Optical activity of small-pitch helical-shaped dielectric media

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A chiral smectic liquid crystal is considered, made of elongated molecules whose directions describe a helix along a given direction. It is shown that for small values of the helix pitch it behaves as a homogeneous medium which is optically active and uniaxial, with maximum rotatory power for light propagating orthogonally to the helix axis. Analytic expressions are given to describe the gyrotropic properties of the medium. The analogies with other helical-shaped structures are discussed. [S0163-1829(96)04939-9]

After the works of Van't Hoff and Le Bel on the tetrahedral shape of carbon atoms, the natural optical activity (or gyrotropy) has been associated with the stereoisomerism of organic compounds. In our century, and, in particular, in the past decades, the attention has gradually shifted from tetrahedral shaped objects to helical structures, involving researchers outside the traditional fields of physical optics, stereochemistry, and crystallography.[1] After the pioneering work of Lindman[2] on the gyrotropy induced by an assembly of small metallic helices, researchers in the field of radio waves propagation have been increasingly interested in gyrotropic media. Similarly, the discovery of the double helix of DNA stimulated new researches in the field of biology. It has been recognized that gyrotropy is, in general, associated with molecules having the shape of helices or of segments of helix,[3] and numerical algorithms have been designed to treat complex dielectric structures.[1]

We approach here a similar problem with a different technique, on the basis of a simple optical model. More precisely, we consider a medium which is locally uniaxial and nongyrotropic, with the optical axis uniformly rotating along the direction of a given axis, say z, in such a way that the components of its versor $\hat{\mathbf{n}}$ are given by

$$n_x = \sin\alpha\cos\varphi, \quad n_y = \sin\alpha\sin\varphi, \quad n_z = \cos\alpha, \tag{1}$$

where α is the tilt angle of the structure, $\varphi = qz + \varphi_0$ and $p = 2\pi/q$ is the helix pitch.

A thin cylinder of such a medium, elongated along z, simulates a helical-shaped macromolecule whose optical activity is related to the rotation of the polarizability direction of its atomic groups and not to their positions. The model also describes a chiral smectic C liquid crystal (LC) and, in the particular case $\alpha = \pi/2$ ($\hat{\mathbf{n}}$ orthogonal to z), a cholesteric LC. The optical properties of these media have been extensively studied in our century for pitches p of the same order of magnitude or greater than the light wavelength λ. Here we consider the case $p < \lambda$, which is interesting to understand the gyrotropy induced by helical-shaped molecules; furthermore, it has been recently shown that short-pitch cholesterics can be used as electro-optical devices.[4]

It has already been shown numerically[5] that small-pitch chiral smectic LC can be well approximated by gyrotropic uniaxial homogeneous media, whose optical activity cannot be derived from the well known de Vries equations.[6] Here, analytic expression for their gyrotropic properties will be explicitly given in the limit $p \ll \lambda$.

According to Landau-Lifshitz[7] and Agranovich-Ginsburg,[8] the electromagnetic properties of the effective homogeneous medium are defined by the constitutive equations

$$\mathbf{D}^{\mathrm{eff}} = \varepsilon_0 \boldsymbol{\varepsilon}^{\mathrm{eff}} \cdot \mathbf{E}^{\mathrm{eff}}, \quad \mathbf{B}^{\mathrm{eff}} = \mu_0 \mathbf{H}^{\mathrm{eff}}, \tag{2}$$

which involve the single tensor $\boldsymbol{\varepsilon}^{\mathrm{eff}}$. The optical activity comes from the nonuniformity in space of the medium (which is assumed as locally nongyrotropic) and of the electromagnetic field. In fact, the polarization at a given point also depends on the field values at neighboring points. We, therefore, write

$$D_i^{\mathrm{eff}} = \varepsilon_0 \left(\tilde{\varepsilon}_{ij} E_j^{\mathrm{eff}} + \gamma_{ijl} \frac{\partial E_j^{\mathrm{eff}}}{\partial x_l} \right), \tag{3}$$

