Photo-induced travelling waves in condensed Langmuir monolayers

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New Journal of Physics 5 (2003) 65.1–65.11 (http://www.njp.org/)
Received 17 March 2003
Published 6 June 2003

Abstract. We report the detailed properties of photo-induced travelling waves in liquid crystalline Langmuir monolayers composed of azobenzene derivatives. When the monolayer, in which the constituent rodlike molecules are coherently tilted from the layer normal, is weakly illuminated to undergo the trans–cis photo-isomerization, spatio-temporal periodic oscillations of the molecular azimuth begin over the entire excited area and propagate as a two-dimensional orientational wave. The wave formation takes place only when the film is formed at an asymmetric interface with broken up–down symmetry and when the chromophores are continuously excited near the long-wavelength edge of absorption to induce repeated photo-isomerizations between the trans and cis forms. Under proper illumination conditions, Langmuir monolayers composed of a wide variety of azobenzene derivatives have been confirmed to exhibit similar travelling waves with velocity proportional to the excitation power irrespective of the degree of amphiphilicity. The dynamics can be qualitatively explained by the modified reaction–diffusion model proposed by Reigada, Sagués and Mikhailov.
1. Introduction

Non-equilibrium dynamic patterns are observable in a wide range of systems such as ordinary fluids [1], semiconductors [2] and chemical reaction systems both in solutions and on solid surfaces [3, 4]. Even though the specific physics underlying these dynamical behaviours are different from one system to the other, they are commonly described by the reaction–diffusion models [5], in which the densities of the reactants are low enough for the particle–particle interaction to be neglected [6]. In contrast to these classical systems, the travelling waves we found in photo-excitable condensed Langmuir monolayers [7] appear quite unique in the sense that the short-range molecular interaction should play an indispensable role in the process of the pattern formation. Soft condensed matter such as polymers, gels, liquid crystals (LCs) and lipid membranes is known to exhibit a variety of self-organized static structures [8], but its dynamic patterns, caused by energy (or mass) dissipation at a state far from equilibrium, have rarely been studied because of their complexity.

In a previous paper [7], we reported the first observation of photo-induced travelling waves in condensed Langmuir monolayers. We showed that the wave formation originates from the molecular photo-isomerization and occurs only by a linearly polarized illumination with the wavelength around 500 nm, i.e. at the long-wavelength edge of absorption. The monolayer must be in the two-dimensional (2D) fluidic LC phase, and the propagation direction undergoes a complete reversal when the polarization of illumination is switched by 90°. The last property, in particular, strongly suggests an intimate connection between the LC order and the wave generation; but no satisfactory explanation has ever been given.

In this paper, we describe the results of more detailed investigation of the wave generation in liquid crystalline Langmuir monolayers with a view to providing an elaborated basis for further understanding of the phenomenon. Dependences of the wave generation and propagation on the excitation power, symmetry condition, temperature and molecular density are elucidated for both amphiphilic and hydrophobic azobenzene compounds by using a homemade simultaneous microscope which is capable of separately detecting the tilt and the azimuthal components of the molecular orientation.
2. Materials and methods

Figure 1 shows the azobenzene derivatives that we synthesized and mainly used in the experiment. On the pure water surface, all these compounds can form softly condensed monolayers independently of their amphiphilicity [9]. As shown in figure 2, both amphiphilic and hydrophobic compounds exhibit smooth isotherms, in which LC phase exists in the wide intermediate regions of area per molecule. Note that the hydrophobic compounds develop a much lower surface pressure compared to their amphiphilic counterparts, although they still form equally stable condensed monolayers. Here, the rodlike molecules (the trans state) are tilted from the layer normal with the long-range orientational order in the azimuth direction along with the fluidic positional packing. This state corresponds to the 2D smectic-C LC phase or polar nematic phase [7, 10]. The full characterization of the orientation states requires the knowledge of both the tilt angle $\beta$ and the tilt azimuth $\alpha$. For simultaneous observation of $\beta$ and $\alpha$, we built a double-beam simultaneous polarizing microscope: one linearly polarized beam for visualizing the molecular azimuth $\alpha$ and the other circularly polarized beam for preferentially displaying the distribution of tilt angle $\beta$ [11]. For the former purpose, p-polarized light from a semiconductor laser (670 nm wavelength, 20 mW) is obliquely incident onto the sample on water and the depolarized reflection is detected by CCD camera through the analyser set in the s-direction. For tilt angle observation, clockwise circularly polarized light from a He–Ne laser (633 nm wavelength, 10 mW) is quasi-normally incident onto the film and the oppositely circularly polarized reflection is detected through the circular analyser consisting of a quarter waveplate and Glan–Tompson prism [11]. The output intensities for these configurations, $I_L$ for the linearly polarized light and $I_C$ for the circularly polarized light, are respectively given by [11, 12]

