

## Natural optical activity and liquid crystals

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**Abstract.** Optical activity of matter is related to the chirality of its constitutive molecules. In liquid crystals, chiral molecules can give rise to superstructures in which the local dielectric tensor rotates in space describing a helix, a fact which greatly enhances the optical activity of the medium. The structures and the optical properties of some helical phases are well-known, as for instance the cholesteric and some chiral smectic phases. For short enough helix pitches, the periodic medium can be considered optically as homogeneous and described by the same constitutive equations used to define the optical properties of solid crystals. Such liquid crystal phases represent an ideal tool to apply the methods, used since a long time in optics, to define homogeneous models for non homogeneous media and to discuss their limits of validity. A brief account is given of the main results recently found in this research area.

**Keywords.** Optical activity; chiral liquid crystals; homogeneous models.

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### 1. Introduction

Natural optical activity is perhaps the most well known but not so well understood optical property. It is treated in any, even elementary, textbook of physics and chemistry, but rarely its explanation goes beyond the observation that it is related to the circular birefringence and to the absence of mirror symmetry. Among physicists, the interest in this property grows since its discovery until the classic work of Max Born, then it seems to decrease, being restricted to a few specialists, mainly Russian. On the contrary, the interest in chiral media has been always growing in chemistry and biology since the fundamental work of Pasteur. Many excellent monographs on chiral molecules are available since many years [1, 2], and more recently in other research fields: microwaves, and more generally electromagnetic wave propagation, so that good monographs closer to the interests of physicists are now available [3, 4].

Optical activity is only displayed by media containing chiral molecules<sup>1</sup>, or more generally by a dissymmetric structure whose symmetry group does not contain an element  $S_n$  – a rotation by an angle  $2\pi/n$  around a given axis followed by reflection in a plane perpendicular to this axis. In particular, it does not contain the element  $S_1$  (a mirror symmetry plane) and  $S_2$  (an inversion symmetry point). Two different molecules related by mirror or by inversion symmetry are optical enantiomers, and rotate the plane of polarization of light in opposite directions.

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<sup>1</sup> In the Russian literature the term *gyrotropy* instead of *chirality* is generally used.

Chirality in molecules leads to a great number of interesting structures, some very simple and regular (crystals), others of great complexity (biological systems). We consider here the simplest ones, and more precisely the cholesteric ( $N^*$ ) and chiral smectic ( $C^*$ ,  $I^*$ ,  $F^*$  and  $K^*$ ) liquid crystals, that are periodic in only one direction. If the helix pitch is smaller than the light wavelength, the periodic medium can be conveniently treated in optics as macroscopically homogeneous, as usual for solid crystals. The description of the macroscopic properties of crystals is a classic problem in optics [5]. From this point of view, the interest in short pitch helical LC-phases is related to the fact that we can use, as a starting point of our analysis, the well-established and universally used model where the molecular structure is neglected and the medium is considered as a continuum. This model, which is non-homogeneous and periodic, will be referred to as *mesoscopic*, whereas the homogeneous model corresponding to a perfect crystal will be referred to as *macroscopic*. The main aim of our research is the definition of macroscopic models for perfect LC crystals and the discussion of their limits of validity, considering as exact the mesoscopic ones.

For this purpose, it has to be noted that many problems in the optics of chiral crystals are still unsolved, since the optical properties of such media are hardly incorporated in the framework of homogeneous models. The main difficulties come from the intrinsic dissymmetry of these media and from the non local nature of optical activity, and are reflected in the surprisingly large number of constitutive equations used to describe optically active media. Any set of constitutive equations defines a possible macroscopic model for the actual periodic structure. The relations between different models have been discussed for a long time in the literature [6, 7], but only in the last decade they have been rather well clarified (see, for instance [3, 4, 8]). A brief account of these developments is given in the next two sections. In the following ones, the mesoscopic models for  $N^*$  and  $C^*$  LCs and the methods used to find the corresponding macroscopic models are defined. Finally, a brief discussion is given of the main results, to show that the LC phases represent indeed ideal systems to discuss the limits of validity of homogeneous models for non-homogeneous media.

## 2. Natural optical activity and helices

Within chiral isotropic media, the field vectors of light describe a helix; as shown by Fresnel, this is a consequence of the fact that the refractive indices for left and right circularly polarized waves are slightly different (*circular dichroism*). The same vectors describe again a helix if we consider circularly polarized light. By considering these facts, Fresnel proposed by analogy that the stereochemical form of chiral crystals, and in particular of crystalline quartz, is essentially helicoidal [9].

