipsometry allowed the use of this technique also to anisotropic materials, like liquid crystals. In this work we present an overview on the ellipsometric studies on nematic liquid crystals characterization and reorientation. The former can be realized with simple reflection measurements: anisotropic refractive indices measurements are presented in the visible and near-infrared wavelength ranges. Moreover, with a temperature control, the nematic-isotropic transition can be measured. The latter, the molecular director distribution, can be measured with a more complex procedure that allows us to measure the values of pretilt and anchoring strength.

1. – Introduction

Most people are familiar with the liquid crystals world, but not many of them have dwelled upon this strange name. Liquid Crystals (LCs) are thought to be a material, even if they are not. This mistake rises from the fact that they are used in common objects like displays and they are presented from the commercial market like materials. To be correct (or more physicist) the “liquid crystal” is a phase of the matter, like the solid, the liquid, the gas and the plasma phases. The liquid crystal phase is an intermediate phase between solid and liquid. Only some materials present these phases, hence these materials are improperly named liquid crystals.

Solids, liquids, and gases respond to electric and magnetic fields, but the response is minimal even when strong fields are applied. On the contrary, LCs respond to even weak electric and magnetic fields with significant structural changes. They have been

(*) E-mail: antigone.marino@na.infn.it

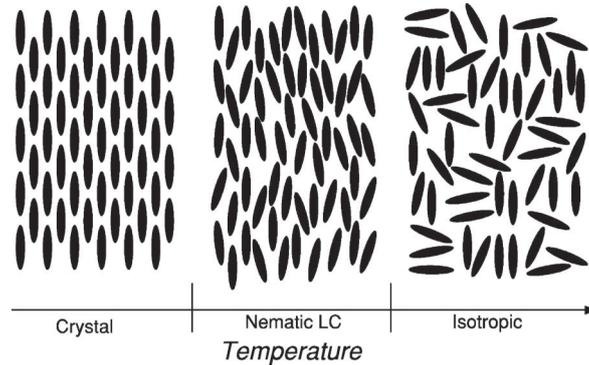


Fig. 1. – The liquid crystal phase appears between the solid and the liquid: increasing the temperature the positional order is lost, while the orientational remains.

known since 1888 when Reinitzer found two melting points in cholesterol benzoate and cholesterol acetate, but it was not until the late 1960's that the development of applications utilizing liquid crystals started. Today liquid crystals displays (LCDs) are very common and almost everyone owns or uses a liquid-crystal-based device. Only few people know that they are used in a diversity of new products, like rolled-up displays, light modulators, switches, optical components, and for plenty of different applications.

The states of matter are distinguishable for the different amount of order among the material molecules. The solid state consists of a rigid arrangement of molecules: they are constrained to occupy a specific position and they are oriented in a specific way. The molecules might vibrate, but the highly ordered arrangement is maintained. This arrangement causes large attractive forces between individual molecules to add them up. Hence, it takes substantial external forces to disrupt the structure. Besides in the liquid phase the molecules neither occupy a specific average position nor remain oriented in a particular orientation. The amount of order is therefore much less than in a solid. Attractive forces still exist, but the random motion of molecules does not allow the forces between individual molecules to add up. That is why a liquid maintains a constant density, even if it takes the shape of its container. Summarizing we can say that a solid possesses positional order, that is molecules are constrained to occupy only certain positions. Moreover it possesses orientational order, because molecules in these specific positions are constrained in the ways they orient themselves with respect to the surroundings. When solid melts to liquid, both types of orders are completely lost. However, during this transition it can happen that the positional order is lost, but some of the orientational order remains: this is the case of liquid crystal phase, which possesses orientational order and not positional order (fig. 1).

Liquid crystals phases often show a high anisotropy, due to the material constituent molecules which are fairly rigid and elongated objects. For pure systems, phase transitions are most easily induced by varying the temperature, these systems are called thermotropic liquid crystals; for systems of rods in solution, phase transitions can be induced also by varying the concentration of rods, these are called lyotropic liquid crystals. In the present work, only thermotropic LCs are considered.