$$I_L = h_1^2(\cos\alpha - f)^2 \sin^2\alpha \sin^2\beta$$
$$I_C = h_2^2 \sin^4\beta,$$

where $h_1$ and $h_2$ are constants, $\theta_t$ is the angle of incidence, and $n_0$ and $n_1$ are the refractive indices of the substrate and the film, respectively. The factors $f = \frac{n_0^2 \tan\theta_t}{n_1^2 \tan\beta}$ are determined experimentally.

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Figure 2. Surface pressure ($\pi$) versus area per molecule ($A$) isotherms of (a) 8ABO5COOH at 25°C and (b) 8ABO6 at 38°C on a water surface. In (a), the 8ABO5COOH film is in the uniform smectic-C phase at $0.31 \text{ nm}^2 \leq A \leq 0.40 \text{ nm}^2$, while it takes the 2D solid-like phase at $A < 0.28 \text{ nm}^2$. In (b), the 8ABO6 film is in the smectic-C phase at $0.20 \text{ nm}^2 < A < 0.35 \text{ nm}^2$, and bulky domains appear at $A < 0.20 \text{ nm}^2$. The different behaviour of the isotherm should be ascribed to the amphiphilicity (see [9]). Amphiphilic compounds 1–4 in figure 1 show isotherms like (a), and dialkylated compounds 5–8 exhibit isotherms similar to (b). The whole experiment was performed in the smectic-C phase: around $A = 0.35 \text{ nm}^2$ for 8ABO5COOH and $A = 0.30 \text{ nm}^2$ for 8ABO6 monolayers, respectively.

Figure 3. The images of tilt (left) and azimuth (right) at exactly the same area in the illuminated Langmuir monolayer composed of 8ABO5COOH, which are taken under the circularly and linearly polarized microscopes, respectively. The scale is given by the white bar of 100 $\mu$m in the tilt image. (See the dynamics in the accompanying movie.)

where $n$ and $\theta_t$ are the refractive index of and the angle of refraction in water, $n_0$ is the ordinary refractive index of the optically uniaxial Langmuir monolayer and $h_1$ and $h_2$ are the Fresnel factors [12]. For excitation of the photo-isomerization, the second harmonic of linearly polarized light from Cd:YAG laser at 532 nm wavelength was normally incident onto the film. The experiment was performed at 25°C unless otherwise mentioned.

Also for the purpose of comparison, we examined freely suspended smectic-C films [13] composed of the same azobenzene derivatives. The thin films were held over a square hole...
formed through a 50 µm thick stainless steel sheet with a changeable area; these films are in a layered structure suspended freely in air just like a soap film. The freely suspended films of a few molecular layers should possess both two-dimensionality and mirror symmetry with regard to the layer plane. We could control the film thickness down to this regime by continuously enlarging the film area. The illuminated free-standing films were observed by the same polarizing microscope as used for the Langmuir films.

3. Result

Here we describe the results in detail with a focus on

(1) whether the tilt angle or the tilt azimuth is the primary carrier of the travelling wave,
(2) what are the conditions of wave generation and
(3) how the wave velocity depends on such parameters as the excitation power.

3.1. Nature of the travelling wave: oscillation of molecular azimuth

By using the simultaneous microscope, we observed the dynamics of the azimuthal angle (given by equation (1)) and the tilt angle (equation (2)) under photo-excitation. The monolayer was uniformly illuminated by the linearly polarized light over an area much bigger than the microscope field of view. Figure 3 gives the typical tilt and azimuth images of the illuminated 8ABO5COOH monolayers, and corresponding to this Fig3.mpg shows their dynamic behaviour. In this animation, we see the travelling wave only on the azimuth (right) associated with the continuous domain growth and propagation from the right to the left of the view, and virtually no sign of the wave was visible on the tilt (left). We studied previously the static stripe textures in detail in terms of the participation of both tilt and azimuthal components, indicating that there exists a strong coupling between these two degrees of freedom in the same Langmuir monolayers [11]. Unlike this static stripe, however, the present result unambiguously reveals that the tilt angle makes no contribution to the dynamic pattern formation. We also examined the other compounds in figure 1 and obtained qualitatively similar results that the travelling waves were associated only with the molecular azimuth variation. By the analysis based on equation (1)
with the fixed tilt angle, the azimuth was found to regularly repeat the pendulum motion with the amplitude of 30°–120° from the surroundings, and the motion continued with a constant rhythm as long as the illumination lasted. In our first report [7], we had circumstantially concluded without the direct tilt image that the wave is of tilt origin, which has to be corrected as mentioned above.

