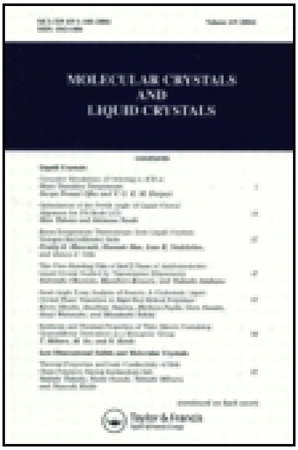

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Magnetic Field Induced Director Reorientation in the Nematic Cell with Time-Dependent Anchoring Due to Adsorption/Desorption of LC Molecules

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The time evolution of director orientation in the cell subject to the external magnetic field in the case of time-dependent boundary conditions is investigated. The case when one substrate has strong anchoring and at other substrate director anchoring is determined by process of adsorption/desorption of LC molecules on it is considered. The problem is solved in one constant approximation and Rapini-type potential for interaction between LC molecules in the cell and adsorbed LC molecules is proposed. During the time evolution the orientational distribution function of molecules adsorbed on the cell substrate possesses two maximums. Time evolution of the director orientation, anchoring energy and easy axis at the substrate is investigated numerically.

Keywords: anchoring energy; liquid crystals; memory-free alignment

1. INTRODUCTION

The possibility to control precisely the anchoring energy of liquid crystals (LC) on photo aligning polymers makes them the most promising materials for weak and memory-free anchoring. The problem, which

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hampers their application, is the strong alignment memory effect. This effect is caused by an anisotropic adsorption of LC molecules on aligning surface and is observed for most aligning materials and different liquid crystals [1–8]. The adsorbed layer behaves as a new anisotropic substrate, imposing strong monostable anchoring [2]. The strength of anchoring depends on the number of adsorbed LC molecules and their orientational distribution function. The memory alignment can be changed due to adsorption and desorption of LC molecules.

The purpose of the present paper is to investigate time evolution of director orientation in the cell subject to the external magnetic (or electric) field in the case of time-dependent boundary conditions. We will concentrate our consideration on the case when one substrate has strong anchoring and at other substrate director anchoring is determined by process of adsorption/desorption of LC molecules on it.

The free energy functional has the usual form

$$F = F_{elast} + F_m + F_S, \tag{1.1}$$

where F_{elast} is the elastic energy, F_m describes the interaction with the magnetic field and has the form

$$F_m = -\int \chi_a (\vec{n}(\vec{r}) \cdot \vec{H}(\vec{r}))^2 dV,$$

and F_S is the part of the free energy that corresponds to the interaction with surface.

To formulate the problem we have to choose some model for F_S and describe the time evolution for the adsorption/desorption process using the kinetic equation for the distribution of the molecules on the surface. The molecules in the volume are described by the function $f_{vol}(\alpha)$, where α is the angle between the director $\vec{n}(\vec{r})$ obtained from the dynamical equations and another direction $\vec{n}'$, the maximum of this function is related to the director orientation. For the molecules near the substrate we have to make the projection of the 3-dimensional distribution f_{vol} onto 2-dimensional one f_V. Evidently, the part F_S of free energy depends on the function f_V and the distribution f_S of LC molecules at the surface. The maximum of f_S plays the role of easy axis on the surface. The function $f_S(\varphi,t)$ (the value $f_S(\varphi,t)$ roughly speaking describes the portion of molecules with the angle φ) obeys the kinetic equation like

$$\frac{\partial f_S(\varphi,t)}{\partial t} = A_+ f_V(\varphi,t) - A_- f_V(\varphi,t), \tag{1.2}$$

where the constants are related to the adsorption/desorption rates. This kinetic equation determines the form of F_S and therefore the boundary condition for Euler-Lagrange equation obtained from the functional (1.1). Finally we arrive to the system of equations: the Euler-Lagrange equation for $\vec{n}(\vec{r})$ (differential), boundary conditions (algebraic and/or integral), and the kinetic equation (1.2) (differential).

In the present work we consider the simplified situation in 1-constant approximation with the planar director orientation. The paper is organized as follows. In Section 2 we present the model and briefly discuss the well-known solution of Euler-Lagrange equation for the case of nematic molecules distributed between two parallel planes. For the sake of simplicity we consider the case strong anchoring on the first plane. Here the model of time-dependent boundary condition is given. Next, in Sec. 2 we also discuss the form of the anchoring energy presented above, this analyzes allows us to rewrite the form of the anchoring energy in Rapini-like form in Sec. 3. Using the kinetic equation the time evolution of all the values can be formulated in terms of the angle related to the director orientation in the volume (see Sec. 4). Simple asymptotical solutions are given in Sec. 5. In Section 6 we discuss the modification of the model when the magnetic field is applied with the angle different from $\pi/2$. The numerical results are discussed in Sec. 7 for the modified kinetic equation Summary and discussion is given in Sec. 8.

2. DESCRIPTION OF THE SYSTEM

1. General Expressions and Geometry of the Model

The bulk elastic energy F_{elast} in one constant approximation is given by

$$F_{elast} = \frac{1}{2}\int k_{22}\partial_i n_j \partial_i n_j dV. \tag{2.1}$$

Consider the following configuration: let the nematic molecules are distributed between the planes $z = 0$ and $z = l$. The director field due to the symmetry can be expressed in terms of the angle $\varphi(z)$:

$$\vec{n}(z) = \vec{e}_x \cos\varphi(z) + \vec{e}_y \sin\varphi(z), \quad \varphi(z) = \angle(\vec{n}, \vec{e}_x)$$

(here φ is an azimuthal angle in spherical coordinates).

The system is in the magnetic field $\vec{H} = \vec{e}_y H$, so that the total functional of the free energy consists of tree parts: the elastic energy F_{elast}, the surface terms F_S and the term caused by the magnetic field F_H:

$$F = F_{elast} + F_H - W_S, \quad F_H = -\frac{1}{2}\int \chi_a (\vec{n}\cdot\vec{H})^2 dV. \tag{2.2}$$

Using notations introduced above

$$F = \frac{1}{2}\int_0^l dz[k_{22}\varphi'^2(z) - \chi_a H^2 \sin^2\varphi(z)] + F_S, \quad F_S = -W_S. \tag{2.3}$$

In the model of the surface potential proposed by Rapini

$$W_S = \frac{1}{2}W_o\cos^2(\varphi(0) - \varphi_o) + \frac{1}{2}W_l\cos^2(\varphi(l) - \varphi_l).$$

where φ_o and φ_l are easy axes at the planes $z = 0$ and $z = l$ correspondingly.

