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Orientational relaxation phenomena in Langmuir-Blodgett films at the air-water interface

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The nature of the orientational relaxation process of the director **n** to its equilibrium orientation $\mathbf{n}_{eq}$, in the mono-(multi)layer(s) Langmuir-Blodgett film, during the lateral compression in absence of flow, is investigated. The relaxation time, during compression of 4-*n*-pentyl-4′-cyanobiphenyl mono-(multi)layer(s) film on the water surface, using the Ericksen-Leslie theory, has been calculated for the number of dynamic regimes.

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I. INTRODUCTION

In absence of flow, the relaxation of the director **n** to their equilibrium orientation $\mathbf{n}_{eq}$ in the liquid crystal (LC) film at the air-water interface, during the lateral compression of the film, is governed by elastic, electric, and hydrodynamic torques exerted per unit LC's volume. If the director is disturbed, for instance, during compression, and then allowed to relax, these torques vanish when the director aligns at an equilibrium angle θ_{eq} with respect to a unit vector **j**, directed perpendicular to the air-water interface (see Fig. 1). Textures of the LC films are produced by the director orientation $\mathbf{n}=\langle \mathbf{u}_i \rangle$, and the fluctuation of the molecular orientation $\mathbf{u}_i$ with respect to **n** is expressed by the order parameters (OPs) $\overline{P_l}=\langle P_l(\mathbf{n}\cdot\mathbf{u}_i)\rangle=\langle P_l(\cos\theta_i)\rangle$, where θ_i is the angle between the long axis of the molecule *i* and the nematic director **n**, $\langle\cdots\rangle$ denotes the statistical average, and P_l are the Legendre polynomials of rank *l*. The orientational order of the mesogenic molecules on the water surface is traditionally quantified in terms of OPs; however, the most complete description of the order is provided by the orientational distribution function (ODF). Recently, different techniques, Maxwell-displacement current (MDC) [1] and optical second-harmonic generation (SHG) [2], have been usefully suggested to observe the dipole mechanism in the organic monolayers with C_∞ symmetry. One important feature of these techniques as a tool to study the relaxation process in the LC monolayers at the air-water interface is an ability to measure the OPs during compression of the *cyanobiphenyls* films [3]. Having obtained the set of non-normalized OPs $S_1(A)$ and $S_3(A)$ of the flexible amphiphilic molecules at the air-water interface, as a function of the molecular area *A*, derived from the MDC and SHG measurements, one can calculate the normalized equilibrium ODF $f(\cos\theta_i)$ of the molecules on the water surface and the normalized OPs $\overline{P_l}$ [4].

In this paper we attempt to answer the question, based upon the Ericksen-Leslie (EL) [5,6] theory, of how the electric, elastic, and hydrodynamic forces affect the orientational relaxation process of the director in the LC film on the water surface during the lateral compression of the film. Taking into account that the relaxation process is governed, among others, by the hydrodynamic torque, where the rotational viscosity coefficients (RVCs) γ_i $(i=1,2)$ play a crucial role, one needs detailed information on reorientation of the molecules in these LC films. The molecular reorientation can be described by the rotational diffusion model [7], which assumes a stochastic Brownian process for molecular reorientations in which each molecule moves in time as a sequence

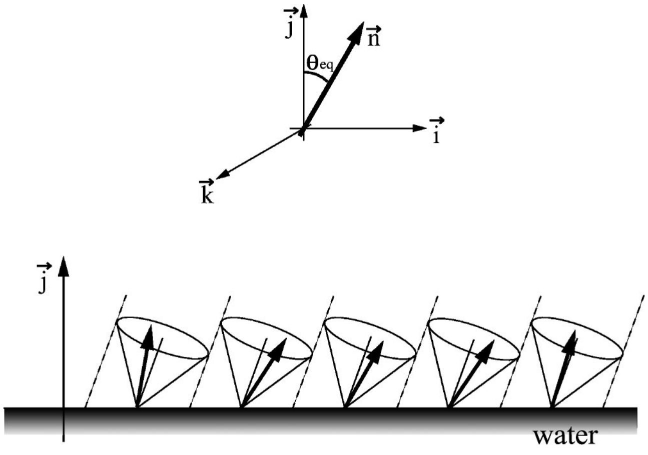

FIG. 1. Coordinate system specifying the orientation of the director and the direction of the electric field and the total polarization vector. The angle between the director **n** and the direction **j** (directed perpendicular to the air-water interface) is $\theta(y,\tau)$.

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of small angular steps caused by collisions with its surrounding molecules and under the influence of a potential of mean torque set up by these molecules. Each molecule is characterized by a rotational diffusion tensor whose principal elements ($D_{xx}=D_{yy}=D_{\perp}, D_{zz}=D_{\parallel}$) are determined in a frame fixed on the molecule. A common approach for determination of viscosity coefficients, in the framework of the statistical-mechanical theory [8], is based on the rotational diffusion model [7]. In such a treatment, the system is determined by the time-dependent single-particle ODF governed by a Fokker-Plank-type kinetic equation and the RVCs are expressed to be inversely proportional to the $D_{\perp}$ in the LC film.