where the suffixes i, j, l run over the Cartesian coordinates x, y, z. Terms in higher order derivatives are neglected since we are considering the case $p \ll \lambda$. For a plane wave we have $E_j^{\mathrm{eff}} = E_{0j}^{\mathrm{eff}} \exp[i(k_l x_l - \omega t)]$ and Eq. (3) gives

$$\varepsilon_{ij}^{\mathrm{eff}} = \tilde{\varepsilon}_{ij} + i\gamma_{ijl} k_l . \tag{4}$$

The effective dielectric tensor $\varepsilon_{ij}^{\mathrm{eff}}$ is complex and depends on the light wave vector $\mathbf{k}$ (spatial dispersion). The imaginary part, responsible for the optical activity, depends on the third rank tensor γ_{ijl}. Energy conservation[9] requires that $\gamma_{ijl} = -\gamma_{jil}$. This reduces the number of independent components of the tensor from 27 to 9, and allows us to write

$$\gamma_{ijl} = e_{ijm} g_{ml} / k_0 , \tag{5}$$

where e_{ijm} is the completely antisymmetric unit pseudotensor, g_{ml} is a second rank pseudotensor, and $k_0 = \omega/c$ the light wave vector in vacuum.

Our aim is to explicitly find the dielectric tensor $\tilde{\boldsymbol{\varepsilon}}$ and the gyrotropy pseudotensor $\mathbf{g}$ of the effective homogeneous medium. To this purpose we recall that the eigenwaves in this medium are plane waves, whereas the eigenwaves in any periodic medium are, in general, Bloch waves with an infinite number of Fourier components. When we consider an effective homogeneous medium we simply neglect all these components except the zeroth order one, which defines an average field smoothly varying over one spatial period. In crystal optics only this average field is of practical interest, because the period is of molecular dimensions. This is not our case, because the pitch of actual helical-shaped LC is usually not negligible with respect to λ. So we will not only define an effective homogeneous model, but also find out the most important effects related to the neglected Fourier components. Such components play a main role in the definition of the boundary conditions. It is, therefore, convenient to consider the optical properties of a finite sample.

Let us first consider a layer of the periodic medium with boundary planes at $z=0$ and $z=Np$, where N is an integer number, and an incident plane wave defined by

$$\begin{pmatrix} \mathbf{E} \\ \mathbf{H} \end{pmatrix} = \begin{pmatrix} Z_0^{1/2}\mathbf{e}(z) \\ Z_0^{-1/2}\mathbf{h}(z) \end{pmatrix} \exp[i(k_x x-\omega t)]+\text{c.c.}, \tag{6}$$

where $Z_0=(\mu_0/\epsilon_0)^{1/2}$ is the vacuum characteristic impedance. Only four components of the electromagnetic field are independent, and Maxwell's equations can be cast in the matrix form[10]

$$\frac{d\beta(z)}{dz}=ik_0 B(z)\beta(z), \tag{7}$$

where $\beta=(e_x, h_y, e_y, -h_x)$ and B is the *Berreman matrix*. In our case $B=B_0+B_a$, where[11]

$$B_0=\begin{pmatrix} 0 & 1-m_x^2/\tilde{\varepsilon}_e & 0 & 0 \\ \tilde{\varepsilon}_o & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & \tilde{\varepsilon}_o-m_x^2 & 0 \end{pmatrix}, \tag{8a}$$

$$B_a=\begin{pmatrix} b_1\cos\varphi & 0 & b_1\sin\varphi & 0 \\ -b_2\cos(2\varphi) & b_1\cos\varphi & -b_2\sin(2\varphi) & 0 \\ 0 & 0 & 0 & 0 \\ -b_2\sin(2\varphi) & b_1\sin\varphi & b_2\cos(2\varphi) & 0 \end{pmatrix}. \tag{8b}$$

