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On Form Birefringence of Some Smectic Liquid Crystals†

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Abstract—The effective dielectric tensor ε, of an unlimited number of l alternate plane layers of arbitrary anisotropic homogeneous materials, has been calculated in the long wavelength limit.

Utilizing the result of the calculations, the form birefringence of three models of smectic liquid crystals (lipid-water systems in smectic A and C configurations, and the herringbone structure) was calculated and it was found that some lipid-water systems and smectic C structures are biaxial. The herringbone structure was also found to exhibit biaxial characteristics.

1. Introduction

The usual method for the investigation of plane monochromatic waves in a stratified medium, starting from Maxwell's equations, leads to the specification of the so-called characteristic matrix$^{(1)}$ of the medium. It relates the components of the electric (or magnetic) vector in some arbitrary plane, to the components in any other plane. The reflection and transmission coefficients of the medium can then be expressed in terms of the elements of the characteristic matrix.

This method outlined above, becomes very difficult if one attempts to solve the most general cases in which the layers are anisotropic. If the principal axes of the electrical permittivity tensors of successive layers do not coincide, there is no simple way to obtain the reflection and transmission coefficients. If one is, however, interested only in the electrical behavior of this structure, then it is possible, for some simple cases, to study the propagation of electromagnetic waves in different directions. Then the square of the ratio of the magnetic to electric field yields an element of the tensor for that

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direction (assuming a non-magnetic medium). Repeating this procedure for different directions one can, in principle, obtain all the elements of the permittivity tensor for the structure as a whole.

Smectic liquid crystals are characterized by their layered structure. In some cases, the layers are a few molecular dimensions in length (thickness) as, for instance, in lipid-water systems.(2) Its structure consists of planar lipid leaflets which are filled by disordered paraffin chains and whose surface is covered by hydrophilic groups of lipid molecules. The lipid leaflets are separated by layers of water with thickness varying from 5 Å to more than 250 Å. Each layer can, so far as the electrical properties are concerned, be adequately described by a tensor ε. The purpose of this paper is to investigate the optical properties of such a layered structure, disregarding the absorption and reflection of electromagnetic waves in the medium.

In the optical frequence range the permittivity arises almost entirely from the electronic polarizability. It depends on the environment in which the atom is situated. For an anisotropic molecule the local polarizability is a tensor. It is reasonable to expect that layers with a thickness of the long molecular axis or less will also be described by a tensor ε under proper conditions of frequency and thermodynamic variables.

2. Theory

We are interested in the electrical properties of a medium that consists of an unlimited number of alternate layers of arbitrary anisotropic materials. This section deals with alternate plane layers of two substances described by the permittivity tensors $\varepsilon,^{(1)}$ $\varepsilon.^{(2)}$ If the thickness of the layers is denoted by t_1 and t_2 respectively, then the medium is periodic with the period $t = t_1 + t_2$. This case is an extension of previous work(3) taking the anisotropic properties of the layers into account.

In order to simplify the calculation, we shall be interested in the case of long wavelengths, i.e. in the optical frequency range. Then $\mu^{(1)}$ and $\mu^{(2)}$ can be approximated by scalars of magnitude very nearly equal to one. In fact, we shall assume nonmagnetic and nonconductive layers. Later, the formalism is extended to include l successively different layers. The formalism presented in this article is also applicable to the purely magnetic case when the electric and magnetic fields are separable.

In the long wavelength limit, which is assumed here, the following relation is valid:

$$t = t_1 + t_2 \ll \lambda. \tag{1}$$

This means that the microscopic field varies slowly across each successive layer. The assumption is made, therefore, that the fields are constant in each region. Then the macroscopic fields are taken as the average of the microscopic fields over the period t, i.e.

$$\mathbf{E} = \int \mathbf{E}\,\mathrm{d}v \Big/ \int \mathrm{d}v = f_1 \mathbf{E}_1 + f_2 \mathbf{E}_2 \tag{2a}$$

$$\mathbf{D} = \int \mathbf{D}\,\mathrm{d}v \Big/ \int \mathrm{d}v = f_1 \mathbf{D}_1 + f_2 \mathbf{D}_2 \tag{2b}$$

where

$$f_i = t_i/(t_1 + t_2) \quad , \quad f_1 + f_2 = 1 \tag{2c}$$

Boundary conditions which the fields must satisfy are

$$\mathbf{n} \times (\mathbf{E}_1 - \mathbf{E}_2) = 0 \tag{3a}$$

$$\mathbf{n} \cdot (\mathbf{D}_1 - \mathbf{D}_2) = 0 \tag{3b}$$

where

$$\mathbf{D}_1 = \boldsymbol{\varepsilon}^{(1)} \cdot \mathbf{E}_1 \quad , \quad \mathbf{D}_2 = \boldsymbol{\varepsilon}^{(2)} \cdot \mathbf{E}_2 \tag{4}$$

and $\mathbf{n}$ denotes the unit vector normal to the boundary surface between the layers.

