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Optical properties of short pitch cholesteric liquid crystals

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The optical properties of short pitch cholesteric liquid crystals are theoretically analysed in the framework of an effective medium theory. It is shown that such properties are well described by a very simple homogeneous model, defined by an effective permittivity tensor $\tilde{\varepsilon}$ having uniaxial symmetry, that is expanded in a power series of the ratio p/λ_0 between the helix pitch and the light wavelength. The linear term is identically zero. This fact gives short pitch cholesterics very unusual properties for their optical activity, which is related to the scaling terms as $(p/\lambda_0)^m$, with m odd and greater than 1. Some problems related to the presence of these terms and concerning boundary effects are discussed but not fully resolved. The limits of validity of the different approximations, obtained by considering only a limited number of terms, are also found.

1. Introduction

Cholesteric liquid crystals (LCs) are probably the most interesting periodic structure found in optics. They have been extensively studied during the last century. The reasons for such interest are historical, theoretical and practical. It is well known that the history of LCs began with the discovery, in 1888, of a cholesteric ester in its cholesteric phase [1]. It is less widely known that before this discovery a cholesteric-like structure had been artificially made by Reusch [2], by superposing identical thin mica sheets, each one rotated by a small angle with respect to the preceding one. This fact demonstrates that the interest in cholesteric-like structures is not restricted to LC physics. Over the last few decades, any property of a cholesteric-like system has been the object of intense theoretical and experimental research, such that now no new optical properties are expected to be found. However, the optical properties of cholesteric samples having a pitch smaller than the light wavelength have received attention only in recent years [3–6], and in the framework of research concerning the optics of crystals. In particular, new methods have been developed to find the effective dielectric tensor $\tilde{\varepsilon}$ of the homogeneous (*macroscopic*) model for short pitch periodic liquid crystals, by assuming their local permittivity tensor field $\varepsilon(\mathbf{r})$. Such a periodic tensor function $\varepsilon(\mathbf{r})$ constitutes a *mesoscopic* model for the crystal, where its molecular (*microscopic*) structure is ignored.

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The aims of the present research are: (i) to apply the Bloch wave method [5, 6], to a particularly simple periodic structure (the existence of analytical solutions for the axial propagation of light in cholesteric LCs will allow us better to test the validity of the method); (ii) to explore the optical properties of short pitch cholesteric LCs for any direction of the light beam, on the basis of expressions as simple as possible; and (iii) to make a contribution to the solution of some unresolved problems concerning basic optics related to the boundary-type effect, that have been described in the cited references.

2. The models

Let us consider a locally biaxial cholesteric with the principal 3-axis parallel everywhere to the z axis of a cartesian frame, while the other two axes are rotating uniformly along z. The optical properties of the medium are fully defined by the relative dielectric tensor

$$\varepsilon(z) = \begin{pmatrix} \varepsilon_m & 0 & 0 \\ 0 & \varepsilon_m & 0 \\ 0 & 0 & \varepsilon_3 \end{pmatrix} + \frac{\varepsilon_a}{2} \begin{pmatrix} \cos(2\phi) & \sin(2\phi) & 0 \\ \sin(2\phi) & -\cos(2\phi) & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{1}$$

where $\varepsilon_m = (\varepsilon_1 + \varepsilon_2)/2$, $\varepsilon_a = (\varepsilon_1 - \varepsilon_2)$, $\phi = qz + \phi_0$, $q = 2\pi/p$, and p is the helix pitch. Equation (1) defines the mesoscopic model of the medium. The effective dielectric tensor $\tilde{\varepsilon}$ of its homogeneous model is found by the Bloch wave method [5, 6]. As a starting point, we consider the normal modes for the electromagnetic field within

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the periodic medium. These are Bloch waves, which can be written as a superposition of plane waves by setting

$$\mathbf{E}(\mathbf{r}) = \sum_{m=-\infty}^{\infty} E_m \exp \mathrm{i}(\mathbf{k} + 2mq\hat{z}) \quad \mathbf{r} \tag{2}$$

and similar expressions can be written for the other field vectors. The effective permittivity $\tilde{\varepsilon}$ of the homogeneous model is implicitly defined by setting $\mathbf{D}_0 = \epsilon_0 \tilde{\varepsilon} \mathbf{E}_0$, i.e. by only considering the plane wave of order zero, that defines the *macroscopic* field.