Recently, the dielectric relaxation time τ_r in organic monolayers on a material surface has been determined to be proportional to the orientational fluctuation of monolayers and inversely proportional to the self-diffusion coefficient $D_{\perp}$ in the LC film [9]. For a small deviation of the relaxation time τ_r from its bulk value $t_0=\tau_{00}^1(T)$, where t_0 is the relaxation time for a hindered rotation of molecules around their molecular short axes in the bulk of the sample, both the RVC γ_1 and the orientational relaxation time τ_r, in the monolayer of 4-*n*-pentyl-4′-cyanobiphenyl (5CB) molecules on the water surface, can be calculated as a function of a small correction of the value t_0. This correction can be caused by interactions between molecules of LC film and the material surface. In turn, the relaxation time $\tau_{00}^1(T)$ can be obtained using molecular-dynamics simulation [10] or NMR technique [11].

The outline of this paper is as follows: a dynamic equation describing the reorientation of a liquid crystalline film on the water surface, in absence of flow, is given in Sec. II. Numerical results for number of relaxation regimes are given in Sec. III. Conclusions are summarized in Sec. IV.

II. FORMULATION OF THE BALANCE OF MOMENTUM EQUATION FOR MONOLAYERS AT THE AIR-WATER INTERFACE

The dynamic equation describing the reorientation of a liquid crystalline film on the water surface can be derived from the balance of elastic, viscous, and electric torques as [5,6] $\mathbf{T}_{vis}+\mathbf{T}_{elast}+\mathbf{T}_{el}+\mathbf{T}_{pol}=0$. In the case of planar geometry $\mathbf{n}=\sin\theta\,\mathbf{i}+\cos\theta\,\mathbf{j}$ and absence of flow, the viscous torque takes the form $\mathbf{T}_{vis}=-\gamma_1\mathbf{n}\times\partial\mathbf{n}/\partial t=\gamma_1\theta_t(y)\mathbf{k}$. Here $\theta(y)$ denotes the polar angle, i.e., the angle between the direction of the unit vector $\mathbf{j}$ (directed perpendicular to the air-water interface) and the director $\mathbf{n}$, and $\theta_t(y)=\partial\theta(y)/\partial t$. The unit vector $\mathbf{i}$ is directed to be parallel to the air-water interface, y is the distance away from the air-water interface in the $\mathbf{j}$ direction, and $\mathbf{k}=\mathbf{i}\times\mathbf{j}$ (see Fig. 1). The torque due to electric field $\mathbf{E}$, for instance, originating from the water surface charge density σ, is given by $\mathbf{T}_{el}=(\epsilon_a/\epsilon_0)\mathbf{n}\times\mathbf{E}(\mathbf{E}\cdot\mathbf{n})=(E_0^2/2)\epsilon_a\epsilon_0\sin 2\theta(y,t)\mathbf{k}$, where $\mathbf{E}=E_0\mathbf{j}=(\sigma/\epsilon_0\bar{\epsilon})\mathbf{j}$ is the surface electric field of the charged water surface, ϵ_0 is the dielectric permittivity of free space, $\bar{\epsilon}=(\epsilon_{\parallel}+2\epsilon_{\perp})/3$ is the average dielectric permittivity, and $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are the dielectric constants parallel and perpendicular to the director $\mathbf{n}$, respectively. The torque due to spontaneous polarization is $\mathbf{T}_{pol}=\mathbf{P}\times\mathbf{E}=PE_0\mathbf{k}$, where $\mathbf{P}$ is the total polarization vector composed of an in-plane spontaneous $\mathbf{P}_s$ and the surface polarization $\mathbf{P}_{surf}$ components. The torque due to elastic forces is [12] $\mathbf{T}_{elast}=\mathbf{n}\times\mathbf{h}$, where the molecular field $\mathbf{h}$ has to be evaluated in term of the Frank elastic coefficients K_i ($i=1,2,3$) for splay, twist, and bend deformations, respectively. It should be noted that accounting for the elastic torque in the torques balance can be justified only in the case of the multilayers Langmuir-Blodgett film.

TABLE I. The values of the splay (K_1) and bend (K_3) Frank elastic coefficients for 5CB, 8CB, and 8OCB nematic liquid crystals as measured in Ref. [13]. The values of the nematic-isotropic (NI) phase transition temperatures are $T_{NI}=306.5$ K, $T_{NI}=313$ K, and 352.2 K, for 5CB, 8CB, and 8OCB molecules, respectively.

T/T_{NI}	0.984	0.992	0.997
K_1 (5CB) [pN]	10.0	7.2	5.5
K_3 (5CB) [pN]	11.7	7.8	5.6
K_1 (8CB) [pN]	12.5	10.0	6.0
K_3 (8CB) [pN]	13.5	10.2	6.15
K_1 (8OCB) [pN]	4.75	3.3	2.5
K_3 8OCB) [pN]	4.8	3.5	2.7

In the case of two-dimensional system, where the molecules of Langmuir-Blodgett film align tilt relative to the unit vector $\mathbf{j}$, thereby defining an array of a unit vectors $\mathbf{u}_i$ in the plane $x-y$ of the film, Eq. (1) can be written as

$$\gamma_1\partial_t\theta(y,t)+\frac{E_0^2}{2}\epsilon_a\epsilon_0\sin 2\theta(y,t)+PE_0\sin\theta(y,t)-\left(\frac{K_3-K_1}{2}\right)\sin 2\theta(y,t)[\partial\theta(y,t)/\partial y]^2-[K_1\cos^2\theta(y,t)+K_3\sin^2\theta(y,t)]\partial^2\theta(y,t)/\partial y^2=0, \tag{1}$$

