Light-induced Fréedericksz transition in a nematic liquid crystal with chiral dopant

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The influence of phototransformed molecules with chiral properties changing on the absorption of light field on the light-induced Fréedericksz transition threshold in a homeotropically oriented nematic cell is considered. It is shown that the appearance of the light-induced chiral molecules can decrease or increase the Fréedericksz threshold value depending on the chirality sign of the phototransformed molecules and of the initial chiral dopant. Expressions for the threshold are obtained for circular and linear polarization of the incident light. The dependence of the threshold on the periodicity of the spatially modulated light intensity is estimated for large periods of modulation. The dependence of dopant threshold chirality on the director anchoring energy has been found.

1. Introduction

It is known that even a small addition of some molecular agents to a nematic liquid crystal (NLC) can drastically change its optical and mechanical properties. Such impurities can be added in several ways: as a diluent in preparing the cell or by modification of some NLC molecules after cell preparation. The latter effect can be realized, in particular, by the absorption of light by some nematics. Indeed, it has been shown experimentally that absorbing dyes have a strong effect on the light-induced reorientation processes in a nematic cell [1]. It was demonstrated that the threshold of the light-induced Fréedericksz transition (LFT) decreased by orders of magnitude on the addition to a NLC of a small percentage of absorbing dyes. Such a decrease in the LFT threshold can arise if the NLC molecules (or dyes) change their conformation as a consequence of the light absorption and gain a permanent electric dipole moment which is absent in the ground state of the molecules (dyes) [2].

Also it was noted and experimentally confirmed that the initial homeotropic alignment of the director can be destabilized by a chiral dopant on exceeding a certain dopant concentration [3, 4]. The addition of such a chiral dopant results in twisting of the NLC structure. The pitch \( p \) of the twisted nematic depends on the dopant concentration \( c \) and on the dilution limit is defined by \( q = 2\pi/p = 4\pi\beta c \), where \( q \) is the chirality of the dopant and \( \beta \) is the microscopic twisting power [5]. Analysis of the twisted nematic director distribution in a cell with homeotropic boundary conditions and infinite anchoring [3] predicts that the homeotropic distribution of the director is stable if \( qL < \pi K_3/K_2 \) (\( L \) is the cell thickness, \( K_2 \) and \( K_3 \) are the Frank elastic constants). If \( qL > \pi K_3/K_2 \) the twisted distribution is realized in the cell. Transition between these structures is first order with hysteresis if \( K_1 < 3(K_3 - K_2) \).

In the present paper we consider the influence of chiral doping on the LFT threshold value in a homeotropic NLC cell. We assume that incident light can be partially absorbed by the NLC molecules (or added dyes) and as a consequence of this phototransformed molecules (PM) with permanent chirality arise in the cell. These chiral PM can compensate the existing chirality
of an initial chiral dopant, increasing the threshold of the Fréedericksz transition, or increase the overall chirality, decreasing the threshold value.

Since the polarization of the incident light has a strong effect on the concentration and sign of the chirality of the PM, we consider the special case of a partially polarized incident light wave. Also we take into account the finite anchoring energy of the interaction of the director with the cell surfaces.

2. Basic equations

The system under consideration is a homeotropically aligned NLC cell bounded by the planes \( z = 0, L \). Let this cell contain a chiral dopant with chirality \( q_0 \) and, moreover, let the incident light induce chiral molecules which create in the NLC additional chirality \( \alpha c \), where \( c \) is the concentration of the PM. The free energy of the cell in the presence of the light wave field inducing the PM has the form

\[
F = F_{el} + F_s + F_l,
\]

where

\[
F_{el} = \frac{1}{2} \int \{ K_1 (\text{div} \, n)^2 + K_2 (n \cdot \text{curl} \, n + q)^2 \}
+ K_3 (n \times \text{curl} \, n)^2 \} \, dV,
\]

\[
F_s = -\frac{1}{2} \int_{S_1, S_2} (n \cdot e_z)^2 \, dS,
\]

\[
F_l = -\frac{1}{16\pi} \int \epsilon_{0l} E_l E_l^* \, dV.
\]

Here \( F_{el} \) is the Frank elastic energy, \( F_s \) is the director anchoring energy with the cell surfaces and is assumed to be like a Rapini potential \([6]\), \( F_l \) is the energy of the light wave in the NLC \([7]\), \( q \) is the total chirality of the initial dopant and the PM, \( q = q_0 + \alpha c \).