From Eq. (3a) it follows that

$$\mathbf{E}_2 = \mathbf{E}_1 + \alpha \mathbf{n} \tag{5}$$

where α is determined by Eq. (3b). Thus we have, using α in Eq. (5),

$$\mathbf{E}_2 = \left[1 + \frac{\mathbf{nn} \cdot (\boldsymbol{\varepsilon}^{(1)} - \boldsymbol{\varepsilon}^{(2)})}{\mathbf{n} \cdot \boldsymbol{\varepsilon}^{(2)} \cdot \mathbf{n}}\right] \cdot \mathbf{E}_1 \tag{6a}$$

or

$$\mathbf{E}_1 = \left[1 - \frac{\mathbf{nn} \cdot (\boldsymbol{\varepsilon}^{(1)} - \boldsymbol{\varepsilon}^{(2)})}{\mathbf{n} \cdot \boldsymbol{\varepsilon}^{(1)} \cdot \mathbf{n}}\right] \cdot \mathbf{E}_2 \tag{6b}$$

where the expression $\mathbf{nn}$ denotes the dyadic of the unit vector $\mathbf{n}$. Combining Eqs. (2a) and (6a) gives

$$\mathbf{E} = \left[1 + f_2 \frac{\mathbf{nn} \cdot (\boldsymbol{\varepsilon}^{(1)} - \boldsymbol{\varepsilon}^{(2)})}{\mathbf{n} \cdot \boldsymbol{\varepsilon}^{(2)} \cdot \mathbf{n}}\right] \cdot \mathbf{E}_1 = \Omega_1 \mathbf{E}_1 \tag{7}$$

and Eqs. (2a) and (6b) give

$$\mathbf{E} = \left[1 - f_1 \frac{\mathbf{nn}\cdot(\boldsymbol{\varepsilon}^{(1)} - \boldsymbol{\varepsilon}^{(2)})}{\mathbf{n}\cdot\boldsymbol{\varepsilon}^{(1)}\cdot\mathbf{n}}\right]\cdot \mathbf{E}_2 = \Omega_2 \mathbf{E}_2 \tag{8}$$

where Ω_1 and Ω_2 are defined by the right sides of Eqs. (7) and (8). Therefore, one can write

$$\mathbf{E}_i = \Omega_i^{-1}\mathbf{E} \qquad i = 1, 2 \tag{9}$$

and Eq. (2b) defines the effective permittivity tensor of the substance formed from the two alternate anisotropic plane layers to be

$$\boldsymbol{\varepsilon} = f_1 \boldsymbol{\varepsilon}^{(1)}\Omega_1^{-1} + f_2 \boldsymbol{\varepsilon}^{(2)}\Omega_2^{-1}. \tag{10}$$

The problem remaining is to find the inverse of the tensor Ω_i. We note that Ω has the form

$$\Omega = 1 + \mathbf{nn}\cdot\mathbf{A} \tag{11}$$

where **A** is any second rank tensor. Then the inverse of Ω is

$$\Omega^{-1} = 1 - (1 + \mathbf{n}\cdot\mathbf{A}\cdot\mathbf{n})^{-1}\mathbf{nn}\cdot\mathbf{A} \tag{12}$$

providing

$$1 + \mathbf{n}\cdot\mathbf{A}\cdot\mathbf{n} \neq 0.$$

Combining Eqs. (10) and (11), we get

$$\boldsymbol{\varepsilon} = f_1 \boldsymbol{\varepsilon}^{(1)} + f_2 \boldsymbol{\varepsilon}^{(2)} - \left[\frac{\mathbf{n}\cdot\boldsymbol{\varepsilon}^{(1)}\cdot\mathbf{n}}{f_1} + \frac{\mathbf{n}\cdot\boldsymbol{\varepsilon}^{(2)}\cdot\mathbf{n}}{f_2}\right]^{-1} \cdot (\boldsymbol{\varepsilon}^{(1)} - \boldsymbol{\varepsilon}^{(2)})\cdot\mathbf{nn}\cdot(\boldsymbol{\varepsilon}^{(1)} - \boldsymbol{\varepsilon}^{(2)}). \tag{13}$$