Here $\mathbf{m}=\mathbf{k}/k_0$, $b_1=-m_x\varepsilon_a\sin(2\alpha)/(2\tilde{\varepsilon}_e)$, $b_2=-\varepsilon_a\varepsilon_0\sin^2\alpha/(2\tilde{\varepsilon}_e)$, and

$$\tilde{\varepsilon}_e=\varepsilon_o+\varepsilon_a\cos^2\alpha, \quad \tilde{\varepsilon}_o=\varepsilon_o(1+\varepsilon_e/\tilde{\varepsilon}_e)/2, \tag{9}$$

where ε_e and ε_o are the principal values of the local dielectric tensor of the periodic medium and $\varepsilon_a=\varepsilon_e-\varepsilon_o$ is the dielectric anisotropy.

The optical properties of the sample are summarized by its transfer matrix $U(Np)=U(p)^N$, which gives the output field as a function of the input field, according to $\beta(z)=U(z)\beta(0)$. The matrix $U(z)$ satisfies the condition $U(0)=\mathbf{1}$, where $\mathbf{1}$ is the identity matrix, and the same propagation equation (7) of the vector β. Its computation requires a numerical integration. An approximate analytical expression can be obtained by a perturbative approach, taking B_0 as the unperturbed matrix. This matrix describes a homogeneous uniaxial medium without optical activity and with principal values of the dielectric tensor equal to $\tilde{\varepsilon}_e$ and $\tilde{\varepsilon}_o$. Since the perturbing matrix B_a depends on z, we make use of a perturbation method very similar to the interaction picture of quantum mechanics for time dependent perturbations. More precisely, we define a new vector α and a new matrix A related to β and B by the equations

$$\alpha(z)=T_0^{-1}(z)\beta(z), \quad A(z)=T_0^{-1}(z)B_a(z)T_0(z), \tag{10}$$

where $T_0(z)$ is the 4×4 matrix whose columns are the β vectors of the four eigenwaves propagating within the unperturbed medium, given by $\beta^{(j)}\exp(ik_0 m_j z)$. Here, $\beta^{(j)}$ and m_j are the eigenvectors and eigenvalues, respectively, of the matrix B_0. The elements of $\alpha(z)$ have a very simple physical meaning, since they are the complex amplitudes of the unpertubed eigenwaves. The nondiagonal elements of $A(z)$ give the coupling between these waves. The vector $\alpha(z)$ and its transfer matrix $U_a(z)$ satisfy an equation formally identical to Eq. (7), with $A(z)$ instead of $B(z)$.

The perturbation approach is obtained by writing the propagation equation for $U_a(z)$ in the integral form

$$U_a(z)=\mathbf{1}+ik_0\int_0^z A(z')U_a(z')dz', \tag{11}$$

and making use of the iteration procedure

$$U_a^{(0)}(z)=\mathbf{1}, \quad U_a^{(n+1)}(z)=\mathbf{1}+ik_0\int_0^z A(z')U_a^{(n)}(z')dz', \tag{12}$$

which, for $p\ll\lambda$, is rapidly converging.

The zeroth order approximation gives an homogeneous model without optical activity, corresponding to the unperturbed medium defined by the matrix B_0. The first iteration gives a transfer matrix $U^{(1)}(Np)$ which depends on the phase constant φ_0 appearing in Eq. (1), which defines the director orientation and the phases of the higher order Fourier components of the Bloch wave at the boundary planes of the sample. A change of φ_0 is equivalent to a shift of the helix along z. The transfer matrix of the homogeneous model is obtained by averaging $U^{(1)}(Np)$ over φ_0, and is exactly the same as for the zeroth order approximation, as discussed below.

