

## Relaxation processes in Langmuir films under lateral compression

A. V. Zakharov\*

Laboratorium voor Akoestiek en Thermische Fysica, Department Natuurkunde en Sterrenkunde, Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium

Mitsumasa Iwamoto<sup>†</sup>

Department of Physical Electronics, Tokyo Institute of Technology, O-okayama 2-12-1, Meguro-ku, Tokyo 152-8552, Japan

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The orientational relaxation process of the director  $\hat{\mathbf{n}}$  to its equilibrium orientation  $\hat{\mathbf{n}}_{eq}$  in the Langmuir film, during the lateral compression in absence of flow, is investigated. The relaxation time, during compression of 4-*n*-pentyl-4'-cyanobiphenyl monolayer (multilayer) films on the water surface, using the Ericksen-Leslie theory, has been calculated for a number of dynamic regimes. It is also shown that the viscous and electric forces exerted per unit volume of the monolayer Langmuir film may excite the solitary wave propagating along the air-water interface.

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### I. INTRODUCTION

The structure of organic monolayer and multilayer systems at the air-water interface has been extensively investigated during the past few years [1–4]. Among the established surface measurement techniques there are two, the Maxwell-displacement current (MDC) technique and the optical second harmonic generation (SHG) technique, that are ideally suited to retrieve information on the orientation of the interfacial region as well as identification of its symmetry [4]. Both these techniques have shed significant light on the role of the dipole and quadrupole interactions in the organic monolayers with  $C_\infty$  symmetry. Taking into account that the molecules in the liquid crystal (LC) phases of Langmuir films either align normal to the air-water interface or they can tilt relative to the interface, thereby defining an array of a unit vectors  $\hat{\mathbf{u}}_i$  in the plane of the film, one can introduce at least two sets of the parameters, positional and orientational order parameters (OPs) [4]. Textures of the LC films are produced by the average molecular orientation  $\hat{\mathbf{n}} = \langle \hat{\mathbf{u}}_i \rangle$ , called the director, and the fluctuation of the molecular orientation  $\hat{\mathbf{u}}_i$  with respect to  $\hat{\mathbf{n}}$  is expressed by the OPs  $\bar{P}_L = \langle P_L[\cos(\hat{\mathbf{n}} \cdot \hat{\mathbf{u}}_i)] \rangle$ , where  $\langle \dots \rangle$  denotes the statistical average, and  $P_L$  are the Legendre polynomials of rank  $L$ . Monolayers at the air-water interface exhibit a number of features during compression of the films. For example, the OP  $\bar{P}_1 = \langle \cos(\hat{\mathbf{n}} \cdot \hat{\mathbf{u}}_i) \rangle$  plays a significant role in the description of the two-dimensional (2D) LC monolayers [4] because of the structural symmetry breaking at the interface, whereas that parameter is not so essential for describing the three-dimensional systems [5]. Since the LC molecules that form

the Langmuir films possess a strong polar group, the dipolar interactions among molecules can influence electrooptical properties of the 2D system. The MDC and SHG signals allow us to determine both the non-OPs and the normalized OPs  $\bar{P}_1(A)$  and  $\bar{P}_3(A)$ , and the surface pressure  $\pi$ -area  $A$  isothermal diagram, during compression of the *cyanobiphenyl* film [6]. In particular, the MDC and SHG investigations of the 4-*n*-pentyl-4'-cyanobiphenyl (5CB) monolayers on the air-water interface during monolayer compression have been reported [1–3], and therefore a large data set is available for comparison with results from the theoretical routes [4,6]. In turn, the past experimental investigations of flow in monolayers during the lateral compression [7] or under shear rate [8–10] has been focused mainly on measurements of effective surface viscosity, with little knowledge of the effects of flow on the underlying structure. The nature of the relaxation process of the director  $\hat{\mathbf{n}}$  to its equilibrium orientation  $\hat{\mathbf{n}}_{eq}$  in the LC film on the water surfaces is also discussed in the separate investigations. With the use of MDC and SHG techniques in combination with the theoretical treatment, based, for instance, upon the Ericksen-Leslie (EL) [11,12] theory, we attempt to answer the question of how the hydrodynamic, elastic, and electric forces affect the orientational relaxation process of the director in the LC film on the water surface during the lateral compression of the film.

