Orientational relaxation processes in Langmuir films under lateral compression

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Abstract

The orientational relaxation process of the director \( \mathbf{n} \) to its equilibrium orientation \( \mathbf{n}_{\text{eq}} \) in the Langmuir film, during the lateral compression, is investigated. The relaxation time and rotational viscosity coefficient, during compression of 4-n-pentyl-4'-cyanobiphenyl (5CB) monolayer film on the water surface has been calculated for a number of dynamic regimes. It is also shown that the viscous and electric torques exerted per unit volume of the monolayer film may excite the solitary wave propagating along the air–water interface.

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1. Introduction

In the absence of flow, the relaxation of the director \( \mathbf{n} \) to their equilibrium orientation \( \mathbf{n}_{\text{eq}} \) in the liquid crystal (LC) monolayer film at the air–water interface, during the lateral compression of the film is governed by an 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 \( \theta_{\text{eq}} \) with respect to a unit vector \( \mathbf{j} \), directed perpendicular to the air–water interface. Among the established surface measurements techniques, there are two techniques, Maxwell-displacement current (MDC) and optical second harmonic generation (SHG), that are ideally suited to retrieve information on the orientation of the interfacial region as well as identification of its symmetry [1]. One important feature of these techniques as a tool to study the relaxation process in the LC monolayer at the air–water interface is an ability to measure the order parameters (OPs) during compression of the cyanobiphenyl films [2,3]. Having obtained the set of non-normalized OPs \( S_l(A) \) and \( S_3(A) \) of the flexible amphiphilic molecules at the air–water interface, as a function of the area \( A \), derived from the MDC and SHG measurements, one can calculate the normalized equilibrium orientational distribution function (ODF) \( f(\cos \theta_i) \) of the molecules on the water surface, the normalized OPs \( \bar{P}_l = \langle P_l(\mathbf{n} \cdot \mathbf{u}_i) \rangle = \langle P_l(\cos \theta_i) \rangle \) [4], the orientational fluctuation of monolayer \( \mathcal{G} = \langle \cos^2 \theta_i \rangle - \langle \cos \theta_i \rangle^2 \) on the water surface, and the orientational relaxation time in the LC monolayer system, during the lateral compression of the film. Here, \( P_l \) are the Legendre polynomials of rank \( l \), \( \theta_i \) is the polar angle between the long axis \( \mathbf{u}_i \) of the molecule \( i \), and the nematic director \( \mathbf{n} = \langle \mathbf{u}_i \rangle \), and \( \langle \ldots \rangle \) denotes the statistical–mechanical average. In this paper, I attempt to answer the question of how the electric and hydrodynamic forces affect the orientational relaxation process of the director in the LC monolayer film on the water surface during the lateral compression of the film.

The outline of this article is as follows: a dynamic equation describing the reorientation of a liquid crystalline monolayer film on the water surface, in absence of flow, is given in Section 2. Numerical results for number of relaxation regimes are also given in Section 2. Conclusions are summarized in Section 3.

2. Formulation of the dynamic equation for monolayer film at the air–water interface

The dynamic equation describing the reorientation of a LC monolayer film on the water surface, in absence of flow, can be derived from the balance of viscous and electric torques as [5,6]

\[
T_{\text{vis}} + T_{\text{el}} + T_{\text{pol}} = 0.
\] (1)
In the case of planar geometry, \( \hat{n} = \sin \theta \hat{i} + \cos \theta \hat{j} \) and the absence of flow, the viscous torque takes the form 

\[
T_{\text{vis}} = -\gamma_{v} \hat{n} \times \dot{\hat{n}} = \gamma_{v} \hat{n} \frac{\partial}{\partial t} \hat{n}.
\]

Here \( \theta(x,t) \) denotes the polar angle, i.e., the angle between the direction of the unit vector \( \hat{n} \) (directed perpendicular to the air–water interface) and the director \( \hat{n} \), \( \dot{\theta}(x,t) = \theta(x,t)/\partial t \) and \( \gamma_{v} \) is the rotational viscosity coefficient (RVC). The unit vector \( \hat{i} \) is directed to be parallel to the air–water interface, \( y \) is the distance away from the air–water interface in the \( \hat{j} \) direction, and \( \hat{k} = \hat{i} \times \hat{j} \). The torque due to electric field \( \mathbf{E} \), for instance, originating from the water surface charge density \( \sigma \), is given by 

\[
T_{\text{el}} = \epsilon_{0} \hat{n} \times \mathbf{E} = \frac{\mathbf{E} \times \hat{n}}{\epsilon_{0}},
\]

where \( \mathbf{E} = E \hat{j} = (\sigma / \epsilon_{0} \varepsilon) \hat{j} \) is the surface electric field of the charged water surface. Here, \( \epsilon_{0} \) is the dielectric permittivity of free space, \( \varepsilon = \epsilon_{||} + 2 \epsilon_{\perp} \) is the average dielectric permittivity, \( \epsilon_{||} \) and \( \epsilon_{\perp} \) are the dielectric constants parallel and perpendicular to the director \( \hat{n} \). The torque due to spontaneous polarization is 

\[
T_{\text{pol}} = \mathbf{P} \times \mathbf{E} = PE \sin(\theta(x,t)) \hat{k}.
\]