The next iteration takes into account the two photon interactions between neighboring molecules. The transfer matrix $U^{(2)}(Np)$, averaged over the phase constant φ_0, has additional terms which couple the two forward propagating unperturbed eigenwaves, giving a rotation of the plane of polarization of the light. The same happens for the bakward waves. This averaged transfer matrix is the same as for a homogeneous medium with optical activity whose dielectric tensor and gyrotropy pseudotensor are given by

$$\boldsymbol{\varepsilon}^{\text{eff}}=\begin{pmatrix} \tilde{\varepsilon}_o & 0 & 0 \\ 0 & \tilde{\varepsilon}_o & 0 \\ 0 & 0 & \tilde{\varepsilon}_e \end{pmatrix}+ig_\perp\begin{pmatrix} 0 & 0 & -m_y \\ 0 & 0 & m_x \\ m_y & -m_x & 0 \end{pmatrix}, \tag{13}$$

$$\mathbf{g}=\begin{pmatrix} g_\perp & 0 & 0 \\ 0 & g_\perp & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{14}$$

where

$$g_{\perp} = -\frac{p}{\lambda}\frac{\varepsilon_a^2}{8\tilde{\varepsilon}_e}\sin^2(2\alpha). \tag{15}$$

No essentially new features are given by the following steps of the iteration procedure, which only give minor corrections to the already found equations.

Comments. (i) Let us first discuss the role of the higher order Fourier components. Interestingly, their effect on the optical properties of the above considered sample is given by a single parameter φ_0, which can be changed by simply rotating the sample with respect to the incidence plane of the light. This fact is a direct consequence of the helical symmetry of the periodic medium. The explicit expression of the transfer matrix is very complicated, even at first order of the perturbation expansion. The optical properties of interest (reflectance and transmittance) are more simply and quickly obtained by a numerical integration of the exact equations. It is however interesting to explicitly write the elements $U_{eo}^{(1)}$ $U_{oe}^{(1)}$ of the matrix $U^{(1)}(d)$ which couple the extraordinary and ordinary forwardly propagating waves, giving a rotation of the plane of polarization of the input beam. To compare this rotation with the one given by the gyrotropy parameter $g_{\perp}$, it is convenient to set $d=\lambda/2\pi$:

$$U_{eo}^{(1)} = -U_{oe}^{(1)} = \frac{p}{\lambda}\tilde{m}_a\left[\frac{1}{2}\frac{\tilde{t}_e}{\tilde{t}_o}b_1\sin\varphi_0 + \frac{1}{4}\frac{1}{\tilde{t}_e\tilde{t}_o}b_2\cos(2\varphi_0)\right] + O((p/\lambda)^2), \tag{16}$$

where $\tilde{m}_a=\tilde{m}_e-\tilde{m}_o=[\tilde{\varepsilon}_o(1-m_x^2/\tilde{\varepsilon}_e)]^{1/2}-(\tilde{\varepsilon}_o-m_x^2)$, $\tilde{t}_e=[\tilde{\varepsilon}_o/(1-m_x^2/\tilde{\varepsilon}_e)]^{1/4}$ and $\tilde{t}_o=(\tilde{\varepsilon}_o-m_x^2)^{1/4}$. These terms, as well as the other terms of the matrix $U^{(1)}(d)$, become identically zero when averaged over φ_0. Their dependence on p/λ and on ε_a is such that they are of the same order of magnitude of the gyrotropy parameter $g_{\perp}$ even in the limit $p\to 0$. This means that, strictly speaking, the homogeneous model for a periodic medium is never valid. However, we know that the optical properties of gyrotropic crystals are well described by a homogeneous model. The paradox is due to the fact that in such crystals only the average field is related to measurable quantities. This obviously occurs for light entering a sample whose boundaries are obliquely oriented with respect to the crystal planes, and for samples where the long range correlation is lost (as a consequence of surface irregularities or impurities, defects, etc.). Our computation suggests therefore that for periodic media the validity and usefulness of the homogeneous model are not related to the vanishing of the higher order Fourier components, but to the fact that their effects are difficult to detect in experiments. Small-pitch chiral smectic LC represent perhaps a unique example of periodic media whose optical properties are, in general, well described by a homogeneous model, except for samples with boundary planes orthogonal to the helix axis. Experiments to test this point are in progress, for media with pitches of the order of 0.1 μm. Preliminary results confirm this fact.