The effective tensor $\tilde{\varepsilon}$ is expressed as a function of the Fourier components of the periodic tensor field $\varepsilon(z)$, which for cholesterics reduce to:

$$\varepsilon_0 = \begin{pmatrix} \varepsilon_m & 0 & 0 \\ 0 & \varepsilon_m & 0 \\ 0 & 0 & \varepsilon_3 \end{pmatrix}$$
$$\varepsilon_{\pm 1} = \frac{\varepsilon_a}{4} \begin{pmatrix} 1 & \mp\mathrm{i} & 0 \\ \mp\mathrm{i} & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \exp(\pm 2\mathrm{i}\phi_0). \tag{3}$$

The zeroth order component ε_0 is the space average $\bar{\varepsilon}$ of $\varepsilon(z)$ and constitutes a first rough approximation for $\tilde{\varepsilon}$. The other approximations are obtained by adding $\bar{\varepsilon}$ terms having the general structure:

$$\varepsilon_{m_1} G_{-m_1} \varepsilon_{m_2} G_{-(m_1+m_2)} \cdots G_{-(m_1+\ldots+m_{N-1})} \varepsilon_{m_N} \tag{4}$$

where

$$G_m = \frac{\omega}{\mathrm{c}} [(\mathbf{k} + 2mq\hat{z})^2 \mathbf{1} - (\mathbf{k} + 2mq\hat{z})(\mathbf{k} + 2mq\hat{z}) - \bar{\varepsilon}]^{-1}. \tag{5}$$

The subscripts $m_1, \ldots, m_N$ run over -1 and $+1$, $\mathbf{1}$ is the 3×3 identity matrix, $(\mathbf{k} + 2mq\hat{z})(\mathbf{k} + 2mq\hat{z})$ is a dyadic product, and the following relations are satisfied:

$$m_1 + \ldots + m_N = 0, \quad \sum_{n=1}^{N'} m_n \neq 0 \quad \forall N' < N. \tag{6}$$

The terms given by equation (4) can be interpreted as the effect of the multiple scattering within the periodic structure, and equation (6) states that only the *forward* scattering with multiplicity $N \geqslant 2$ gives a contribution to $\tilde{\varepsilon}$. The formal expression of $\tilde{\varepsilon}$ can be written as:

$$\tilde{\varepsilon} = \bar{\varepsilon} + \sum_{N=2}^{\infty} \sum_{m_1} \cdots \sum_{m_{N-1}} \varepsilon_{m_1} G_{-m_1} \varepsilon_{m_2} G_{-(m_1+m_2)} \cdots \times G_{-(m_1+\ldots+m_{N-1})} \varepsilon_{-(m_1+\ldots+m_{N-1})}. \tag{7}$$

The tensor $\tilde{\varepsilon}$ explicitly depends on $\mathbf{k}$ through the matrices G_m, as shown by equation (5), i.e. $\tilde{\varepsilon} = \tilde{\varepsilon}(\mathbf{n})$, where $\mathbf{n} = \mathbf{k}/k_0$ is the normalized wave vector and $k_0 = 2\pi/\lambda_0$ is the light wave vector in free space. The dominant contribution to $\tilde{\varepsilon}(\mathbf{n})$ is given in general by the terms with $N = 2$, i.e. by the double scattering (two-photon scattering). Within this approximation, equation (7) assumes the simple form

$$\tilde{\varepsilon}(\mathbf{n}) = \bar{\varepsilon} + \varepsilon_{-1} G_1(\mathbf{n}) \varepsilon_1 + \varepsilon_1 G_{-1}(\mathbf{n}) \varepsilon_{-1}. \tag{8}$$

A further simplification is obtained by expanding G_m as a power series of the small parameter p/λ_0, since only the first terms of such an expansion are expected to give a non-negligible contribution to $\tilde{\varepsilon}(\mathbf{n})$. In the following we consider a homogeneous model where only the terms up to $(p/\lambda_0)^3$ are considered. Equation (8) now gives:

$$\tilde{\varepsilon}(\mathbf{n}) = \bar{\varepsilon} + \left(\frac{p}{\lambda_0}\right)^2 \tilde{\varepsilon}^{(2)} + \left(\frac{p}{\lambda_0}\right)^3 \tilde{\varepsilon}^{(3)} + O\left(\frac{p}{\lambda_0}\right)^4 \tag{9}$$

where

$$\tilde{\varepsilon}^{(2)} = a \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \tilde{\varepsilon}^{(3)} = a n_z \begin{pmatrix} 0 & \mathrm{i} & 0 \\ -\mathrm{i} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{10}$$
$$a = \frac{\varepsilon_a^2}{32\varepsilon_3}(2\varepsilon_3 - n_x^2 - n_y^2)$$

and n_x, n_y, n_z are the components of $\mathbf{n}$. The effective homogeneous medium is uniaxial, with the symmetry axis coincident with the helix axis of the periodic structure, and the $\mathbf{n}$-independent component is given by:

$$\tilde{\varepsilon}(\mathbf{0}) = \begin{pmatrix} \tilde{\varepsilon}_o & 0 & 0 \\ 0 & \tilde{\varepsilon}_o & 0 \\ 0 & 0 & \tilde{\varepsilon}_e \end{pmatrix} \tag{11}$$

where

$$\tilde{\varepsilon}_o = \varepsilon_m + \frac{\varepsilon_a^2}{16}\left(\frac{p}{\lambda_0}\right)^2; \quad \tilde{\varepsilon}_e = \varepsilon_3. \tag{12}$$

The $\mathbf{n}$-dependent component of $\tilde{\varepsilon}^{(2)}$ becomes important if $\tilde{\varepsilon}(\mathbf{0})$ defines an isotropic medium, i.e. if $\tilde{\varepsilon}_e = \tilde{\varepsilon}_o$, because in this case it gives a small anisotropy to the medium. This condition is never met by the N* phase, where $\varepsilon_2 \approx \varepsilon_3 \neq \varepsilon_1$.

