

Effect of backflow on the orientational and dissipation processes in Langmuir films

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The numerical study of the system of hydrodynamic equations that include both director motion and fluid flow, for a number of dynamic regimes in the 4-*n*-pentyl-4'-cyanobiphenyl multilayer film on the water surface has been carried out. Calculations show that the relaxation time over which the torques exerted per unit of liquid crystals volume puts the director $\hat{\mathbf{n}}$ to be normal to the air-water interface, is one order of magnitude less in the case of accounting for the backflow effect than without accounting for that effect. The role of the charged water surface potential on the orientational relaxation process in the 5CB multilayer film on the water surface also has been investigated.

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I. INTRODUCTION

The flow behavior of monolayer (multilayers) liquid crystal (LC) films at the air-fluid interface is of fundamental and technological significance [1,2]. Many applications of ultrathin films require the fabrication of films with a high degree of orientational order and it has become apparent over years that the orientational order processing of Langmuir films at the air-water interface can influence the orientational relaxation phenomena in the LC films. In absence of an external flow, the relaxation of the director $\hat{\mathbf{n}}(\mathbf{r}, t)$ to their equilibrium orientation $\hat{\mathbf{n}}_{\text{eq}}(\mathbf{r})$ in the LC film on the water surface, for instance, during the lateral compression of the film, is governed by elastic, electric, and viscous torques exerted per unit of LC's volume. If the director is disturbed during compression, or by the laser beam pulse, and then allowed to relax, these torques vanish when the director aligns at the equilibrium angle $\theta_{\text{eq}}(\mathbf{r})$ with respect to the normal $\hat{\mathbf{k}}$ to the air-water interface. But any physical effect that reorients the director induces flow in the LC phase, which, in turn, is coupled to the director. This is the so-called backflow [3]. While having a subordinate role, backflow has been found to qualitatively change the orientational behavior of the director in electrically driven reorientation. To the lowest order, backflow can be considered in a theory by renormalizing the rotational viscosity coefficient γ_1 [4], but this approach is valid only if reorientation is small. To the high order, backflow can be accounted for by a numerical study of the full system of hydrodynamic equations that include both director reorientation and the velocity field [5]. So, one should expect that the backflow will also play a crucial role on the reorientation relaxation on Langmuir films. Measurements of flow-induced orientation at the molecular level have normally been performed on Langmuir films where the material ex-

posed by the flow has been fixed to a solid substrate [6]. However, such an approach does not readily lend itself to the examination of relaxation phenomena on Langmuir films on the water surface.

In an attempt to bring the theory and experiment closer and to gain insight into the importance of the backflow effect in the relaxation process in the LC film on the water surface, we have performed a numerical study of the system of hydrodynamic equations that include both director motion and fluid flow. To calculate it, one must include the equation for the velocity \mathbf{v} and consider the coupled director-velocity equations in the framework of the well-established Ericksen-Leslie theory [7,8]. So, our main aim is to clarify the influence of the backflow effect on the orientational relaxation in the LC film on the water surface.

The outline of this paper is as follows: a system of hydrodynamic equations describing both director motion and fluid flow of a liquid crystal film on the water surface is given in Sec. II. Numerical results for the number of relaxation regimes describing both the orientational relaxation of the director and velocity fields as well as the total stress tensor components are given in Sec. III and IV, respectively. Conclusions are summarized in Sec. V.

II. FORMULATION OF THE BALANCE OF THE MOMENTUM EQUATIONS FOR MULTILAYER LC FILM ON THE WATER SURFACE

We consider a system composed of asymmetric polar molecules, such as *cyanobiphenyls* which are confined to a flat layer on the water surface. When the LC film is in contact with the water surface, selective ion adsorption takes place. For instance, the positive ions are attracted by the water surface, whereas the negative ones are repelled. In this case, the surface electric field \mathbf{E} , originating from the surface charge density κ , will penetrate the film on the order of the Debye screening length λ_D [9], owing to ions present in the LC film (a weak electrolyte). The distance dependence of the surface electric field with bulk screening is given by [9]

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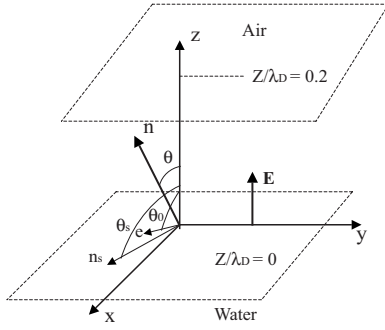


FIG. 1. The coordinate system specifying the orientation of the director $\hat{\mathbf{n}}$ and the angle $\theta(\tau, z)$ between the director and the normal $\hat{\mathbf{k}}$ to the air-water interface.