The helical model for optical activity first suggested by Fresnel has become more and more important in our century. In his *Lehrbuch der optik* [10], Drude explains the optical activity by assuming that the electrons within chiral molecules oscillate along a helix. This gives a polarization vector  $\mathbf{P}$  containing a term proportional to curl  $\mathbf{E}$ . In SI units, the constitutive equations are

$$\mathbf{D} = \varepsilon_0(\varepsilon^{(0)} + a\nabla \times)\mathbf{E}; \quad \mathbf{B} = \mu_0\mathbf{H}. \quad (1)$$

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The chiral parameter  $a$  has the dimension of a length. As a very rough estimate of its order of magnitude in the optical frequency range, we can assume it to be of the dimension of the chiral molecular group. The circular birefringence, defined as the difference  $\Delta n$  between the refractive indices for right and left circularly polarized waves, is generally very small and given by

$$\Delta n = 2\pi a/\lambda, \quad (2)$$

where  $\lambda$  is the light wavelength within the medium. The rotatory power, i.e. the rotation of the plane of polarization per unit path length of the linearly polarized beam, is

$$\rho = \frac{2\pi^2}{n^{(0)}} \frac{a}{\lambda^2}, \quad (3)$$

where  $n^{(0)} = \sqrt{\varepsilon^{(0)}}$ .

The chiral parameters  $a$  and  $\rho$  are the most important optical parameters explicitly depending on the molecular size. The scaling laws, given by eqs. (2), (3), were first found by Boltzmann [11] on the basis of a simple molecular model. It is however to be observed that according to Drude's model of oscillating electrons, the parameters  $\varepsilon^{(0)}$  and  $a$  depend on the light wavelength, owing to the frequency dispersion. This gives a more complicated dependence of  $\Delta n$  and  $\rho$  on  $\lambda$ . For the one-electron model of Drude, the parameter  $a$  changes its sign at the proper frequency of the oscillating electron, giving a dependence of  $\rho$  on  $\lambda$  of the type  $(\lambda^2 - \lambda_1^2)^{-1}$ , where  $\lambda_1$  is the wavelength corresponding to the proper frequency. In the quantum mechanical treatment, the number of proper frequencies becomes infinite.

An interesting realization of the Drude model has been given by Lindman [12]. He shows that a box containing small randomly oriented helices of copper wires rotates the plane of polarization of microwaves. The oscillation of the conducting electrons within the wire can be treated classically, and the optical rotatory dispersion follows the Drude equation.

More recently, the advances in digital computers opened a new area of research on scattering by helices (for an essential bibliography, see [3,4]). These studies on helices have been of great help to better understand natural optical activity successfully in terms of the 'helical model'. Most optically active molecules or radicals have indeed helical conformations; in other chiral molecules, the disposition of the atoms or atomic groups can be used to define a left-or right-handed helical ensemble, which governs the optical activity [1, 2].

Let us now consider chiral liquid crystals. The history of liquid crystals begins with the discovery of a cholesteric compound, in 1888 [13], and Fresnel's ideas on the origin of optical activity seem to materialize in cholesteric LCs. The director field within a cholesteric and the field vectors  $\mathbf{E}$  and  $\mathbf{B}$  within a circularly polarized wave have exactly the same morphology. The one-dimensional  $N^*$  and  $C^*$  phases are perhaps the simplest helical objects existing in nature and, for light propagating along the helix axis, they are the only periodic structures whose optical properties are described by exact and simple analytic expressions. In particular, the rotatory power is given by an expression containing the Drude factor  $(\lambda^2 - \lambda_1^2)^{-1}$ , where the critical wavelength  $\lambda_1$  is equal to the helix pitch and has therefore a very simple geometric meaning [14]. It is interesting to observe that also for Lindman's helices the quantity  $\lambda_1$  is related to purely geometric

quantities (pitch and radius of the helix, length and radius of the wire), but its expression is extremely complicated. Strangely enough, the optical activity of helical liquid crystals for a general direction of the light beam has only been studied recently [15]. It is given by very simple expressions, and will be discussed in § 7.

### 3. Constitutive equations

Natural optical activity is related to the space derivatives of the electric field appearing in eq. (1), a fact which gives rise to spatial dispersion. In other words, optical activity is a non local property coming from the molecular structure of matter or, more generally, from its non-uniformity in space.

The constitutive equations, eq. (1), are easily generalized to anisotropic media by simply considering the quantities  $\varepsilon^{(0)}$  and  $a$  as second rank tensors. A further generalization is also obtained by considering higher order space derivatives. The most general linear relation between  $\mathbf{D}$  and  $\mathbf{E}$  can be written as:

$$D_i = \varepsilon_0(\varepsilon_{ij}^{(0)} E_j + \gamma_{ijl} \partial_l E_j + \eta_{ijlm} \partial_l \partial_m E_j + \dots). \quad (4)$$

For plane waves, we assume for the vectors  $\mathbf{D}$  and  $\mathbf{E}$  a dependence on  $\mathbf{r}$  and  $t$  of the type  $\exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)]$ . Inserting this expression into eq. (4), we obtain an explicit dependence of the relative dielectric tensor on the wavevector  $\mathbf{k}$

$$\varepsilon_{ij} = \varepsilon_{ij}^{(0)} + i\gamma_{ijl} k_l - \eta_{ijlm} k_l k_m + \dots. \quad (5)$$

The quantities  $\gamma_{ijl}$  depend on the molecular size and, for periodic media, on the period  $p$ . By neglecting the dependence of  $\gamma_{ijl}$  on  $\omega$  (i.e. the frequency dispersion), we find for the term  $\gamma_{ijl} k_l$  the Boltzmann scaling law. Similarly, the terms coming from the derivative of order  $m$  scale as  $(p/\lambda)^m$ . Optical activity is related to the odd-order terms, which are identically zero for media with inversion symmetry.