In the case of two-dimensional system, where the molecules of Langmuir film align tilt relative to the unit vector \( \hat{n} \), thereby defining an array of unit vectors \( \hat{n} \), in the plane \( x-y \) of the film, the balance of the torques can be written as 

\[
\gamma_{v} \frac{\partial}{\partial t} \theta(x,t) + \frac{E^{2}}{2} \epsilon_{0} \epsilon_{||} \sin 2\theta(x,t) + PE \sin \theta(x,t) = 0.
\]

It allows us to rewrite the last equation in a dimensionless form as 

\[
\frac{\partial}{\partial t} \theta(x,t) = -\sin \theta(x,t) - \sin 2\theta(x,t),
\]

where \( \partial_{t} \theta(x,t) = \partial \theta(x,t)/\partial t \) is the dimensionless time, \( x = x/d \) is the dimensionless distance along the air–water interface, \( \partial = \epsilon_{||} \epsilon_{\perp} \varepsilon / 2P \) is the parameter of the system, which in the following is to be considered as a positive constant, and \( d \) is the size of the LC monolayer.

### 2.1. Case of \( \delta \ll 1 \)

In this case, the electric torque can be safely disregarded \( (E \ll P) \) and the relaxation of the director to its equilibrium orientation in the LC monolayer film at the air–water interface is governed by the polarization and viscous forces, and one can determine a solution of Eq. (3) \( (\delta \ll 1) \) in the form 

\[
\theta(t) = 2\tan^{-1} [\exp(-t)] + \theta_{\text{eq}},
\]

where \( \theta_{\text{eq}} \) is the equilibrium value of the angle \( \theta(t) \) at a particular temperature and molecular area \( A \), which determine the equilibrium orientation of the director in the LC monolayer film. It should be noted here that the equilibrium value of the angle \( \theta_{\text{eq}}(A) \) can be determined as 

\[
\theta_{\text{eq}}(A) = \cos^{-1} \left( \frac{d(A)}{l} \right)
\]

where \( l \) is the length of the LC molecule and \( d(A) \) is the thickness of the LC monolayer film. In turn, the magnitude of \( d(A) \) can be determined, for instance, by using the X-ray diffraction measurements [1].

But there is another exact solution of Eq. (3) \( (\delta \ll 1) \) [6],

\[
\theta(x,t) = \tan^{-1} \left[ 1/\sinh(\sqrt{v}t - x + \theta_{0}) \right],
\]

where \( \theta_{0} \) is a constant. Solution (5) describes the solitary kink \( \theta(x,t) \), which is spreading along the \( x \)-axis with the velocity

\[
v = PE \frac{d}{\gamma_{s}}.
\]

Physically, this means that the film has initially 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 \( v \). In the case of the monolayer film 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, I use the molecular model of collective tilted rodlike polar molecules hinged by their ends to a water surface and separated by a certain distance each other. In the wide range of the molecular area, the MDC signals allows us to determine the dipole moment \( \Delta(A) \) of the cyanobiphenyl molecule at the air–water interface. It has been found from the MDC measurements [2,3], that with decreasing of the molecular area, the dipole moment of 4-n-pentyl-4’-cyanobiphenyl (5CB) increases from zero, at the molecular area 0.6 nm\(^2\) \( \leq A \leq 0.9 \) nm\(^2\), up to 0.5D per molecule, at the molecular area 0.2 nm\(^2\) \( \leq A \leq 0.6 \) nm\(^2\) (see, for instance, Ref. [2] Fig. 4). Physically, this means that the initial dipole moment of the 5CB molecule \( (A \sim 5D) \) is fully compensated, due to interactions with the water molecules, at the molecular area 0.6 nm\(^2\) \( \leq A \leq 0.9 \) nm\(^2\), and that compensation is decreased up to 0.5D per 5CB molecule, with decreasing molecular area.