In the present paper we suggest that the energy W_S depends on the values $\varphi(0)$, $\varphi(l)$ and the properties of a surface that determine the easy axis orientation. For the sake of simplicity we consider the case when at the surface $z = 0$ we have strong anchoring with $\varphi_o = 0$. So that

$$F = \frac{1}{2}\int_0^l dz[k_{22}\varphi'^2(z) - \chi_a H^2 \sin^2\varphi(z)] - W_S[\varphi(l)]. \tag{2.4}$$

Taking the variation of this functional one will arrive to the following Euler-Lagrange equation

$$\begin{aligned} &\varphi''(z) + \frac{\chi_a H^2}{k_{22}}\sin\varphi(z)\cos\varphi(z) = 0, \\ &\alpha^2 = \frac{\chi_a H^2}{k_{22}} \text{ (we suppose that } \chi_a > 0), \end{aligned} \tag{2.5}$$

with boundary conditions

$$\varphi(0) = 0, \quad k_{22}\varphi'(l) - \frac{dW_S[\varphi(l)]}{d\varphi(l)} = 0. \tag{2.6}$$

The solution of the Eq. (2.5) is well-known. Using its first integral we get

$$\varphi'^2(z) + \alpha^2\sin^2\varphi(z) = C^2 = \text{const},$$

the constant is related to the maximum of the function $\varphi(z)$, $C = \sin\varphi_m$, for $\varphi_m = \varphi(z_m)$, where $\varphi'(z_m) = 0$. Using the boundary condition for $z = 0$ we can write the solution in the form

$$\alpha z = \int_0^{\varphi(z)} \frac{d\varphi}{[\sin^2\varphi_m - \sin^2\varphi]^{1/2}},$$

or

$$\alpha z = \int_0^{\arcsin(\sin\varphi(z)/k)} \frac{d\varphi}{[1-k^2\sin^2\varphi]^{1/2}}$$
$$\equiv F\left(\operatorname{arc}\sin\frac{\sin\varphi(z)}{k}, k\right), \quad k = \sin\varphi_m \tag{2.7}$$

(we can see that $z_m = K(\alpha l)$). In the equivalent form of the Eq. (2.7) can be written as

$$\sin\varphi(z) = k\, sn(\alpha z, k). \tag{2.8}$$

The parameter k of the elliptic integral can be determined from the second boundary condition. Taking into account (2.8) we can rewrite this in the form

$$\alpha k\, cn(\alpha l, k) - \frac{1}{k_{22}} \frac{dW[\varphi(l)]}{d\varphi(l)}\bigg|_{\varphi(l)=\arcsin(k\, sn(\alpha l, k))} = 0. \tag{2.9}$$

In Rapini model (2.9) reads

$$\alpha k\, cn(\alpha l, k) + \frac{W_l}{k_{22}} \sin(\varphi(l)-\varphi_l)\cos(\varphi(l)-\varphi_l)\bigg|_{\varphi(l)=\arcsin(k\, sn(\alpha l, k))} = 0. \tag{2.10}$$

In two simplest cases $W \to 0$ and $W \to \infty$ this equation can be rewritten in more simple one. When $W \to 0$, (2.9) is reduced to $k\, cn(\alpha l, k) = 0$, so that k obeys the equation $K(k) = \alpha l$. When $W_l \to \infty$, $\varphi(l) = \varphi_l$, where φ_l is the solution of the equation $dW[\varphi]/d\varphi = 0$. In Rapini model this equation holds due to (2.10).

In all of these cases the value k determines the director distribution completely.

2. Time Evolution

In the present paper we will analyze the time-dependent boundary condition at $z = l$. Time evolution of the easy axis at the surface $z = l$ is governed by the process of adsorption/desorbtion of the molecules at the surface. Therefore the functions like to director orientation, the easy axis at the surface, the anchoring energy, are time-dependent.

Free energy functional has the form

$$F(t) = \frac{1}{2}\int_0^l dz \left[k_{22}\left(\frac{\partial\varphi(z,t)}{\partial z}\right)^2 - \chi_a H^2 \sin^2\varphi(z,t)\right] + F_S(t). \tag{2.11}$$

All the equations determining the director orientation preserves their form, but the parameter k becomes time-dependent.

We assume the following expression for the anchoring energy

$$W(t) = W_o \int d\Omega_1 \int d\Omega_2 (\vec{n}_1 \cdot \vec{n}_2)^2 f_{surf}(\Omega_1, t) f_{vol}(\Omega_2, t), \tag{2.12}$$

where $\vec{n}_{1,2}$ are determined by $\Omega_{1,2} = (\varphi_{1,2}, \theta_{1,2})$ in spherical coordinates, f_{vol} and f_{surf} are distribution functions in the cell (for some z) and at the substrate.

For $f_{vol}(\Omega, t)$ we choose

$$f_{vol}(\Omega', t) = \frac{1}{N_{vol}} \exp(\beta P_2(\vec{n} \cdot \vec{n}')), \quad \int f_{vol}(\Omega, t) d\Omega = 1, \quad \beta = \frac{aS}{kT}. \tag{2.13}$$

Here N_{vol} is a normalization constant, S is the order parameter, a is some constant, $\vec{n}$ is the director orientation (solution of Euler-Lagrange equations), $\vec{n}'$ is orientation of LC molecules determined by $\Omega' = (\varphi', \theta')$. Using

$$\vec{n} = (\cos\varphi, \sin\varphi, 0), \quad \vec{n}' = (\cos\varphi' \sin\theta', \sin\varphi' \sin\theta', \cos\theta')$$

we get

$$\vec{n} \cdot \vec{n}' = \sin\theta' \cos(\varphi - \varphi'),$$

so that

$$f_{vol}(\Omega', t) = \frac{1}{N_{vol}} \exp(\beta P_2(\sin\theta' \cos(\varphi - \varphi')), \tag{2.14}$$

the real time dependence is included in $\vec{n}$ (or $\varphi(t)$).

The LC molecules can be adsorbed on the surface with different values of θ' but with the same φ'. Distribution on the surface is planar so that we have to make a 2-dimensional projection of (2.14) integrating on the variable θ', i.e., to describe these molecules we have to consider the averaged distribution for $z = l$:

$$f_V(\varphi', t) = \langle f_{vol}(\Omega', t) \rangle_{\theta'} = \int_0^\pi f_{vol}(\Omega', t) \sin\theta' d\theta'. \tag{2.15}$$

Further we will denote $\varphi(l, t)$ by $\varphi_V(t)$.