This formalism can be readily extended to the case of plane layers of l substances, providing the long wave-limit is still valid, i.e. the field variables do not change considerably over the distance

$$t = \sum_1^l t_i \ll \lambda:$$

After some calculation, one obtains the following expression for the effective tensor $\boldsymbol{\varepsilon}$

$$\boldsymbol{\varepsilon} = \sum f_i \boldsymbol{\varepsilon}^{(i)} - \left[\sum_i (f_i/\mathbf{n}\cdot\boldsymbol{\varepsilon}^{(i)}\cdot\mathbf{n})\right]^{-1} \times \sum_{i<j} [f_i f_j/(\mathbf{n}\cdot\boldsymbol{\varepsilon}^{(i)}\cdot\mathbf{n})(\mathbf{n}\cdot\boldsymbol{\varepsilon}^{(j)}\cdot\mathbf{n})](\boldsymbol{\varepsilon}^{(i)} - \boldsymbol{\varepsilon}^{(j)})\cdot\mathbf{nn}\cdot(\boldsymbol{\varepsilon}^{(i)} - \boldsymbol{\varepsilon}^{(j)}) \tag{14}$$

The magnetic characteristics of the periodic multilayered structure can be obtained in analogy with the derivations above and the permeability tensor μ would then be given for l substances by Eq. (14) with $\mu^{(i)}$ replacing $\varepsilon^{(i)}$.

Let us consider a special case of l alternating layers in which the principal axes of the tensors $\varepsilon^{(i)}$ in each successive layer have the same orientation with respect to some laboratory frame. Furthermore, let us assume that one of the principal axes is parallel to the boundary normal $\mathbf{n}$. Then the effective permittivity tensor ε of the whole structure is given by

$$\varepsilon = \begin{pmatrix} \sum_i^l f_i \epsilon_x^{(i)} & 0 & 0 \\ 0 & \sum_i^l f_i \epsilon_y^{(i)} & 0 \\ 0 & 0 & (\sum_i^l f_i/\epsilon_z^{(i)})^{-1} \end{pmatrix} \tag{15}$$

3. Optical Characteristics of the Periodically Anisotropic Layers. Application to Liquid Crystals of the Smectic Types A and C.

Optical observation of liquid crystalline systems have shown that they are strongly birefringent.(5) Nematic mesophases were experimentally determined to be uniaxial. M. T. Freiser,(6) starting from an effective orientational interaction between two asymmetrical molecules, has investigated an interaction in which each molecule interacts with an effective coordination number of neighbors. He has shown that the ground state of a system with such pairwise interactions (nematic phase) is biaxial. However, this has not yet been verified experimentally. Smectic phase *A* (characterized by the normal to the layer being colinear with the long molecular axis) is observed to be also uniaxial. However, for smectic phase *C* (long molecular axis is tilted at some angle α with respect to the layer normal), the argument was made(7) that it should be biaxial. That this is truly the case for three compounds was later experimentally observed by Taylor, Fergason and Arora.(5) All three compounds exhibited nematic and smectic *C* phases. The tilt angle was found to be nearly 45 degrees for each of them. They are optically positive and the optic axial angle $2V$ is of the order of 20 degrees for all three compounds in the smectic *C* phase. The authors have proposed that, at least to some extent, the biaxial character of smectic *C* phases is due to " anisotropy of the degree of order ". Nematic phases were uniaxial and also optically positive. The experimentors ruled out the herringbone structure of the smectic *C* type.

A molecular theory of birefringence of nematic phases has been proposed by Chandrasekhar *et al.*(8) They have shown that dispersion and repulsion forces play the predominant role in explaining the experimentally observed results. Taking into account the dispersion, dipole–dipole, induction and repulsive interactions for an assembly of anisotropic molecules in the nematic phase, they showed that the potential energy of any molecule is a function of its orientation with respect to the mean directions of the molecules in the medium. Clearly, the birefringent properties may be explained in terms of the anisotropic electrical properties of the molecules from which the compound is formed.

In crystal optics the form birefringence, which is due to the ordered arrangement of similar particles of optically isotropic material, plays an important role. Because smectic liquid crystals are ordered arrangements of molecular layers, one is led to the question as to what extent these ordered anisotropic layers reflect the optical properties of such a structure. In analogy with crystal optics this will be called form birefringence. Each molecular layer can be described by a single degenerate permittivity tensor $\boldsymbol{\varepsilon}$. We shall consider the following cases (always assuming that the x-principal axes of successive layers coincide):

(i) Lamellar system of the anisotropic (uniaxial) layer and an isotropic layer.

A representation of this model may be taken to be the smectic phase of the lipid-water system.(8) We shall be interested in two examples—smectic *A* and smectic *C*.