For a real $\varepsilon(z)$, the term scaling as $(p/\lambda_0)^3$ is purely imaginary, and gives the $\tilde{\varepsilon}(\mathbf{n})$ an hermitian part that defines the optical activity of the medium.

3. Eigenwaves for the electromagnetic field: plane wave solutions

The eigenmodes for the electromagnetic field in the effective homogeneous medium have the simple form of plane waves. However, the dependence of $\tilde{\varepsilon}(\mathbf{n})$ on $\mathbf{n}$ gives a Fresnel equation that is no longer biquadratic: for any given direction $\hat{n}$, the equation has more than two plane wave solutions, with different values of $|\mathbf{n}|$. In expansion

(9), $\tilde{\varepsilon}(\mathbf{n})$ contains powers of $\mathbf{n}$ up to $\mathbf{n}^3$, and a Fresnel equation of the fifth degree in n^2 is expected. To find out the five independent solutions, it is convenient to consider the displacement vector $\mathbf{D}$, which is orthogonal to $\hat{n}$, instead of the vector $\mathbf{E}$. For plane harmonic waves, the Maxwell equations can be written,

$$\mathbf{n} \times [\mathbf{n} \times (\varepsilon^{-1}\mathbf{D})] = -\mathbf{D}. \tag{13}$$

Since the helix axis z is a symmetry axis of $\tilde{\varepsilon}(\mathbf{n})$, it is not restrictive to assume that the vector $\hat{n}$ is contained in the plane (y, z). With such an assumption, equation (13) can be written as:

$$\begin{cases} a_{11} D_x + a_{12} D_{y'} = 0 \\ a_{21} D_x + a_{22} D_{y'} = 0 \end{cases} \tag{14}$$

where the axis y' is orthogonal to the plane $(\hat{x}, \hat{n})$ and such that $\hat{x}, \hat{y}', \hat{n}$ define a right-handed cartesian frame. The coefficients a_{ij} are

$$\begin{aligned} a_{11} &= \tilde{\eta}_o + bn^2 (p/\lambda_0)^2 \sin^2\theta - 1/n^2; \\ a_{22} &= (\tilde{\eta}_o \cos^2\theta + \tilde{\eta}_e \sin^2\theta) \\ &\quad + bn^2 (p/\lambda_0)^2 \sin^2\theta \cos^2\theta - 1/n^2; \\ a_{12} &= -a_{21} = \mathrm{i} bn (p/\lambda_0)^3 (2\varepsilon_3 - n^2 \sin^2\theta) \cos^2\theta \end{aligned} \tag{15}$$

where θ is the angle $(\hat{n}, \hat{z})$ and

$$\begin{aligned} &\tilde{\eta}_o = \tilde{\varepsilon}_o^{-1} = \varepsilon_m^{-1} - \frac{\varepsilon_a^2}{16\varepsilon_m^2}\left(\frac{p}{\lambda_0}\right)^2 + O\left(\frac{p}{\lambda_0}\right)^4; \\ &\tilde{\eta}_e = \tilde{\varepsilon}_e^{-1} = \varepsilon_3^{-1}; \quad b = \frac{1}{32\varepsilon_3}\frac{\varepsilon_a^2}{\varepsilon_m^2}. \end{aligned} \tag{16}$$

Setting the determinant of the coefficients a_{ij} to zero, one indeed obtains a Fresnel equation of the fifth degree in the unknown n^2. To discuss the structure and the meaning of its solutions, it is convenient first to neglect the term scaling as $(p/\lambda_0)^3$ in the expression of $\tilde{\varepsilon}(\mathbf{n})$, thus obtaining an equation system where the off-diagonal elements a_{12}, a_{21} are identically zero. The eigenvalue equation is now of the fourth degree, and its four roots correspond to four linearly polarized waves, with polarization planes parallel or orthogonal to the plane $(\hat{n}, \hat{z})$. The wave vector of the last ones satisfies the biquadratic equation

$$\tilde{\eta}_o + b(p/\lambda_0)^2 \sin^2\theta n^2 - 1/n^2 = 0 \tag{17}$$

whose roots are:

$$\begin{aligned} n_1^2 &= \tilde{\eta}_o^{-1} - b(p/\lambda_0)^2 \sin^2\theta \tilde{\eta}_o^{-3} + O(p/\lambda_0)^4 \\ n_2^2 &\approx -\tilde{\eta}_o (p/\lambda_0)^{-2} (b \sin^2\theta)^{-1}. \end{aligned} \tag{18}$$