$$\mathbf{E}(z) = E \exp(-z/\lambda_D) \hat{\mathbf{k}}, \quad (1)$$

where $E = \kappa/(\epsilon_0 \bar{\epsilon})$ is the electric field at the charged plane, ϵ_0 is the dielectric permittivity of free space, $\bar{\epsilon} = (\epsilon_{\parallel} + 2\epsilon_{\perp})/3$ is the average dielectric permittivity, and ϵ_{\parallel} and ϵ_{\perp} are the dielectric constants parallel and perpendicular to the director $\hat{\mathbf{n}}$, respectively, $\hat{\mathbf{k}}$ is a unit vector directed away and perpendicular to the LC film-water interface, and z is the distance away from the water surface in the $\hat{\mathbf{k}}$ direction (Fig. 1). So, the coordinate system defined by our task assumed that the electric field is applied normal to the LC film-water interface, and the director $\hat{\mathbf{n}}$ is in the xz plane (or in the yz plane). Assuming that the electric field \mathbf{E} varies only in the z direction, we can suppose that the components of the director $\hat{\mathbf{n}} = \sin \theta(z, t) \hat{\mathbf{i}} + \cos \theta(z, t) \hat{\mathbf{k}}$, as well as the rest of the physical quantities, also depend only on the z coordinate. Here θ denotes the polar angle, i.e., the angle between the direction of the director $\hat{\mathbf{n}}$ and the normal $\hat{\mathbf{k}}$ to the air-water interface, $\hat{\mathbf{i}}$ is the unit vector directed parallel to the air-water interface, and $\hat{\mathbf{j}} = \hat{\mathbf{k}} \times \hat{\mathbf{i}}$ (Fig. 1). If the director is disturbed, for instance, during compression, or by the laser beam pulse, and then allowed to relax, in presence only the external electric field \mathbf{E} , originating from the surface charge density κ , the relaxation of the director $\hat{\mathbf{n}}$ to their equilibrium orientation $\hat{\mathbf{n}}_{\text{eq}}$, is governed by electric \mathbf{T}_{el} , elastic $\mathbf{T}_{\text{elast}}$, and viscous \mathbf{T}_{vis} torques exerted per unit of LC's volume. But any physical effect that reorients the director induces flow in the LC phase, which, in turn, is coupled to the director. By assuming an incompressible fluid, the hydrodynamic equations describing the reorientation of the LC film on the water surface can be derived from the balance of elastic, viscous, and electric torques $\mathbf{T}_{\text{elast}} + \mathbf{T}_{\text{vis}} + \mathbf{T}_{\text{el}} = 0$, and the Navier-Stokes equation for the velocity field \mathbf{v} . Taking into account that the velocity field $\mathbf{v}(z, t)$ in the LC film on the water surface is excited by only the director reorientation, together with the incompressibility condition $\nabla \cdot \mathbf{v} = 0$, which implies that only one nonzero component of the vector \mathbf{v} exist, viz. $\mathbf{v}(z, t) = v_x(z, t) \hat{\mathbf{k}}$, the Navier-Stokes equation reduces to

$$\rho_m \partial_t v_x(z, t) = \partial_z \sigma_{zx}, \quad (2)$$

where $\partial_t = \partial/\partial t$, ρ_m is the mass density, $u(z, t) = v_x(z, t)$, and σ_{zx} is the viscosity stress tensor component, which can be

expressed in terms of the six Leslie coefficients α_i ($i = 1, \dots, 6$) as

$$\sigma_{zx} = h(\theta) u_z - 2f(\theta) \theta_t, \quad (3)$$

where $u_z = \partial u(z, t)/\partial z$, $h(\theta) = \alpha_1 \sin^2 \theta \cos^2 \theta + f(\theta) + \frac{1}{2} \alpha_4 + g(\theta)$, and $f(\theta) = \frac{1}{2} (\alpha_3 \sin^2 \theta - \alpha_2 \cos^2 \theta)$ and $g(\theta) = \frac{1}{2} (\alpha_6 \sin^2 \theta + \alpha_5 \cos^2 \theta)$, respectively. In the case of planar geometry, the viscous and elastic torques takes the form $\mathbf{T}_{\text{vis}} + \mathbf{T}_{\text{elast}} = [\gamma_1 \theta_t - \frac{1}{2} (\gamma_1 - \gamma_2 \cos 2\theta) u_z - \frac{1}{2} \mathcal{G}_\theta(\theta) \theta_z^2 - \mathcal{G}(\theta) \theta_{zz}] \hat{\mathbf{j}}$, where $\mathcal{G}(\theta) = (K_1 \sin^2 \theta + K_3 \cos^2 \theta)$, $\theta_z = \partial \theta(z, t)/\partial z$, $\theta_{zz} = \partial^2 \theta(z, t)/\partial z^2$, γ_1 and γ_2 are the rotational viscosity coefficients, and K_1 and K_3 are the splay and bend elastic constants of the LC film, respectively. The torque due to electric field \mathbf{E} , originating from the water surface charge density κ , is given by $\mathbf{T}_{\text{el}} = \epsilon_0 \epsilon_a \hat{\mathbf{n}} \times \mathbf{E}(\hat{\mathbf{n}} \cdot \mathbf{E}) = E^2(z)/2\epsilon_0 \bar{\epsilon} \sin 2\theta(z, t) \hat{\mathbf{j}}$. The torque due to polarization is given by $\mathbf{T}_{\text{pol}} = \mathbf{P} \times \mathbf{E} = -P_x E(z) \hat{\mathbf{j}}$, where \mathbf{P} is the polarization vector, and P_x is the x component of this vector. The spontaneous polarization in the LC film, composed of asymmetric polar molecules arises in response to elastic deformation, and is known as the flexoelectric effect [10]. In the case of polar molecules (which is the case for all *cyanobiphenyls*), splay and bend deformations give rise to two independent flexoelectric coefficients (e_1, e_3), and their combinations to induced polarization can be written as $\mathbf{P} = e_1 \hat{\mathbf{n}} \cdot \nabla \hat{\mathbf{n}} - e_3 \hat{\mathbf{n}} \times \nabla \times \hat{\mathbf{n}} = P_x \hat{\mathbf{i}} + P_z \hat{\mathbf{k}} = \mathcal{F}(\theta) \theta_z \hat{\mathbf{i}} - \frac{1}{2} (e_1 + e_3) \sin(2\theta) \theta_z \hat{\mathbf{k}}$. So, the torque due to polarization \mathbf{P} takes the form $\mathbf{T}_{\text{pol}} = -(\kappa/\epsilon_0 \bar{\epsilon}) \exp(-z/\lambda_D) \mathcal{F}(\theta) \theta_z \hat{\mathbf{j}}$, where $\mathcal{F}(\theta) = (e_3 \cos^2 \theta - e_1 \sin^2 \theta)$. It should be pointed out that accounting for the elastic and spontaneous polarization torques in the torque balance can be justified only in the case of the multilayer Langmuir film. In the case of the quasi-two-dimensional system, where the molecules of the Langmuir film align and tilt relative to the normal $\hat{\mathbf{k}}$, and thereby define an array of unit vectors $\hat{\mathbf{a}}_i$ in the plane x - z of the film, the torque balance equation describing the reorientation of the liquid crystal film can be written as

$$\gamma_1 \theta_t = \mathcal{A}(\theta) u_z + \frac{1}{2} \mathcal{G}_\theta(\theta) \theta_z^2 + \mathcal{G}(\theta) \theta_{zz} + \mathcal{B}(\theta) \theta_z + C(z) \sin 2\theta, \quad (4)$$

where $\mathcal{A}(\theta) = \frac{1}{2} (\gamma_1 - \gamma_2 \cos 2\theta)$, $\mathcal{B}(\theta) = \mathcal{F}(\theta) (\kappa/\epsilon_0 \bar{\epsilon}) \times \exp(-z/\lambda_D)$, and $C(z) = \frac{1}{2} (\kappa^2 \epsilon_a / \epsilon_0 \bar{\epsilon}^2) \exp(-2z/\lambda_D)$, respectively.