For solid crystals the terms scaling as  $(p/\lambda)^m$ , with  $m > 1$  have always been considered to be of purely academic interest. As an illuminating example, the term with  $m = 2$  gives a small optical anisotropy to cubic crystals, a fact predicted by Lorentz as early as 1878 [16] and experimentally observed only in 1960 [17]. On the other hand, for helical liquid crystals the ratio  $(p/\lambda)$  is generally not a small quantity. The higher order terms could therefore be of interest. In particular, for light propagating along the helix axis of cholesteric LCs the term with  $m = 1$  is identically zero and the optical activity is given by the term scaling as  $(p/\lambda)^3$ . The presence of higher order terms gives rise to non simple problems for the boundary conditions of finite samples, and more generally for non-homogeneous media displaying spatial dispersion. Here we only consider the first two terms.

Let us first discuss the constitutive equations (1) suggested by Drude. The equations are indeed very simple, but their simplicity has rather heavy counterparts. As shown by Fedorov [18], a new term must be added to  $\mathbf{S} = \mathbf{E} \times \mathbf{H}$  to obtain a Poynting vector having the meaning of power flux density. Further, the equations are non-invariant with respect to Lorentz transformation. Fedorov suggested new equations, which are now generally written in the form (for more details, see [3,4])

$$\mathbf{D} = \underline{\underline{\varepsilon}}(\mathbf{I} + \underline{\underline{\alpha}} \cdot \nabla \times) \mathbf{E}, \quad \mathbf{B} = \underline{\underline{\mu}}(\mathbf{I} + \underline{\underline{\alpha}}^T \cdot \nabla \times) \mathbf{H}, \quad (6)$$

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where  $\underline{\mathbf{I}}$  is the identity matrix and the superscript  $T$  stands for transpose. Many other sets of constitutive equations have been suggested. The simplest one is

$$\underline{\mathbf{D}} = \underline{\underline{\epsilon}} \underline{\mathbf{E}} + i \underline{\underline{\chi}} \underline{\mathbf{H}}, \quad \underline{\mathbf{B}} = -i \underline{\underline{\chi}}^T \underline{\mathbf{E}} + \underline{\underline{\mu}} \underline{\mathbf{H}}. \quad (7)$$

For uniform media the equations (1), (6) and (7) are equivalent, after suitable redefinition of the field vectors. To explain this fact, let us consider the Maxwell equations

$$\nabla \times \underline{\mathbf{E}} + \frac{\partial \underline{\mathbf{B}}}{\partial t} = 0, \quad (8a)$$

$$\mu_0^{-1} \nabla \times \underline{\mathbf{B}} - \epsilon_0 \frac{\partial \underline{\mathbf{E}}}{\partial t} = \underline{\mathbf{j}}, \quad (8b)$$

where the vector  $\underline{\mathbf{j}}$  takes into account the motion of all charged particles within the medium. Equation (8a) can obviously be used to substitute in eq. (6) the term  $\underline{\underline{\alpha}} \cdot \nabla \times \underline{\mathbf{E}}$ , which is responsible for optical activity, by  $-\underline{\underline{\alpha}} \partial \underline{\mathbf{B}} / \partial t$ , thus giving rise to a new and fully equivalent set of equations. For time harmonic fields this last quantity can in turn be written as  $i\omega \underline{\mathbf{B}}$ , obtaining a linear dependence of  $\underline{\mathbf{D}}$  on  $\underline{\mathbf{E}}$  and  $\underline{\mathbf{B}}$ . A similar equation has been suggested by Post [19], whereas an equation where  $\underline{\mathbf{D}}$  linearly depends on  $\underline{\mathbf{E}}$  and  $\underline{\mathbf{H}}$  has been suggested by Tellegen [20]. The above transformations are rather formal, but the underlying physics is not trivial. In fact the equations containing the space derivatives of the vector fields emphasize the non local character of the optical activity, i.e. the fact that the response of the medium to the impressed fields at any given point also depends on the field values at the neighboring points. The Tellegen equations, instead, have been suggested on the assumption that chiral objects contain both electric and magnetic dipoles.