where K_1 and K_3 are the splay and bend elastic constants of the LC film. According to the experimental data for elastic coefficients K_1 and K_3, determined using the Freedericksz transition method [13], the values of the splay and bend coefficients, at least for *cyanobiphenyls*, at temperatures far from the second-order nematic-smectic-*A* phase transition in the nematic phase, are approximately equal and collected in Table I. It allows us to rewrite the last equation in a dimensionless form as

$$\partial_\tau\theta(\overline{y},\tau)=-\sin\theta(\overline{y},\tau)-\epsilon\sin 2\theta(\overline{y},\tau)+\delta\partial^2\theta(\overline{y},\tau)/\partial\overline{y}^2, \tag{2}$$

where $\partial_\tau\theta(\overline{y},\tau)=\partial\theta(\overline{y},\tau)/\partial\tau$, $\tau=tPE_0/\gamma_1$ is the dimensionless time, $\overline{y}=y/d$ is the dimensionless distance away from the water surface in the LC film, $\epsilon=\epsilon_a\epsilon_0E_0/(2P)$ and $\delta=K_3/(PE_0d^2)$ are the parameters of the system, which are considered as positive constants, in the following and d is the size of the LC monolayer, i.e., the length of the molecule.

A. Case of $\delta \ll 1$ $(\epsilon > 0)$

In this case the elastic torque can be safely disregarded and the relaxation of the director **n** to its equilibrium orientation $\mathbf{n}_{eq}$, in the LC film at the air-water interface, is governed by the electric forces, and one can determine a solution of Eq. (1) in the form

$$-\int \frac{d\theta}{\sin\theta+\epsilon\sin 2\theta}=\tau+\tau_0, \tag{3}$$

where τ_0 can be chosen from the value $\theta(\tau\to\infty)=\theta_{eq}$, where θ_{eq} is the equilibrium value of the angle $\theta(\tau)$ at a particular temperature and molecular area A, which determine the equilibrium orientation of the director in the LC film.

In the case $\epsilon < 1/2$, i.e., $\epsilon_0\epsilon_a E_0 < P$, which implies that the torque on the director due to polarization forces prevails over torque due to electric forces, Eq. (3) gives the solution [14]

$$-\tau-\tau_0=\ln\tan\frac{\theta}{2}-\frac{4\epsilon}{(1-4\epsilon^2)^{1/2}}\tan^{-1}\left[\frac{\tan\dfrac{\theta}{2}+2\epsilon}{(1-4\epsilon^2)^{1/2}}\right], \tag{4}$$

whereas in the case $\epsilon > 1/2$, i.e., $\epsilon_0\epsilon_a E_0 > P$, which implies that the torque on the director due to electric forces prevails over torque due to polarization forces, Eq. (3) gives the solution [14]

$$-\tau-\tau_0=\ln\tan\frac{\theta}{2}-\frac{2\epsilon}{(4\epsilon^2-1)^{1/2}}\times\ln\left[\frac{\tan\dfrac{\theta}{2}+2\epsilon-(4\epsilon^2-1)^{1/2}}{\tan\dfrac{\theta}{2}+2\epsilon+(4\epsilon^2-1)^{1/2}}\right]. \tag{5}$$

It should be pointed out that in the case $\epsilon = 1/2$, i.e., $\epsilon_0\epsilon_a E_0 = P$, which implies that the torques on the director due to both electric and polarization forces are equal, the relaxation of the initially disturbed director **n** to its equilibrium orientation $\mathbf{n}_{eq}$ can be determined as

$$-\tau-\tau_0=\frac{1}{2}\left[\frac{1}{1+\cos\theta}+\ln\tan\frac{\theta}{2}\right]. \tag{6}$$

In the case $\epsilon \gg 1$, i.e., $\epsilon_0\epsilon_a E_0 \gg P$, which implies that the elastic torque and torque due to the spontaneous polarization forces (in the form $\mathbf{T}_{pol}$) can be safely disregarded, and the relaxation of the director **n** to its equilibrium position $\mathbf{n}_{eq}$ in the LC film is governed by only the electric forces, one may determine a solution of Eq. (2) in the form

$$\theta(\tau)=\tan^{-1}[\exp(-2\tau)]+\theta_{eq}. \tag{7}$$

B. Case of $\delta \ll 1$ and $\epsilon \ll 1$

In this case both elastic and electric torques (later in the form of $\mathbf{T}_{el}$) can be safely disregarded and the relaxation of the director **n** to its equilibrium orientation $\mathbf{n}_{eq}$ in the LC film, at the air-water interface, is governed by only the polarization forces, and one can also determine a solution of Eq. (2) in the form

$$\theta(\tau)=2\ \tan^{-1}[\exp(-\tau)]+\theta_{eq}, \tag{8}$$

where θ_{eq} is the equilibrium value of the angle $\theta(\tau)$ at a particular temperature and molecular area A, which determine the equilibrium orientation of the director in the LC film.

C. Case of $\delta \gg 1$

In this case the electric torques, both due to the polarization forces (in the form of $\mathbf{T}_{pol}$) and due to electric forces (in the form of $\mathbf{T}_{el}$), can be safely disregarded and the relaxation of the director **n** to their equilibrium orientation $\mathbf{n}_{eq}$ in the LC film is governed by only the elastic forces, and the diffusion equation (2) with $\delta > 0$ has a solution with a single exponential decaying time:

$$\theta(\tau)=\exp(-\kappa\tau)c_1(\sin c_2\overline{y}+\cos c_2\overline{y}), \tag{9}$$

with a positive coefficient κ $(\kappa=\delta c_2^2>0)$. Here c_1 and c_2 are only temperature-dependent coefficients. This solution shows that the influence of the elastic torque in the relaxation regime, in the case of only multilayers LC film with approximately equal splay and bend elastic deformations, leads to dissipative processes in the system, and the value of the angle $\theta(\overline{y},\tau)$ is exponentially decaying with time, and the director, therefore, aligns under elastic torques perpendicular to the interface $[\lim_{\tau\to\infty}\theta(\overline{y},\tau)=0]$. It is important to stress again that accounting for the elastic forces can be justified only in the case of the multilayer Langmuir-Blodgett films.