As to the distribution f_{surf} it is evident that that its form is

$$f_{surf}(\Omega', t) = f_S(\varphi', t) \delta(\cos\theta'),$$

here the last multiplier displays the fact that all the molecules lie at the substrate.

Therefore using the properties of $f_{vol}(\Omega, t)$ and $f_{surf}(\Omega, t)$ we can rewrite $W(t)$ as

$$W(t) = W_o \int_{-\pi/2}^{\pi/2} d\varphi_1 \int_{-\pi/2}^{\pi/2} d\varphi_2 \cos^2(\varphi_1 - \varphi_2) f_S(\varphi_1, t) \times \int_0^{\pi} \sin^3\theta_2 f_{vol}(\Omega_2, t) d\theta_2,$$

or, denoting

$$\overline{f}_V(\varphi, t) = \int_0^{\pi} f_{vol}(\Omega, t) \sin^3\theta \, d\theta \tag{2.16}$$

we can present (2.2) as

$$W(t) = W_o \int_{-\pi/2}^{\pi/2} d\varphi_1 \int_{-\pi/2}^{\pi/2} d\varphi_2 f_S(\varphi_1, t) \overline{f}_V(\varphi_2, t) \cos^2(\varphi_1 - \varphi_2). \tag{2.17}$$

The functions $f_V(\varphi', t)$ and $\overline{f}_V(\varphi', t)$ are given and we can introduce more convenient notations motivated as follows. Maximum values both of them are reached when $\varphi' = \varphi_V$ and they are symmetric with respect to extremum. Moreover, their real time dependencies are included into $\varphi_V(t)$. So we denote

$$f_V(\varphi' - \varphi_V(t)) \equiv f_V(\varphi', t), \quad \overline{f}_V(\varphi' - \varphi_V(t)) \equiv \overline{f}_V(\varphi', t),$$

where

$$f_V(\alpha) = \frac{1}{N_{vol}} \int_0^{\pi} e^{\beta P_2(\sin\theta \cos\alpha)} \sin\theta \, d\theta,$$
$$\bar{f}_V(\alpha) = \frac{1}{N_{vol}} \int_0^{\pi} e^{\beta P_2(\sin\theta \cos\alpha)} \sin^3\theta \, d\theta.$$

With these notations for a fixed moment of time W_S as the function of φ_V reads

$$W[\varphi_V(t)] = W_o \int_{-\pi/2}^{\pi/2} d\varphi_1 \int_{-\pi/2}^{\pi/2} d\varphi_2 f_S(\varphi_1, t) f_V(\varphi_2 - \varphi_V(t)) \cos^2(\varphi_1 - \varphi_2). \tag{2.18}$$

The function $f_S(\varphi, t)$ obeys the kinetic equation

$$\frac{\partial f_S(\varphi, t)}{\partial t} = A_+ f_V(\varphi - \varphi_V(t)) - A_- f_S(\varphi, t), \tag{2.19}$$

where $A_\pm$ are the coefficients describing velocities of the adsorption/desorbtion process. In the equilibrium case $f_S(\varphi, t)$ is simply proportional to $f_V(\varphi - \varphi_V)$, namely

$$f_S(\varphi, t) = \frac{A_+}{A_-} f_V(\varphi - \varphi_V(t))$$

so that $\varphi = \varphi_V$ is the maximum of this distribution and corresponds to the easy axis on a surface.

To find the director orientation we have to solve the boundary condition for all time values, this equation depends on function $W(t)$, to write its explicit form in order to find the energy $W(t)$ we have to solve the kinetic equation. The initial condition we choose

$$f_S(\varphi, 0) = \frac{A_+}{A_-} f_V(\varphi - \varphi_S(0), 0)$$

where the value $\varphi_S(0)$ is given. Molecules, adsorbed on a surface, are not so mobile as the volume ones so that at $t = 0$ the function $f_S(\varphi)$ describes the equilibrium distribution. At the same time the magnetic field changes the orientation of the molecules in the cell.

It should be noted here that the functions $f_V(\varphi)$ and $\overline{f}_V(\varphi)$ can be expressed in terms of error-function integral. Calculating the integral over θ directly one will arrive to the following expressions:

$$f_V(\varphi) = \frac{1}{N_{vol}} \frac{\sqrt{\pi}}{\xi} e^{\beta P_2(\cos\beta)} erf(\xi), \tag{2.20}$$

$$\overline{f}_V(\varphi) = -\frac{1}{N_{vol}} \frac{1}{\xi^2} e^{-\beta/2} + \frac{1}{2\xi^2} f_V(\varphi), \tag{2.21}$$

where

$$\xi^2 = \frac{3\beta}{2}\cos^2\varphi, \quad -\frac{\pi}{2}\varphi\frac{\pi}{2}, \quad erf(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2} dt.$$

For $\varphi \to \pi/2$ ($\alpha \to 0$) there are not any singularity. Indeed,

$$f_V(\varphi) \to \frac{2}{N_V} e^{-\beta/2}, \quad \overline{f}_V(\varphi) \to 0 \quad \text{for} \quad \varphi \to \frac{\pi}{2}.$$

Using (2.20, 2.21) and the properties of the error function we can write down power series expansions

$$f_V(\varphi) = \frac{2}{N_{vol}} e^{-\beta/2} \sum_{n=0}^{\infty} \frac{2^n}{(2n+1)!!} \xi^{2n} \equiv \frac{2}{N_{vol}} e^{-\beta/2} \times \sum_{n=0}^{\infty} \frac{2^n}{(2n+1)!!} \left(\frac{3\beta}{2}\right)^n \cos^{2n}\varphi, \tag{2.22}$$

$$\bar{f}_V(\varphi) = \frac{2}{N_{vol}} e^{-\beta/2} \sum_{n=0}^{\infty} \frac{2^n}{(2n+3)!!} \xi^{2n} \equiv \frac{2}{N_{vol}} e^{-\beta/2} \times \sum_{n=0}^{\infty} \frac{2^n}{(2n+3)!!} \left(\frac{3\beta}{2}\right)^n \cos^{2n} \varphi, \tag{2.23}$$

(these functions differ from each other on the factor $2n+3$ in Tailor series).