The geometrical anisotropy of LC molecules gives rise to various liquid crystal mesophases, all of them characterized by a different degree of positional order. In general, the order of the subsequent phases decreases with increasing temperature, going from the crystal phase to the isotropic phase passing through the Smectic C, Smectic A and

Nematic. In the Nematic phase molecules have no positional order but long-range orientational order. Here all the molecules tend to align with their long axes in a preferred direction described by the unit vector \hat{n} called the molecular director. The nematic is a uniaxial medium where the states \hat{n} and $-\hat{n}$ are indistinguishable. In this work only the nematic LC phase will be treated.

At a given temperature T , the $\mathbf{n}(\mathbf{r})$ distribution of a liquid crystal can be found describing the system by its free energy density, imposing the boundary conditions, and minimizing the free energy density [1].

As said before, the reason why LCs are so widely used for displays and telecom applications lies in their extremely sensitive response to electric and magnetic fields by means of a redistribution of the molecular director. Ordered structures of anisotropic molecules make the macroscopic physical properties also anisotropic. Nematic liquid crystals might show both positive and negative values of the dielectric anisotropy. If $\Delta\varepsilon > 0$, the molecular director tends to orient parallel to electric field, while if $\Delta\varepsilon < 0$, the molecular director tends to orient perpendicular to electric field.

Consider now what happens when a small amount of nematic liquid crystal is placed between two pieces of glass which have been previously treated to produce the alignment of the director parallel to the surface. Near the two glass surfaces, the director is constrained to point in a certain direction (parallel to the surface). Now imagine that the nematic LC has positive anisotropy, $\Delta\varepsilon > 0$, and an electric field is applied perpendicular to the glass surfaces: the field tends to orient the director parallel to the field. The molecules near the surface are not very free to reorient with the field like the ones in the middle of the cell. The electric field thus causes the director to change its orientation mostly in the middle, with diminishing change closer to the surfaces. The most interesting aspect of this deformation is that it does not occur gradually as the strength of the field is gradually increased. For fields with strengths below a certain value, the LC remains undeformed. Then at some threshold value of the field, the deformation begins and then gets bigger as the field strength is increased. The transition from an undeformed structure to a deformed one is called Fréedericksz transition.

The optical properties of liquid crystals and the way they affect light are also the basis for just about all their applications. Two aspects are extremely relevant: due to anisotropy, light propagates in a different way with respect to the molecular director orientation; light itself can reorient the liquid crystal, because light is an electro-magnetic field, and this reorientation of the LC modifies the propagation of light giving rise to a non-linear optical effect.

As said before, nematic LC are uniaxial, and the optic axis coincides with the molecular director. If we take z -direction parallel to the optic axis, the dielectric tensor ε_{ij} of a nematic LC is

$$(1) \quad \varepsilon_{ij} = \begin{pmatrix} \varepsilon_{\perp} & 0 & 0 \\ 0 & \varepsilon_{\perp} & 0 \\ 0 & 0 & \varepsilon_{\parallel} \end{pmatrix}.$$

Solving the Fresnel equation (1) for such system, we find two different solutions

$$n_o = \sqrt{\varepsilon_{\perp}},$$

$$n_e(\theta) = \frac{n_o n_e}{\sqrt{n_e^2 \cos^2 \theta + n_o^2 \sin^2 \theta}} = \sqrt{\varepsilon_{\parallel}}.$$

Corresponding to these solutions there are two values of the wavevector

$$\begin{aligned} k_1 &= \frac{\omega}{c} n_o, \\ k_2 &= \frac{\omega}{c} n_e(\theta). \end{aligned}$$