For $(p/\lambda_0) \ll 1$, the effective refractive indices are $n_1 \sim \sqrt{\tilde{\varepsilon}_o}$ and n_2, with $|n_2| \gg 1$. This last solution is physically meaningless, because its wave vector is outside the limits of validity of the effective medium theory. Formally identical equations are found for the two waves having polarization parallel to the plane $(\hat{n}, \hat{z})$, with the quantity $\tilde{\eta}_o$ substituted by $\tilde{\eta}_o \cos^2\theta + \tilde{\eta}_e \sin^2\theta$. In conclusion, only two solutions are physically meaningful. They can be obtained more easily by considering the terms depending on (p/λ_0) as perturbing terms in the equation that defines $\tilde{\varepsilon}(\mathbf{n})$, equation (9). The Fresnel equation is biquadratic, and gives the zeroth order solutions $n_1^{(0)}$ and $n_2^{(0)}$. Each one of these solutions, say $n_i^{(0)}$, is now inserted into the expressions for the matrices $G_{\pm 1}(\mathbf{n})$, equation (5), thus again obtaining a biquadratic Fresnel equation. Its root closest to $n_i^{(0)}$ is assumed to be the first order solution $n_i^{(1)}$. The next approximation can be obtained by inserting $n_i^{(1)}$ in the expression of $G_{\pm 1}(\mathbf{n})$, but in our case this is unnecessary because the second order corrections are of the order of $(p/\lambda_0)^4$. This perturbation–iteration procedure automatically selects the physical solutions, and seems, therefore, more appropriate to finding out $\tilde{\varepsilon}(\mathbf{n})$. The matrices $G_m(\mathbf{n})$ are contained in terms which act indeed as perturbing terms.

A similar iteration procedure has been used to find the transmission and the reflection coefficients at the boundaries of the cholesteric sample, where the tangential component of $\mathbf{n}$, instead of the direction $\hat{n}$, is the known quantity and dictated by the phase matching condition.

Finally we observe that the terms of $\tilde{\varepsilon}(\mathbf{n})$ scaling as $(p/\lambda_0)^3$ are related to the optical activity of the medium. In fact, in the presence of such terms the eigenwaves become elliptically polarized, as clearly shown by equations (14–16).

4. Optical activity and its scaling law

The cholesteric phase can be obtained only with chiral compounds that are optically active even in their isotropic phase. This fact implies the presence of an imaginary and hermitian part in the local dielectric tensor $\varepsilon(z)$. However, the contribution to the optical activity coming from the helical arrangement of the molecules in the N* phase is generally many orders of magnitude greater than the contribution arising from the chirality of the constituent molecules. For lossless media, the tensor $\varepsilon(z)$ can therefore be assumed as real.

A cholesteric sample gives uniform or quasi-uniform rotation of the polarization plane of linearly polarized light propagating along the helix axis (axial propagation), in a p-range from zero to nearly $\lambda_0/\Delta n$, where Δn is the local optical anisotropy. The rotatory power, i.e. the optical rotation per unit length ψ/d, is equal to $(k_1 - k_2)/2$, where k_1 and k_2 are the wave vectors of the eigenmodes for axial propagation, whose polarization states are nearly circular (except within the Bragg band; however a sufficiently thin sample gives optical rotation even in this band). The dependence of ψ/d on p and λ_0

is given by the de Vries equation [7]

$$\psi/d = \frac{k_o}{32}\left(\frac{p}{\lambda_0}\right)^3 \frac{\varepsilon_a^2}{[(p/\lambda_0)^2\varepsilon_m - 1]}. \tag{19}$$

The dependence of ψ/d on p is complicated, but simplifies in the short pitch limit, where $n_1 - n_2$ scales as $(p/\lambda_0)^3$ and $\psi/d \equiv (k_1 - k_2)/2$ scales as p^3/λ_0^4.

A scaling law of the type p^3/λ_0^4 is quite unusual. In fact, in most chiral compounds the rotatory power scales as λ_0^{-2}, a fact known experimentally since the early research of Biot on rotatory power [8]. The dependence of ψ/d on the size of the chiral molecules was first shown by Boltzmann in 1874 (see, for example, [9]) on the basis of a simple molecular model. Therefore for chiral crystals a scaling law of the type p/λ_0^2 is expected, and actually found in most media. The p^3/λ_0^4 scaling law in short pitch cholesterics is a further example of the unique optical properties of the cholesteric phase, and appears even more surprising in the framework of the approach given here. In fact, equation (9) is obtained by expanding the matrices G_m in a power series of p/λ_0. It is easily shown that: (i) for real $\varepsilon(z)$ the contribution to the optical activity only comes from the terms containing odd powers of (p/λ_0), which are purely imaginary, and (ii) for **n** parallel to the periodicity axis of 1D crystals the term linear in (p/λ_0) is identically zero. These facts explain the well known but unusual scaling law found in the N* phase for axial propagation, at least in the sense that this property is displayed by all short-pitch 1D crystals. The peculiarity of N* crystals is due to the fact that the term linear in (p/λ_0) is absent for *any direction of the light beam*. This property appears very strange indeed if we consider the following facts: (i) the optical activity is related in general to helical shaped structures because any chiral object, for example a chiral molecular group, defines a left- or right-handed helix which governs the optical activity [9]; (ii) the cholesteric phase is the simplest and the best known example of periodic helical structures. Despite these facts, the main term related to the optical activity of short pitch cholesterics is lacking, and only smaller contributions scaling as the third or higher powers of p/λ_0 are present in the expression of $\tilde{\varepsilon}(\mathbf{n})$.