Normalization constant N_{vol} can be calculated from the condition $\int_{-\pi/2}^{\pi/2} f_V(\varphi)d\varphi = 1$. The result is

$$N_{vol} = 2\pi e^{-\beta/2} \frac{erfi(\sqrt{3\beta/2})}{\sqrt{3\beta/2}}, \quad erfi(x) = \int_0^x e^{t^2} dt. \tag{2.24}$$

3. THE ANCHORING ENERGY

For each fixed moment of time the integral (2.12) can be considered as the function of the parameter φ_V, so that we can transform $W(t) \equiv W[\varphi_V]$ using general properties of the distributions f_{vol} and f_{surf}.

Making a substitution $\alpha_2 = \varphi_2 - \varphi_V$ into the inner integral and performing the simple calculations with trigonometric functions we obtain

$$\begin{aligned} W[\varphi_V] = W_o \int_{-\pi/2}^{\pi/2} f_S(\varphi_1, t) d\varphi_1 \Bigg[& \int_{-\pi/2-\varphi_V}^{\pi/2-\varphi_V} \bar{f}_V(\alpha_2, 0) d\alpha_2 \\ & + \cos 2(\varphi_1 - \varphi_V) \int_{-\pi/2-\varphi_V}^{\pi/2-\varphi_V} \bar{f}_V(\alpha_2) \cos 2\alpha_2 \, d\alpha_2 \\ & + \sin 2(\varphi_1 - \varphi_V) \int_{-\pi/2-\varphi_V}^{\pi/2-\varphi_V} \bar{f}_V(\alpha_2) \sin 2\alpha_2 \, d\alpha_2 \Bigg]. \end{aligned}$$

The functions $\sin 2\theta, \cos 2\theta$ and $\bar{f}_V(\theta)$ are periodic with the period π, so that we can change the range of integrals from $[-\pi/2 - \varphi_V, \pi/2 - \varphi_V]$ to $[-\pi/2, \pi/2]$. Further, $\bar{f}_V(\theta) = \bar{f}_V(-\theta)$ so that the integral with the sine function vanishes due to antisymmetry of $\sin 2\theta$.

Finally, we arrive to the following form of the anchoring energy

$$W[\varphi_V] = \frac{1}{2} W_o \left[I_S \bar{I}_V + \bar{C}_{2V} (C_{2S} \cos 2\varphi_V + S_{2S} \sin 2\varphi_V) \right], \tag{3.1}$$

where

$$I_S(t) = \int_{-\pi/2}^{\pi/2} f_S(\theta,t)d\theta, \quad \overline{I}_V = \int_{-\pi/2}^{\pi/2} \overline{f}_V(\theta)d\theta = \text{const},$$
$$\overline{C}_{2V} = \int_{-\pi/2}^{\pi/2} \overline{f}_V(\theta)\cos 2\theta d\theta = \text{const}, \quad \overline{S}_{2V} = \int_{-\pi/2}^{\pi/2} \overline{f}_V(\theta)\sin 2\theta d\theta \equiv 0, \quad (3.2)$$
$$C_{2S}(t) = \int_{-\pi/2}^{\pi/2} f_S(\theta,t)\cos 2\theta d\theta, \quad S_{2S}(t) = \int_{-\pi/2}^{\pi/2} f_S(\theta,t)\sin 2\theta d\theta.$$

Using (2.20, 2.21) we can find the following connection between I_V, $\overline{I}_V$ and $\overline{C}_{2V}$:

$$\frac{3\beta}{2}(\overline{I}_V + \overline{C}_{2V}) = \frac{\pi}{N_{vol}} e^{-\beta/2} - \frac{1}{2} I_V.$$

The integral $\overline{I}_V$ can be calculated with the use of expansion (0.9), we get

$$\overline{I}_V = \frac{2\pi e^{-\beta/2}}{N_{vol}} \sum_{n=0}^{\infty} \frac{1}{(2n+1)(2n+3)n!} \left(\frac{3\beta}{2}\right)^n.$$

In these denotations one can rewrite the formula for the anchoring energy in the special form that is similar to usual Rapini expression. Let us define the angle $\varphi_S(t)$:

$$\sin 2\varphi_S(t) = \frac{S_{2S}(t)}{[C_{2S}^2(t) + S_{2S}^2(t)]^{1/2}}, \quad \cos 2\varphi_S(t) = \frac{C_{2S}(t)}{[C_{2S}^2(t) + S_{2S}^2(t)]^{1/2}} \quad (3.3)$$

Therefore (3.2) reads

$$W[\varphi_V] = \frac{1}{2} W_o \left[I_S \overline{I}_V + \overline{C}_{2V} \sqrt{C_{2S}^2(t) + S_{2S}^2(t)} \cos 2(\varphi_V(t) - \varphi_S(t)) \right]. \quad (3.4)$$

The boundary condition at the plane $z = l$ has the form

$$k_{22} \frac{\partial \varphi(z,t)}{\partial z}\bigg|_{z=l} - \frac{\partial W[\varphi_V(t)]}{\partial \varphi_V(t)} = 0. \quad (3.5)$$

The last term in l.h.s. of (3.5) can be calculated by the direct differentiation (0.4) or (1.1) on the parameter φ_V. So we get

$$\frac{\partial W}{\partial \varphi_V} = W_o \overline{C}_{2V} (S_{2S} \cos 2\varphi_V - C_{2S} \sin 2\varphi_V) \quad (3.6)$$

(here we use only the formal properties of $f_V(\theta)$ without its explicit form).

From (3.6) we can conclude that $dWd\varphi_V = 0$ when $\varphi_V = \varphi_S$, so that the function $\varphi_S(t)$ defined in (3.3) plays the rule of the easy axis on a surface at the time moment t. Using the definition of φ_S and the expression (3.6) we can rewrite the boundary condition as

$$k_{22}\frac{\partial\varphi(z,t)}{\partial z}\bigg|_{z=l} + W_o\overline{C}_{2V}\sqrt{C_{2S}^2(t) + S_{2S}^2(t)}\sin 2(\varphi_V(t) - \varphi_S(t)) = 0 \quad (3.7)$$

that formally coincides with Rapini expression.