A linearly polarized wave propagating perpendicular to the optic axis and with its \mathbf{E} -vector parallel to the optic axis sees the refractive index n_e : the wave is called *extraordinary* wave. If, instead, the \mathbf{E} -vector is perpendicular to the optic axis, the wave sees the refractive index n_o , the wave is *ordinary*. If the \mathbf{E} -vector makes some angle with the optic axis, the wave is split up into two waves, which simultaneously propagate through the medium with different speeds. Hence, an optically anisotropic medium is said to be birefringent, where birefringence can be evaluated as

$$\Delta n = n_{\parallel} - n_{\perp}.$$

In liquid crystals the birefringence is typically 0.1–0.2, an extremely high value compared with other materials. The idea to use LCs dates back to the 70's: after the first impressive success of LC materials in the display area, scientists thought to exploit them in the design of photonic devices. The advantages of using liquid crystals are many: they are transparent, hence they exhibit a low absorption; they are birefringent; they can be driven by low electric fields; their low-viscosity liquid nature makes them easy to integrate; they are cheap; they show so many mesophases and composites, that they are almost every time adaptable to the required device necessities. Drawbacks in the use of LCs are mainly due to scattering losses and to response times.

The LC optical characterization in a wide spectral range is becoming a very important technical task because of their spreading applications in displays, optical telecommunication and other advanced areas of science and engineering. In this paper, ellipsometry is presented as one of the best techniques to achieve this goal.

2. – Ellipsometry

Standard Spectroscopic Ellipsometry is based on measurements of two physical quantities: the relative phase change, Δ , and the relative amplitude change, Ψ , suffered by incident light when reflected (or transmitted) by a layered structure [2]. These two parameters are linked to the reflection (or transmission) coefficients, which are themselves related to the optical response of the surface: the Ψ 's and Δ 's spectra depend on the refractive indices of the layers, on their thickness and, in the case of anisotropic films, on the orientation of their optics axis (of course, they depend on any physical parameters that affect the optical behavior of the material, for instance on temperature).

By the adoption of the 2×2 Jones matrix formalism, it is possible to extend ellipsometry application to anisotropic media, Generalized Ellipsometry (GE) [3]. In this way it is possible to generalize the Standard Ellipsometry parameters, Δ and Ψ , suffered by incident light after transmission or reflection by a sample, to the case when a change occurs in light polarization. The six GE parameters, Δ , Ψ , Δ_{ps} , Ψ_{ps} , Δ_{sp} , Ψ_{sp} , are linked to the Jones matrices of reflected (J_r) or transmitted (J_t) beam through the following

equations:

$$(4) \quad \begin{aligned} \tan \Psi \cdot e^{i\Delta} &= \frac{J_{pp}}{J_{ss}}, \\ \tan \Psi_{ps} \cdot e^{i\Delta_{ps}} &= \frac{J_{ps}}{J_{pp}}, \\ \tan \Psi_{sp} \cdot e^{i\Delta_{sp}} &= \frac{J_{sp}}{J_{ss}}, \end{aligned}$$

where $J = J_r, J_t$ and

$$J_r = \begin{pmatrix} r_{pp} & r_{sp} \\ r_{ps} & r_{ss} \end{pmatrix} \quad \text{and} \quad J_t = \begin{pmatrix} t_{pp} & t_{sp} \\ t_{ps} & t_{ss} \end{pmatrix},$$

with $r_{pp}, r_{ss}, r_{ps}, r_{sp}$ ($t_{pp}, t_{ss}, t_{ps}, t_{sp}$) representing the reflection (transmission) coefficients for p -, s -, and cross-polarizations respectively. In the isotropic case we have $n_x = n_y = n_z$ and the Jones matrix will be diagonal:

$$J_r = \begin{pmatrix} r_{pp} & 0 \\ 0 & r_{ss} \end{pmatrix} \quad \text{and} \quad J_t = \begin{pmatrix} t_{pp} & 0 \\ 0 & t_{ss} \end{pmatrix}.$$

The equations written in (4) are reduced to the first one and only two parameters are meaningful. We remark that off-diagonal elements in Jones matrices represent the conversion of the p - and s -polarized light into s - and p -polarized respectively; those elements vanish also for anisotropic media in highly symmetric configuration, *i.e.* when the optics axis is oriented parallel or perpendicular to the plane of incidence.

The Jones matrix formalism is based on the assumption of a completely polarized light. When a significant amount of reflected or transmitted light becomes depolarized, it may be necessary to introduce the Mueller matrix representation [4].