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

### II. FORMULATION OF THE BALANCE OF THE MOMENTUM EQUATION FOR MULTILAYERS 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]  $\mathbf{T}_{vis} + \mathbf{T}_{elast} + \mathbf{T}_{el} + \mathbf{T}_{pol} = \mathbf{0}$ . In the case of planar geom-

\*Author to whom correspondence should be addressed. Permanent address: Saint Petersburg Institute for Machine Sciences, the Russian Academy of Sciences, Saint Petersburg 199178, Russia. Electronic address: Alexandre.Zakharov@fys.kuleuven.ac.be

<sup>†</sup>Electronic address: iwamoto@pe.titech.ac.jp

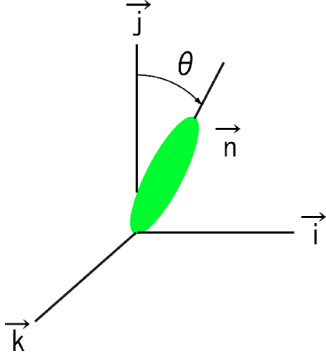


FIG. 1. Coordinate system specifying the orientation of the director and the direction of the electric field and the total polarization vector. The angle between the director  $\hat{\mathbf{n}}$  and the direction  $\hat{\mathbf{j}}$  (directed perpendicular to the air-water interface) is  $\theta(y,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

entry  $\hat{\mathbf{n}} = \sin \theta \hat{\mathbf{i}} + \cos \theta \hat{\mathbf{j}}$  and the absence of flow, the viscous torque takes the form  $\mathbf{T}_{vis} = -\gamma_1 \hat{\mathbf{n}} \times \partial \hat{\mathbf{n}} / \partial t = \gamma_1 \partial_t \theta(y, t) \hat{\mathbf{k}}$ . Here  $\theta(y, t)$  denotes the polar angle, i.e., the angle between the direction of the unit vector  $\hat{\mathbf{j}}$  (directed perpendicular to the air-water interface) and the director  $\hat{\mathbf{n}}$ ,  $\partial_t \theta(y, t) = \partial \theta(y, t) / \partial t$ , and  $\gamma_1$  is the rotational viscosity coefficient (RVC). The unit vector  $\hat{\mathbf{i}}$  is directed to be parallel to the air-water interface,  $y$  is the distance away from the air-water interface in the  $\hat{\mathbf{j}}$  direction, and  $\hat{\mathbf{k}} = \hat{\mathbf{i}} \times \hat{\mathbf{j}}$  (see Fig. 1). The torque due to electric field  $\mathbf{E}$ , for instance, originating from the water surface charge density  $\sigma$ , is given by  $\mathbf{T}_{el} = (\epsilon_a / \epsilon_0) \hat{\mathbf{n}} \times \mathbf{E} (\mathbf{E} \cdot \hat{\mathbf{n}}) = [E^2(y)/2] \epsilon_a \epsilon_0 \sin 2\theta(y, t) \hat{\mathbf{k}}$ , where  $\mathbf{E} = E(y) \hat{\mathbf{j}} = (\sigma / \epsilon_0 \bar{\epsilon}) \times \exp(-y/\lambda_D) \hat{\mathbf{j}}$  is the surface electric field of the charged water surface, and penetrates the LC film, due to ions present in the organic film (a weak electrolyte), on the order of the Debye screening length  $\lambda_D$  [13]. Here  $\epsilon_0$  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  $\hat{\mathbf{n}}$ , respectively. The torque due to elastic forces is [5]  $\mathbf{T}_{elast} = \hat{\mathbf{n}} \times \mathbf{h}$ , where the molecular field  $\mathbf{h}$  has to be evaluated in terms of the Frank elastic coefficients  $K_i$  ( $i=1, 2, 3$ ) for splay, twist, and bend deformations, respectively. The torque due to spontaneous polarization is  $\mathbf{T}_{pol} = \mathbf{P} \times \mathbf{E} = P_x E(y) \hat{\mathbf{k}}$ , 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, and  $P_x$  is the  $x$  component of the vector  $\mathbf{P}$ .  $\mathbf{P}_s$  is the spontaneous polarization in the Langmuir film, composed of asymmetric polar molecules in response to elastic deformation, and is known as the flexoelectric effect [14]. In the case of polar molecules (which is the case for all cyanobiofenyls), splay and bend deformations give rise to two independent flexoelectric (FE) coefficients ( $e_1, e_3$ ), and their contributions to induced polarization can be written as [14,15]

$$\begin{aligned} \mathbf{P}_s &= e_1 \hat{\mathbf{n}} \cdot \nabla \hat{\mathbf{n}} - e_3 \hat{\mathbf{n}} \times \nabla \times \hat{\mathbf{n}} \\ &= (e_3 \cos^2 \theta - e_1 \sin^2 \theta) \partial_y \theta(y) \hat{\mathbf{i}} \\ &\quad - (e_3 + e_1) \cos \theta \sin \theta \partial_y \theta(y) \hat{\mathbf{j}}. \end{aligned} \quad (1)$$