Smectic *A*:

$$\mathbf{n} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \qquad \boldsymbol{\varepsilon}^{(1)} = \begin{pmatrix} \epsilon_x^{(1)} & 0 & 0 \\ 0 & \epsilon_x^{(1)} & 0 \\ 0 & 0 & \epsilon_z^{(1)} \end{pmatrix} \tag{16}$$

Eq. (13) reduces in this case to

$$\boldsymbol{\varepsilon} = \begin{pmatrix} f_1 \epsilon_x^{(1)} + f_2 \epsilon^{(2)} & 0 & 0 \\ 0 & f_1 \epsilon_x^{(1)} + f_2 \epsilon^{(2)} & 0 \\ 0 & 0 & (f_2 \epsilon_z^{(1)} + f_1 \epsilon^{(2)})^{-1} \epsilon_z^{(1)} \epsilon^{(2)} \end{pmatrix}$$

This is the uniaxial structure. If the second layer is also anisotropic and the principal axes of the two layers coincide, then

$$\boldsymbol{\varepsilon} = \begin{pmatrix} f_1\epsilon_x^{(1)}+f_2\epsilon_x^{(2)} & 0 & 0 \\ 0 & f_1\epsilon_x^{(1)}+f_2\epsilon_x^{(2)} & 0 \\ 0 & 0 & (f_1\epsilon_z^{(2)}+f_2\epsilon_z^{(1)})^{-1}\epsilon_z^{(1)}\epsilon_z^{(2)} \end{pmatrix} \qquad (18)$$

This is still a uniaxial structure.

Smectic *C*:

The axes of the Cartesian coordinate system are chosen to coincide with the principle axis system of the electric permittivity tensor $\boldsymbol{\varepsilon}$ of the first layer of thickness t_1. (The tilt angle $\alpha = 45°$). The second layer is an isotropic one characterized by the scalar $\epsilon^{(2)}$ and the thickness t_2. In this system (Fig. 1) the normal $\mathbf{n}$ is

$$\mathbf{n} = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix} \qquad \boldsymbol{\varepsilon}^{(1)} = \begin{pmatrix} \epsilon_x^{(1)} & 0 & 0 \\ 0 & \epsilon_x^{(1)} & 0 \\ 0 & 0 & \epsilon_z^{(1)} \end{pmatrix}$$

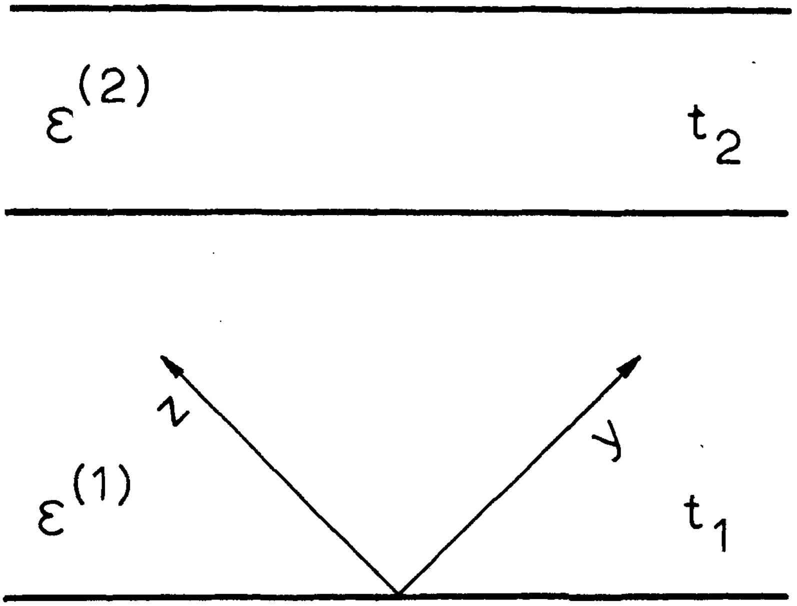

Figure 1. Model of the smectic C liquid crystal. One of the two alternating layers is isotropic, denoted by the scalar $\varepsilon^{(2)}$ and the thickness t_2. The molecular axis (z-principal axis of the tensor $\varepsilon^{(1)}$) is tilted at the angle $\alpha = 45°$ with respect to the boundary normal.