In the last ten years, our group specialized in the ellipsometric study of LCs and their reorientation. Experimental data were measured on a Variable-Angle Spectroscopic Ellipsometer (VASE®) manufactured by the Woollam Company. Measurements have been performed as a function of both wavelength and angle of incidence, in the spectral range from 300 nm to 1700 nm. This instrument is equipped with an AutoretarderTM, which utilizes patented technology to achieve maximum measurement accuracy.

Once the experimental data are acquired, ellipsometry needs an inversion procedure to obtain from Ψ and Δ the physical quantities of interest. It is necessary to draw up a multilayer optical model, which carefully describes the sample structure. A specifically designed software generates theoretical data and unknown parameters, such as thickness or optical constants values, are adjusted in the optical model to better fit the experimental data. Parameters values are fixed once the iteration process minimizes the difference between experimental and model-generated data (fig. 2). The software determines the sample refractive index and eventually thickness, by means of a multiple-fitting procedure. This procedure ends providing a numerical value for the discrepancy between experimental and generated data, called Mean Square Error (MSE), which we use to check the goodness of the fit. The main possible drawbacks in SE, GE and MME analysis could be the dependence of final results on: accuracy of the optical model; starting points in fitting procedures; statistical correlation between fit parameters.

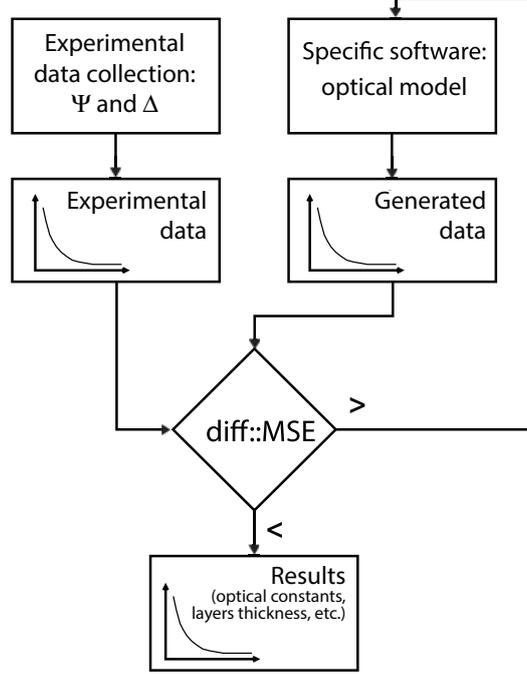


Fig. 2. – Ellipsometry needs an inversion procedure to calculate the physical qualities from the measured ones. The data analysis flow chart shows this inversion procedure.

3. – LC optical constants

In order to measure the LC anisotropy and estimate the ordinary and extraordinary refractive indexes, an appropriate model for the multilayer stack composing the LC cell has to be considered. Typically we have a 7 layers model: 1) the lower glass substrate, 2) a possible electrode layer, like ITO (Indium Tin Oxide), 3) the lower alignment layer, 4) the LC layer, 5) the upper alignment layer, 6) the upper electrode, 7) the upper glass.

As shown in [5], ellipsometry allows to measure the material optical constants. Moreover it is possible to distinguish the two configurations of the LC cell: the homeotropic one, with the molecular director perpendicular to the cell plane; and the planar one with the director in the cell plane. In both configurations, we can consider the off-diagonal elements of the Jones matrices to be vanishing. Due to the absence of any resonances in the examined spectral range, we can describe the ordinary and extraordinary indices of the nematic by using the simplest 2-parameter Cauchy formula (where the subscripts o and e stand for ordinary and extraordinary, respectively)

$$(5) \quad n_{o,e} = a_{o,e} + \frac{b_{o,e}}{\lambda^2}.$$

Trials made with the three-parameter Cauchy formula did not give any significant difference in the obtained dispersion curves; furthermore, the third fitted parameter was always quite strongly correlated to the previous ones, especially the second one, decreasing according to the degree of confidence in the fit.