On the other hand, when the mirror symmetry is broken at the interface, the surface polarization  $\mathbf{P}_{surf}$  may arise in a thin surface layer  $\lambda_l \sim 10-100$  nm, for any (planar, homeotropic, or oblique) alignment of a liquid crystal [16]. The microscopic reason for this polarization might be the preferential asymmetric attachment of dipolar molecules to the water surface, ion adsorption, or spatial dependence of the nematic OP  $\bar{P}_2(y)$  (the so-called ordo-electric polarization [16]). In the quadrupolar approximation, the surface (ordo-electric) polarization (SP) of LCs takes the form [17]

$$\mathbf{P}_{surf} = \frac{3}{2} e^* \nabla \bar{P}_2(y) \cdot \left( \hat{\mathbf{n}} \hat{\mathbf{n}} - \frac{1}{3} \mathbf{I} \right), \quad (2)$$

where  $e^*$  is the quadrupolar coefficient of a nematic. Although the difference in the direction of the  $\mathbf{P}_{surf}$  vector for homeotropic and planar alignments follows, of course, from the dipolar nature of the surface layers [17], it can also be explained in the framework of the ordo-electric polarization model [Eq. (2)]. By setting the director normal to the substrate and on the  $xy$  plane to give  $\hat{\mathbf{n}} = (\sin \theta, \cos \theta, 0)$ , and by integrating over  $y$  component of the  $\mathbf{P}_{surf}$  vector  $P_{surf} \hat{\mathbf{j}}$ , one has [16]  $\langle P_{surf}^y \rangle = \frac{3}{2} e^* (\cos^2 \theta_s - \frac{1}{3}) \Delta \bar{P}_2$ , where  $\theta_s$  is the polar angle of a surface director  $\hat{\mathbf{n}}_s$ ,  $\Delta \bar{P}_2 = \bar{P}_{2,b} - \bar{P}_2(0)$ , and  $\bar{P}_{2,b}$  and  $\bar{P}_2(0)$  are the bulk and surface OPs, respectively. For the homeotropic alignment ( $\theta_s = 0$ ),  $\langle P_{surf}^y \rangle_h = e^* \Delta \bar{P}_2$ , whereas for the planar one ( $\theta_s = \pi/2$ ),  $\langle P_{surf}^y \rangle_p = -\frac{1}{2} e^* \Delta \bar{P}_2$ . Since the quadrupolar coefficient  $e^*$  and the flexoelectric coefficients  $e_1$  and  $e_3$  related to the splay and bend distortions of the LC are connected by a simple relationship [18]  $e^* = (e_1 + e_3)/3 \bar{P}_2(y)$ , the following expressions for the  $y$  components of  $\mathbf{P}_{surf}$  vector are obtained:  $\langle P_{surf}^y \rangle_h = e_+ \Delta \bar{P}_2 / 3 \bar{P}_2(y)$  and  $\langle P_{surf}^y \rangle_p = -e_+ \Delta \bar{P}_2 / 6 \bar{P}_2(y)$ , respectively. Here  $e_+ = e_1 + e_3$ . Now the SP takes the form [16]  $\mathbf{P}_{surf} = A \hat{\mathbf{j}}_1 \cdot (\hat{\mathbf{n}} \hat{\mathbf{n}} - \frac{1}{3} \mathbf{I}) = A \xi [(\cos^2 \theta - \frac{1}{3}) \hat{\mathbf{i}} + \frac{1}{2} \sin 2\theta \hat{\mathbf{j}}]$ , where  $A = (e_+/2) [d \ln \bar{P}_2(y) / dy]$ ,  $\hat{\mathbf{j}}_1$  is a unit vector which defines the direction of the  $y$  component SP vector, and  $\hat{\mathbf{i}}$  is a unit vector perpendicular to  $\hat{\mathbf{j}}$ . The coefficients  $\xi = 1$  when  $\hat{\mathbf{j}}_1$  is parallel to  $\hat{\mathbf{j}}$  and  $\xi = -1$  when  $\hat{\mathbf{j}}_1$  is antiparallel to  $\hat{\mathbf{j}}$ . In the simplest case of the electric field  $\mathbf{E}(y) = E(y) \hat{\mathbf{j}}$ , the torque due to polarization  $\mathbf{P}$  is

$$\mathbf{T}_{pol} = \mathbf{P} \times \mathbf{E} = (\mathbf{P}_s + \mathbf{P}_{surf}) \times \mathbf{E} = \frac{\sigma}{\epsilon_0 \bar{\epsilon}} \exp(-y/\lambda_D) \mathcal{F}(\theta) \hat{\mathbf{k}}, \quad (3)$$