To be able to observe the evolution of the polar angle $\theta(z, t)$ to their equilibrium orientation $\theta_{\text{eq}}(z)$ and the evolution of the velocity field $u(z, t)$, caused by the director $\hat{\mathbf{n}}$ reorientation to the equilibrium position, we consider the dimensionless analog of these equations (2) and (4) in the form

$$\theta_\tau = \bar{\mathcal{A}}(\theta) u_z + \delta_1 \left[\frac{1}{2} \bar{\mathcal{G}}_\theta(\theta) \theta_z^2 + \bar{\mathcal{G}}(\theta) \theta_{zz} \right] + \delta_2 \bar{\mathcal{B}}(\theta) \theta_z + \bar{C}(z) \sin 2\theta, \quad (5)$$

$$\delta_3 \partial_\tau \mu(z, \tau) = \partial_z \bar{\sigma}_{zx}, \quad (6)$$

where $\bar{\mathcal{A}}(\theta) = \mathcal{A}(\theta)/\gamma_1$, $\bar{\mathcal{G}}(\theta) = \mathcal{G}(\theta)/K_1$, $\bar{\mathcal{B}}(\theta) = \mathcal{F}(\theta)/e_1 \times \exp(-z)$, $\bar{C} = \frac{1}{2} \exp(-2z)$, $\bar{\sigma}_{zx} = \sigma_{zx}/\gamma_1$. Here τ

$=(\epsilon_a \epsilon_0 E^2 / \gamma_1)t$ is the dimensionless time, $\bar{z}=z/\lambda_D$ is the dimensionless distance away from the water surface in the LC film, $E=\kappa/\epsilon_0 \bar{\epsilon}$, $\delta_1=K_1/(\epsilon_0 \epsilon_a E^2 \lambda_D^2)$, $\delta_2=e_1/(\epsilon_0 \epsilon_a E^2 \lambda_D)$, $\delta_3=\rho \epsilon_a \kappa^2 \lambda_D^2/(\epsilon_0 \bar{\epsilon}^2 \gamma_1^2)$ are three parameters of the system, and $\lambda_D=\sqrt{\epsilon_0 \epsilon_k k_B T/2q^2 n_{\text{ions}}}$ is the Debye screening length [9]. Here q is the proton charge, k_B is the Boltzmann constant, $\epsilon=\epsilon_0(\epsilon_{\parallel} \cos^2 \theta_s + \epsilon_{\perp} \sin^2 \theta_s)$ (a case of the bulk screening), and n_{ions} is the bulk ions concentration. Note that the overbars in the space variable z , in the last two Eqs. (5) and (6), have been eliminated.

Consider now the LC film on the water surface when the director $\hat{\mathbf{n}}$ is weakly anchored to the water surface and the anchoring energy takes the form [3] $W=\frac{1}{2}A \sin^2(\theta_s - \theta_0)$, where A is the anchoring strength, θ_s and θ_0 are the polar angles corresponding to the director orientation on the water surface $\hat{\mathbf{n}}_s$ and easy axis $\hat{\mathbf{e}}$, respectively. The torque balance transmitted to the surface assumed that the director angle must satisfy the boundary conditions (see the Appendix)

$$\begin{aligned} [\partial\theta(z)/\partial z]_{z=0} &= \frac{A\lambda_D}{2K_3} \sin 2\Delta\theta, \\ \theta(z)_{z=0} &= 0, \end{aligned} \quad (7)$$

where $\Delta\theta=\theta_s - \theta_0$, whereas the initial orientation of the director is disturbed parallel to the interface, with $\theta(\tau=0, z)=\frac{\pi}{2}$, and then allowed to relax to its equilibrium value $\theta_{\text{eq}}(z)$. Taking into account the case of *cyanobiphenyls* on the water surface the more preferable director orientations are homeotropic or oblique [11], and the fact that the velocity field in the LC film is excited by only the director reorientation, the no-slip boundary condition on \mathbf{v} seems quite reasonable. So, velocity on the water surface must satisfy the boundary condition

$$\begin{aligned} [\partial u(z)/\partial z]_{z=0} &= 0, \\ u(z)_{z=0} \equiv v_x(z)_{z=0} &= 0. \end{aligned} \quad (8)$$

Now the 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, and with accounting for the backflow, can be obtained by solving the system of the nonlinear partial differential equations (5) and (6), with the appropriate boundary and initial $\theta(0, z)=\frac{\pi}{2}$ conditions, both for the polar angle $\theta(\tau, z)$ [Eq. (7)] and velocity $u(\tau, z)$ [Eq. (8)].

For the case of 4-*n*-pentyl-4'-cyanobiphenyl (5CB), at temperature $T=300$ K and density 10^3 kg/m³, the experimental data for elastic constants are $K_1=10.5$ pN and $K_3=13.8$ pN [12], whereas the experimental data for A , obtained using different experimental techniques, are varied between 10^{-4} and 10^{-6} J/m². In the following we use the calculated data for both flexoelectric coefficients $e_1=-11.6$ pC/m and $e_3=4.3$ pC/m [13], and the dielectric constants $\epsilon_{\parallel}=18$ and $\epsilon_{\perp}=8$ [14], as well as the measured $\gamma_1 \sim 0.072$ Pa s and $\gamma_2 \sim -0.079$ Pa s [15], at $T=300$ K. At temperature 300 K and density 10^3 kg/m³, the values of the six Leslie coefficients were found to be (in Pa s) [15] $\alpha_1 \sim -0.0066$, $\alpha_2 \sim -0.075$, $\alpha_3 \sim -0.0035$, $\alpha_4 \sim 0.072$,

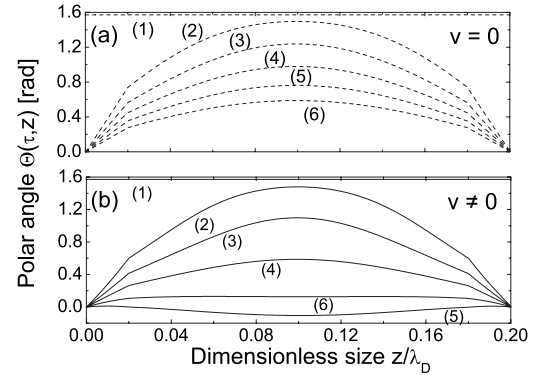


FIG. 2. The polar angle $\theta(\tau, z)$ [$\tau=(\kappa^2 \epsilon_a / \epsilon_0 \bar{\epsilon}^2 \gamma_1)t$ is a dimensionless time] vs the distance z/λ_D away from the water surface, for the case of the multilayer 5CB film with the homeotropic alignment [$(A\lambda_D/2K_3)\sin 2(\theta_s - \theta_0)=0.01$] on the water surface, during the first time term $\Delta\tau=0.01$, without accounting for the backflow effect (a), and with accounting for the backflow effect (b), respectively.