4. KINETIC EQUATION

Time evolution is governed by the kinetic equation

$$\frac{\partial f_S(\varphi,t)}{\partial t} = A_+ f_V(\varphi - \varphi_V) - A_- f_S(\varphi,t), \quad f_S(\varphi,0) = \frac{A_+}{A_-} f_V(\varphi - \varphi_S(0)).$$

Multiplying all sides of the kinetic equation on $\sin 2\varphi$ and $\cos 2\varphi$ and integrating on φ in the range $[-\pi/2, \pi/2]$ one can find the differential equations

$$\begin{aligned}\frac{d}{dt}S_{2S}(t) + A_- S_{2S}(t) &= A_+ C_{2V}\sin 2\varphi_V(t),\\ \frac{d}{dt}C_{2S}(t) + A_- C_{2S}(t) &= A_+ C_{2V}\cos 2\varphi_V(t),\end{aligned} \quad (4.1)$$

with formal solutions

$$\begin{aligned}S_{2S}(t) &= S_{2S}(0)e^{-A_- t} + A_+ C_{2V}\int_0^t e^{-A_-(t-\tau)}\sin 2\varphi_V(\tau)d\tau,\\ C_{2S}(t) &= C_{2S}(0)e^{-A_- t} + A_+ C_{2V}\int_0^t e^{-A_-(t-\tau)}\cos 2\varphi_V(\tau)d\tau.\end{aligned} \quad (4.2)$$

Here analogously to (3.2) we have introduced the following constants

$$\begin{aligned}I_V &= \int_{-\pi/2}^{\pi/2} f_V(\theta)d\theta = \text{const},\\ C_{2V} &= \int_{-\pi/2}^{\pi/2} f_V(\theta)\cos 2\theta\, d\theta = \text{const},\\ S_{2V} &= \int_{-\pi/2}^{\pi/2} f_V(\theta)\sin 2\theta\, d\theta \equiv 0.\end{aligned} \quad (4.3)$$

The constant C_{2V} can be calculated from the identity

$$\int_{-\pi/2}^{\pi/2} f_V(\varphi)\cos^2\varphi d\varphi \equiv \frac{1}{2}(I_V + C_{2V}) = \frac{1}{N_{vol}}\frac{\pi e^{-\beta/2}}{3\beta/2}(e^{3\beta/2} - 1),$$

so that

$$C_{2V} = \frac{2}{N_{vol}}\frac{\pi e^{-\beta/2}}{3\beta/2}(e^{3\beta/2} - 1) - I_V.$$

Similarly, integrating the kinetic equation directly, we obtain the equation for the integral $I_S(t) = \int_{-\pi/2}^{\pi/2} f_S(\varphi, t)d\varphi$,

$$\frac{d}{dt}I_S(t) + A_- I_S(t) = A_+ I_V,$$

therefore,

$$I_S(t) = \left(I_S(0) - \frac{A_+}{A_-}\right)e^{-A_- t} + \frac{A_+}{A_-}I_V. \tag{4.4}$$

Assuming $f_S(\varphi, 0) = A_+ A_- f_V(\varphi - \varphi_S(0))$ we get $I_S(0) = (A_+/A_-)I_V$, so that

$$I_S(t) = \frac{A_+}{A_-}I_V = \text{const.} \tag{4.5}$$

Note that the kinetic equation one can rewrite by the following way, making the substitution $f_S(\varphi, t) = e^{A_- t}\hat{f}_S(\varphi, t)$:

$$f_S(\varphi, t) = f_S(\varphi, 0)e^{-A_- t} + A_+\int_0^t e^{-A_-(t-\tau)} f_V(\varphi, \varphi_V(\tau))d\tau. \tag{4.6}$$

Integrating this equation with 1, $\sin 2\varphi$ and $\cos 2\varphi$ we will arrive to the results obtained above. Using the formal solutions for $S_{2S}(t)$ and $C_{2S}(t)$ one can present the energy and its derivative with respect to φ_V as

$$\begin{aligned} W[\varphi_V] = \frac{1}{2}W_o[I_S\bar{I}_V &+ \bar{C}_{2V}[\cos 2\varphi_V(t)C_{2S}(0) + \sin 2\varphi_V(t)S_{2S}(0)]e^{-A_- t} \\ &+ C_{2V}\bar{C}_{2V}\int_0^t e^{-A_-(t-\tau)}\cos 2(\varphi_V(t) - \varphi_V(\tau))d\tau], \end{aligned} \tag{4.7}$$

$$\begin{aligned} \frac{dW[\varphi_V]}{d\varphi_V} = W_o\overline{C}_{2V}&[\cos 2\varphi_V(t)S_{2S}(0) - \sin 2\varphi_V(t)C_{2S}(0)]e^{-A_- t} \\ &- W_o A_+ C_{2V}\overline{C}_{2V}\int_0^t e^{-A_-(t-\tau)}\sin 2(\varphi_V(t) - \varphi_V(\tau))d\tau. \end{aligned} \tag{4.8}$$

Using the formal time dependencies, we are able to reformulate the initial problem as following. To calculate the director orientation for any time moment we need $k(t)$. This function satisfies the integral equation

$$\begin{aligned}&\alpha k(t)cn(\alpha l, k(t)) - W_o\overline{C}_{2V}(\cos 2\varphi_V(t)S_{2S}(0) - \sin 2\varphi_V(t)C_{2S}(0))e^{-A_- t}\\&\quad + W_o C_{2V}\overline{C}_{2V}\int_0^t e^{-A_-(t-\tau)}\sin 2(\varphi_V(t) - \varphi_V(\tau))d\tau = 0.\end{aligned} \tag{4.9}$$

When $t \to \infty$ the first term can be neglected.

5. ASYMPTOTIC

Let us consider the asymptotic behaviour of the solution when $t \to \infty$. In this case

$$\lim_{t\to\infty} tg\, 2\varphi_S(t) = \lim_{t\to\infty}\frac{\int_0^t e^{-A_-(t-\tau)}\sin 2\varphi_V(\tau)d\tau}{\int_0^t e^{-A_-(t-\tau)}\cos 2\varphi_V(\tau)d\tau} = \lim_{t\to\infty} tg\, 2\varphi_V(t).$$

Therefore $\varphi_S(t) \to \varphi_V(t)$, when $t \to \infty$ and the boundary condition at $z = l$ in this case reads

$$k_{22}\frac{\partial\varphi_V(z,\infty)}{\partial z}\bigg|_{z=l} = \alpha k_{22}\cdot k(\infty)cn(\alpha l, k(\infty)) = 0,$$

so that $\alpha l = K(k(\infty))$. This means that for $t \to \infty$ angles φ_S and φ_V are equal and are independent on the properties of a surface.