where  $\mathcal{F}(\theta) = (e_3 \cos^2 \theta - e_1 \sin^2 \theta) \partial_y \theta(y) + A \xi (\cos^2 \theta - \frac{1}{3})$ . It should be noted that accounting for the elastic and spontaneous polarization torques in the torques balance can be justified only in the case of the multilayer Langmuir film. In the case of the two-dimensional system, where the molecules of the Langmuir film align and tilt relative to the unit vector  $\hat{\mathbf{j}}$ , and thereby define an array of unit vectors  $\hat{\mathbf{u}}_i$  in the plane  $x-y$  of the film, the dynamic equation describing the reorientation of the liquid crystalline film can be written as

$$\begin{aligned} \gamma_1 \partial_t \theta(y, t) + \frac{E^2(y)}{2} \epsilon_a \epsilon_0 \sin 2\theta(y, t) + E(y) \mathcal{F}(\theta(y, t)) \\ - \left( \frac{K_3 - K_1}{2} \right) \sin 2\theta(y, t) (\partial \theta(y, t) / \partial y)^2 \\ - [K_1 \cos^2 \theta(y, t) + K_3 \sin^2 \theta(y, t)] \partial_{yy} \theta(y, t) = 0, \quad (4) \end{aligned}$$

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 [19], 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. It allows us to rewrite the last equation in a dimensionless form as

$$\begin{aligned} \partial_\tau \theta(\bar{y}, \tau) = -\delta \exp(-2\bar{y}) \sin 2\theta(\bar{y}, \tau) + \delta_1 \exp(-\bar{y}) \\ \times \{ \sin^2 \theta(\bar{y}, \tau) \partial_{\bar{y}} \theta(\bar{y}, \tau) - \delta_2 \partial_{\bar{y}} \ln \bar{P}_2(\bar{y}) \\ \times [\cos^2 \theta(\bar{y}, \tau) - 1/3] \} + \delta_3 \partial_{\bar{y}\bar{y}} \theta(\bar{y}, \tau), \quad (5) \end{aligned}$$

where  $\partial_\tau \theta(\bar{y}, \tau) = \partial \theta(\bar{y}, \tau) / \partial \tau$ ,  $\tau = t \sigma^2 / \gamma_1$  is the dimensionless time,  $\bar{y} = y / \lambda_D$  is the dimensionless distance away from the water surface in the LC film,  $\delta = \epsilon_a / (2 \epsilon_0 \bar{\epsilon}^2)$ ,  $\delta_1 = e_1 / (\epsilon_0 \bar{\epsilon} \sigma \lambda_D)$ ,  $\delta_2 = e_+ / (2 e_1) \xi$ ,  $\delta_3 = K_3 / (\sigma \lambda_D)^2$ , and  $\lambda_D = \sqrt{\epsilon_0 \epsilon k_B T / 2 q^2 n_{ions}}$  [13]. Here  $q$  is the proton charge,  $k_B$  is the Boltzmann constant,  $\bar{\epsilon} = \epsilon_0 (\epsilon_{\parallel} \cos^2 \theta_s + \epsilon_{\perp} \sin^2 \theta_s)$  (a case of the bulk screening), and  $n_{ions}$  is the bulk ion concentration. If one further supposes that the nematic OP  $\bar{P}_2$  changes from its values at the surface to that of the bulk film, the distance dependences of the  $\bar{P}_2(y)$  and can be expressed as [16]

$$\begin{aligned} \bar{P}_2(y) = \bar{P}_2(0) \left( \frac{\Delta \bar{P}_2}{\bar{P}_2(0) \lambda_D} y + 1 \right), \\ y \leq \lambda_D = \bar{P}_{2,b}, \quad y > \lambda_D, \quad (6) \end{aligned}$$

with the following expression for the  $\partial_{\bar{y}} \ln \bar{P}_2(\bar{y}) = f(\bar{y}) = \Delta \bar{P}_2 / [\Delta \bar{P}_2 \bar{y} + \bar{P}_2(0)]$ , for  $\bar{y} \leq 1$ , and 0, for  $\bar{y} > 1$ . In this case Eq. (5) can be written as

$$\begin{aligned} \partial_\tau \theta(y, \tau) = -\delta \exp(-2y) \sin 2\theta(y, \tau) + \delta_1 \exp(-y) \\ \times \{ \sin^2 \theta(y, \tau) \partial_y \theta(y, \tau) - \delta_2 f(y) [\cos^2 \theta(y, \tau) - 1/3] \} \\ + \delta_3 \partial_{yy} \theta(y, \tau). \quad (7) \end{aligned}$$

The overbars in the space variable  $y$  have been eliminated. 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 (7), with an appropriate boundary conditions [for instance,  $\theta(\tau, y)_{y=0} = 0$  (homeotropic anchoring) or  $\theta(\tau, y)_{y=0} = \pi/2$  (planar anchoring), and the initial  $\theta(0, y) = \pi/2$  condition]. 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  $\theta_{eq}$ .