3.2. Conditions of the wave generation: 1. Symmetry

The air–water interface does not have up–down symmetry, and it has been previously shown that the spontaneous formation of the static orientational stripes is essentially connected with this asymmetry of the interface. Is it also essential for the photo-induced wave generation? The following experimental results show that this is likely to be the case.

We prepared few-molecular-layer-thick freely suspended films of the same compounds. The thin films suspended in air have the up–down mirror symmetry. Figure 4 shows the behaviour of a five-molecular-layer-thick film of 8ABO6 (see figure 1) under linearly polarized illumination. Although the photo-excitation agitated the film, the induced motions appeared largely random, more fluidic than orientational, and never developed into coherent waves as we see in the Langmuir monolayers. Even when the film thickness was decreased down to a bilayer\(^3\), the behaviour remained essentially the same. It is interesting to note that a similar random behaviour has also been observed in the Langmuir monolayers when the excitation was made either by circularly polarized or non-polarized light. Also taking into account the fact that we could observe the orientational waves even in multilayer Langmuir films, these observations of the suspended films suggest that the up–down asymmetry must be an essential ingredient of the coherent wave generation. The coupling between the broken up–down and in-plane symmetry and the polarization of excitation light must be playing a decisive role in developing the coherent motion.

3.3. Conditions of the wave generation: 2. Density of the excited molecules

As mentioned at the beginning, the coherent wave generation can occur only when the wavelength of the excitation light is so chosen as to meet the absorption edge of azobenzene. This means that during the wave propagation, the average fraction of the \textit{cis}-isomer must be kept at a few per cent, while more than 95% of molecules should be in the \textit{trans} state. Since photo-kinetics dictates the temporal probability by which one molecule is found in the \textit{trans} or \textit{cis} form, it does not mean that only a small group of molecules contributes to the wave generation, but means that every single molecule should participate in the wave by spending a few per cent of its time in the \textit{cis} form, transforming itself back and forth between the \textit{trans} and \textit{cis} isomers. The following experiments conducted on mixtures substantiate this picture.

The binary mixtures of one of the azobenzene compounds in figure 1 and a photo-inactive additive, 5-\textit{n}-octyl-2-(4-\textit{n}-hexyloxyphenyl)pyrimidine (hereafter referred to as P608), were prepared at various ratios, and examined on the water surface under illumination\(^4\). P608 has a roughly identical molecular shape with azobenzene derivatives and forms by itself a stable liquid

\(^3\) Unlike the Langmuir films, it is impossible to make a stable monolayer in the free-standing films, and the minimum obtainable thickness is a bilayer.

\(^4\) Fortunately, the azobenzene derivatives and P608 compounds are completely miscible on the scale of visible light wavelength.
crystalline Langmuir monolayer at room temperature. In monolayers composed of a mixture with the mole fraction of less than 10% azobenzene, no dynamical behaviour was observed even under strong excitations at over ten times higher power than that used for neat azobenzene monolayers. When the azobenzene ratio was increased to more than 20%, the embryos of the waves became noticeable, which, however, could not propagate over a long distance. Figure 5 shows the dynamics of the illuminated monolayer composed of 8ABO6 and P6O8 mixed at 1:1 mole fraction. The excited domains showed up all over the illuminated area, but they could propagate only a short distance before they disappeared. Increasing the excitation power does not alleviate the poor propagation. We then gradually decreased the fraction of the photo-inactive component and found that, only below 10%, the travelling waves could emerge. Even above 10%, the additional component had little influence on the monolayer properties; nevertheless, it effectively disrupted the wave propagation. These findings suggest the significance of proximity interaction between photoactive molecules in generating the travelling orientational waves. The 2D LC monolayers bear inherently strong orientational fluctuations, which are immediately manifest under the polarizing microscope. The photo-induced trans–cis isomerization may enhance a certain mode of orientational fluctuations that would grow into the collective rotation of the azimuth.