By the similar way we can consider the limit $t \to 0$, the boundary condition is reduced to

$$\begin{aligned}&k_{22}\alpha k(0)cn(\alpha l, k(0)) + W_o\overline{C}_{2V}[C_{2S}^2(0) + S_{2S}^2(0)]^{1/2}\\&\quad\times \sin 2(\varphi_V(0) - \varphi_S(0)) = 0.\end{aligned}$$

This equation receives the simplest form when $\varphi_S(0) = 0$:

$$k_{22}\alpha k(0)cn(\alpha l, k(0)) + W_o\overline{C}_{2V}C_{2S}(0)\sin 2\varphi_V(0) = 0.$$

Taking into account the solution $\varphi_V = \arcsin(k\, sn(\alpha l, k))$ we get

$$\frac{sn(\alpha l)cn(\alpha l)}{dn(\alpha l)} = -\frac{\alpha k_{22}}{2W_o\overline{C}_{2V}C_{2S}(0)} := \xi = \text{const},$$

so that

$$cn(2\alpha l, k) = \frac{1-\xi^2}{1+\xi^2}$$

or, equivalently

$$2\alpha l = F\left(\arccos\frac{1-\xi^2}{1+\xi^2}, k(0)\right).$$

This equation allows one to find $k(0)$ and investigate the properties of the critical field.

6. NON-ORTHOGONAL FIELD CONFIGURATION

Let us now consider the simple modification of the problem. In all the calculations performed above the direction of the magnetic field was orthogonal to the easy axis at the plane $z = 0$. In more general case

$$\vec{H} = H(\vec{e}_x \cos\varphi_H + \vec{e}_y \sin\varphi_H),$$

so that the free energy functional receives the form

$$F = \frac{1}{2}\int_0^l dz[k_{22}\varphi'^2(z) - \chi_a H^2 \cos^2(\varphi(z) - \varphi_H)] - W_S. \qquad (6.1)$$

With the use of standard procedure we will arrive to the Euler-Lagrange equation with the following boundary conditions

$$\varphi(0,\, t) = 0 \ \ (\text{for } z = 0), \quad k_{22}\varphi'_z(l,t) - \frac{dW_S[\varphi(l,t)]}{d\varphi(l,t)} = 0 \ \ (\text{for } z = l).$$

For arbitrary φ_H we introduce the substitution

$$\psi(z,t) = \varphi_H - \varphi(z,t), \qquad (6.2)$$

so that the Euler-Lagrange equation reads

$$\psi''_z(z,t) + \frac{\chi_a H^2}{k_{22}}\sin\psi(z,t)\cos\psi(z,t) = 0, \quad \alpha^2 = \frac{\chi_a H^2}{k_{22}} \qquad (6.3)$$

the boundary conditions (2.2) are reduced to

$$\psi(0,\, t) \equiv \psi_o = \varphi_H, \quad k_{22}\psi'_z(l,t) - \frac{dW_S[\psi(l,t)]}{d\psi(l,t)} = 0. \qquad (6.4)$$

Using the periodicity properties of distribution functions one can easily show that the anchoring energy will be the same, we can simply substitute $\psi = \varphi_H - \varphi$, $\psi_V = \varphi_H - \varphi_V$ instead of φ, φ_V and denote again

$$f_S(\psi,t) \equiv f_S(\varphi_H - \psi, t).$$

Integrating the equation (6.3) we obtain the well-known formula

$$\alpha(z-a) = \pm\int_0^{\psi(z)} \frac{d\psi}{[\sin^2\psi_m - \sin^2\psi]^{1/2}},$$

where $\psi'(z_m) = 0$, $\psi_m = \psi(z_m)$. In R.H.S. of this expression we have to choose the sign "$+$" for $z < z_m$, and "$-$" for $z > z_m$. When $z = 0$ we find

$$-\alpha a = F\left(\arcsin\frac{\sin\psi_o}{k}, k\right), \quad k = \sin\psi_m. \tag{6.5}$$

Requiring the total solution being continuous at $z = z_m$, we can write

$$\sin\psi(z) = k\,\mathrm{sn}(\alpha(z-a), k) \tag{6.6}$$

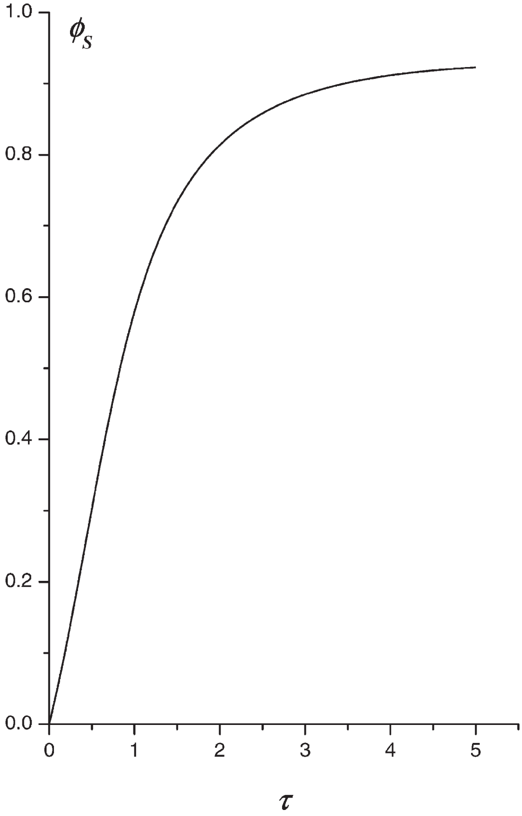

FIGURE 1 The function $\varphi_S(\tau)$ for initially ordered surface distribution.

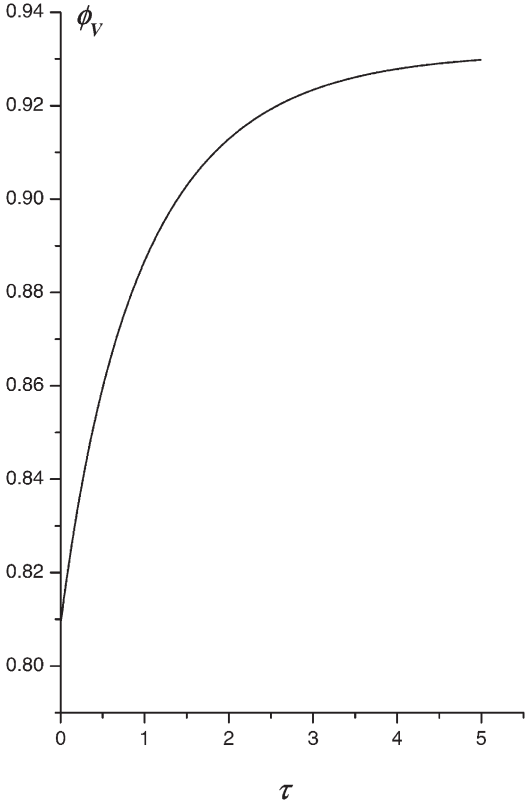

FIGURE 2 The function $\varphi_V(\tau)$ for initially ordered surface distribution.