Minimizing the free energy (1), one can obtain the following equations for the director \( n \)

\[
-\kappa_1 \text{grad}(\text{div} \, n) + K_2 (Q \cdot \text{curl} \, n + \text{curl}(Qn))
+ K_3 (\text{curl} \, n \times \text{R}) + \text{curl}(\text{R} \times n)]
- \frac{\epsilon_0}{16\pi} [(n \cdot E^*)E + (n \cdot E) \cdot E^*] + \mu(r)n = 0 \tag{2}
\]

\[
\{W \cdot (n - \text{n} \cdot e_z) \cdot e_z \} \pm K_2 (n \times e_z) \, \text{div} \, n \pm K_2 Q (n \times e_z)
\pm K_3 [(\text{R} \times n) \cdot e_z] + \lambda(r)n|_{z=\pm L} = 0. \tag{3}
\]

Here \( Q = n \cdot \text{curl} \, n + q_0 + \alpha c \), \( \text{R} = [n \times \text{curl} \, n] \). The unknown multipliers \( \mu(r) \) and \( \lambda(r) \) must be found from the condition \( n^2 = 1 \) in the cell volume and on the surfaces.

Further we consider the stability of the initial director distribution \( n_0 = e_z \) which is the solution to equations (2) and (3). It is convenient to present the director in the form \( n = n_0 + \delta n \) where \( \delta n \ll 1 \). In order to obtain the threshold value of the electric field of the light wave, it is sufficient to keep in the variational equations (2) and (3) only the terms linear in \( \delta n \).

Assuming the characteristic times concentration change of the PM are small in comparison with the director reorientation time, we can write that the PM concentration \( c \) is the solution to the next equation \([2]\)

\[
\frac{\partial c}{\partial t} = -\frac{c}{\tau} + D \frac{\partial c}{\partial x} + \delta \chi y I y (1 - c) \tag{4}
\]

where \( D \) is the PM diffusion coefficient, \( \tau \) is the PM lifetime, \( \chi_y = \chi_3^y + \chi_1^y q_i n_i \), \( \chi_y = \chi_0 - \chi_1^y \), \( \chi_0 \) are the absorption coefficients for the light polarized along and perpendicular to the director, respectively, \( I_y = \langle E_l E_l^* \rangle \) is the time-averaged light intensity tensor, and \( \delta \) is the quantum efficiency of the phototransformation of the NLC molecule.

We assume that the partially polarized monochromatic light wave is incident on the cell along the \( OZ \) axis: \( E = E_0(t) \exp\{i(kz - \omega t)\} \). Then the light intensity tensor \( I_y = \langle E_l E_l^* \rangle \) has the form

\[
\hat{I} = \frac{1}{2} I_0 (1 \pm \xi_1 \hat{\sigma}_1 + \xi_2 \hat{\sigma}_2 + \xi_3 \hat{\sigma}_3)
\]

where \( \xi_1 = \langle |E_x|^2 - |E_y|^2 \rangle / |E_0|^2 \), \( \xi_2 = \langle 2 \text{Re}(E_x E_y^*) / |E_0|^2 \rangle \), \( \xi_3 = \langle 2 \text{Im}(E_x E_y^*) / |E_0|^2 \rangle \), are the reduced Stokes parameters, \( \xi_0 = |E_x|^2 + |E_y|^2 \), \( I_0 = \langle E_0 E_0^* \rangle = S \hat{P} \), and \( \hat{\sigma} \) are Pauli matrices \([8]\).

It should be noted that in the pure NLC the linearly polarized light wave produces equal concentrations of PM with positive and negative chirality, so that the total light-induced chiral ability of the PM is zero. One can take this into account by assuming that the chirality of PM is a function of the Stokes parameters.