Every layer in the model needs to be described by a dispersion formula. The presence of two oxide layers as electrodes makes things much more complicated [6]. In fact the ITO needs to be fitted using two absorbing Lorentz oscillators. Moreover, if we assume homogeneity for the ITO film, the model does not fit well the experimental data. Several authors report strong indications that ITO mass density, microstructure and film continuity, degree of oxidation, and hence also its optical properties, are generally varying along the stratification direction [7]. Adding a Bruggeman Effective Medium Approximation (EMA) to the ITO layer [8] it is possible to introduce a linear variation of the optical parameters within the film's depth, which describes a different level of oxidation depending on the film's interaction with air.

The accuracy of the optical parameter values obtained by the experimental data inversion procedure depends dramatically both on the chosen physical model of the sample and on the initial guess for the parameters to be determined. To improve the reliability and accuracy of the sample characterization, the VASE is recommended to be complemented with other techniques. At this aim, we have integrated it with the Half Leaky Guided Mode (HLGM) spectroscopy. The dispersion curves of nematic LC E7 have been estimated in the 450–1700 nm wavelength interval with both precision and accuracy of 10^{-4} [9]. To modify the commercial ellipsometer for the HLGm method we have developed one component that mounts the equilateral SF6 prism on the upper side of the sample and another one that places the converging lens between the sample and the ellipsometer detector [10]. The integration of HLGm with ellipsometry on the same device gives the evident advantage of the simultaneous and complementary use of both the techniques to overcome most of the problems in applying ellipsometry to LC. The HLGm data can be interpreted easily and so they give more reliable results for the refractive-indices measurements. These results can be used as the starting point for the fitting procedure in ellipsometry. The most important result of the integration of these two techniques is overcoming their accuracy limitation using the results of each method as an initial guess for the other method, in a feedback loop. In fact, our quoted refractive-index values show the same accuracy level, namely 10^{-4} , in the whole spectral range [11], while previous measurements of the LC optical parameters were given with an accuracy lower in the NIR (not exceeding 10^{-3}) than in the visible. Furthermore, we stress that our modification of the commercial ellipsometer allows oneself to realize not only HLGm but also M-line technique for the optical characterization of guiding structures. In this case the waveguide must have a solid core to be pressed against the base of high-index SF6 prism to make a thin air gap [6].

We measured 5CB refractive indices at different wavelengths in visible and NIR spectral regions in a wide temperature range providing both the nematic and isotropic phases of LCs. The temperature effect on the LC refractive indices can be described by a four-parameter model [12]

$$\begin{aligned}
 n_o &= \alpha - \beta T - \frac{\Delta\nu}{3} \left(1 - \frac{T}{T_c}\right)^\gamma, \\
 n_e &= \alpha - \beta T + \frac{2\Delta\nu}{3} \left(1 - \frac{T}{T_c}\right)^\gamma, \\
 n_{\text{mean}} &= (n_e + 2n_o)/3 = \alpha - \beta T,
 \end{aligned}
 \tag{6}$$

where parameters α and β can be obtained from fitting the temperature-dependent n_{mean} data at a given wavelength, and parameters $\Delta\nu$ and γ can be obtained by fitting the

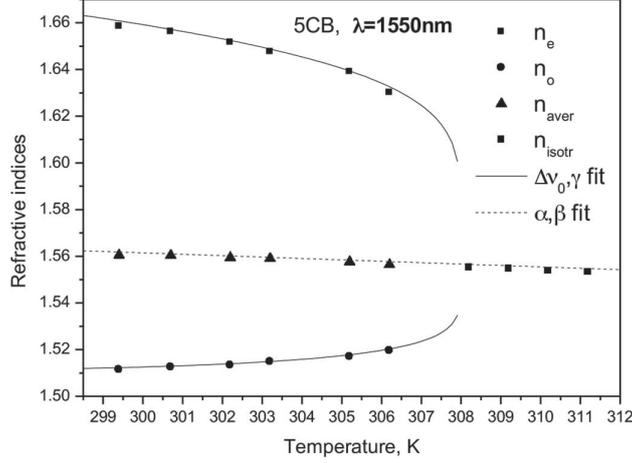


Fig. 3. – Experimental (points) and approximated by the four-parameter model temperature dependence (lines) of the 5CB refractive indices for $\lambda = 1550$ nm.

temperature-dependent Δn data. Figure 3 shows the experimental 5CB refractive-index dependence on temperature as well as approximation by the four-parameter model for $\lambda = 1550$ nm.