where a satisfies (6.5). The parameter $k(t)$ can be calculated from the boundary condition at $z = l$

$$\alpha k\, cn(\alpha(l-a)) - \frac{1}{k_{22}}\frac{dW[\psi_V]}{d\psi_V} = 0, \quad \psi_V \equiv \psi(l) = \arcsin[k \sin(\alpha(l-a))],$$

or, taking into account general expression of W

$$\alpha k\, cn(\alpha(l-a)) + \frac{W_o}{k_{22}}\overline{C}_{2V}(C_{2S}\sin 2\psi_V - S_{2S}\cos 2\psi_V) = 0. \qquad (6.7)$$

Here $C_{2S}(t)$, $S_{2S}(t)$ and $\overline{C}_{2V}$ are the same as in (3.2). Functions $C_{2S}(t)$, $S_{2S}(t)$ (and the anchoring energy) can be determined from the kinetic equation as described in Sec. 4.

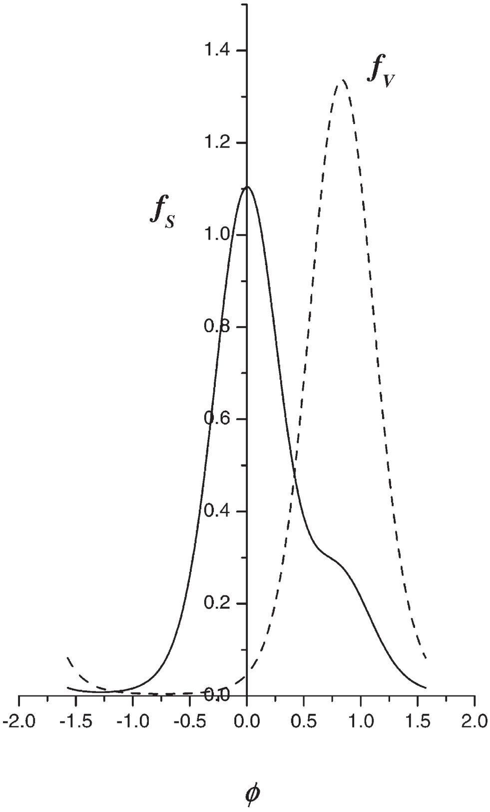

FIGURE 3 The distributions $f_V(\tau)$ and $f_S(\tau)$ for initially ordered surface distribution for middle moment of time.

7. MODIFICATION OF KINETIC EQUATION

To describe the adsorption/desorbtion process more precisely we use the generalized kinetic equation in the following form

$$\frac{\partial f_S(\varphi,t)}{\partial t} = A_+(\varphi,t)f_V(\varphi,t) - A_-(\varphi,t)f_S(\varphi,t), \tag{7.1}$$

where we denote

$$A_+(\varphi,t) = a_+P_+(\varphi,t), \quad A_-(\varphi,t) = a_-P_-(\varphi,t), \tag{7.2}$$

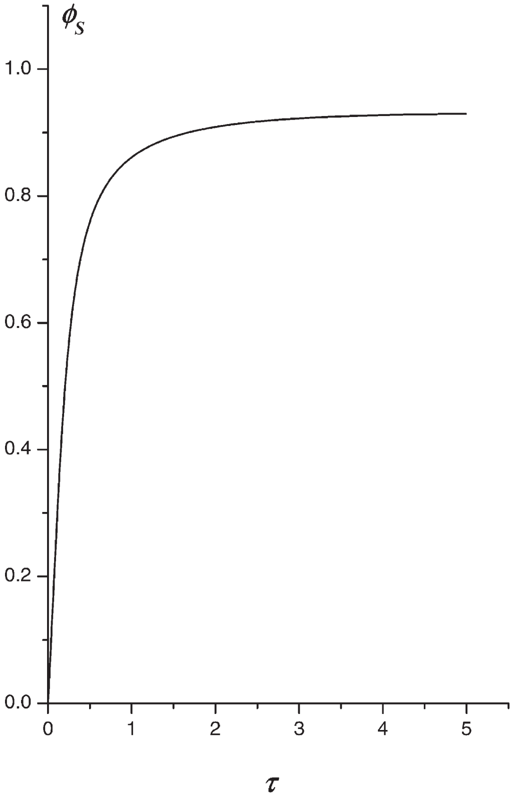

FIGURE 4 The function $\varphi_S(\tau)$ for initially chaotic surface distribution.

and

$$P_+(\varphi,t) = \exp\left[\frac{\alpha_s S_s}{kT}\cos^2(\varphi-\varphi_S)\right] \times \int_{-\pi/2}^{\pi/2}\exp\left[-\frac{\alpha_s S_s}{kT}\cos^2(\varphi_1-\varphi_S)\right] f_S(\varphi_1,t)d\varphi_1, \tag{7.3}$$

$$P_-(\varphi,t) = \exp\left[-\frac{\alpha_s S_s}{kT}\cos^2(\varphi-\varphi_S)\right] \times \int_{-\pi/2}^{\pi/2}\exp\left[\frac{\alpha_s S_s}{kT}\cos^2(\varphi_1-\varphi_S)\right] f_V(\varphi_1,t)d\varphi_1. \tag{7.4}$$

The functions $P_\pm(\varphi,t)$ can be interpreted as follows. The probability for given LC molecule to be desorbed from the surface depends on the

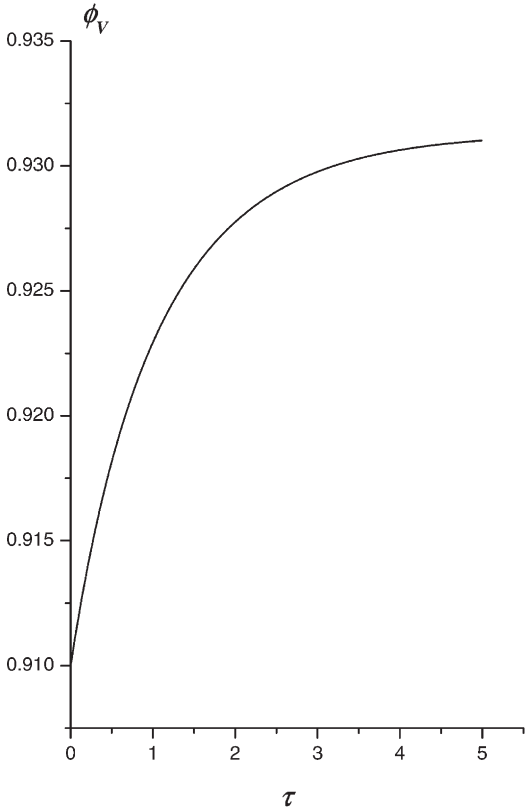

FIGURE 5 The function $\varphi_V(\tau)$ for initially chaotic surface distribution.