The incident light beam has only components \( E_x \) and \( E_y \), but inside the NLC it possesses \( E_z \) component due to the director fluctuations. We must take this into account in considering the stability of the initial director configuration. Solving the Maxwell’s equations [curl(curl E) = (o^2 / e^2) \delta E] in a linear in \( \delta n \) approximation, one can obtain the next dependence of the field inside the NLC on the components of the undisturbed incident field \([7]\)

\[
E^{in} = \begin{bmatrix}
E_x, E_y, \frac{-\delta n_x E_x + \delta n_y E_y}{e_z}
\end{bmatrix}.
\tag{5}
\]

Thus, when solving the equations (2)–(4) we must use the field (5) inside the NLC. Substituting this field in (4) we obtain in the stationary case the following
expressions for the PM concentration and its first derivative (we keep only the terms linear in \( \delta n \))

\[
e = \frac{\tau \delta \chi \delta n}{1 + \tau \delta \chi} \frac{L_0}{L_0}
\]

Using \( \delta n = \delta n(z) \) and substituting the expressions (5) into the equations (2), (3) for the director and keeping only the terms linear in \( \delta n \), we obtain the following system of linear equations and boundary conditions for the director disturbance \( \delta n \)

\[
L^2 \frac{\partial^2 \delta n}{\partial z^2} + 2tL \frac{\partial \delta n}{\partial z} + \hat{B} \delta n = 0,
\]

where \( \hat{B} = B_0(\hat{T}^\dagger I_0) \), \( \hat{T}^\dagger = \frac{1}{2} \langle E^*_i E^*_j + E^*_j E^*_i \rangle \) is the symmetric part of the light intensity tensor,

\[
B_0 = \frac{1}{16\pi K_3} \overline{\overline{E}}_L I_0,
\]

\[
\hat{\chi}_4 = i \sigma_2 = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix},
\]

\[
t = \frac{K_3}{K_3} (q_0 + \alpha c) \quad \text{and} \quad \omega = \frac{W L}{K_3}.
\]

Let us define the following column vector

\[
x = \left( \delta n_x, \delta n_y, L \frac{\partial \delta n_x}{\partial z}, L \frac{\partial \delta n_y}{\partial z} \right)^T.
\]

Thus (7) takes the form

\[
L \frac{\partial x}{\partial z} = \hat{A} x,
\]

where the matrix \( \hat{A} \) is

\[
\hat{A} = \begin{pmatrix}
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
- B_0(1 + \xi_3) & - \xi_1 B_0 & 0 & -2t \\
- \xi_1 B_0 & - B_0(1 - \xi_3) & 2t & 0
\end{pmatrix}
\]

Putting \( x = c \exp(\lambda z/L) \) as a solution to equation (9) provided that \( \lambda \) is an eigenvalue of the matrix \( \hat{A} \) we obtain the following expressions for the eigenvalues and eigenvectors

\[
\lambda_k = \pm i(B_0 + 2t^2 \pm [(B_0 + 2t^2)^2 - B_0^2(1 - \xi_1^2 - \xi_3^2)])^{1/2} \]

\[
e_k = \{ \xi_1 B_0 + 2t \lambda_k, (1 + \xi_3) B_0 + \lambda_k^2, (\xi_1 B_0 + 2t \lambda_k) \lambda_k, \}

\times [(1 + \xi_3) B_0 + \lambda_k^2] \lambda_k \}^T.
\]

Thus the general solution is

\[
x = \sum_{i=1}^{4} a_i e_i \exp(\lambda_i z/L),
\]

where \( a_i \) are the constants that must be chosen to satisfy the boundary conditions (8). The condition of existence of the non-trivial solution to the equations for \( a_i \) gives us the equation for the threshold value of the light wave intensity \( I_0 \).

If we have four different eigenvalues \( \lambda_i \) this equation is as follows

\[
\begin{pmatrix}
\alpha_1 & \alpha_1^* & \alpha_2 & \alpha_2^* \\
\beta_1 & \beta_1^* & \beta_2 & \beta_2^* \\
\gamma_1 & \gamma_1^* & \gamma_2 & \gamma_2^* \\
\delta_1 & \delta_1^* & \delta_2 & \delta_2^*
\end{pmatrix} = 0
\]

where

\[
\alpha_i = \exp(\lambda_i) \{(w + \lambda_i)(\xi_1 B_0 + 2t \lambda_i) + t[(1 + \xi_3) B_0 + \lambda_i^2]\}
\]

\[
\beta_i = \exp(\lambda_i) \{(w + \lambda_i)[(1 + \xi_3) B_0 + \lambda_i^2] - t(\xi_1 B_0 + 2t \lambda_i)\}
\]

\[
\gamma_i = (w - \lambda_i)(\xi_1 B_0 + 2t \lambda_i) - t[(1 + \xi_3) B_0 + \lambda_i^2]
\]

\[
\delta_i = (w - \lambda_i)[(1 + \xi_3) B_0 + \lambda_i^2] + t(\xi_1 B_0 + 2t \lambda_i).
\]

If we define \( L_{12} = \text{Im}(\alpha_1 \beta_1^*) - \text{Im}(\alpha_1^* \beta_1) \), equation (13) takes the more simple form \( L_{12} + L_{21} = 0 \).