Using eqs. (6) and the obtained interpolation formulas for α , β , $\Delta\nu$ and γ , refractive indices for any value of T and λ can be calculated with an error smaller than ± 0.001 .

4. – LC reorientation

In many physical studies dealing with LCs, as well as in practical devices like displays, it is necessary to anchor the orientation of the nematic director to appropriate surfaces in specific directions and with specific anchoring energies. This is accomplished in different ways, usually by deposition of an alignment layer functionalized to tilt the nematic director in some direction. The accurate knowledge of the orientation of the nematic director at the interface and its anchoring energy is quite important for the optimal design of the LC cell that in turn determines the device performance.

Variable-angle spectroscopic ellipsometry is a suitable technique for such measures. In Vertical-Aligned Nematic (VAN) cells the LC director sets itself perpendicular to the alignment layer, showing, in some cases, a small angle θ with the normal to the sample plane, called tilt, that may vary throughout the cell bulk. The director tilt profile is ultimately determined by the pretilt, defined as the tilt angle at the cell walls when no voltage is applied. The control of tilt angle distribution inside VAN LC thin films is essential for many applications. If the pretilt is null, the LC orientation upon electric switching is undefined, therefore the cell usually generates domains. Higher pretilts lead to faster displays, because the dynamic response time decreases. However, increasing the pretilt, the quality of the dark state is reduced, because the birefringence in the off state increases too. Thus a delicate balance between response time and contrast has to be sought in manufacturing VAN displays. Optimizing pretilt and anchoring energy, possibly independently on each boundary surface, is crucial for VAN cell performance. With this aim, we have investigated the pretilt and the director tilt angle distribution in

several VAN cells under the action of an applied electric field [13]. Exploiting jointly these ellipsometric measurements and simulations, it is possible to give an accurate evaluation of the anchoring energy [14].

Adding this reorientational information to the optical characterization of LCs allows us to make a complete analysis of the LC device [15, 16].

The LC display market is trying to push more and more towards the device optimization, trying to solve the two biggest problems: to obtain faster response times and bigger contrast ratios. Nowadays, to this purpose, researcher are testing LC mixtures with other materials, such as carbon nanotubes (CNT). It has been observed that the LC spontaneous alignment induces the same alignment in CNT dispersed into it. Moreover, when an external electric field above the Fréedericksz threshold is applied to the LC, the molecules reorient accordingly, and the CNT orientation changes likewise. A recent study, of ellipsometry merged with Raman Spectroscopy, analyzes the formation of topological defects in LC matrices induced by multiwalled carbon nanotubes (MWCNTs) and external electric fields [17]. The defects are ascribable to a distortion of the LC molecular director in proximity of the MWCNT surface. The system is analyzed macroscopically using VASE, and confocal micro-Raman spectroscopy is used to study the system state at the microscale. This allows to acquire a three-dimensional, spatially-resolved map of the topological defect, determining scale length variations and orientation topography of the LC molecules around the MWCNT [17]. Likewise, the reorientation of single-walled carbon nanotubes in negative anisotropy liquid crystals has been studied [18].

5. – Conclusions

We proposed spectroscopic ellipsometry as a reference technique for liquid-crystal characterization. The measure of the optical constants, their dependence on temperature, pretilt, tilt distribution, and anchoring strength in nematic LC cells can be carried out with a good accuracy. A meaningful ellipsometric data inversion is strictly dependent on the choice of a proper physical model, and, above all, the final multi-parameter fitting procedure may critically depend on a good initial guess. That is why, to improve the reliability and accuracy of the optical-constants measurements, we have integrated the variable-angle spectroscopic ellipsometry with other techniques.

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