It should be pointed out that in the case of $\delta \gg 1$, Eq. (1) can be written as

$$\frac{\partial\theta}{\partial\tau}-\delta\left\{\frac{\partial^2\theta}{\partial\overline{y}^2}+\delta_1\left[\sin\theta\cos\theta\left(\frac{\partial\theta}{\partial\overline{y}}\right)^2-\cos^2\theta\frac{\partial^2\theta}{\partial\overline{y}^2}\right]\right\}=0, \tag{10}$$

where $\delta=K_3/PEd^2$ is the large and $\delta_1=(K_3-K_1)/K_3$ is the small parameter of the system. In the temperature range where the values of the splay and bend deformations are approximately equal, $\delta_1 \ll 1$, and one may determine a power series solution of Eq. (10) in the form $\theta(\tau,\overline{y})=\theta_1(\tau,\overline{y})+\delta_1\theta_2(\tau,\overline{y})+\cdots$. Substituting the last expression for the $\theta(\tau,\overline{y})$ into Eq. (10) we obtain

$$\frac{\partial\theta_1}{\partial\tau}-\delta\frac{\partial^2\theta_1}{\partial\overline{y}^2}=0, \tag{11}$$

$$\frac{\partial\theta_2}{\partial\tau} - \delta\frac{\partial^2\theta_2}{\partial\overline{y}^2} - \delta\left[\frac{1}{2}\sin 2\theta_1\left(\frac{\partial\theta_1}{\partial\overline{y}}\right)^2 - \cos^2\theta_1\frac{\partial^2\theta_1}{\partial\overline{y}^2}\right] = 0. \tag{12}$$

The diffusion equation (11) with $\delta > 0$ has a solution with a single exponential decaying time [see Eq. (9)], which shows that the influence of the elastic torque leads to dissipative processes in the multilayers system, and the value of the angle θ_{eq} is $\lim_{\tau\to\infty}\theta(\overline{y},\tau)=0$. Physically, this means that the director, in the case of the multilayers system, aligns under the action of only elastic torques, perpendicular to the interface. The analysis of the experimental data for the elastic coefficients K_1 and K_3, determined in Ref. [13] for the homologous series (nCB,$n=5$–8) in the nematic phase, shows that the highest value of δ_1 is ~ 0.17. This means that one may determine a power series solution of Eq. (10), for the temperature range in which *cyanobiphenyls* exhibit a nematic phase, and that the influence of the elastic forces on the relaxation process in the LC films during the lateral compression leads to dissipative processes in the system.

D. Case of $\delta\sim 1$ and $\epsilon\sim 1$

A reorientation of the director in the multilayer LC film on the water surface, when the relaxation regime is governed by the viscous, elastic, and electric forces, can be obtained by solving the full nonlinear partial differential equation (2) with an appropriate boundary conditions [for instance, $\theta(\overline{y},\tau)_{\overline{y}=0} = \theta(\overline{y},\tau)_{\overline{y}=L/d} = 0$ (homeotropic anchoring) and the initial $\theta(\overline{y},0)=\pi/2$ condition]. Here L is the size of the multilayer film. The last condition means that the initial orientation of the director is disturbed parallel to the interface, and then allowed to relax to its equilibrium value θ_{eq}.

III. ORIENTATIONAL RELAXATION IN LC FILMS ON THE WATER SURFACE; NUMERICAL RESULTS

In the case of the monolayer 5CB film, when the elastic torque can be safely disregarded (case I), the polarization contribution to the toque balance is composed of only the surface polarization $\mathbf{P}_s = n_s\Delta(A)\mathbf{j}$ (in our case directed away from the water surface) contribution, where $n_s = 1/Ad$ is the film charge density, d is the size of the LC monolayer film, A is the molecular area, and $\Delta(A)$ is the magnitude of the molecular dipole moment corresponding to the 5CB molecule at the air-water interface. In the wide region of the molecular area, the MDC and SHG signals allow us to determine the dipole moment $\Delta(A)$ and the set of non-normalized OPs $S_1(A)$ and $S_3(A)$ of the flexible amphiphilic 5CB molecules in the monolayer on the water surface (see Fig. 2), during compression of the *cyanobiphenyl* film. Having obtained the set of non-normalized OPs, one can calculate the normalized equilibrium ODF $f(\cos\theta_i)$ of the molecules on the water surface as

$$f(\cos\theta_i) = \frac{1}{4\pi}\sum_{l=0}^{\infty}\frac{2l+1}{2}\overline{P}_l P_l(\cos\theta_i), \tag{13}$$