That experimental observation 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 the hydrophilic tails are directed away from the water surface, I use the molecular model of collective tilted rodlike polar molecules hinged by their ends to a water surface and separated by a certain distance each other. In the wide range of the molecular area, the MDC signals allows us to determine the dipole moment \( \Delta(A) \) of the cyanobiphenyl molecule at the air–water interface, and the velocity takes the form

\[
v = PE \frac{d}{\gamma_{s}} = \sigma \frac{\Delta(A)}{\epsilon_{0} \epsilon_{||} A \gamma_{s}}.
\]

Here \( \sigma = q n_{w} \), where \( q = 1.602 \times 10^{-19} \) C is the proton charge, and \( n_{w} \) is the water surface charge density. The values of the charge density, for example, in \( \sigma = 10^{-3} \) C/m\(^2\) at \( T = 300 \) K, correspond to the water surface density \( n_{w} \sim 1.6 \times 10^{16} \) m\(^{-2}\), which agrees with experimental values \( \sim 10^{15} - 10^{16} \) m\(^{-2}\) [7]. While values of the static constants in Eq. (7) are usually fairly easily found, the determination of the motional constant for rotational viscosity is still a formidable task. Recently, the rotational viscosity coefficient \( \gamma_{s} \) has been calculated in the form [5]
where $\mathcal{B} = \frac{k_B T_0}{\hbar}$, $k_B$ is the Boltzmann constant, $T$ is the temperature, and $|v| \ll 1$ is the small deviation of the relaxation time $\tau = t_0 (1 + v)$ from its bulk value $t_0 = \tau_0^{-1}$. Here $v = \Delta \tau / t_0$, and $\Delta \tau$ is the small correction of the $t_0$ due to interaction between molecules of LC monolayer film and the water surface. The bulk relaxation time has been calculated to be equal to 28 ns ($T = 300$ K) [8]. 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 of $\Lambda(A)$ up to $\sim 0.5D$ per SCB molecule, the orientational fluctuation of monolayer $G(A) = \langle \cos^2 \theta_i(A) \rangle - \langle \cos \theta_i(A) \rangle^2$ on the water surface, can be calculated using the normalized equilibrium ODF [4] $f(\cos \theta_i)$. Having obtained the set of non-normalized OPs, obtained from MDC and SHG measurements in monolayer film on the water surface, during compression of the film [2–4], one can calculate the normalized equilibrium ODF $f(\cos \theta_i)$ of the molecules on the water surface as [4]

$$
\begin{align*}
\mathcal{P}(t) = \frac{1}{4\pi} \sum_{i=0}^{\infty} \frac{2i+1}{2} \mathcal{P}_i(\cos \theta_i),
\end{align*}
$$

(9)

where $\theta_i$ is the polar angle of the unit vector $\hat{u}_i$ along the molecular symmetry axis. The normalized OPs can be written as [4] $\mathcal{P}_i = \int_{-\infty}^{\infty} \mathcal{P}_i(x)\mathcal{f}(x)dx/\int_{-\infty}^{\infty} \mathcal{f}(x)dx$, where the function $f(x)$ as in Eq. (9), but with the non-normalized OPs, $i=1,3$, and $\mathcal{P}_1(x) = \left\{ \begin{array}{ll} x & i = 1, \\ \frac{1}{2} (5x^3 - 3x) & i = 3. \end{array} \right.$

Fig. 1 shows the normalized OPs $\mathcal{P}_1(A)$ and $\mathcal{P}_3(A)$ as function of the molecular area.

Combining Eqs. (7) and (8) yields the velocity of the kink spreading along the $x$ axis in the form

$$
\begin{align*}
\psi(a) = \mathcal{F}(A) \frac{\mathcal{G}(A)}{1 + \nu} \sigma,
\end{align*}
$$

(10)

where $\mathcal{F}(A) = 2\Lambda(A)d/(\varepsilon_0 k_B T_0)$. In the case of SCB monolayer film on the water surface, with charge density in $\sigma = 10^{-3} \text{ [C/m}^2\text{]},$ one obtains $\mathcal{F} \sigma \sim 54 \mu \text{m/s}$. The magnitude of the velocity $\nu$ of the solitary wave propagating along the $x$-axis, at two different $\nu = 0.05, 0.1$, is shown in Fig. 2.

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 SCB monolayer film on the water surface and the magnitude of the solitary wave velocity is proportional to the strength of the electric field, originating from the water surface charge density $\sigma$.

It should be noted out that the relaxation behavior of $\theta(x, t)$ in the form of Eq. (5) assumes that the director has been initially disturbed at the left end of the monolayer film, with the condition $\theta(x,0)$, whereas the relaxation behavior of $\theta(t)$ in the form of Eq. (4) assumes that the director has been initially disturbed, with the condition $\theta(0, x) = \pi/2$ for $x \in [-\infty, \infty]$, at any point of the monolayer film.