In the next section we consider some relevant problems related to the presence of the higher order terms in the expression of $\tilde{\varepsilon}(\mathbf{n})$. Here, we discuss the limits of the validity of equations (10), whose simplicity is due to the fact that two different types of approximation have been made. Firstly, only the two-photon scattering has been considered and secondly, the matrices G_m have been expanded in a power series of p/λ_0, up to $(p/\lambda_0)^3$. The cholesteric phase is an ideal tool to test the validity limits of the expressions obtained, because exact analytical expressions have been known for axial propagation since 1951 [7]. We recall that the de Vries equation gives an approximate expression of ψ/d, where only the term scaling as ε_a^2 is considered. This term strictly corresponds to two-photon scattering, because the multiple scattering with multiplicity N gives terms scaling as ε_a^N in the expression of $\tilde{\varepsilon}(\mathbf{n})$. Figure 1 gives the rotatory power ψ/d as a function of the normalized pitch p/λ_0, for fixed λ_0, calculated using the exact equations (full lines), using the de Vries equation (upper dotted line), and using the expressions of $\tilde{\varepsilon}(\mathbf{n})$ obtained by considering the power expansions up to $(p/\lambda_0)^m$, for $m = 3$ (lower dotted line), $m = 5$ (asterisks), and $m = \infty$ (circles). The coefficient of the term scaling as $(p/\lambda_0)^5$ for axial propagation is

$$\tilde{\varepsilon}^{(5)} = \frac{1}{32} n(\varepsilon_m + n^2)\varepsilon_a^2. \tag{20}$$

The full expansion with $m = \infty$ has been obtained as the first order approximation of the perturbation approach described in § 3, by inserting the expression $\tilde{\varepsilon}(\mathbf{n}_i^{(0)})$ given by equation (8) in the Fresnel equation. The computations are very simple because for axial propagation $n_1^{(0)} = n_2^{(0)}$, since the unperturbed solutions are degenerate.

The discontinuity in the full curve occurs at the left hand side of the Bragg band, where p becomes identical to the internal wavelength λ and the medium gives selective reflection. The approximation with $m = \infty$, and the de Vries equation, give practically everywhere the same values, very close to the exact ones up to p nearly equal to λ. The limits of validity of the homogeneous model are larger than expected, at least for the rotatory power. The model fails only at the Bragg band, where no homogeneous model can be valid, as can be seen. The approximations with $m = 3$ and $m = 5$ are valid up to $p \sim \lambda/5$ and $p \sim \lambda/3$, respectively.

5. Spatial dispersion and boundary conditions

The spatial dispersion, i.e. the explicit dependence of the effective dielectric tensor $\tilde{\varepsilon}(\mathbf{n})$ on the wave vector of the plane waves, is a manifestation of the non-local character of the interactions of matter with the electric field. The polarization induced by the electric field **E** at any given point **r** depends on the value of **E** at **r** and also at the neighbouring points. The simplest way to take into account the spatial dispersion is to develop **E**(**r**) as a Taylor series, and to define a displacement vector **D** dependent explicitly on the space derivatives of **E**:

$$D_\alpha = \varepsilon_{\alpha\beta}E_\beta + \gamma_{\alpha\beta\gamma}\partial_\beta E_\gamma + \ldots \tag{21}$$

For plane waves, ∂_β corresponds to $ik_0 n_\beta$, since the space dependence of $E_\gamma(x_1, x_2, x_3)$ is given by the factor