$\alpha_5 \sim 0.048$, and $\alpha_6 \sim -0.03$, respectively. The values of the charge density, estimated to be of the order of $\kappa=10^{-4}-10^{-3}$ (C/m²) at $T=300$ K, corresponds to the water surface charge density n_w in $\sim 10^{15}-10^{16}$ m⁻², which agrees with experimental values $\sim 10^{15}-10^{16}$ m⁻² [9]. Here $\kappa=qn_w$, where $q=1.602 \times 10^{-19}$ C is the proton charge. The magnitude of the Debye length depends solely on the properties of the LC and not on any property of the surface. In the case of homeotropic alignment of the 5CB film on the water surface ($\theta_s=0$), the Debye length $\lambda_D=45$ nm. In the case of homeotropic alignment, when the polar angles θ_s and θ_0 are both close to 0, $\Delta\theta$ is rather small, $\Delta\theta \sim 1^\circ - 3^\circ$, and therefore $\sin 2\Delta\theta \sim 2\Delta\theta$, so the combination of $A\lambda_D/K_3$ values varied between 0.04 and 4×10^{-4} . The set of parameters, which are involved in Eqs. (5) and (6), are equal to $\delta_1 \sim 0.53$, $\delta_2 \sim -0.55$, and $\delta_3 \sim 10^{-5}$. Using the fact that $\delta_3 \ll 1$, the Navier-Stokes equation (6) can be considerably simplified as the velocity follows adiabatically the motion of the director. Thus, the whole left-hand side of Eq. (6) can be neglected and Eq. (6) takes the form

$$\bar{\sigma}_{zx} = [h(\theta)u_z - 2f(\theta)\theta_\tau]/\gamma_1 = -\mathcal{C}(\tau), \quad (9)$$

where $\mathcal{C}(\tau)$ is the function that does not depend on z and will be fixed by the boundary conditions.

III. ORIENTATIONAL RELAXATION OF BOTH THE DIRECTOR AND VELOCITY FIELDS IN THE LC FILM: NUMERICAL RESULTS

The relaxation of the director $\hat{\mathbf{n}}$ to its equilibrium orientation $\hat{\mathbf{n}}_{\text{eq}}$, which is described by the polar angle $\theta(\tau, z)$ from the initial condition $\theta(0, z)=\frac{\pi}{2}$ to zero in the multilayer 5CB film on the water surface at different times ($\{\tau=0.0$ [curve (1)], ..., 0.01 [curve (6)], see Fig. 2, $\{\tau=0.012$ [curve (7)], ..., 0.02 [curve (11)], see Fig. 3, $\{\tau=0.024$ [curve (12)]; 0.028 [curve (13)]; 0.032 [curve (14)]; 0.036 [curve (15)]; 0.04 [curve (16)], see Fig. 4}) have been investigated by a standard numerical relaxation method [16], at

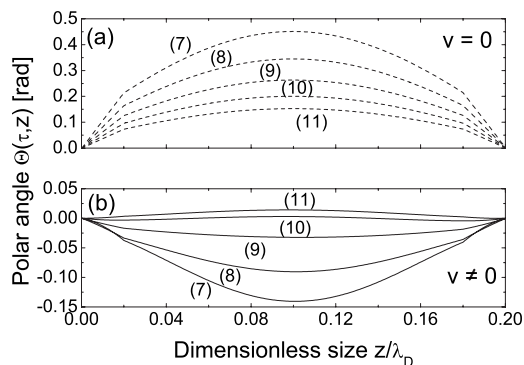


FIG. 3. Same as Fig. 2, but the evolution of the polar angle $\theta(\tau, z)$ is shown during the second time term $\Delta\tau=0.02$ [$\tau=0.012$ [curve (7)]; 0.014 [curve (8)]; 0.016 [curve (9)]; 0.018 [curve (10)]; and 0.02 [curve (11)], respectively].

the value $\frac{A\lambda_D}{2K_3} \sin(2\Delta\theta)=0.01$, and results are shown in Figs. 2–4. In all these cases the effect of the backflow on the relaxation process of the polar angle $\theta(\tau, z)$ in the LC film are shown in Figs. 2(b), 3(b), and 4(b), whereas the same relaxation processes, but without accounting for the backflow, are shown in Figs. 2(a), 3(a), and 4(a), respectively. The velocity field $u(\tau, z)$ excited by reorientation of the director $\hat{\mathbf{n}}$ to its equilibrium orientation $\hat{\mathbf{n}}_{\text{eq}}$, also relaxed with time to zero, and the results of the calculations are shown in Fig. 6. In the case of 5CB film on the water surface, with charge density in $\kappa=10^{-3}$ C/m², and without accounting for the backflow effect, the director reorientation to its equilibrium orientation is characterized by a monotonic decreasing of the polar angle $\theta(\tau, z)$ with time to zero [Figs. 2(a), 3(a), and 4(a), respectively], whereas accounting for the backflow effect is characterized by oscillated decreasing to zero of the polar angle $\theta(\tau, z)$ with respect to the interface normal [see Figs. 2(b), 3(b), and 4(b), respectively], and the electric, elastic, and viscous torques finally puts the director into an orientation normal to the interface, with time in one order of the magnitude smaller than one for the case without accounting for the backflow. The relaxation of the director $\hat{\mathbf{n}}(\tau, z)$ to its equilibrium orientation $\hat{\mathbf{n}}_{\text{eq}}(z)$ in the multilayer 5CB film on