order parameter of surrounding it other adsorbed molecules, and also site for desorption should be vacant in other words is may be written as $a_- P_-(\varphi, t)$, where $a_- = \text{const}$. The surface order parameter is defined as

$$S_s = \int_{-\pi/2}^{\pi/2} [\cos^2 \varphi - 1/2] f_S(\varphi, t) d\varphi. \tag{7.5}$$

The probability for given LC molecule to be adsorbed depends on its orientational state before adsorption, the order parameter of already adsorbed molecules, and also site for adsorption should be vacant (some adsorbed molecule should go away before new molecule from the bulk comes to that site). So that it is $a_+ P_+(\varphi, t)$, where $a_- = \text{const}$.

In stationary case we can put $\partial f_S/\partial t = 0$ and the kinetic equation became

$$a_+ P_+(\varphi, t) = a_- P_-(\varphi, t).$$

Integrating this expression over φ we arrive to the result that $a_+ = a_-$.

It seems that this form of the kinetic equation describes the experimental data more realistically than the equation with $A_\pm = \text{const}$. Some results of the numerical calculations are presented on Figures 1–6. The solution of the differential equation was developed with the use of standard Runge-Kutta method, and at each step of this procedure we solve the algebraic equation to find the parameter k of the elliptic functions.

In all the figures the following values of constants are chosen:

$$\frac{l}{\xi} = 2, \quad \frac{W_o \xi}{k_{22}} = 0.1, \quad \beta_V = 4.55, \quad \beta_S = 1.$$

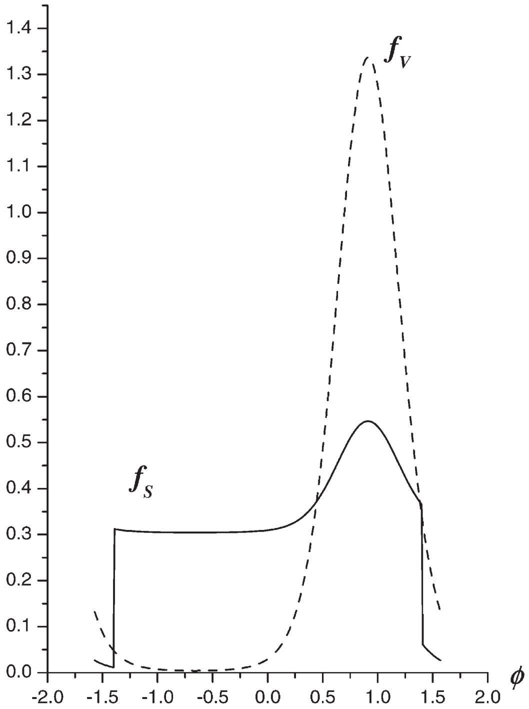

FIGURE 6 The distributions $f_V(\tau)$ and $f_S(\tau)$ for initially chaotic surface distribution for middle moment of time.

(the magnetic field is orthogonal to director distribution). In the kinetic equation (modified) we put $A_{\pm,0} = 1$. Time variable is dimensionless, we denote $\tau = A_{-,0}t$.

In the Figures 1–3 the initial orientation of LC molecules at the plane is the same as in the nearest layer in the volume (i.e., $f_S(\varphi, 0) = f_V(\varphi, 0)$). Time evolution of distributions is given for $\tau \cong 0.2$. The function $\varphi_S(t)$ can be fitted by the stretch exponent

$$\varphi_S(\tau) = \varphi_S(\infty) + A\exp[-(\tau/\tau_0)^{\gamma}]$$

with $\gamma = 1.18$.

In the Figures 4–6 the initial orientation at the plane is chaotic, we describe this by the function

$$f_s(\varphi, 0) = \begin{cases} 1, |\varphi| < 1.4, \\ 0, |\varphi| > 1.4. \end{cases}$$

(further we normalize this function requiring $\int_{-\pi/2}^{+\pi/2} f_S(\varphi, 0)d\varphi = 1$). Time evolution of distributions is given for $\tau \cong 0.2$. The function $\varphi_S(t)$ can be fitted by the stretch exponent with $\gamma = 0.79$.

Note that the parameter γ in the stretch exponent essentially depends on all the parameters of the model. It may be larger or smaller than 1.

8. SUMMARY

We have studied time evolution of director orientation in the cell subject to the external magnetic field in the case of time-dependent boundary conditions. Boundary conditions change is due to processes of LC molecules adsorption/desorption. Director reorientation may have stretch-exponential character. This agrees qualitatively with experimental data of [11]. Characteristics of stretch exponent significantly depend on model's parameters, in particular on order parameter of adsorbed LC molecules.

REFERENCES

[1] Cheng, J. & Boyd, G. D. (1979). *Appl. Phys. Lett.*, *35*, 444.
[2] Stoenescu, D. (1998). *Ph.D. Thesis*, Univ. P. Sabatier, Toulouse.
[3] Clark, N. A. (1985). *Phys. Rev. Lett.*, *55*, 292.
[4] Ouchi, Y., Feller, B. B., Moses, T., & Shen, Y. R. (1992). *Phys. Rev. Lett.*, *68*, 3040.
[5] Sato, Y., Sato, K., & Uchida, T. (1992). *Jpn. J. Appl. Phys.*, *31*, L579.
[6] Nose, T., Masuda, S., & Sato, S. (1991). *Jpn. J. Appl. Phys.*, *30*, 3450.

[7] Vetter, P., Ohmura, Y., & Uchida, T. (1993). *Jpn. J. Appl. Phys.*, *32*, L1239.

[8] Reznikov, Yu., Ostroverkhova, O., Singer, K., Kim, J.-H., Kumar, S., Lavrentovich, O., Wang, B., & West, J. (2000). *Phys. Rev. Lett.*, *84*, 1930.

[9] Rapini, A. & Papoular, M. (1969). *J. Phys. Colloq.*, *30*, 54.

[10] de Gennes, P. G. (1974). *The Physics of Liquid Crystals*, Clarendon Press: Oxford.

[11] Faetti, S., Gerus, I., & Mutinati, C. (2004). *Mol. Cryst. Liq. Cryst., 421*, 81.