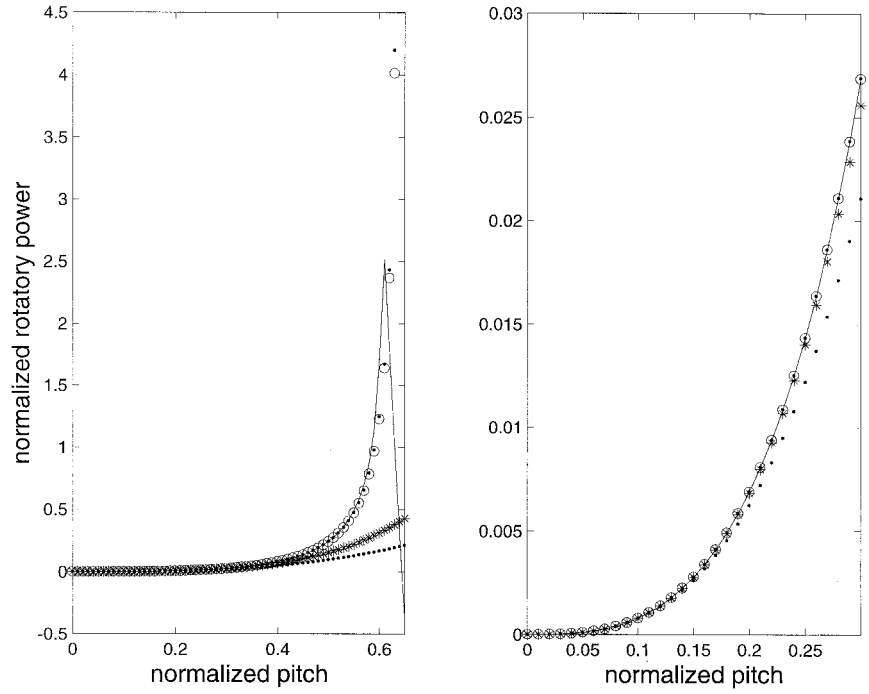

Figure 1. Optical rotatory power ψ/d versus p, where both d and p are measured in units λ_0 and ψ is in degrees, for a medium with $\varepsilon_1 = (1.75)^2$, $\varepsilon_2 = \varepsilon_3 = (1.55)^2$. The full line gives the exact values, the other curves the approximated ones (see text). All the approximations consider only terms linear in $\varepsilon_a^2 \equiv (\varepsilon_1 - \varepsilon_2)^2$.

$\exp(ik_0 n_\beta x_\beta)$. An approximation up to $(p/\lambda_0)^m$ corresponds, therefore, to a Taylor expansion up to the derivatives of order m. As far as we know, only the first order derivatives have been considered to date to define the optical properties of chiral media; the second order derivatives have been taken into account in cubic crystals, since they give a small optical anisotropy to such crystals [10]. To take into account the optical activity of short pitch cholesterics, we must consider at least the third order derivatives, as discussed in the preceding sections.

The presence of derivative-dependent terms in the constitutive equations gives problems which are not simple, in particular concerning the boundary conditions and the reflection properties of the medium. Such problems have been solved, at least partially, only for the first order derivatives by the Russian school [11, 12] and more recently by Raab and Graham, on the basis of a different set of constitutive equations [13]. More precisely, those workers make use of a covariant multipole form for the vectors **D** and **H**, that are written as

$$D_\alpha = \epsilon_0 E_\alpha + P_\alpha - \frac{1}{2}\nabla_\beta Q_{\alpha\beta} + \ldots; \qquad H_\alpha = \mu_0^{-1} B_\alpha - M_\alpha + \ldots \tag{22}$$

where **P** and **M** are the electric and magnetic dipole densities, respectively, and **Q** is the electric quadrupole density. Such equations are easily transformed in the Landau-type constitutive equations used here, where $\mathbf{B} = \mu_0 \mathbf{H}$ and **D** is given by equation (21). In particular, to eliminate the vector **M** from equation (22) it is sufficient to add to **P** a vector $\mathbf{P}'$ such that $\partial \mathbf{P}'/\partial t = \text{rot } \mathbf{M}$, i.e. to reinterpret the magnetization current density $\mathbf{J}_m = \text{rot } \mathbf{M}$ as a polarization current density $\partial \mathbf{P}'/\partial t$.

These approaches, and in particular the most recent one of Raab and Graham, are particularly suitable with which to treat the contribution to spatial dispersion given by the chirality of the molecules, where the *non-locality* is restricted to the molecular size. For N* crystals, this contribution is negligibly small, and the non-locality has a different origin. In fact, the assumption that the optical properties of a N* crystal are fully defined by a tensor field $\varepsilon(z)$ is, in a sense, an assumption of locality, but a further and more important contribution to the spatial dispersion comes from the inhomogeneity of the medium on a scale intermediate between the molecular and the macroscopic one (mesoscopic scale). The non-local character of our system is mainly due therefore to the mesoscopic inhomogeneity of the medium, and more precisely to the multiple scattering among its different parts. This gives a suitably averaged value of $\tilde{\varepsilon}(\mathbf{n})$, where the averaging must be performed, at least in principle, over the entire crystal. These long range interactions greatly complicate the problems related to the presence of the sample boundaries. The homogeneous model considered here has been found by considering an unlimited periodic medium. Strictly speaking, in a semi-infinite medium the effective tensor $\tilde{\varepsilon}(\mathbf{n})$ becomes **r**-dependent, since a dependence on the distance of the

considered point from the boundary plane is expected. The evaluation of the macroscopic dielectric tensor gives the same problems found for the evaluation of any other macroscopic quantity, as for instance the Frank elastic constants, in the presence of long range interactions.

The presence of a *boundary layer* having a thickness of the order of the pitch has been shown [4] by the optical properties of short pitch smectic C* phases. In the same paper, even more important optical effects are seen in samples between parallel planes orthogonal to the helix axis. Such effects are also present in N* samples. They are shown in figure 2, which gives the depolarized transmittance $T(\phi_0)$ and reflectance $R(\phi_0)$ of a sample with thickness $d = \lambda_0$, as a function of the angle ϕ_0 between the boundary direction of the local optic axis and the polarization plane of normally incident light. For $p \gg \lambda_0$ the dependence of the reflectance on ϕ_0 is obvious, because a ϕ_0 change has the same effect as the rotation of the optic axis of a uniaxial homogeneous crystal. Unexpectedly, this dependence is still very strong for p-values as small as $\lambda_0/10$, where the homogeneous model is expected to be valid. Despite the fact that $\varepsilon(z)$ is changing rapidly along z, T and R strongly depend on the boundary value of $\varepsilon(z)$. The figure gives an impressive demonstration of the difficulty in defining homogeneous models for crystals, and more generally for inhomogeneous media whose local properties are still correlated over distances large with respect to the wavelength of light. In fact, the optical properties of homogeneous models cannot depend on ϕ_0.