2.2. Case of $\delta < 1/2$

In this case, the relaxation of the director $\hat{n}$ to its equilibrium orientation $\hat{n}_\text{eq}$ in the LC film at the air–water interface, is governed by the viscous and electric forces, and one can determine a solution of Eq. (3) in the form

$$
\begin{align*}
- \int \frac{d\theta}{\sin \theta + \delta \sin 2\theta} = \tau + \tau_0,
\end{align*}
$$

(11)

here $\tau_0$ can be chosen from the value $\theta(\tau \rightarrow \infty) = \theta_\text{eq}$, where $\theta_\text{eq}$ is the equilibrium value of the angle $\theta(t)$ at a particular temperature and area $A$, which determine the equilibrium orientation of the director in the LC film.

In the case $\delta < 1/2$, i.e., $\varepsilon_0 \epsilon \kappa < P$, which implies that the torque on the director due to polarization forces prevails over torque due to electric forces, Eq. (11) gives the solution [9]

$$
\begin{align*}
\tau - \tau_0 = \ln \tan \frac{\theta}{2} - \frac{4\delta}{(1 - 4\delta^2)^{1/2}} \tan^{-1} \left[ \tan \frac{\theta}{2} + 2\delta \left( 1 - 4\delta^2 \right)^{1/2} \right],
\end{align*}
$$

(12)
whereas in the case $\delta > 1/2$, i.e., $\epsilon_0\epsilon_r E > P$, which implies that the torque on the director due to electric forces prevails over torque due to polar forces, Eq. (11) gives the solution [9]

$$
\tau - \tau_0 = \ln \frac{\tan \frac{\theta}{2}}{\tan \frac{\theta}{2} + 2\delta - (4\delta^2 - 1)^{1/2}} \times \ln \frac{\tan \frac{\theta}{2} + 2\delta - (4\delta^2 - 1)^{1/2}}{\tan \frac{\theta}{2} + 2\delta + (4\delta^2 - 1)^{1/2}}.
$$

(13)

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

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

(14)

In the case $\delta > 1$, i.e., $\epsilon_0\epsilon_r E > P$, which implies that the electric torque prevails over torque due to the polarization forces, and the relaxation of the director $\hat{n}$ to its equilibrium position $\hat{n}_{eq}$ in the LC monolayer film is governed by only the electric forces, and one may determine a solution of Eq. (11) in the form

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

(15)

In the case of 5CB monolayer film on the water surface, with the charge density in $\sigma = 10^{-3}$ C/m$^2$, one obtains the $\delta$ to be equal $\delta = \epsilon_0\epsilon_r E/(2P_s) \sim 1.08[4]$. So, finally, one has a different relaxation processes, which can be determined by Eqs. (12)–(14), in three different molecular areas: 0.2 nm$^2 < A < 0.463$ nm$^2$ ($\delta < 1/2$), $A = 0.463$ nm$^2$ ($\delta = 1/2$), and $0.463$ nm$^2 < A < 0.6$ nm$^2$ ($\delta > 1/2$), respectively. The relaxation behavior of $\theta(\tau)$ ($\tau = tP/s_1$) has been studied and found that the dimensionless relaxation time decrease with increasing $\delta$, i.e., with increasing electric forces: from 12, for $\delta < 1/2$, to 6, for both $\delta > 1/2$ and $\delta > 1$. The dimension value of the orientational relaxation time $\tau$ of the director to the equilibrium orientation can be written as

$$
t_A(\tau) = \frac{\gamma_A d_0 \epsilon_0 E}{\sigma A(A)} = \tau = \frac{\mathcal{L}(A)}{\mathcal{G}(A)} \frac{1 + v}{\sigma - \tau},
$$

where $\mathcal{L}(A) = \frac{2}{2} \frac{d_0}{d_1} t_0$. The orientational relaxation time $\tau$ of the director to the equilibrium orientation, as a function of the molecular area $A$, at two different $v = 0.05, 0.1$, are shown in Fig. 3.

In the case of 5CB monolayer film on the water surface, the electric and viscous torques puts the director into the equilibrium orientation with different relaxation times, which increase with increasing $v$, up to 0.7 ms. It is important to stress that the inclusion of the surface electric field, originating from the water surface charge density $\sigma$, has an important influence on the relaxation time.

3. Conclusion

In this paper, I investigate the orientational relaxation process in the organic LC monolayer film on the water surface, during the lateral compression. In the case of the monolayer system, 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 of 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. Note 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, 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 rodlike polar molecules hinged by their end to a water surface allows us to determine the dimension values of both the relaxation time and velocity of the kink solitary wave in that system. It is important to stress that the inclusion of the surface electric field, originating from the water surface charge density, has an important influence both on the relaxation time and velocity of the solitary wave spreading on the water surface. A balance between the frictional and electric torques exerted on the director is reflected in a linear growth of the velocity $v$ and an inversely proportional decrease of the relaxation time upon increasing the strength of the electric field.

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