Consider now eq. (8b). For stationary and low frequency fields it is possible and convenient to separate the contributions to the total density  $\underline{\mathbf{j}}$ , arising from the free electrons (conduction current), the bound electrons whose displacement gives rise to the electric polarization (displacement current), and the electron rotations giving rise to the magnetic polarization (Ampere's current). For a perfect insulator  $\underline{\mathbf{j}}$  is generally expressed as:

$$\underline{\mathbf{j}} = \frac{\partial \underline{\mathbf{P}}}{\partial t} + \nabla \times \underline{\mathbf{M}}, \quad (9)$$

where  $\underline{\mathbf{P}}$  and  $\underline{\mathbf{M}}$  are the electric and magnetic polarization vectors. This enables us to write eq. (8b) in the usual form:

$$\nabla \times \underline{\mathbf{H}} - \frac{\partial \underline{\mathbf{D}}}{\partial t} = 0 \quad (10)$$

where  $\underline{\mathbf{D}} = \epsilon_0 \underline{\mathbf{E}} + \underline{\mathbf{P}}$  and  $\underline{\mathbf{H}} = \mu_0^{-1} \underline{\mathbf{B}} - \underline{\mathbf{M}}$ . With such definitions, the tangential components of the vector  $\underline{\mathbf{H}}$  are continuous at the boundaries of the considered medium, while the vector  $\underline{\mathbf{M}}$  (and consequently,  $\underline{\mathbf{B}}$ ) becomes discontinuous owing to a  $\delta$ -type discontinuity for the current density  $\underline{\mathbf{j}}_M = \nabla \times \underline{\mathbf{M}}$ . Similar considerations can be employed for the normal components of the vectors  $\underline{\mathbf{D}}$ ,  $\underline{\mathbf{P}}$  and  $\underline{\mathbf{E}}$ , by using the other pair of Maxwell's equations and the polarization charge related to the surface discontinuity of the vector  $\underline{\mathbf{P}}$ . However, at optical frequencies the current magnetization  $\underline{\mathbf{j}}_M$  is small and its separation from the main current  $\underline{\mathbf{j}}_p = \partial \underline{\mathbf{P}} / \partial t$  becomes questionable [21]. It would therefore be convenient to incorporate the current  $\underline{\mathbf{j}}_M$  into a suitably defined new vector  $\tilde{\underline{\mathbf{P}}}$  and write the constitutive equations in the simple form of eq. (1). Formally, it is enough to define a

new vector  $\tilde{\mathbf{P}}$  such as  $\partial\tilde{\mathbf{P}}/\partial t = \partial\mathbf{P}/\partial t + \nabla \times \mathbf{M}$  and, accordingly, define new vectors  $\tilde{\mathbf{H}}$ ,  $\tilde{\mathbf{D}}$  and new tensors  $\tilde{\underline{\underline{\varepsilon}}}$ ,  $\tilde{\underline{\underline{\mu}}}$ .

Let us finally consider the more general equation (4). The presence of higher order terms generates more complex and not yet fully solved problems, in particular those concerning the boundary conditions. If we only consider the first two terms, this equation is fully equivalent to eq. (1), where  $\varepsilon^{(0)}$  and  $a$  are second rank tensors. This has been shown by Landau–Lifshitz on the basis of symmetry laws [21], and by Fedorov on the basis of energy considerations [18].

#### 4. Mesoscopic and macroscopic models for helical liquid crystals

Chiral molecules in liquid crystals can give rise to new chiral phases, in which the average orientation of the molecular long axis (nematic director  $\hat{\mathbf{n}}$ ) rotates in space, describing a helix. The chiral phase arising from nematics is the cholesteric phase ( $N^*$ ), the corresponding one for smectic C is the chiral smectic phase ( $C^*$ ). From the point of view of optics, the main difference between these phases is in the direction of  $\hat{\mathbf{n}}$ , which is orthogonal to the helix axis, say  $z$ , for  $N^*$  liquid crystals and obliquely oriented for  $C^*$ . The angle  $\alpha$  between  $\hat{\mathbf{n}}$  and  $z$  is the *tilt angle* of the helical structure. The components of  $\hat{\mathbf{n}}$  are given by

$$n_x = \sin \alpha \cos(qz + \varphi_0), \quad (11a)$$

$$n_y = \sin \alpha \sin(qz + \varphi_0), \quad (11b)$$

$$n_z = \cos \alpha, \quad (11c)$$

where  $q = 2\pi/p$ , and the phase constant  $\varphi_0$  defines the direction of  $\hat{\mathbf{n}}$  at the plane  $z = 0$ . For cholesterics,  $\alpha = \pi/2$ .

In the following we consider the medium as locally uniaxial and fully defined by its dielectric tensor, given by

$$\underline{\underline{\varepsilon}} = \varepsilon_o + \varepsilon_a \hat{\mathbf{n}}(z) \hat{\mathbf{n}}(z), \quad (12)$$

where  $\varepsilon_a$  is the local dielectric anisotropy, defined as the difference  $\varepsilon_e - \varepsilon_o$  between the principal values of  $\underline{\underline{\varepsilon}}$ . The components of the tensor  $\underline{\underline{\varepsilon}}(z)$  are periodic functions of  $z$ , with period equal to the helix pitch. The magnetic polarizability of actually available compounds is negligibly small, whereas their local biaxiality and gyrotropy are in general non negligible. However, their influence on the optical properties of the smectic samples considered here is very small. The intrinsic optical activity (coming from the chirality of the individual molecules) gives non-negligible effects only in the limit where the pitch becomes comparable to the molecular size. Even in this limit it will be neglected, because our aim is to find out and discuss the optical activity arising from the helical arrangement of the molecules.