However, strong discrepancies between the actual periodic medium and its homogeneous model are found only if we consider small effects that are, in general, of little macroscopic interest and not easily detected experimentally. This statement is well illustrated by figure 3, which gives the optical rotation and the rotatory power of a finite sample as a function of its thickness. The full line refers to the macroscopic model in the $(p/\lambda_0)^3$ approximation, and the dotted lines to the exact values computed for three different values of ϕ_0. Large discrepancies between the different curves are found only for a very small optical rotation ψ, of the order of 0.1 degree or lower. It must be noted that the curves for the homogeneous model have been obtained by making use of 'wrong' boundary conditions, obtained by assuming the tangential continuity of the vectors **E** and **H**, or equivalently the normal continuity of the Poyting vector. It is in fact well known that such conditions are not consistent with the Landau-type constitutive equations (21), because the conservation of the energy flux at the boundary plane requires the addition of a new small term to $\mathbf{E} \times \mathbf{H}$, to obtain a self-consistent set of bulk

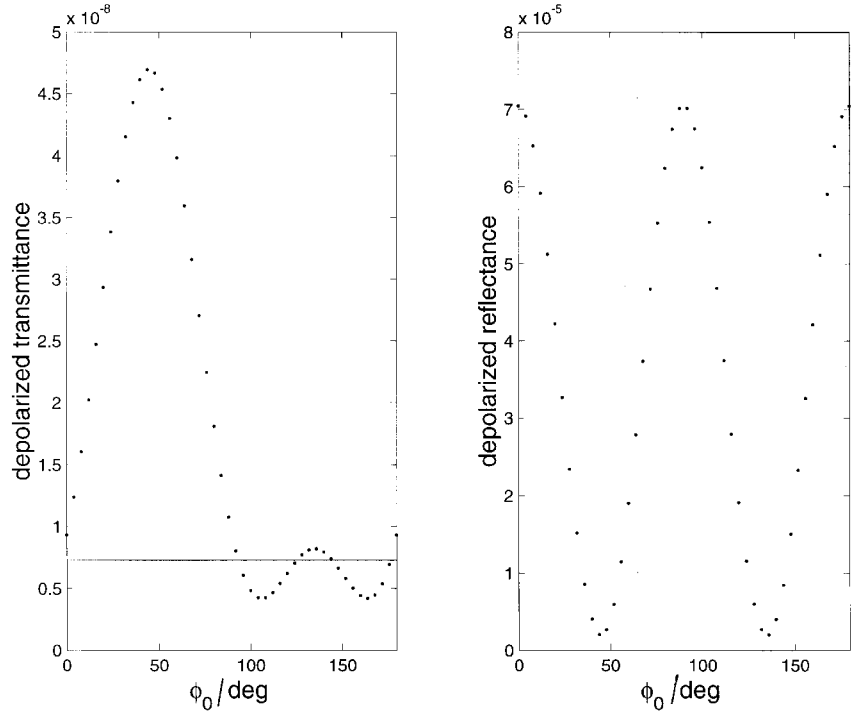

Figure 2. Depolarized transmittance and reflectance versus ϕ_0, defined as intensity ratios, with input linear polarization and orthogonal output polarization, for a sample of thickness $d = \lambda_0$ and pitch $p = 0.1\lambda_0$ between two glasses with refractive index $n_g = 1.5$. The other parameter values are the same as in figure 1. The dotted lines refer to the periodic medium, the full line to its homogeneous model in the $(p/\lambda_0)^3$ approximation, which gives a reflectance equal to 1.8×10^{-10}, such that the full line in the left hand figure is practically coincident with the horizontal axis.