If we introduce the notation

$$\begin{aligned} u &= f_1 \epsilon_x^{(1)} + f_2 \epsilon^{(2)} \\ v &= f_1 \epsilon_z^{(1)} + f_2 \epsilon^{(2)} \\ l &= f_1 f_2 [f_2(\epsilon_x^{(1)} + \epsilon_z^{(1)}) + 2 f_1 \epsilon^{(2)}]^{-1} \\ a &= \epsilon_x^{(1)} - \epsilon^{(2)} \\ b &= \epsilon_z^{(1)} - \epsilon^{(2)} \end{aligned} \tag{19}$$

Then Eq. (13) gives

$$\boldsymbol{\varepsilon} = \begin{pmatrix} u & 0 & 0 \\ 0 & u - la^2 & -lab \\ 0 & -lab & v - lb^2 \end{pmatrix} \tag{20}$$

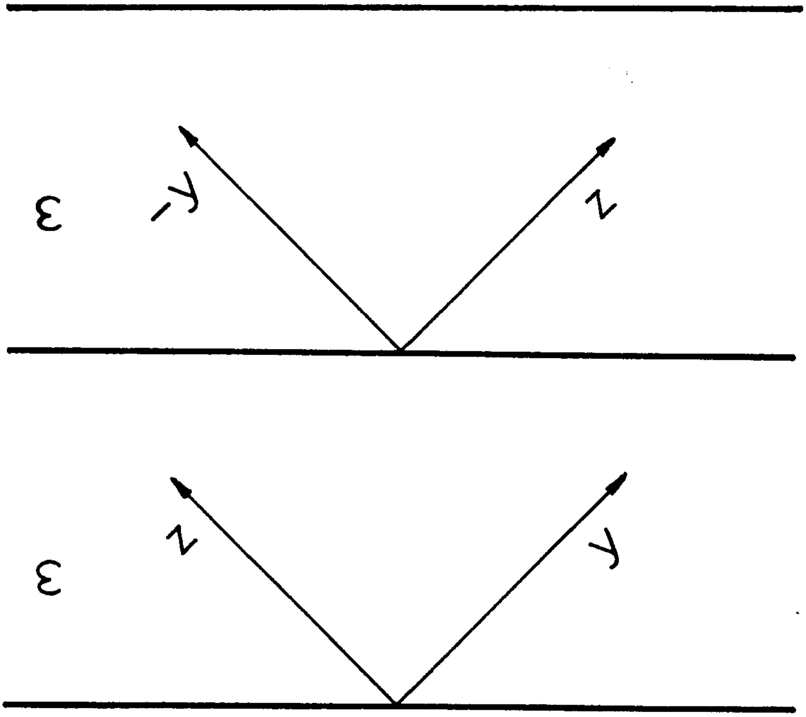

Figure 2. Model of the herringbone structure. The layers are of equal thickness and the molecular axes (z-principal axes of electric permittivity tensors) are at 90° angles to one another.

Diagonalization of this tensor gives the three principal values, which are

$$\lambda_1 = u$$

$$\lambda_{2,3} = \tfrac{1}{2}\{[u+v-l(b^2+a^2)] \pm [(v-u)^2 - 2(v-u)\,l(b^2-a^2) + l^2(a^2+b^2)^2]^{1/2}\} \tag{21}$$

where u, v, l, a and b are defined by Eq. (19). For $\epsilon_x^{(1)} \neq \epsilon_z^{(1)}$ this structure exhibits, in general, biaxial properties.

(ii) Herringbone structure.

Let us consider the herringbone structure such that the tilt angle $\alpha = 45°$ (Fig. 2). Then $f_1 = f_2 = \frac{1}{2}$ and after the diagonalization the following result is obtained:

$$\epsilon = \begin{pmatrix} \epsilon_x & 0 & 0 \\ 0 & 2(\epsilon_x+\epsilon_z)^{-1}\epsilon_x\epsilon_z & 0 \\ 0 & 0 & \frac{1}{2}(\epsilon_x+\epsilon_z) \end{pmatrix} \tag{22}$$

Herringbone structures are, therefore, biaxial. The angle γ between the optical axes is given by

$$\operatorname{tg}\frac{\gamma}{2} = \left[\frac{\epsilon^{(z)}(\epsilon^{(y)}-\epsilon^{(x)})}{\epsilon^{(x)}(\epsilon^{(z)}-\epsilon^{(y)})}\right]^{1/2} = \left(\frac{\epsilon_z+\epsilon_x}{\epsilon_z-\epsilon_x}\right)^{1/2} \tag{23}$$

when the principal axes in Eq. (22) are so oriented that

$$\epsilon^{(x)} < \epsilon^{(y)} < \epsilon^{(z)}$$

4. Summary

Because of the multilayer structure of smectic liquid crystals one would expect that the form birefringence might play, in some cases, an important role. The form birefringence was then calculated for three models of the smectic phases (lipid-water systems in smectic A and C configurations and the herringbone structure) and it was found that these structures, under appropriate conditions, may be biaxial.

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