Equations (11), (12) define the mesoscopic model. Our aim is to find out the corresponding macroscopic model in the limit  $p \ll \lambda$  and to discuss its limits of validity, assuming as exact the mesoscopic one. For this purpose, two different methods have been used, based on the Bloch waves within the periodic medium [22] and on the transfer matrices for finite samples between parallel plates [15]. The two methods have given the same results for the bulk properties of different periodic LCs. The first method can be

used in principle for any crystal, whereas the other one has only been developed for one dimensional crystals (it could be extended to higher dimensional crystals, but it becomes rather involved). However, the transfer matrix method is more suitable to bring out the validity limits of the macroscopic model and possible boundary effects. Both methods are therefore of interest and will be described in the following sections.

## 5. Bloch wave method

Any electromagnetic field vector  $\mathbf{F}$  can be decomposed in plane waves within homogeneous media, in Bloch waves within perfectly periodic media. The Bloch waves can be considered as a superposition of plane waves:

$$\mathbf{F}(\mathbf{r}) = \sum_{\mathbf{q}} \mathbf{F}_{\mathbf{q}} \exp[i(\mathbf{k} + \mathbf{q}) \cdot \mathbf{r}], \quad (13)$$

where  $\mathbf{k}$  is the Bloch vector, the summation runs over all the  $\mathbf{q}$ -vectors of the reciprocal lattice and the time dependence  $\exp(-i\omega t)$  is assumed.

The Bloch-wave method consists in retaining a single plane wave, that implicitly defines the macroscopic (homogeneous) medium. All the other plane waves are neglected. In fact, for decreasing values of the pitch the amplitudes of the higher order plane waves decrease. The homogeneous model would be well justified if all the amplitudes of the neglected components went to zero for  $p \rightarrow 0$ . Unfortunately, this is not true for crystals [7]. To show this fact it is enough to insert the expression

$$\underline{\underline{\varepsilon}}(\mathbf{r}) = \sum_{\mathbf{q}} \underline{\underline{\varepsilon}}_{\mathbf{q}} \exp(i\mathbf{q} \cdot \mathbf{r}) \quad (14)$$

into the equation  $\mathbf{D}(\mathbf{r}) = \underline{\underline{\varepsilon}}(\mathbf{r})\varepsilon_0 \mathbf{E}(\mathbf{r})$ , where  $\mathbf{D}(\mathbf{r})$  and  $\mathbf{E}(\mathbf{r})$  are given by eq. (13). We obtain

$$\mathbf{D}_{\mathbf{q}} = \varepsilon_0 \sum_{\mathbf{q}'} \underline{\underline{\varepsilon}}_{\mathbf{q}-\mathbf{q}'} \cdot \mathbf{E}_{\mathbf{q}'}. \quad (15)$$

Even if only one Fourier component of the vector  $\mathbf{E}(\mathbf{r})$  is different from zero, we have a set of non-zero Fourier components for the vector  $\mathbf{D}(\mathbf{r})$ , each one corresponding to a component  $\underline{\underline{\varepsilon}}_{\mathbf{q}}$  of the tensor  $\underline{\underline{\varepsilon}}$ .

For  $p \ll \lambda$ , the effects of the neglected Fourier components are negligible in experiments in which only an average of the field vectors, over a large volume with respect to  $p$ , is involved. This *averaged* field corresponds to the zero-th order Fourier component. However, experiments depending on the exact field values are not to be excluded, in principle. The possible discrepancies between exact and approximated (*averaged*) expressions will be discussed later because they are more easily found by the transfer matrix approach.

A method to define the effective dielectric tensor of the macroscopic medium is given in [22] and can be summarized as follows.

By inserting eqs. (14) and (13) into Maxwell's equations, one obtains the following propagation equation for each  $\mathbf{q}$  component of a Bloch wave of the electric field

$$(\mathbf{k}_{\mathbf{q}}^2 \mathbf{I} - \mathbf{k}_{\mathbf{q}} \otimes \mathbf{k}_{\mathbf{q}} - k_0^2 \underline{\underline{\varepsilon}}_0) \cdot \mathbf{E}_{\mathbf{q}} = k_0^2 \underline{\underline{\varepsilon}}_{\mathbf{q}} \mathbf{E}_0 + k_0^2 \sum_{\mathbf{q}' \neq \mathbf{q}, 0} \underline{\underline{\varepsilon}}_{\mathbf{q}-\mathbf{q}'} \cdot \mathbf{E}_{\mathbf{q}'}, \quad (16)$$

where  $k_0 = \omega/c$  is the vacuum wavevector,  $\mathbf{I}$  is the  $3 \times 3$  identity tensor and  $\mathbf{k}_q = \mathbf{k} + \mathbf{q}$ . Equation (16) is similar to the wave equation used in the dynamical theory of X-ray scattering, except that in this theory a two-wave approximation close to a Bragg reflection band is generally considered. Here, instead, we shall suppose that we are far from a Bragg band and that the modulation of the dielectric tensor is sufficiently small,  $|\underline{\underline{\epsilon}}_q| \ll 1$  for  $\mathbf{q} \neq 0$ . Under these conditions we can solve perturbatively eq. (16) by first neglecting the summation on the right-hand side, i.e. the effect of multiple scattering events: at this stage this amounts to a Born approximation. We can thus express each Fourier component  $\mathbf{q} \neq 0$  of the  $\mathbf{q}$ th Bloch wave of the electric field as a function of the zeroth order component alone