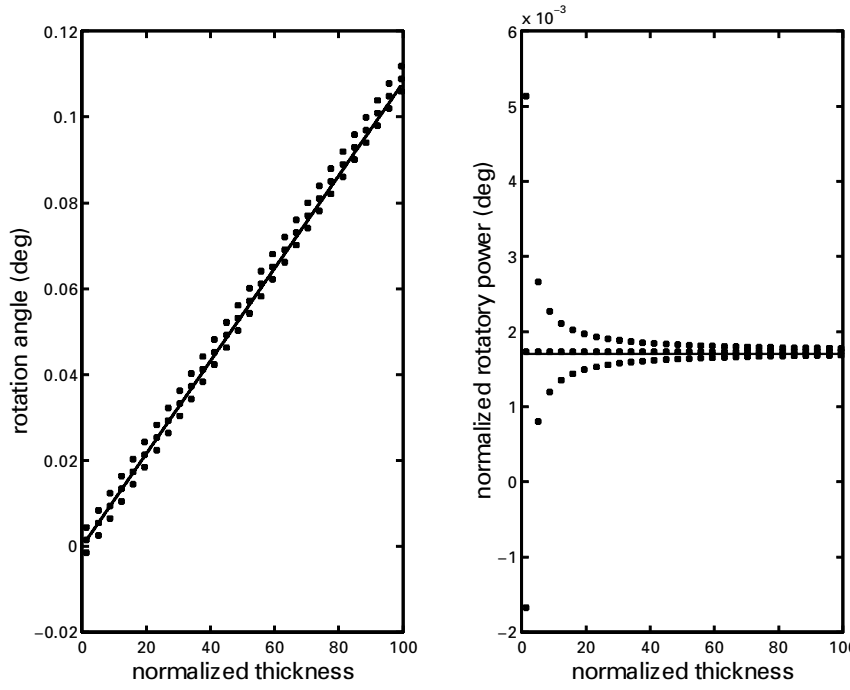

Figure 3. Optical rotation $/d$ (right-hand figure) versus $d/_0$. The other parameter values are the same as in figure 2. The dotted lines refer to the periodic medium with $\phi_0 = 0°, 60°, 120°$, the full lines to the homogeneous model in the $(p/\lambda_0)^3$ approximation.

and boundary relations for chiral media. The additional term has been calculated by Fedorov [12] for the simple case where the bulk equations contain only first order derivatives. The search for the corresponding term in the presence of higher order derivatives is still an open question. Despite its omission, the homogeneous model gives, in general, very good results. In fact it must be noted that the discrepancies shown by figures 2 and 3 are not due to the omission of the above term, but to a completely different and stronger effect, related to the role of the angle ϕ_0.

6. Conclusions

The Bloch wave method, developed recently to explore homogeneous models for crystals having periods short with respect to the wavelength of light, has been applied to short pitch N* liquid crystals. Very simple expressions are found for the effective permittivity $\tilde{\varepsilon}(\mathbf{n})$, that explicitly depend on the normalized wave vector $\mathbf{n}$ of the plane waves propagating in the medium. The simplicity of the equations giving $\tilde{\varepsilon}(\mathbf{n})$ is a consequence of the simplicity of the cholesteric structure, whose optical properties are fully defined by a permittivity function $\varepsilon(\mathbf{r})$ that only contains the Fourier components of order $-1, 0, +1$.

The most interesting optical property of short pitch cholesterics is related to their optical activity, that is given by terms of $\tilde{\varepsilon}(\mathbf{n})$ scaling as $(p/\lambda_0)^m$, with $m = 3, 5, 7, \ldots$ This property constitutes a further example of the unique optical properties of the cholesteric phase. In fact the main contribution to the optical activity of any other chiral medium is given by a term scaling as (p/λ_0). The terms with even m-values are of minor interest, because they only give a small correction to the linear birefringence.

The limits of validity of the homogeneous model have been carefully tested, at least for what influences the rotatory power for light propagating along the helix axis. Such limits depend on the number of terms used to define $\tilde{\varepsilon}(\mathbf{n})$. If we consider only terms with $m \leqslant 3$, the model is valid up to $p \approx \lambda/5$, there λ is the internal wavelength. The term with $m = 5$ extends its validity up to $p \approx \lambda/3$. The full expression of $\tilde{\varepsilon}(\mathbf{n})$, corresponding to $m = \infty$, is still reasonably simple and is valid up to p nearly equal to λ, i.e. up to the p-value that gives the Bragg reflection band. For higher p-values the homogeneous medium loses any meaning, as is evident.

A great emphasis is given to some problems concerning basic optics related to the presence of multiple roots for the Fresnel equation and to the presence of boundary effects. The homogeneous model allows, for any given direction, many plane wave solutions with different effective refractive indices. However only two solutions are physically meaningful, and can be found by a simple perturbation approach. The problems related to the presence of boundary effects have been discussed but not fully resolved. The great interest of a term scaling as $(p/\lambda_0)^3$ poses in fact not trivial problems for the definition of a self-consistent set of boundary and bulk equations, and could stimulate further research.

With reference to the aims declared in the introduction, the results obtained can be summarized as follows:

(i) The Bloch wave method seems very efficient, since it can generate many approximations for the effective dielectric tensor; in fact $\tilde{\varepsilon}(\mathbf{n})$ is expanded in a power series of two parameters, the local optical anisotropy ε_a and of the ratio p/λ_0. The different approximations are obtained by only considering some terms of the series.

(ii) The optical properties of short pitch cholesteric LCs are well described by equations (9–12), where only terms up to ε_a^2 and $(p/\lambda_0)^3$ are considered; this approximation for $\tilde{\varepsilon}(\mathbf{n})$ is based on very simple expressions, and it is sufficient to interpret experiments up to $p \approx \lambda_0/5$. The additional terms simply extend the validity of the model up to p nearly equal to the internal wavelength, but do not give any new insights.

(iii) The term scaling as $(p/\lambda_0)^3$, which is essential to account for the optical rotatory power of the chiral medium, gives new not yet fully resolved problems. Indeed, from the point of view of the boundary effects, the problems solved here appear not to be as important as the new ones highlighted.

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