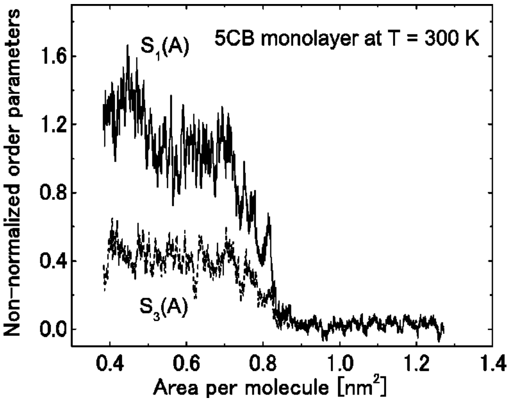

FIG. 2. Measured non-normalized OPs $S_1(A)$ and $S_3(A)$ vs molecular area A of 5CB monolayer at the air-water interface.

where θ_i is the polar angle of the unit vector $\mathbf{u}_i$ along the molecular symmetry axis and $P_l(\cos\theta_i)$ denote Legendre polynomials of any rank. The normalized OPs

$$\overline{P}_i = \frac{\int_{-1}^{+1} p_i(x) f(x)\,dx}{\int_{-1}^{+1} f(x)\,dx}, \tag{14}$$

where the function $f(x)$ as in Eq. (13), but with the non-normalized OPs, $i=1,3$,

$$p_i(x) = \begin{cases} x, & i=1 \\ \frac{1}{2}(5x^3-3x), & i=3, \end{cases}$$

and shown in Fig. 3(b). On the other hand, our two-

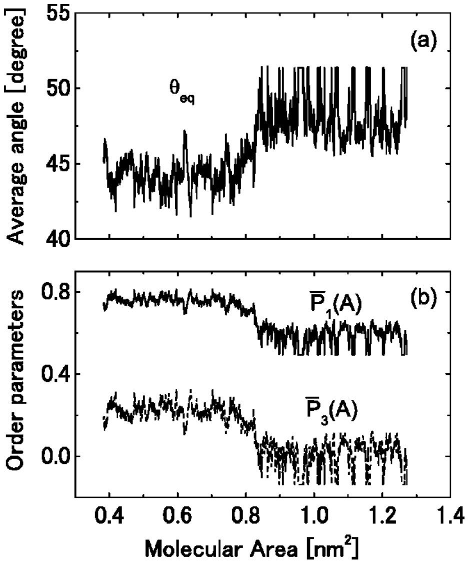

FIG. 3. (a) Plot of the average $\theta_{eq}(A)$ during compression of the film. (b) Normalized OPs $\overline{P}_1(A)$ (upper curve) and $\overline{P}_3(A)$ (lower curve) vs molecular area A of 5CB monolayer at the air-water interface.

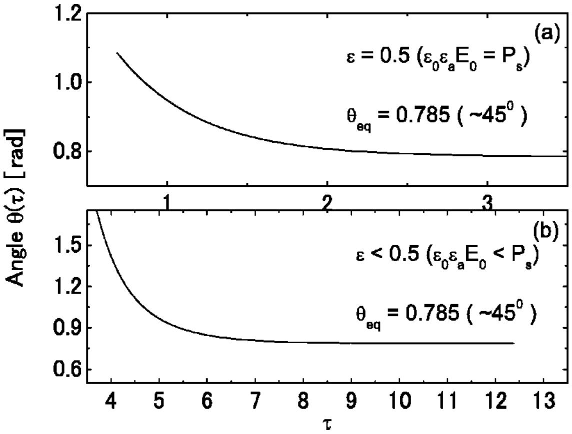

FIG. 4. Plot of relaxation of the angle $\theta(\tau)$ ($\tau = tP_sE_0/\gamma_1$ is a dimensionless time) to its equilibrium value $\theta_{eq} \sim 0.785$ ($\theta_{eq} \sim 45°$, corresponding to molecular area in ~ 0.463 nm^2) during compression of the film, at $\epsilon = 1/2$, i.e., $\epsilon_0\epsilon_aE_0 = P_s$, and calculated using Eq. (6). (b) Same as (a), but the angle $\theta(\tau)$ is calculated using Eq. (4), with the value of $\epsilon < 1/2$, i.e., $\epsilon_0\epsilon_aE_0 < P_s$.

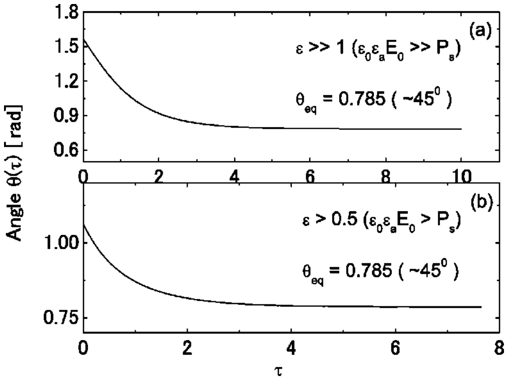

FIG. 5. (a) Same as Fig. 4(a), but the angle $\theta(\tau)$ is calculated using Eq. (7), with the value of $\epsilon \gg 1$, i.e., $\epsilon_0\epsilon_aE_0 \gg P_s$. (b) Same as (a), but the angle $\theta(\tau)$ is calculated using Eq. (5), with the value of $\epsilon > 1/2$, i.e., $\epsilon_0\epsilon_aE_0 > P_s$.