(ii) We have tested the limits of validity of the homogeneous model, defined by Eqs. (13), (9), and (15), by comparing its optical properties of practical interest with the corresponding properties of the actual periodic medium. In particular, we have computed the intensities and polarizations of the transmitted and reflected beams for different sample parameters and different orientations of the helix axis with respect to the boundary planes. For samples with the helix axis orthogonal to these planes, the Berreman equation (7) has been integrated numerically and the optical properties of the sample, such as the rotation angle of the input polarization, have been averaged over φ_0, as previously explained. For the other orientations, the equations for anisotropic gratings have been used, in which φ_0 plays no role.[12]

According to our computations, the homogeneous model fits all the considered properties within one percent up to $p<\lambda/5$. Large deviations are only found for p approaching the value where the periodic medium gives the first Bragg diffraction peak. Here, obviously, no homogeneous model is valid. The range of validity of the model is unexpectedly large, if we consider that it has been derived by an iteration procedure which is meaningful only for $p\ll\lambda$. We further observe that the rotatory power is very large, compared to typical values for isotropic liquids and crystals. The gyrotropy parameter $g_{\perp}$ of the actually available small-pitch smectic LC is of the order of 0.01. This gives a rotatory power of the order of one degree over a thichness of one wavelength, which, in general, cannot be neglected in experiments. The possible contribution coming from the chirality of the constitutive molecules is therefore negligible.

We further observe that the small local biaxiality of smectic LC, which here has been neglected, does not greatly change the gyrotropy parameter $g_{\perp}$, and that the sample generally transforms linear into elliptic polarization, owing to the dielectric anisotropy of the effective homogeneous medium. An experimental verification of the given theory requires, therefore, the evaluation of the rotation of the ellipse's axes. A simpler experiment could be done by considering a suitable polidomain crystal with random orientation of the helix axis. In fact, the medium obtained by averaging the effective dielectric tensor over all helix directions behaves as an isotropic optically active medium, whose gyrotropy pseudotensor has diagonal terms equal to $2g_{\perp}/3$ (*biisotropic* medium, i.e., isotropic for both the real and imaginary parts of the dielectric tensor).

(iii) The most interesting and unexpected result of our computations lies in the great simplicity of the basic equations, if we consider that the optical activity comes from the interactions between neighboring molecules, and is therefore a second order effect, given by the second iteration. In fact the effective medium is uniaxial in both the real and imaginary parts of the dielectric tensor (*biuniaxial*), and the gyrotropy pseudotensor **g** depends on a single parameter $g_{\perp}$, as shown by Eq. (14). The index $\perp$ refers to the optical axis, which is coincident with the helix axis. The absence of the parallel component means that the rotatory power is zero for light propagating along the optical axis.

The gyrotropy parameter $g_{\perp}$ (i) is a linear function of p/λ, as expected, since it derives from linear terms in the first order derivative appearing in Eq. (3); (ii) depends on the square of the local dielectric anisotropy of the medium. Its sign is therefore the same for media having positive and negative local anisotropy, and only depends on the handedness of the helix, defined by the sign of p. We recall that $p=2\pi/q$, and that, according to Eq. (1), positive or negative q values correspond to right- or left-handed helices, respectively; (iii) is maximum for $\alpha=45°$, zero for $\alpha=0°$, and $\alpha=90°$ (namely, for a cholesteric LC).