In the case of linear polarization of the incident light or in the absence of the incident light wave \( (B_0 = 0) \), matrix (10) has the eigenvalue \( \lambda = 0 \) of multiplicity two, so we must seek the general solution in the form

\[
x = c_1(a_1 z + a_2) + \sum_{i=3}^{4} a_i e_i \exp \left( \frac{-\lambda_i z}{L} \right).
\]

Putting \( x \) in this form to the boundary conditions (8) we obtain the following equation for the threshold value

\[
\begin{pmatrix}
t_\mu & 2tw & B_0 - t^2 & w \\
w_\mu & 2r - \mu^2 & tw & t \\
-2tw \sin \mu & 2tw \cos \mu & t^2 - B_0 & w \\
-t_\mu \cos \mu & -t_\mu \sin \mu & -B_0 w & -t
\end{pmatrix} = 0
\]

where \( \mu^2 = 2B_0^2 + 4t^2 \).

3. Expressions for the threshold value

Equations (13) and (14) give us the principal opportunity to find the threshold value \( B_0 \) and thus the threshold of the director stability as a function of the incident light polarization, the director anchoring energy and the initial and induced concentration of chiral dopant. But in the general case it is difficult to calculate the threshold value from these equations even numerically. For this reason we consider here some particular cases.
3.1. Infinite director anchoring and circular light polarization

Putting in equation (13) the director anchoring energy \( W = \infty \) we obtain the following equation for the threshold

\[
2r^2(1 - r^2)^{1/2}(1 - \cos \mu_1 \cos \mu_2) \\
+ \sin \mu_1 \sin \mu_2 (B_0^2 + 2 r^2) = 0
\]

(15)

where \( \mu_{1,2} = \{B_0 + 2 r^2 \pm [(B_0 + 2 r^2)^2 - B_0^2 (1 - r^2)]^{1/2}\}^{1/2} \) and \( r^2 = \chi_1^2 + \chi_2^2 \) defines the degree of linear polarization of the light. In particular, if the initial chiral dopant and PM molecules are absent \((r = 0)\), we obtain from equation (15) the threshold value of the incident light wave intensity in the case of partially polarized incident light [7]

\[
I_{th}^0 = I_0(t) = \frac{8 \pi^3 K_3}{L^2 \varepsilon_a} \frac{\varepsilon_\perp}{\varepsilon_\parallel} \left( \frac{2}{1 + l} \right),
\]

(16)

If the incident light is circularly polarized \((l = 0)\) equation (15) takes the form

\[
B_0 = \pi^2 - r^2.
\]

(17)

Let the concentration of PM be small so that \( r \delta \chi_\perp I_0 \ll 1 \). Then with an accuracy to terms \( \sim (r \delta \chi_\perp I_0)^2 \) the threshold value obtained from equation (17) is

\[
I_{th}^0 = I_0(0) \left[ 1 - \left( \frac{K_2 L q_0}{K_3} \right)^2 \right] \\
\times \left[ 1 - \frac{4}{\pi^2} \left( \frac{K_2}{K_3} \right)^2 \alpha q_0 L^2 \tau \delta \chi_\perp I_0(0) \right], \quad q_0 L < \pi K_3/K_2
\]

(18)

where \( I_0(0) \) is defined by the formula (16). Here we have the linear dependence of the threshold value on the PM concentration \( c = \tau \delta \chi_\perp I_0(0) \). One can see that this value decreases with increasing PM concentration, if PM and initial dopant have chirality of the same sign, and increases in the opposite case. Thus, the appearance of PM in the presence of initial chiral dopant can either increase or decrease the threshold value. In the absence of PM the threshold value \( I_{th}^0 \) decreases with increasing dopant chirality according to a simple square law (18).