$$\mathbf{E}_q = k_0^2 \mathbf{G}(\mathbf{q}) \underline{\underline{\epsilon}}_q \mathbf{E}_0, \quad (17)$$

where we have defined the tensor

$$\mathbf{G}(\mathbf{q}) = (k_q^2 \mathbf{I} - k_q \otimes k_q - k_0^2 \underline{\underline{\epsilon}}_0)^{-1}. \quad (18)$$

The electric field components, eq. (17), will in turn induce a polarization and thus give rise to the dielectric displacement  $\mathbf{D}$ , whose Fourier components are given by eq. (15). The macroscopic model is obtained by considering only the component  $\mathbf{q} = 0$  in eq. (15). With this approximation, the periodic medium behaves like an effective homogeneous medium whose relative dielectric tensor is given by

$$\underline{\underline{\tilde{\epsilon}}} = \underline{\underline{\epsilon}}_0 + k_0^2 \sum_{\mathbf{q} \neq 0} \underline{\underline{\epsilon}}_{-\mathbf{q}} \mathbf{G}(\mathbf{q}) \underline{\underline{\epsilon}}_q. \quad (19)$$

## 6. Transfer matrix method

The transfer-matrix approach is particularly suitable to find out and discuss possible boundary effects. In fact, the transfer matrix gives the output field, at  $z = d$ , as a function of the input field, at  $z = 0$ , for a finite sample between the planes  $z = 0$  and  $z = d$ . For  $p > \lambda$  the periodic sample acts in general as a grating. The transfer matrix is infinite dimensional and a suitably truncated matrix is used [23, 24]. An incident plane wave gives rise in fact to a finite number of homogeneous (propagating) waves and to an infinite number of non-homogeneous (evanescent) waves. The field at  $z = 0$  is the superposition of the input and the reflected waves, the field at  $z = d$  is the superposition of the transmitted waves. By decreasing the pitch, the number of homogenous waves decreases. The sample can be conveniently treated as homogeneous only if all these waves disappear, except two, corresponding to the waves reflected and transmitted by homogeneous layers. This occurs for small enough pitches, whose actual value strongly depends on the direction of the grating wave vector  $\mathbf{q}$  with respect to  $z$ .

Here we consider one-dimensional crystals with  $\mathbf{q}$  parallel to  $z$ . The periodic sample can be treated as a stratified medium, and the transfer matrix becomes four-dimensional. The transfer matrix  $U(z)$  between the planes  $z = 0$  and  $z$  satisfies the propagation equation

$$\frac{dU(z)}{dz} = ik_0 B(z) U(z), \quad (20)$$

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where  $k_0 = \omega/c$  and  $B(z)$  is the propagation matrix, referred to as *Berreman matrix* [25] in the liquid crystal literature. The same equation holds for homogeneous layers, where the Berreman matrix is  $z$ -independent.

Two samples having the same transfer matrix for any direction of the input plane wave are optically identical. The macroscopic properties of the periodic medium are therefore fully defined by a matrix  $U(\theta_i, \varphi_i)$ , where  $\theta_i$  and  $\varphi_i$  are the polar and azimuthal angles of the input plane wave. The effective macroscopic medium is in principle defined as the homogeneous medium giving the same transfer matrix. Obviously, no homogeneous medium is fully equivalent to a periodic one, and some approximations are required.

As a first simplifying assumption, we have considered samples containing an integral number  $N$  of pitches. Their transfer matrix is equal to  $U(p)^N$ , where  $U(p)$  is the transfer matrix over one pitch.

For  $p \ll \lambda$ , it is convenient to expand the transfer matrix  $U(p)$  in ascending powers of the small parameter  $p/\lambda$ , by making use of an iteration procedure. For the sake of definiteness, let us consider the smectic structure defined in § 4. The transfer matrix can be written as

$$U(p, \varphi_0) = I + \sum_{n=1}^{\infty} \left( i \frac{p}{\lambda} \right)^n u_n(\varphi_0), \quad (21)$$

where the dependence of the matrix on the angle  $\varphi_0$ , which plays a major role in our theory, is evidenced. In other words, we stress the fact that the transfer matrices of the smectic sample depend on the average molecular directions at the boundary planes.