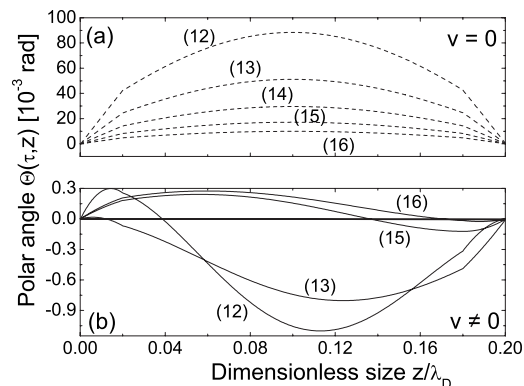


FIG. 4. Same as Fig. 2, but the evolution of the polar angle $\theta(\tau, z)$ is shown during the third time term $\Delta\tau=0.04$ [$\tau=0.024$ [curve (12)]; 0.028 [curve (13)]; 0.032 [curve (14)]; 0.036 [curve (15)]; and 0.04 [curve (16)], respectively].

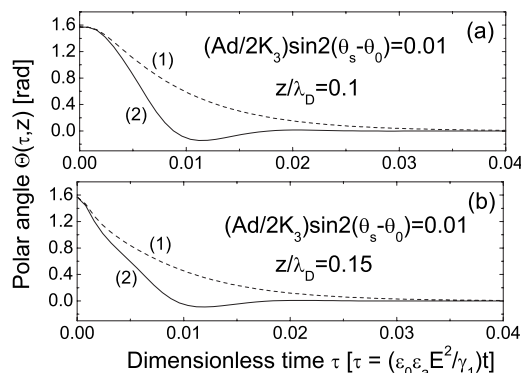


FIG. 5. Plot of relaxation of the polar angle $\theta(\tau, z)$ [$\tau=(\kappa^2\epsilon_a/\epsilon_0\epsilon^2\gamma_1)t$ is a dimensionless time] to its equilibrium value $\theta_{\text{eq}}(z)=0$, for the case of the multilayer 5CB film on the water surface, at two dimensionless distances away from the water surface; $z/\lambda_D=0.1$ (a) and 0.15 (b), both without [curves (1)] and with [curves (2)] accounting for the backflow effect, respectively.

the water surface, being initially disturbed $\theta(0, z)=\frac{\pi}{2}$, at two different distances, $z/\lambda_D=0.1$ and 0.15 away from the water surface, are shown in Fig. 5. Calculations show that the electric, elastic, and viscous torques exerted per LC's volume are vanished when the director aligns to be normal to the interface ($\theta=0$). In the case of the homeotropic alignment [$(A\lambda_D/2K_3)\sin 2(\theta_s-\theta_0)=0.01$] and with accounting for the backflow effect, the torques exerted per unit volume puts the director into an equilibrium orientation with different relaxation times; at $z/\lambda_D=0.1$ with $\tau_R=0.025$, whereas at $z/\lambda_D=0.15$ with $\tau_R=0.022$, respectively. It corresponds to dimension values of the relaxation time in 0.20 μs and 0.18 μs , respectively. The relaxation criterion $\epsilon=|(\theta(\tau_R)-\theta_{\text{eq}})/\theta_{\text{eq}}|$ for calculating procedure was chosen to be equal to 10^{-4} , and the numerical procedure was then carried out until a prescribed accuracy was achieved. According to our calculations, the relaxation time over which the torques exerted per unit volume vanish, in one order of the magnitude less in the case of accounting for the backflow effect than in the case of without accounting for that effect. The relaxation process of the velocity field $u(\tau, z)$ in the LC film on the water surface at the initial stage up to $\Delta\tau\sim 0.02$ is also characterized by the oscillating behavior of $u(\tau, z)$ with changing both τ and z , but with growth of the time τ , the range of these oscillations decrease, and finally take a more smooth character [see curves (3) and (4), of Fig. 6], before getting to the zero value. The absolute magnitude of the dimension velocity field $v_x(t, z)=(\lambda_D\epsilon_a\kappa^2/\gamma_1\epsilon_0\epsilon^2)u(\tau, z)$ in the LC film on the water surface, at the final stage of the relaxation process [see, curves (3) and (4), of Fig. 6] is equal to ~ 200 $\mu\text{m/s}$. Note that the velocity with the first derivative is satisfied by the boundary conditions (8), on the water surface. Calculations show that oscillating contribution to the viscous torque, due to accounting for the backflow effect, leads to decreasing, at least, in one order of the magnitude, of the relaxation time during which the torques exerted per unit LC volume puts the director into an orientation normal to the interface. Note that the time dependence $\theta(\tau, z)$ in the LC film with size

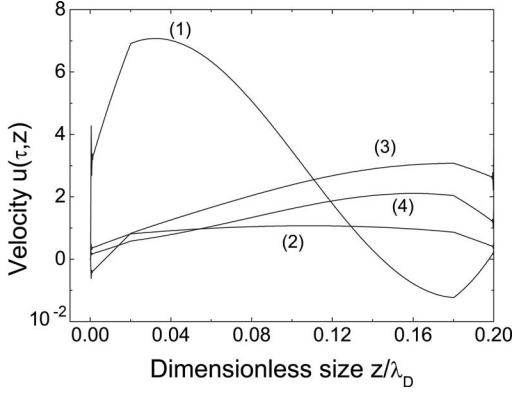


FIG. 6. The dimensionless velocity $u(\tau, z)$ [$u(\tau, z) = (\gamma_1 \epsilon_0 \bar{\epsilon}^2 / \lambda_D \epsilon_a \kappa^2) v_x(t, z)$ is the dimensionless velocity] vs the distance z/λ_D away from the water surface, for the case of the multilayer 5CB film with the homeotropic alignment [$(A\lambda_D/2K_3)\sin 2(\theta_s - \theta_0) = 0.01$] on the water surface, during the time term $\Delta = \tau_2 - \tau_1 = 0.012$ $\{\tau_1 = 0.028$ [curve (1)]; 0.032 [curve (2)]; 0.036 [curve (3)]; and $\tau_2 = 0.04$ [curve (4)], respectively}, when the magnitude of $u(\tau, z)$ decreases to zero.