### III. ORIENTATIONAL RELAXATION IN THE LC FILM ON THE WATER SURFACE

#### A. Case of multilayer film

Let us consider the relaxation process in the multilayer 5CB film on the water surface during the lateral compression. In order to discuss the homeotropic alignment of 5CB molecules on the water surface, one needs the data for  $e_+$ ,  $\gamma_1$ ,  $\epsilon_{\parallel}$ ,  $\epsilon_{\perp}$ ,  $K_3$ ,  $\lambda_D$ ,  $\bar{P}_2(0)$ , and the bulk OP  $\bar{P}_{2,b}$ . At temperature 300 K and density  $10^3 \text{ kg m}^{-3}$ , the order parameter was found to be  $\bar{P}_{2,b} = 0.51$  [20]. In the following we use the calculated data  $e_+ = -15.9 \text{ pC m}^{-1}$  [21] and  $\gamma_1 = 0.05 \text{ Pa s}$  [20], at  $T = 300 \text{ K}$ , the calculated  $\epsilon_{\parallel} = 18$ ,  $\epsilon_{\perp} = 8$ ,  $\bar{\epsilon} = 11.3$ , and  $\epsilon_a = 10$  [20], as well as the calculated  $K_3 = 13.8 \text{ pN}$ , using the molecular dynamics simulation of 5CB [20] at the same temperature. 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 is  $\lambda_D \approx 45 \text{ nm}$ ,  $f(y) = 1/(y-2)$ , for  $y < 1$ , and 0, for  $y \geq 1$ , and the set of parameters, which is involved in Eq. (7) is equal to  $\delta \sim 0.52$ ,  $\delta_1 \sim -0.252$ ,  $\delta_2 \sim 0.68$ , and  $\delta_3 \sim 0.75$ . The values of the charge density, estimated to be of the order of  $\sigma \sim 10^{-4} - 10^{-3} \text{ C/m}^2$  at  $T = 300 \text{ K}$ , corresponds to the water surface charge density  $n_w$  in  $\sim 10^{15} - 10^{16} \text{ m}^{-2}$ , which agrees with experimental values  $\sim 10^{15} - 10^{16} \text{ m}^{-2}$  [13]. Here  $\sigma = q n_w$ , where  $q = 1.602 \times 10^{-19} \text{ C}$  is the proton charge. In the case of planar alignment ( $\theta_s = \pi/2$ ), the Debye length is  $\lambda_D \approx 30 \text{ nm}$ ,  $f(y) = -1/(y+4)$ , for  $y < 1$ , and 0, for  $y \geq 1$ , whereas the set of parameters, which is involved in Eq. (7) is equal to be  $\delta \sim 0.52$ ,  $\delta_1 \sim -0.378$ ,  $\delta_2 \sim -0.68$ , and  $\delta_3 \sim 1.12$ . The relaxation of the director  $\hat{\mathbf{n}}$  to its equilibrium orientation  $\hat{\mathbf{n}}_{eq}$ , which is described by the angle  $\theta(\tau, y)$  from the initial condition  $\theta(0, y) = \pi/2$  to zero during the lateral compression of the multilayer 5CB film on the water surface at different film sizes  $L/\lambda_D = 0.2, 0.4, 0.5, 0.8, 1.0, 1.6$ , and 2.0, have been investigated by a standard numerical relaxation method [22], and results are shown in Figs. 2 and 3 [23]. Calculations show that the viscous, elastic, and electric torques exerted per unit volume are vanished when the director aligns at an angle  $\theta(y, \tau) = 0$  with respect to the interface normal. In the case of homeotropic alignment on the water surface, the torques exerted per unit volume puts the director into an orientation normal to the interface, with the different relaxation times  $\tau = t \sigma^2 / \gamma_1$ , and the torque increases as the size of the film  $L/\lambda_D$  increases from 1 up to 10. Calculations also show that the relaxation processes in the Langmuir films on the water surface, for planar alignment of 5CB molecules, is approximately two times longer than that for the homeotropic alignment. It is noted that the time dependence  $\theta(y, \tau)$  in the Langmuir film with size  $L/\lambda_D = 2.0$  corresponds to the case of the multilayer 5CB film in  $\sim 45$  layers on the water surface, and the relaxation time is equal to be  $\sim 56 \mu\text{s}$ .