dimensional (2D) LC system is composed of axially symmetric molecules, the hydrophilic heads of which are uniformly distributed on the water surface and the hydrophobic tails are directed away from the water surface. It allows us to consider the model of axially symmetric molecular rods, the hydrophilic heads of which are uniformly distributed on the water surface and the hydrophobic tails are directed away from the water surface and tilted at the average equilibrium angle $\theta_{eq}(A)$ with respect to the unit vector $\mathbf{j}$ directed perpendicular to the interface, and the equilibrium orientation of the director $\mathbf{n}_{eq}$ in the monolayer film can be determined as $\mathbf{n}_{eq} = \mathbf{i}\sin\theta_{eq} + \mathbf{j}\cos\theta_{eq}$. Now, one may calculate θ_{eq} as $\int_0^{\pi}\theta_i f(\cos\theta_i)\sin\theta_i d\theta_i$ [see Fig. 3(a)]. We also found that with decreasing of the molecular area that dipole moment increases from zero, at the molecular area $0.6\ \mathrm{nm}^2 \leqslant A \leqslant 0.9\ \mathrm{nm}^2$, up to 0.5 D per molecule, at the molecular area $0.2\ \mathrm{nm}^2 \leqslant A \leqslant 0.6\ \mathrm{nm}^2$. Physically, this means that the initial dipole moment of the 5CB molecule ($\Delta \sim 5$ D) is the fully compensated, due to interactions with the water molecules, at the molecular area $0.6\ \mathrm{nm}^2 \leqslant A \leqslant 0.9\ \mathrm{nm}^2$, and that compensation decreases up to 0.5 D per 5CB molecule, with decreasing of the molecular area. The values of the charge density, for example, in $\sigma = 10^{-3}$ C/m^2 at $T = 300$ K, correspond to the water surface charge density n_w in $\sim 1.6 \times 10^{16}\ \mathrm{m}^{-2}$, which agrees with experimental values $\sim 10^{15} - 10^{16}\ \mathrm{m}^{-2}$ [15]. Here $\sigma = qn_w$, where $q = 1.602 \times 10^{-19}$ C is the proton charge. In the following, we use the dipole moment $\Delta(A) \leqslant 0.5$ D per 5CB molecule on the water surface, restricted by the molecular area $0.2\ \mathrm{nm}^2 \leqslant A \leqslant 0.6\ \mathrm{nm}^2$ and the value of $\overline{\epsilon}$ which has been determined using the temperature-dependent coefficients $\epsilon_\parallel$ and $\epsilon_\perp$ for 5CB obtained in Ref. [16]. In the case of 5CB monolayer film on the water surface, with the charge density in $\sigma = 10^{-3}$ C/m^2, one obtains $\epsilon = \epsilon_a\epsilon_0E_0/(2P_s) \sim 1.08|A|$. So, finally, one has a different relaxation process, which can be determined by Eqs. (4), (5), and (6), in three different molecular areas; $0.463\ \mathrm{nm}^2 < A \leqslant 0.6\ \mathrm{nm}^2$ ($\epsilon < 1/2$ [see Fig. 4(b)]), $A = 0.463\ \mathrm{nm}^2$ ($\epsilon = 1/2$ [see Fig. 4(a)]), and $0.2\ \mathrm{nm}^2 \leqslant A < 0.463\ \mathrm{nm}^2$ ($\epsilon > 1/2$ [see Fig. 5(b)]), respectively. The case $\epsilon \gg 1$, i.e., $\epsilon_0\epsilon_aE_0 \gg P$, which implies that the torque on the director in the monolayer LC film on the water surface, due to electric forces (for instance, due to external electric field), prevails over the polarization forces, and the relaxation of the initially disturbed director $\mathbf{n}$ to its equilibrium orientation is shown in Fig. 5(a). We have studied the relaxation behavior of $\theta(\tau)$ ($\tau = tPE_0/\gamma_1$) and found that the dimensionless relaxation time decreases with increasing ϵ, i.e., with increasing of the electric forces from 12, for $\epsilon < 1/2$, to 6, for both $\epsilon > 1/2$ and $\epsilon \gg 1$. The time of the orientational relaxation of the director to the equilibrium can be written as

$$t_r = \frac{\gamma_1 A d \epsilon_0 \overline{\epsilon}}{\sigma\Delta(A)}\tau. \tag{15}$$

While values of the static constants in Eq. (15) are usually fairly easily found, the determination of the motional constant for rotational diffusion is still a formidable task. Recently, the dielectric relaxation time τ_r, for an organic film on a material surface, in the framework of the statistical-mechanical theory [9], based on the rotational diffusion model [7], has been calculated. As a result, τ_r can be found to be proportional to the orientational fluctuation of monolayers $f = \langle\cos^2\theta_i\rangle - \langle\cos\theta_i\rangle^2$, and inversely proportional to the self-diffusion coefficient $D_\perp$ in the LC film. For the small deviation of the relaxation time τ_r from its bulk value t_0, one can write $\tau_r = t_0(1+\nu)$, where $t_0 = \tau_{00}^1(T)$ is the bulk dielectric relaxation time and depends only on the temperature, and $\nu = \Delta\tau/t_0$, where $\Delta\tau$ is the small correction of the value t_0, due to interaction between molecules of LC film and the material surface. So, in our case, the expression for the self-diffusion coefficient $D_\perp$ takes the form [9]

$$D_\perp = \frac{2f}{t_0}\frac{1}{1+\nu}, \tag{16}$$

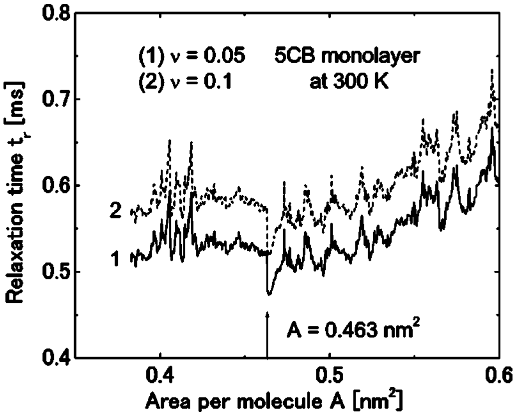

FIG. 6. Plot of the relaxation time t_r of the director to its equilibrium orientation during compression of 5CB monolayer at the air-water interface, calculated using Eq. (15), with the value of $\nu = 0.05$ (curve 1) and 0.1 (curve 2), respectively.