$d/\lambda_D = 0.2$ corresponds to the case of the multilayer 5CB film in approximately five layers on the water surface, and the relaxation time with accounting for the backflow effect is equal to $\sim 0.15 \mu\text{s}$, whereas the same time, but without accounting for the backflow effect is equal to $\sim 2 \mu\text{s}$. Calculations also show that the effect of the backflow on the relaxation of the director field $\hat{\mathbf{n}}(z, \tau)$ to its equilibrium orientation increases with increasing of the distance away from the water surface. Note that the relaxation processes in the multilayer 5CB film on the water surface have been investigated at the value of the anchoring energy $\frac{A\lambda_D}{2K_3} \sin 2\Delta\theta = 0.01$, the charge density $\kappa = 10^{-3} \text{ C/m}^2$, and fixed temperature $\sim 300 \text{ K}$.

IV. ORIENTATIONAL RELAXATION OF THE TOTAL STRESS TENSOR COMPONENTS: NUMERICAL RESULTS

Our attention now turns to the viscous stress tensor σ_{ij} which also can be obtained directly from the Rayleigh dissipation function \mathcal{D} as [17]

$$\bar{\sigma}_{zx}(\tau) = \partial \mathcal{D}(\tau) / \partial u_z. \quad (10)$$

In our case the dissipation function \mathcal{D} takes the form $\mathcal{D}(\tau) = \mathcal{R}(\theta)u_z^2 - [2f(\theta)/\gamma_1]\theta_z u_z + \frac{1}{2}\theta_z^2$, where $\mathcal{R}(\theta) = \frac{1}{2\gamma_1}h(\theta)$. Having obtained both the dimensionless polar angle $\theta(\tau, z)$ and velocity $u(\tau, z)$, one can calculate the integral dissipation function $\Delta(\tau) = \int_0^\tau \mathcal{D}(\xi) d\xi$, and two dimensionless stress tensor components $\bar{\sigma}_{zz}^f$ and $\bar{\sigma}_{xx}^f$, respectively. Figure 7 shows the dimensionless integral dissipation function $\Delta(\tau)$ which monotonically increases with growth of time and saturates at different times τ_R ; in the case of accounting for the backflow effect with $\tau_R \sim 0.012$, whereas in the case without accounting for that effect with time $\tau_R \sim 0.1$, respectively. Such behavior of the integrated dissipation function shows that the system with accounting for the backflow relaxed to the equi-

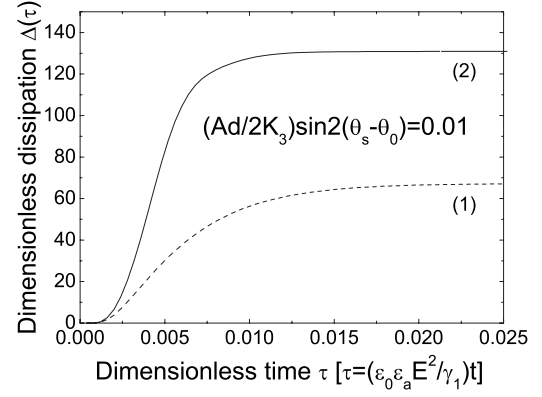


FIG. 7. The dependence of the integrated dissipation function $\Delta(\tau)$ for the 5CB multilayer film with the homeotropic alignment [$(A\lambda_D/2K_3)\sin 2(\theta_s - \theta_0) = 0.01$] on the water surface, both without [curve (1)] and with [curve (2)] accounting for backflow effect.

librium state, approximately, in one order of the magnitude faster than the system without accounting for that effect. In the case of planar geometry $\hat{\mathbf{n}} = \sin \theta(z, t)\hat{\mathbf{i}} + \cos \theta(z, t)\hat{\mathbf{k}}$, the balance of linear momentum becomes $\bar{P}_z = -[\partial \mathcal{D}(\tau) / \partial \theta_z]\theta_z$, where $\bar{P}_z = \partial \bar{P}(z, \tau) / \partial z$, and $\bar{P}(z, \tau)$ is the viscous contribution to the total pressure $P(z, \tau)$. The total pressure P may then take the form [15]

$$P(z, \tau) = W_{el} + W_{pol} - W_{elast} - \int [\partial \mathcal{D}(\tau) / \partial \theta_z]\theta_z dz, \quad (11)$$

where $W_{el} = \frac{1}{2}\epsilon_0(\epsilon_\perp + \epsilon_a \cos^2 \theta)E^2(z)$, $W_{pol} = \frac{1}{2}P_z E(z)$, and $W_{elast} = \frac{1}{2}\mathcal{G}(\theta)\theta_z^2$ are the electric, polarization, and elastic potentials, respectively. Having obtained the total pressure $P(z, \tau)$, one can calculate, using the Ericksen-Leslie theory [7,8], the normal components of the total stress tensor σ_{zz}^f and σ_{xx}^f . Note that in our case $\sigma_{yy}^f = 0$. Taking into account that in the vicinity of the LC film-air interface the component of the total stress tensor σ_{zz}^f is equal to zero, and in our case the dimensionless stress tensor components $\bar{\sigma}_{zz}^f(z, \tau)$ and $\bar{\sigma}_{xx}^f(z, \tau)$ take the form

$$\begin{aligned} \bar{\sigma}_{zz}^f &= \mathcal{K}_1(z) - \mathcal{K}_1(d/\lambda_D) - \bar{C}(z)(\epsilon_\perp/\epsilon_a + \cos^2 \theta) \\ &\quad + \bar{C}(d/\lambda_D)(1 + \epsilon_\perp/\epsilon_a) + \frac{1}{2} \sin 2\theta \mathcal{K}_2(\theta, u) \\ &\quad + \delta_2[\mathcal{K}_3(z) - \mathcal{K}_3(d/\lambda_D) + \mathcal{K}_4(\theta)], \end{aligned} \quad (12)$$