#### B. Case of monolayer film

In the case of the monolayer 5CB film, when the elastic torque and the torque due to spontaneous polarization  $\mathbf{P}_s$  can be safely disregarded, the polarization contribution to the

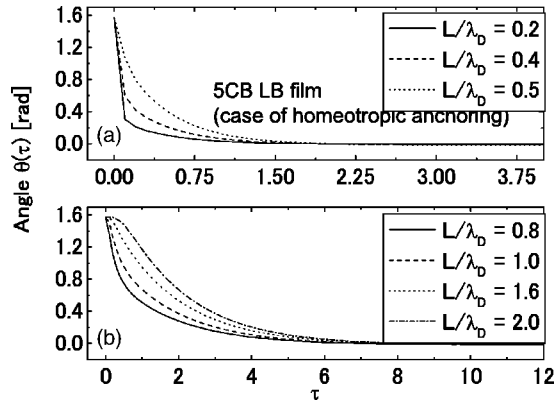


FIG. 2. (a) Plot of relaxation of the angle  $\theta(\tau)$  ( $\tau = t\sigma^2/\gamma_1$  is a dimensionless time) to its equilibrium value  $\theta_{eq} \sim 0$  in the multilayer 5CB film on the water surface, calculated using Eq. (7), for the case of the homeotropic alignment on the water surface at different film sizes  $L/\lambda_s = 0.2, 0.4,$  and  $0.5$ . (b) Same as (a), but the film sizes are  $L/\lambda_s = 0.8, 1.0, 1.6,$  and  $2.0$ .

toque balance is composed of only the surface polarization  $\mathbf{P}_{surf} = \rho\Delta(A)\hat{\mathbf{n}}(t, A)$  (in our case directed away from the water surface) contribution, where  $\rho = 1/Ad$  is the number density of molecules in the film,  $d$  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, 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 [6]

$$f(\cos \theta_i) = \frac{1}{4\pi} \sum_{l=0}^{\infty} \frac{2l+1}{2} \bar{P}_l P_l(\cos \theta_i), \quad (8)$$

where  $\theta_i$  is the polar angle of the unit vector  $\hat{\mathbf{u}}_i$  along the molecular symmetry axis, and  $P_l(\cos \theta_i)$  denote Legendre

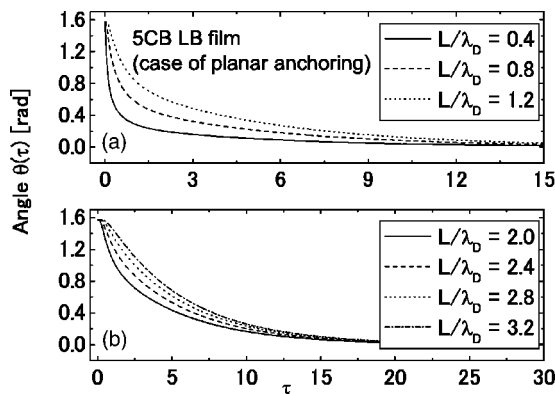


FIG. 3. (a) Same as Fig. 2, but for the planar alignment on the water surface at different film sizes  $L/\lambda_s = 0.4, 0.8,$  and  $1.2$ . (b) Same as (a), but the film sizes are  $L/\lambda_s = 2.0, 2.4, 2.8,$  and  $3.2$ .

polynomials of any rank. The normalized OPs can be written as [6]  $\bar{P}_i = \int_{-1}^1 p_i(x)f(x)dx / \int_{-1}^1 f(x)dx$ , where the function  $f(x)$  is as in Eq. (8), but with the non-normalized OPs,  $i = 1, 3,$  and

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

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 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. The hydrophobic tails are directed away from the water surface and tilted at the average equilibrium angle  $\theta(\tau, A)$  with respect to the unit vector  $\hat{\mathbf{j}}$  directed perpendicular to the interface, and the orientation of the director  $\hat{\mathbf{n}}(\tau, A) = \sin \theta(\tau, A)\hat{\mathbf{i}} + \cos \theta(\tau, A)\hat{\mathbf{j}}$  in the monolayer film on the water surface, when the relaxation regime is governed by the viscous and electric forces, can be obtained by solving the nonlinear equation [see Eq. 2 [24]]

$$\partial_\tau \theta(\bar{x}, \tau) = -\sin \theta(\bar{x}, \tau) - \delta \sin 2\theta(\bar{x}, \tau), \quad (9)$$

where  $\partial_\tau \theta(\bar{x}, \tau) = \partial \theta(\bar{x}, \tau) / \partial \tau$ ,  $\tau = tPE_0/\gamma_1$  is the dimensionless time,  $\bar{x} = x/d$  is the dimensionless distance along the air-water interface,  $\delta = \epsilon_a \epsilon_0 E_0 / (2P) = (\epsilon_a q n_w Ad) / [2\bar{\epsilon} \Delta(A)] = \chi|A|$ . Here  $\chi \sim 0.05$ , at the left end of the water surface charge density interval ( $10^{15} - 10^{16} \text{ m}^{-2}$ ), and the molecular area is restricted by the values  $0.4 \leq |A| \leq 0.8$ . In that case the electric torques can be safely disregarded ( $E_0 \ll P$ ) and the relaxation of the director to its equilibrium orientation 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. (9) ( $\delta \ll 1$ ) in the form