In the absence of the initial chiral dopant \((q_0 = 0)\) the expression for the threshold which follows from equation (17) is

\[
I_{th}^0 = I_0(0) \left\{ 1 - \frac{4}{\pi^2} \left( \frac{K_2}{K_3} \right)^2 \alpha L \tau \delta \chi_\perp I_0(0) \right\}.
\]

(19)

In this case the dependence of the threshold value \( I_{th}^0 \) on the concentration of PM molecules and their chirality is quadratic. Thus the threshold value only decreases due to PM and does not depend on the sign of the PM chirality.

3.2. Infinite director anchoring and linear light polarization

Under infinite director anchoring \((W = \infty)\) we obtain from equation (14) the next transcendental equation for the threshold value

\[
B_0 = 2(x^2 - r^2), \quad \tan x = \frac{x(2 - x^2)}{r^2}
\]

(20)

where \( x \in (\pi/2, \pi) \).

The dependence of the threshold value on the initial and PM chirality is shown in figure 1. The decrease in the threshold obtained for linear light polarization with increasing dopant chirality has been experimentally observed in [9].

3.3. Dopant threshold chirality

The initial stable homeotropically aligned director configuration becomes unstable at some concentration of chiral dopant (some value of the chiral parameter \( q_0 L \)). We can find this threshold value of \( q_0 \) by putting \( B_0 = 0 \) into equation (14). As a result we obtain the dependence of the threshold chirality on the director anchoring energy \( W \) in the form

\[
\tan t_0 = \frac{2t_0 w}{t_0^2 - w^2}
\]

(21)

where \( t_0 = (K_2/K_3) \alpha L q_0 \). A solution to this equation is shown in figure 2. Under absolutely rigid anchoring \((W = \infty)\) we find from (21) the known expression \( q_{th}^0 = \pi K_3/K_2 L \) [3] for the threshold value.
One can see that a dynamical diffraction grating of the PM concentration with spatial period $2\pi/\Delta q$ appears in the NLC cell. Omitting the intermediate results, it is noted that the linearization of the bulk equations and boundary conditions (2), (3) in this case can be carried out in the same way as for linearly polarized light in §3.2. The existence requirement of a periodicity with respect to the coordinate $x$ solution to these equations gives the equation for the threshold value of $I_0$. In the case of large periods of light intensity modulation ($\Delta q$ is small), the final expression for the threshold is defined by formula (14) where it is necessary to change $e_d/\varepsilon_d$ to $e_d \sin^2 h/\varepsilon_d \cos^2 h$ (note that $h = \pi - \gamma$ where $\gamma \ll 1$).

Thus the dependence of the threshold light intensity on its spatial periodicity is given by the expression

$$I_{th} = I_{th}^{(h = \pi)} \left( \frac{\varepsilon_d}{\varepsilon_d - \varepsilon_{\perp} \sin^2 \theta/\varepsilon_{\perp} \cos^2 \theta} \right).$$

where $I_{th}^{(h = \pi)}$ is the threshold for the linear light polarization obtained in §3.2.

4. Conclusions

We have studied theoretically the influence of phototransformed molecules (PM) with chirality on the light-induced Fréedericksz transition threshold in a NLC cell. It was found that the presence of chiral dopant in the NLC as well as the chiral PM can significantly influence the LFT threshold value.

The general expressions for the threshold obtained for finite director anchoring and partially polarized incident light wave were simplified for circular polarization of the light and infinite anchoring and gained clear analytical form. As a result, in the absence of the phototransformation of the NLC molecules, the threshold value decreases quadratically with respect to the initial dopant concentration. If the incident light induces formation of the chiral PM, the LFT threshold value decreases if the PM chirality has the same sign as the dopant and increases in the opposite case. If only the chiral PM are present in the cell, the threshold decreases and does not depend on the sign of PM chirality.

For linearly polarized incident light, the expressions for threshold value were obtained as a set of implicit equations which were calculated numerically. Solutions to these equations exhibited the same qualitative behavior as in the case of circularly polarized light.

In the absence of a light wave, the chiral dopant produces the twist torque which can destabilize the initial homeotropic configuration. The dependence of the dopant threshold chirality on the director anchoring energy was also obtained and it was shown that with a small anchoring parameter the LFT threshold strongly decreases.
The dependence of the LFT threshold on the period of modulation of the incident light intensity was obtained in the case of large periods of modulation.

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