$$\begin{aligned} \bar{\sigma}_{xx}^f &= \mathcal{K}_1(z) + \mathcal{K}_1(d/\lambda_D) - \bar{C}(z)(\epsilon_\perp/\epsilon_a + \cos^2 \theta) \\ &\quad + \bar{C}(d/\lambda_D)(1 + \epsilon_\perp/\epsilon_a) + \frac{1}{2} \sin 2\theta \mathcal{K}_5(\theta, u) + \delta_2[\mathcal{K}_3(z) \\ &\quad + \mathcal{K}_3(d/\lambda_D) + \mathcal{K}_5(\theta)] + (\delta_1 \bar{G}(\theta) - \delta_4)\theta_z^2, \end{aligned} \quad (13)$$

where $\mathcal{K}_1(z) = \int_0^z \bar{C}(z)\sin(2\theta)\theta_z dz$, $\mathcal{K}_2(\theta, u) = [(\alpha_1 \cos^2 \theta + \alpha_6)u_z - \gamma_2 \theta_z]/\gamma_1$, $\mathcal{K}_3(z) = \int_0^z \bar{B}(\theta)\theta_z^2 dz$, $\mathcal{K}_4(\theta) = \frac{1}{2}(1 + e_3/e_1)\sin(2\theta)\theta_z \exp(-z)$, $\mathcal{K}_5(\theta, u) = [(\alpha_1 \sin^2 \theta + \alpha_5)u_z - \gamma_2 \theta_z]/\gamma_1$, and $\delta_4 = (\frac{A\lambda_D \bar{\epsilon}}{2\lambda_D \sigma})^2 \frac{\epsilon_0}{K_3 \epsilon_a}$. In our case the last parameter $\delta_4 = 0.0012$. The relaxation of the dimensionless components of the total stress tensor $\bar{\sigma}_{zz}^f(z, \tau)$ and $\bar{\sigma}_{xx}^f(z, \tau)$ to their

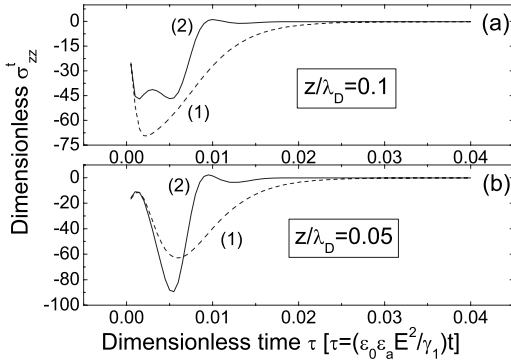


FIG. 8. Plot of relaxation of the dimensionless component of the stress tensor $\bar{\sigma}_{zz}^t(z, \tau)$ [$\tau = (\kappa^2 \epsilon_a / \epsilon_0 \bar{\epsilon}^2 \gamma_1) t$ is a dimensionless time] to its equilibrium value, for the case of the multilayer 5CB film on the water surface, at dimensionless distance away from the water surface $z/\lambda_D = 0.1$ (a) and 0.05 (b), both without [curves (1)] and with [curves (2)] accounting for the backflow effect, respectively.

equilibrium values in the multilayer 5CB film on the water surface, at two different distances, $z/\lambda_D = 0.1$ and 0.05 away from the water surface, are shown in Figs. 8 and 9. The relaxation process of the total stress tensor component $\bar{\sigma}_{zz}^t(z, \tau)$ in the LC film on the water surface, in the case of accounting for the backflow effect, at the initial stage up to $\Delta\tau_{zz} \sim 0.02$ is characterized by oscillating behavior of $\bar{\sigma}_{zz}^t(z, \tau)$ with changing of τ . Calculations of the absolute magnitude of $\sigma_{ii}^t = (\epsilon_a \kappa^2) / (\epsilon_0 \bar{\epsilon}^2) \bar{\sigma}_{ii}^t$ ($i = x, z$) shows that under the influence of the forces exerted per LC's unit volume the component of the total stress tensor σ_{zz}^t is characterized by the increase of $|\sigma_{zz}^t|$ up to 7×10^4 Pa within the initial stage of the relaxation process ($\Delta\tau_{zz} \sim 0.01$), and fast decreasing of $|\sigma_{zz}^t|$ up to zero, within the last stage of the relaxation process. Note that in the vicinity of the air-LC film interface $\lim_{z \rightarrow d} \bar{\sigma}_{zz}^t(z) = 0$. Figure 9 show that the dimensionless component of the total stress tensor $\bar{\sigma}_{xx}^t(z, \tau)$ relaxed to zero with the relaxation time $\Delta\tau_{xx} \sim 0.016$ ($\sim 0.12 \mu\text{s}$), and the relaxation process in the case of accounting for the backflow effect is characterized by oscillating behavior of $\bar{\sigma}_{xx}^t$ at the initial stage of evolution up to $\Delta\tau_{xx} \sim 0.014$ ($\sim 0.105 \mu\text{s}$). Having obtained the relaxation time of the stress tensor component $\bar{\sigma}_{xx}^t$ directed parallel to the x axis, the relaxation time of the LC film on the water surface during the lateral com-

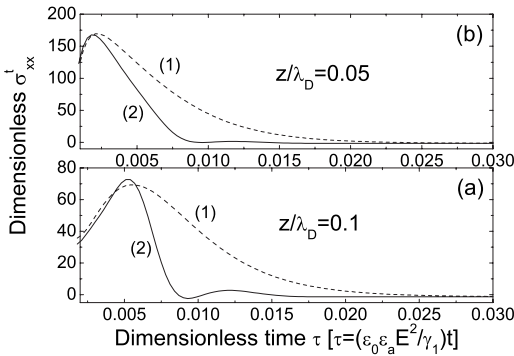


FIG. 9. Same as Fig. 8, but the evolution of the dimensionless component of the stress tensor $\bar{\sigma}_{xx}^t(z, \tau)$ to its equilibrium value.