$$\theta(\tau) = 2 \tan^{-1} [\exp(-\tau)] + \theta_{eq}, \quad (10)$$

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

But there is another exact solution of Eq. (9) ( $\delta \ll 1$ ),

$$\theta(\bar{x}, \tau) = \tan^{-1} \{1 / (\sinh[\tau - \bar{x} + \bar{x}_0])\}, \quad (11)$$

where  $\bar{x}_0$  is a constant. Indeed,  $\partial_\tau \theta(\bar{x}, \tau) = -\cosh^{-1}[\tau - \bar{x} + \bar{x}_0]$ , and taking into account relation  $\tan \theta(\bar{x}, \tau) = \sinh^{-1}[\tau - \bar{x} + \bar{x}_0] = \mathcal{A}$ , one has that  $\sin \theta(\bar{x}, \tau) = \mathcal{A} / (1 + \mathcal{A}^2)^{1/2} = \cosh^{-1}[\tau - \bar{x} + \bar{x}_0]$ . Finally, one can rewrite Eq. (9) in the following way:  $\partial_\tau \theta(\bar{x}, \tau) = -\cosh^{-1}[\tau - \bar{x} + \bar{x}_0] = -\sin \theta(\bar{x}, \tau)$ . Solution (11) describes the solitary kink  $\theta(\bar{x}, \tau)$ , which is spreading along the  $x$  axis with the velocity

$$v = PE_0 d / \gamma_1 = q n_w \Delta(A) / (\epsilon_0 \bar{\epsilon} A \gamma_1). \quad (12)$$

Physically, this means that the film has initially been disturbed, for instance, at the left end of the monolayer film, with the condition  $\theta(0, 0) = \pi/2$ , and that disturbance must propagate in the form of the solitary wave along the  $x$  axis with the velocity  $v$ . We also found that with a decrease of the

molecular area that the dipole moment increases from zero at the molecular area  $0.6 \text{ nm}^2 \leq A \leq 0.9 \text{ nm}^2$ , up to 0.5 D per molecule, at the molecular area  $0.2 \text{ nm}^2 \leq A \leq 0.6 \text{ nm}^2$ . Physically, this means that the initial dipole moment of the 5CB molecule ( $\Delta \sim 5 \text{ D}$ ) is fully compensated, due to interactions with the water molecules, at the molecular area  $0.6 \text{ nm}^2 \leq A \leq 0.9 \text{ nm}^2$ , and that compensation increases up to 0.5 D per 5CB molecule, with a decrease of the molecular area. The values of the charge density, for example, in  $\sigma = 10^{-4} - 10^{-3} \text{ C/m}^2$  at  $T=300 \text{ K}$ , corresponds to the water surface charge density  $n_w$  in  $\sim 10^{15} - 10^{16} \text{ m}^{-2}$ . Here  $\sigma = qn_w$ , where  $q = 1.602 \times 10^{-19} \text{ C}$  is the proton charge. In the following, we use the dipole moment  $\Delta(A) \leq 0.5 \text{ D}$  per 5CB molecule on the water surface, restricted by the molecular area  $0.2 \text{ nm}^2 \leq A \leq 0.6 \text{ nm}^2$  and the value of  $\bar{\epsilon}$  which has been determined using the temperature-dependent coefficients  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$  for 5CB obtained in Ref. [20].

While values of the static constants in Eq. (12) are usually fairly easily found, the determination of the motional constant for rotational viscosity is still a formidable task. Recently, the rotational viscosity coefficient  $\gamma_1$ , has been calculated in the form [24]

$$\gamma_1 \sim \frac{\rho k_B T}{2\mathcal{G}} (1 + \nu)t_0, \quad (13)$$

where  $\rho = 1/(Ad)$  is the number density of molecules,  $k_B$  is the Boltzmann constant,  $T$  is the temperature, and  $|\nu| \ll 1$  is the small deviation of the relaxation time  $\tau_r$  from its bulk value  $t_0 = \tau_{00}^1(T)$ . The bulk relaxation time has been calculated to be equal to 28 ns ( $T=300 \text{ K}$ ) [20]. In the wide region of the molecular area  $0.2 \text{ nm}^2 \leq A \leq 0.6 \text{ nm}^2$ , which is characterized by increasing  $\Delta(A)$  up to  $\sim 0.5 \text{ D}$  per 5CB molecule, the orientational fluctuation of monolayer  $\mathcal{G} = \langle \cos^2 \theta_i \rangle - \langle \cos \theta_i \rangle^2$  on the water surface, can be calculated using the normalized equilibrium ODF [23]  $f(\cos \theta_i)$ . Combining Eqs. (12) and (13) yields the velocity of the kink spreading along the  $x$  axis in the form

$$v = \mathcal{F} \mathcal{G} / [1 + \nu], \quad (14)$$

where  $\mathcal{F} = 2\Delta(A)qn_w d / (\epsilon_0 \bar{\epsilon} k_B T t_0)$ . In the case of the 5CB monolayer film on the water surface, with charge density in  $\sigma = 10^{-3} \text{ C/m}^2$ , one obtains  $\mathcal{F} \sim 54 \mu\text{m/s}$ .