where $|\nu| \ll 1$. On the other hand, γ_1 is proportional to the $\rho k_B T/D_\perp$, and, as a result, can be written in the form

$$\gamma_1 \sim \frac{\rho k_B T}{2f}(1+\nu)t_0, \tag{17}$$

where $\rho = N/V$ is the number density of molecules, k_B is the Boltzmann constant, and T is the temperature. The number density ρ of 5CB ($T \sim 300$ K) has been fixed to the value 1.8×10^{27} m^{-3}, whereas the relaxation time t_0 is equal to 28 ns ($T=300$ K) [10]. In the wide region of the molecular area 0.2 nm$^2 \leqslant A \leqslant 0.6$ nm^2, which is characterized by increasing of $\Delta(A)$ up to $\sim$0.5 D per 5CB molecule, the orientational fluctuation of monolayer $f = \langle \cos^2\theta_i \rangle - \langle \cos\theta_i \rangle^2$ on the water surface can be calculated using the normalized equilibrium ODF $f(\cos\theta_i)$ [see Eq. (13)]. The orientational relaxation time t_r [see Eq. (15)] of the director to the equilibrium orientation, as a function of the molecular area A, at two different $\nu = 0.05, 0.1$, is shown in Fig. 6. In the case of 5CB monolayer film on the water surface, the electric torque puts the director into the equilibrium orientation with different relaxation times, which increase with increasing ν, up to 0.7 ms.

In the case of the multilayers of 5CB molecules on the water surface, at $T=300$ K, by accounting for only the surface polarization $\mathbf{P}_s$ contribution to the torque balance, one obtains that $K_3 \gg P_s E_0 d^2$ $(\delta = K_3 A \overline{\epsilon}\epsilon_0/(\Delta(A) d\sigma) \sim 346 \gg 1)$, and the relaxation of the director $\mathbf{n}$ to their equilibrium orientation $\mathbf{n}_{eq}$ in the LC film is governed by only the elastic forces, and the diffusion equation (2) with $\delta \gg 1$ has a solution with a single exponential decaying time τ [see Eq. (9)]. In both these cases, in the region of the molecular area 0.2 nm$^2 \leqslant A \leqslant 0.6$ nm^2, which is characterized by increasing of $\Delta(A)$ up to $\sim$0.5 D per 5CB molecule, the time of the orientational relaxation t_r of the director to the equilibrium can be also calculated using Eq. (15).

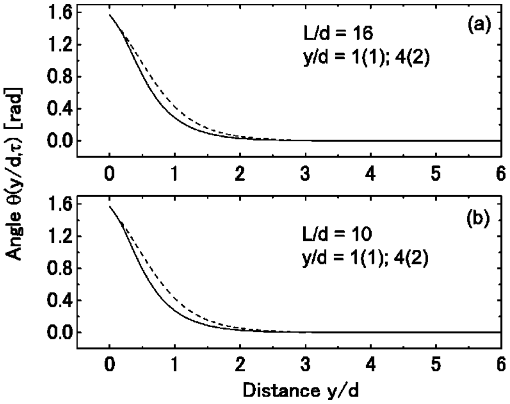

FIG. 7. (a) Plot of relaxation of the angle $\theta(\overline{y},\tau)$ ($\tau = tP_sE_0/\gamma_1$ is a dimensionless time and $\overline{y} = y/d$ is a dimensionless distance away from the water surface) during the lateral compression of the multilayers 5CB film on the water surface, calculated using Eq. (2), for the case of the homeotropic alignment on both the boundaries, $\overline{y}=0$ (water-LC interface) and $\overline{y} = L/d = 16$ (LC-air interface). (b) Same as (a), but the size of the LC film is $\overline{y} = L/d = 10$.

In the case of the multilayers film, c omposed of 5CB molecules on the water surface, when a high spontaneous polarization $\mathbf{P}_s$ (estimated to be of the order of 10^{-2} C/m^2) prevails over the surface polarization $\mathbf{P}_{surf}$ (estimated to be of the order of 10^{-3} C/m^2), one obtains that $\delta \sim \epsilon \sim 1$, and the relaxation of the director $\mathbf{n}$ to its equilibrium orientation $\mathbf{n}_{eq}$ can be described by the nonlinear partial differential equation (2), with an appropriate boundary condition. Calculations of the relaxation process, with the boundary $\theta(\overline{y},\tau)_{\overline{y}=0} = \theta(\overline{y},\tau)_{\overline{y}=L/d} = 0$ (at two different sizes $L/d = 10$ and 16) and the initial $\theta(\overline{y},0) = \pi/2$ conditions, have been investigated by a standard numerical relaxation method [17]. Calculations show (Figs. 7 and 8) that the viscous, elastic, and electric torques exerted per unit volume are vanished when the director aligns at an angle $\theta(\overline{y},\tau) = 0$, with respect to the interface normal. The torques exerted per unit volume