Equation (21) recalls the expansion given by eq. (5) for the dielectric tensor  $\underline{\underline{\tilde{\epsilon}}}$  of the effective macroscopic medium, where the term of order  $n$  scales as  $(p/\lambda)^n$ . The evaluation of the tensors  $\tilde{\epsilon}_{ij}^{(0)}$ ,  $\tilde{\gamma}_{ijl}, \dots$  appearing in the expression of  $\underline{\underline{\tilde{\epsilon}}}$  requires rather involved but straightforward computations, which will be published in a separate paper. We only discuss here one important point. From the expansion of  $\underline{\underline{\tilde{\epsilon}}}$  in powers of  $p/\lambda$ , a similar expansion for the Berreman matrix  $\tilde{B}$  of the effective medium is easily obtained. It can be written as

$$\tilde{B} = \tilde{b}_0 + \left( i \frac{p}{\lambda} \right) \tilde{b}_1 + \left( i \frac{p}{\lambda} \right)^2 \tilde{b}_2 + \dots, \quad (22)$$

where  $\tilde{b}_0$  only depends on  $\underline{\underline{\tilde{\epsilon}}}^{(0)}$ ,  $\tilde{b}_1$  also depends on the chiral tensor  $\tilde{\gamma}$ , and so on. To obtain identical transfer matrices, the following identities are required for the first two terms:

$$\tilde{b}_0 = b_0; \quad (23a)$$

$$\tilde{b}_1 = \sum_{m=1}^{\infty} \left\{ \frac{1}{m} \left[ \frac{1}{2} (b_m a_m - a_m b_m) + \cos m\varphi_0 (b_0 b_m - b_m b_0) - \sin m\varphi_0 (b_0 a_m - a_m b_0) \right] \right\}, \quad (23b)$$

where  $a_m$  and  $b_m$  are the matrices appearing in the following Fourier expansion of the Berreman matrix  $B(z)$  of the periodic (mesoscopic) medium:

$$B(z) = b_0 + \sum_{m=1}^{\infty} \{ a_m \cos[m(qz + \varphi_0)] + b_m \sin[m(qz + \varphi_0)] \}. \quad (24)$$

From eqs (23a), (23b) some very interesting conclusions can be drawn, that are valid for any crystal. A well defined macroscopic model for crystals can be obtained only if we neglect the dependence of its dielectric tensor on the crystal period, i.e. spatial dispersion. In our case it is defined by the matrix  $\tilde{b}_0$ , given by eq. (23a). The matrix  $\tilde{b}_1$ , that appears in the term depending on  $p/\lambda$  and defines the optical activity of the medium, explicitly depends on  $\varphi_0$ . Obviously, the bulk properties of the macroscopic model must be independent of the boundary conditions, defined here by  $\varphi_0$ . This means that we must neglect the  $\varphi_0$ -dependent terms. Surprisingly, these terms are generally not small with respect to the other ones appearing in the expression of  $\tilde{b}_1$ . In fact the elements of  $b_0$  are generally at least one order of magnitude greater than the elements of the matrices  $a_m$  and  $b_m$ . This means that no homogeneous model is able to fully account for the optical activity of gyrotropic crystals even in the limit  $p \rightarrow 0$ , since the  $p$ -dependence of all the terms in  $\tilde{b}_1$  is exactly the same. It has been shown, theoretically and experimentally, that the homogeneous model for chiral smectics completely fails in the particular geometry where the screw axis of the helical structure is orthogonal or nearly orthogonal to the boundary planes [26]. However, in all the other geometries the macroscopic model considered here works very well. In fact the omission of the  $\varphi_0$ -dependent terms is equivalent to an averaging over  $\varphi_0$ . If the boundary plane is not orthogonal to the screw axis of the helical structure, the direction of the local optic axis changes along the boundary planes, and an averaging over  $\varphi_0$  takes place automatically. The omission of the terms depending on  $\varphi_0$  has the same role as the omission of the higher Fourier components in the Bloch wave approach, as is evident.

## 7. Macroscopic model for chiral smectics

The macroscopic model for short-pitch chiral smectics has been first derived by making use of the matrix method [15], under the simplifying assumption that the periodic medium is locally uniaxial.

Only the first two terms of the expansion of eq. (5) are considered. In the orthogonal Cartesian frame whose  $z$ -axis coincides with the helical axis of the  $C^*$  LCs the real part of the dielectric tensor is

$$\tilde{\epsilon} = \begin{pmatrix} \tilde{\epsilon}_\perp & 0 & 0 \\ 0 & \tilde{\epsilon}_\perp & 0 \\ 0 & 0 & \tilde{\epsilon}_\parallel \end{pmatrix}, \quad (25)$$

with

$$\tilde{\epsilon}_\perp = \epsilon_o + \frac{\epsilon_a \epsilon_o \sin^2 \alpha}{2(\epsilon_e - \epsilon_a \sin^2 \alpha)}, \quad (26a)$$

$$\tilde{\epsilon}_\parallel = \epsilon_e - \epsilon_a \sin^2 \alpha. \quad (26b)$$