The velocity  $v$  of the solitary wave propagating along the  $x$  axis, at two different  $\nu = 0.05, 0.1$ , is shown in Fig. 4. If the solitary wave is excited by the viscous and electric torques, that solitary wave can propagate with the largest velocity up to  $25 \mu\text{m/s}$ , at least for a 5CB monolayer film on the water surface.

It should be noted that the relaxation behavior of  $\theta(\bar{x}, \tau)$  in the form of Eq. (11) assumes that the director has been initially disturbed at the left end of the monolayer film, with the condition  $\theta(0, 0) = \pi/2$ , whereas the relaxation behavior of  $\theta(\tau)$  in the form of Eq. (10) assumes that the director has been initially disturbed, with the condition  $\theta(0, \bar{x}) = \pi/2$  for  $\bar{x} \in [-\infty, +\infty]$  at any point of the monolayer film.

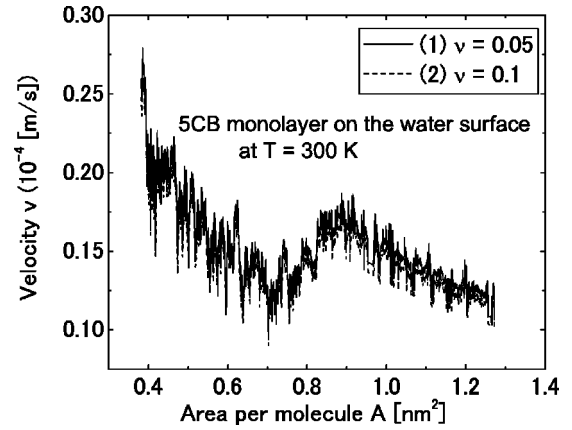


FIG. 4. Plot of the kink velocity  $v$  during compression of the 5CB monolayer at the air-water interface, calculated using Eq. (14), with the values of  $\nu = 0.05$  (curve 1) and  $0.1$  (curve 2), respectively.

#### 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  $\hat{\mathbf{n}}$  to its equilibrium orientation  $\hat{\mathbf{n}}_{eq}$ , during compression of 4-*n*-pentyl-4'-cyanobiphenyl 5CB monolayer (multilayer) films at the air-water interface is calculated using the Ericksen-Leslie theory. 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 between the electric and hydrodynamic torques exerted on the director is reflected in the growth of the time relaxation upon increasing the size of the Langmuir film. 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 and electric forces, in the multilayers LC film, leads to a dissipative process in that system, and the director, therefore, aligns under these torques perpendicular to the interface. On the other hand, in the case of the monolayer LC system, which 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 polar angle  $\theta(A, \tau)$  with respect to the normal to the interface, one deals with a twofold result. First, the viscous and electric forces exerted per unit volume of the monolayer Langmuir film vanish when the director aligns at an equilibrium angle  $\theta_{eq}$  with respect to the normal. Second, these forces may excite the solitary wave which is spreading along the air-water interface. Notes that the relaxation behavior of  $\theta(A, \tau)$  in the kink shape form probably can be observed in polarized white light. Taking into account that the director reorientation takes place in the narrow area of the LC film (the width of kink), propagating through the rectangular Langmuir film, though, the kink can be visualized in polarized white light as a dark strip, running along the air-water interface. So, a simple 2D LC model of collective tilted rod-like polar molecules hinged by their end to a water surface

allow us to determine the dimension values of both the relaxation time and the velocity of the kink solitary wave in that system.

It should be pointed out that the nematic-isotropic (NI) phase transition in the monolayer (multilayer) film on the water surface has been initiated by the lateral compression of the film, whereas the NI phase transition in the bulk of the LC sample was initiated by the temperature field. This difference originates from the symmetry of monolayers at the air-water interface, and results in the generation of the surface potential across the monolayers. The local electric field  $E_{dd}$ , due to the dipole-dipole interaction, should also be accounted for by an additional contribution to the torque balance equation. In the case of the monolayer 5CB film on the

water surface, the initial dipole moment of the 5CB molecules is compensated up to 0.5 D, and the influence of the  $E_{dd}$  can be safely disregarded, but this problem certainly deserves further investigation.

Our analysis also shows that the relatively simple molecular model in combination with the experimental data obtained with high accuracy can provide a powerful tool for investigations of both the structural and relaxation properties of real monolayer (multilayer) systems.

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