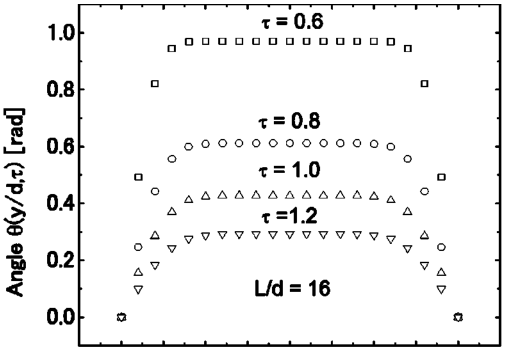

FIG. 8. The distance dependence of the angle $\theta(\overline{y},\tau)$ during the lateral compression of the multilayers 5CB film on the water surface, calculated using Eq. (2), for the case of the homeotropic alignment on both the boundaries, $\overline{y}=0$ (water-LC interface) and $\overline{y} = L/d = 16$ (LC-air interface), at four values of the dimensionless time τ: 0.6 (squares), 0.8 (circles), 1.0 (upper triangles), and 1.2 (down triangles).

put the director into an orientation normal to the interface,practically, with the same relaxation time $\tau = \sigma\Delta(A)/\gamma_1 A d \epsilon_0 \overline{\epsilon} t_r \sim 3.0$, for sizes $L/d = 10$ and 16, respectively. Figure 8 shows the dependence of the angle $\theta(\overline{y},\tau)$, calculated with Eq. (2), on the distance y/d away from the boundary $(\overline{y}=0)$, for the case of the homeotropic alignment ($\theta(\overline{y},\tau)_{\overline{y}=0} = \theta(\overline{y},\tau)_{\overline{y}=L} = 0, L/d = 16$), and for the following values for dimensionless time $\tau = 0.6$, 0.8, 1.0, and 1.2. The values of $\theta(\overline{y},\tau)$ vary rapidly between the boundary and center $\theta(\overline{y},\tau)$ values, within the first four molecular layers from both the water surface and LC-air interface. We are aware of the fact that the macroscopic description of the relaxation processes masks the role of the mesogenic interactions among the LC molecules in the film, as well as among the LC and the water molecules. However, at the phenomenological description this limitation is counterbalanced by the simplicity of the present approach, which can be used to calculate many material parameters of the ultrathin LC film on the water surface.

It should also be noted that the relaxation process of the director $\mathbf{n}$ to its equilibrium orientation $\mathbf{n}_{eq}$, in the mono- (multi) layer(s) of 5CB molecules on the water surface, has been investigated at fixed temperature ~ 300 K. Since the number of material coefficients such as the OPs $\overline{P_l}$, the self-diffusion coefficient $D_\perp$, the RVC γ_1, and the relaxation time τ^1_{00} have a strong temperature dependence, a role of the temperature, during the lateral compression of the LC film, should be examined separately. Fortunately, both SHG and MDC techniques allow us to carry out such measurements in the temperature range corresponding to the nematic phase of 5CB.

IV. CONCLUSION

In this paper, we investigate the orientational relaxation phenomena in the organic LC film on the water surface, during the lateral compression. The relaxation of the director $\mathbf{n}$ to its equilibrium orientation $\mathbf{n}_{eq}$, during compression of 4-*n*-pentyl-4′-cyanobiphenyl (5CB) mono- (multi)layer(s) film at the air-water interface is calculated using the Ericksen-Leslie theory. The average angle θ_{eq} corresponding to $\mathbf{n}_{eq}$ is evaluated based on the Maxwell displacement current and optical second-harmonic generation techniques. In order to elucidate the role of charged water surface on the relaxation process, we take into account only the long-range component (due to the surface electric field) of the surface potential. A balance between the electric and hydrodynamic torques exerted on the director is reflected in the growth of the time relaxation upon decreasing the strength of the electric field. The influence of the elastic forces on the dynamics of the director, during the lateral compression of the LC film, is reflected in the relaxation of the director to its equilibrium position to be normal to the interface. It is important to stress that the influence of the elastic forces, in the multilayers LC film, leads to dissipative process in that system, and the director, therefore, aligns under elastic torques perpendicular to the interface. While the experimentally obtained values of the order parameters for flexible amphiphilic *cyanobiphenyl* systems on the water surface, can be provided by both the MDC and SHG methods, the determination of motional constants is still a formidable task [1]. It should be pointed out that the state of the monolayer composed of the flexible polar molecules on the water surface is reflected in the set of the non-normalized OPs, obtained from MDC and SHG measurements. On the other hand, our 2D LC system is composed of axially symmetric molecules, the hydrophilic heads of which are uniformly distributed on the water surface and the hydrophobic tails are directed at the average equilibrium angle $\theta_{eq}(A)$ with respect to the normal to the interface. This implies that the volumes of $\theta_{eq}(A)$ can be obtained from MDC and SHG measurements in the monolayer film on the water as a function of the area *A*. Physically, this means that the dimensionless value of the relaxation time can be obtained using the phenomenological EL theory, whereas a simple 2D LC model of collective tilted rodlike polar molecules hinged by their end to a water surface allows us to determine the dimension value of the relaxation time in that system.

So, the relatively simple molecular model in combination with the experimental data obtained with high accuracy can provide a powerful tool for investigation of both the structural and relaxation properties of real mono- (multi)layer(s) systems.

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