These properties are interesting from many points of view, and some are rather unexpected, compared with the properties of the same medium at higher p values. In fact, it is well known that cholesteric and chiral smectic LC with $p \geqslant \lambda$ give a huge rotation of the plane of polarization of light,[6] which is maximum for light propagating along the helix axis, and disappears if the light beam is rotated above a given angle.[13] Here it has been shown that for $p \ll \lambda$ the rotatory power is zero for light propagating along the helix axis, maximum in the orthogonal directions, and completely absent for the cholesteric phase. Let us discuss separately these points.

Exact analytic expressions are available for light propagating along the helix axis of cholesteric and chiral smectic LC. They show that an optical activity actually exists also for $p<\lambda$, but decreases as $(p/\lambda)^3$, and becomes practically negligible for $p<\lambda/10$. A full description of the optical activity for any direction of the light beam and for any p value requires a more complex theory. For $p \geqslant \lambda$, the rotatory power along the helix axis is essentially a first order effect, in the sense that the rotation of the polarization plane within any thin layer of the sample does not practically depend on the presence of neighboring layers. It cannot be accounted for in the framework of our theory since the iteration procedure loses its meaning for $p>\lambda$. In the opposite limit $p \ll \lambda$, the interaction between neighboring layers becomes important.

The fact that the gyrotropy parameter $g_\perp$ goes to zero for $\alpha=0°$ and $\alpha=90°$ is not surprising if we compare the medium M considered here with a medium M' made of well oriented dielectric helices with uniaxial polarizability tangent to the helix. In fact, the angle α' between the helix axis and any small segment of the helix, which depends on the ratio between the radius and the pitch of the helices, plays a role similar to the tilt angle α with respect to the polarization properties. Now, M'-type media display optical activity except for $\alpha'=0°$, where the helix becomes a straight line, and for $\alpha'=90°$, where the helix collapses into a circle. (A similar behavior is also found in biuniaxial media made of well oriented conducting helices.[14])

Other analogies between media of type M and M' exist. By increasing α' the dielectric anisotropy of M' changes its sign, from positive to negative values, whereas the sign of the gyrotropy parameters remains unchanged. A particular angle α'_c therefore exists, where the medium becomes isotropic for what concerns the real part of the dielectric tensor and anisotropic for what concerns the optical activity (*isotropic-anisotropic*). M-type media exactly display a similar behavior. The corresponding angle α_c is obtained by setting $\tilde{\varepsilon}_e=\tilde{\varepsilon}_o$, and is given by $\cos^2\alpha_c=[(\varepsilon_o^2+8\varepsilon_e^2)^{1/2}-3\varepsilon_o]\varepsilon_a^{-1}/4$. For this particular value of α the medium simply rotates the plane of polarization of linearly polarized light, and the rotation angle depends on the direction of the light beam. The conceptual (and perhaps also practical) interest of this fact is evident. This value of α is of great interest also for the optical properties of smectic LC at higher values of the pitch.[11]

Owing to the above analogies, we expect that the obtained results will be of help for a better understanding of the optical properties of other helical-shaped media, despite the structural differences between them. In particular, it would be of most interest to inquire to what extent the gyrotropy of different types of helical conformations can be described by expressions having the simple structure of Eq. (15).

(iv) As a final comment, let us recall that the optical properties of cholesteric and chiral smectic LC have been first understood for light propagating along the helix axis, and that it is generally thought that no essentially new optical property arises for obliquely propagating light.[15] The gyrotropic properties of small-pitch chiral smectics LC represent perhaps the most important effect which cannot be found if we only consider light propagating along to the helical axis. They are given by expressions which are at same time very simple and of great generality, since they can describe biuniaxial, isotropic-anisotropic, and bi-isotropic media. Other types of periodic helical structures have recently been considered, where the medium is locally gyrotropic and magnetic, in connection with the increasing interest for chiral media in the field of microwaves.[16] Only the case where $\alpha=90°$ and the light beam propagates along the helix axis has been considered. According to our analysis, structures having different α values could be of even greater interest.

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