The third-rank tensor  $\gamma_{mnr}$  can be expressed as

$$\gamma_{ijk} = k_0^{-1} e_{ijm} g_{mk}, \quad (27)$$

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where  $k_0 = 2\pi/\lambda$  is the vacuum wave vector,  $e_{ijm}$  the totally antisymmetric Levi-Civita tensor, and  $g_{ij}$  are the components of the second rank gyration tensor [21]

$$g = \begin{pmatrix} g_{\perp} & 0 & 0 \\ 0 & g_{\perp} & 0 \\ 0 & 0 & g_{\parallel} \end{pmatrix}, \quad (28)$$

with

$$g_{\perp} = -\frac{p}{\lambda} \frac{\varepsilon_a^2 \sin^2(2\alpha)}{8(\varepsilon_e - \varepsilon_a \sin^2 \alpha)}; \quad g_{\parallel} = 0. \quad (29)$$

The effective homogeneous medium defined by eqs. (25)–(29) is uniaxial and its optic axis is coincident with the helix axis. A similar behavior is in general exhibited by the crystal classes  $C_n, D_n$ , with  $n > 2$  [7]. The subscripts used to define the two parameters  $g_{\parallel}$  and  $g_{\perp}$  correspond to the components of the vector  $\mathbf{k}$  parallel and orthogonal to the helix axis. The fact that  $g_{\parallel}$  is equal to zero means that optical activity is zero for light propagating along this axis, and reaches its maximum value for light propagating orthogonally to the helix axis.

For  $\alpha = \pi/2$ , i.e. for cholesterics,  $g_{\perp} = 0$ : up to terms scaling as  $p/\lambda$ , short pitch cholesterics are not optically active.

For  $\alpha = \alpha_c$ , where  $\alpha_c$  is given by

$$\cos^2 \alpha_c = \frac{(\varepsilon_o^2 + 8\varepsilon_e^2)^{1/2} - 3\varepsilon_o}{4\varepsilon_a} \quad (30)$$

we obtain  $\tilde{\varepsilon}_{\perp} = \tilde{\varepsilon}_{\parallel}$ . The linear birefringence disappears, as for usual liquids, and the medium displays pure optical rotation: its eigenwaves are circularly polarized. For any other  $\alpha$ -value the eigenwaves are elliptically polarized.

It is interesting to compare the optical properties of chiral smectics with those of a medium made of small, identical and parallel helices. For this purpose, let us consider one of the helices used by Lindman, in the long wavelength limit. The radiation field of an helix is the same as for a small helical antenna, which behaves as a set of two dipolar antennas, electric and magnetic respectively, whose electric and magnetic moments are parallel and dephased, with a phase difference  $\delta = \pm\pi/2$ . The ratio between the corresponding radiation fields depends on the frequency and on the geometry of the helix. The radiation field at any point is elliptically polarized, with the ellipse's axes parallel and orthogonal to the plane defined by the point and the helix axis. In fact, the two electric vectors generated by the dipolar antennas are orthogonal and dephased, with a phase difference  $\delta = \pm\pi/2$ .

A plane electromagnetic wave excites all the antennas. To obtain the total field, we must add the forwardly scattered waves to the incident one. As is evident, the medium is macroscopically uniaxial and chiral, with the optic axis parallel to the averaged axis of the helices, and with eigenwaves elliptically polarized. Their two polarization states are defined by the same ellipse considered above, and by the orthogonal one.

Let us now discuss the analogies with short pitch chiral smectics. Along the helix axis, the field scattered by the helices vanishes. This fact corresponds to the vanishing of  $g_{\parallel}$  for smectics. If the angle  $\beta$  between the helix axis and the oscillation direction of the

electrons along the wire is equal to 0 or to  $\pi/2$ , the helical antennas become electric or magnetic dipolar antennas, respectively, giving linear polarizations in orthogonal directions. The medium is no more chiral, similarly to a smectic in the limits  $\alpha = 0$  and  $\alpha = \pi/2$ . Further, an intermediate value  $\beta_c$  of  $\beta$  exists, corresponding to circularly polarized eigenwaves.

The same properties are expected for dielectric helices having uniaxial polarizability tangent to the wire, and for an helical arrangement of isotropic small spheres, with many spheres per turn. Here again the easy polarizability is along the helix, due to the dipolar interaction between any pair of nearest spheres.

## 8. Conclusions

Optical activity is the most important non local optical property. It explicitly depends on the molecular size in liquids and on the spatial period  $p$  in crystals. To take into account this fact, an expansion of the dielectric tensor in ascending powers of the parameter  $p/\lambda$  is generally used. In the optical frequency range, this parameter is very small for solid crystals, whereas no upper limit exists for periodic liquid crystal phases. The interest of such phases in optics is due to the following facts:

- their rotatory power is some orders of magnitude greater than those of other chiral media;
- higher order terms are experimentally detectable, whereas they are of no practical interest in solid crystals;
- a great variety of chiral LC phases exists and, in particular, phases that are periodic in only one direction and have a very simple and well known structure.

Hence the helical LC phases are unique, in particular for discussing the following:

- the equations to be used to describe the optical properties of chiral media;
- the methods allowing to find out the macroscopic model for short pitch samples;
- the limits of validity of the macroscopic models;
- the boundary conditions in the presence of higher order terms.

Here, we have essentially discussed the first two points, since they are needed for taking up the other ones, which are up to now not completely solved.

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