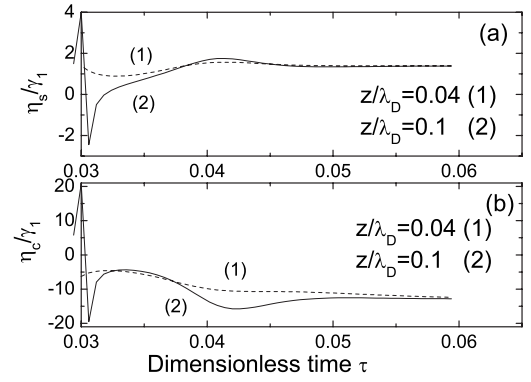


FIG. 10. Plot of relaxation of the dimensionless shear $\bar{\eta}_s(\tau, z) = \eta_s / \gamma_1$ (a) and compression $\bar{\eta}_c(\tau, z) = \eta_c / \gamma_1$ (b) [$\tau = (\kappa^2 \epsilon_a / \epsilon_0 \bar{\epsilon}^2 \gamma_1) t$ is a dimensionless time] viscosities to their equilibrium values $\bar{\eta}_{s(c)}(\text{eq})$, at dimensionless distance away from the water surface $z/\lambda_D = 0.04$ [curve (1)] and 0.1 [curve (2)], respectively, for the case of homeotropic alignment $(A\lambda_D / 2K_3) \sin 2(\theta_s - \theta_0) = 0.01$ of 5CB molecules at the water surface.

pression can be estimated as $\Delta\tau_c = \Delta\tau_{xx} \sim 0.016$ ($\sim 0.12 \mu\text{s}$).

In an attempt to bring the theory and experiment closer we have performed a numerical study of the viscous coefficients, one for compression η_c , and another for shear η_s . Having obtained both the dimensionless stress tensor component $\bar{\sigma}_{xx}(\tau) = \mathcal{R}(\theta) u_z - [2f(\theta) / \gamma_1] \theta_\tau$ and the velocity $u(\tau, z)$, one can calculate the dimensionless shear viscosity coefficient $\eta_s (\equiv \eta_{zx})$ as $\bar{\sigma}_{zx}(\tau, z) = \bar{\eta}_s \partial u(\tau, z) / \partial z = \bar{\eta}_s u_z(\tau, z)$, or

$$\bar{\eta}_s = \mathcal{R}(\theta) - 2f(\theta) \theta_\tau / (\gamma_1 u_z), \quad (14)$$

and the compression viscosity $\bar{\eta}_c (\equiv \eta_{xx})$ as

$$\bar{\eta}_c = \bar{\sigma}_{xx}(\tau, z) / u_z(\tau, z). \quad (15)$$

The relaxation of the dimensionless viscosities $\bar{\eta}_s = \eta_s / \gamma_1$ and $\bar{\eta}_c = \eta_c / \gamma_1$ to their equilibrium values in the multilayer 5CB LC film on the water surface, at two different distances $z/\lambda_D = 0.04$ (close to the water surface) and 0.1 (in the middle part of the film) are shown in Figs. 10(a) and 10(b). The relaxation processes of these viscosities, at initial stage, up to $\Delta\tau \sim 0.03$ ($\sim 0.23 \mu\text{s}$) are characterized by oscillating behavior both $\bar{\eta}_c(\tau)$ and $\bar{\eta}_s(\tau)$ with changing of τ . Figure 10 shows that the dimension shear viscosity $\eta_s(\tau)$ relaxed to $\lim_{\tau \rightarrow \Delta\tau_s} \eta_s(\tau) \rightarrow \eta_s(\text{eq}) \sim 1.4 \gamma_1$, whereas the dimension compression viscosity $\eta_c(\tau)$ relaxed to $\lim_{\tau \rightarrow \Delta\tau_c} \eta_c(\tau) \rightarrow \eta_c(\text{eq}) \sim 12.4 \gamma_1$, practically with the same relaxation time $\Delta\tau_{s(c)} \sim 0.06$ ($\sim 0.45 \mu\text{s}$).

V. CONCLUSION

In summary, we have investigated the relaxation of the director $\hat{\mathbf{n}}(\mathbf{r}, t)$ to its equilibrium orientation $\hat{\mathbf{n}}_{\text{eq}}(\mathbf{r})$ on 4-*n*-pentyl-4'-cyanobiphenyl multilayer film on the water surface during the lateral compression of the film. Our simulations, in the framework of the classical Ericksen-Leslie theory, prove that to describe dynamical reorientation of the

director correctly, one must include a proper treatment of backflow. To the high order, backflow must be accounted for by a numerical study of the full system of the hydrodynamic equations that include both the director reorientation and the velocity flow. In order to elucidate the role of the 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 among the electric, elastic, and viscous torques exerted on the director is reflected in the relaxation of the director to its equilibrium position to be normal to the interface. We believe that the present investigation can shed some light on the problem of the reorientation processes in Langmuir films at the air-liquid interface.

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APPENDIX

In the case of the weak anchoring the relevant boundary equilibrium condition for the polar angle θ is given by [3,17,18] $\frac{\partial W_t}{\partial \theta} - \frac{\partial W}{\partial \theta} = 0$, at $z=0$, where $W_t = W_{el} + W_{pol} + W_{elast}$ is the total energy of the LC system composed by electric $W_{el} = \frac{1}{2}\epsilon_0(\epsilon_{\perp} + \epsilon_a \cos^2 \theta)E^2(z)$, polarization $W_{pol} = \mathcal{F}(\theta)\theta_z E(z)$, and elastic $W_{elast} = \frac{1}{2}\mathcal{G}(\theta)\theta_z^2$ potentials, whereas $W = \frac{1}{2}A \sin^2(\theta_s - \theta_0)$ is the anchoring energy, respectively. In the limiting case $\lim_{z \rightarrow 0} \theta \rightarrow 0$, this leads to the boundary requirement $(\frac{\partial \theta}{\partial z})_{z=0} = \frac{A\lambda_D}{2K_3} \sin 2\Delta\theta + \Delta\epsilon$, where the last term $\Delta\epsilon = e_3\lambda_D\kappa/K_3 \sim 10^{-4}$ is the effect of the polarization to the torque balance equation transmitted to the LC film/water interface. The combination of $\frac{A\lambda_D}{2K_3}$ values varied between 0.2 and 0.02, so, the last term on the right-hand side of the torque equation can be neglected and the boundary condition for the polar angle θ must satisfy Eq. (7). In the case of no-slip boundary condition on \mathbf{v} and the limiting case $\lim_{z \rightarrow 0} \theta \rightarrow 0$, the interfacial linear momentum balance provide the extra condition on $(u_z)_{z=0}$ as $\frac{1}{2\gamma_1}(-\alpha_3 + \alpha_4 + \alpha_5) \times (u_z)_{z=0} = 0$ or $(u_z)_{z=0} = 0$.

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