3.4. Wave properties: velocity versus excitation power

Along with the polarization and wavelength, the intensity of the excitation light also significantly affects the properties of the travelling wave. Figure 6 shows the waves excited at relatively low and high excitation powers, exhibiting a marked increase of the wave velocity with the excitation power. A systematic investigation utilizing a fast image analysis revealed a quasi-linear dependence of the phase velocity of the wave on the excitation power as shown in figure 7. In terms of the frequency $\nu$ and the wavelength $\lambda$, the phase velocity is written as their product, $v = \lambda \nu$. We found a weak power dependence of the wavelength showing a twofold reduction on the order of 10 $\mu$m associated with one order of increase in power from $I = 15$ to 150 mW cm$^{-2}$; consequently, the frequency underwent a 20-fold increase. The same line of behaviours was
Figure 6. The dynamics observed in 8ABO6 Langmuir monolayers when illuminated at the power of (a) $I = 20\ \text{mW cm}^{-2}$ (movie1) and (b) $I = 150\ \text{mW cm}^{-2}$ (movie2). The film is identical but the observation area is different.

obtained for all other compounds in figure 1, although the appropriate power for wave generation was slightly varied in each case$^5$.

Inasmuch as the thermal conversions are negligible, the photo-chemical rate equation for azobenzenes can be written as follows $[14, 15]$:

$$\frac{\partial c_{\text{cis}}}{\partial t} = k_{t \rightarrow c} c_{\text{trans}} - k_{c \rightarrow t} c_{\text{cis}} \quad (3)$$

$$\frac{\partial c_{\text{trans}}}{\partial t} = k_{c \rightarrow t} c_{\text{cis}} - k_{t \rightarrow c} c_{\text{trans}} \quad (4)$$

where $c_{\text{cis}}$ and $c_{\text{trans}}$ are the fraction of the $\text{cis}$ and the $\text{trans}$ isomers, respectively, which satisfy $c_{\text{cis}} + c_{\text{trans}} = 1$, and $k_{t \rightarrow c}$ and $k_{c \rightarrow t}$ are the rate constants for the $\text{trans}$-to-$\text{cis}$ and $\text{cis}$-to-$\text{trans}$ transformation $[15]$, which are proportional to the light intensity. In the steady state under uniform illumination, the fractions of $\text{trans}$ and $\text{cis}$ isomers are determined only by the ratio, $k_{\text{trans}}/k_{\text{cis}}$.

$^5$ Azobenzene molecules with various end-groups have different stabilities in the Langmuir monolayer state under illumination. When the excitation power is increased, the amphiphilic molecules such as 8ABO5COOH firstly increase the wave velocity linearly with the power and then, above a certain threshold, break into a granular structure losing the LC order, while the non-amphiphiles with long alkyl chains such as 8ABO6 continue the linear relation up to higher power than 200 mW cm$^{-2}$ as shown in figure 5. On the other hand, non-amphiphiles with short chain length like 4ABO1 in figure 1 show the linear relation only when the power is low, for instance lower than 0.1 mW cm$^{-2}$ in the case of 4ABO1, and they stand up normally to the surface under high excitation. The region in which the wave velocity is proportional to the excitation power varies in the azobenzene compounds with different structures.
that is a function of the wavelength only. The fraction actually determines the probability that one particular molecule is found in either the cis or the trans form as it is monitored over a long enough time. In contrast, the rates of conversion from the trans to cis and vice versa increases linearly with the excitation power.

Our observation of the power dependent behaviour is a clear indicative of the fact that the conversion dynamics is essential in generating the waves; this is consistent with the observation that the waves never be generated under ultraviolet light illumination no matter how carefully the intensity has been controlled. The specific dependences of $v$, $\nu$ and $\lambda$ on the power are hard to explain based on the simple rate equation as above which neglects the coupling between photo-excitation and the liquid crystalline order. In the simplest extension into the diffusion–reaction scheme that transforms the rate equations as

$$\frac{\partial c_{cis}}{\partial t} = D_{cis} \frac{\partial^2 c_{cis}}{\partial x^2} + k_{t\rightarrow c} c_{trans} - k_{c\rightarrow t} c_{cis}$$

(5)

$$\frac{\partial c_{trans}}{\partial t} = D_{trans} \frac{\partial^2 c_{trans}}{\partial x^2} + k_{c\rightarrow t} c_{cis} - k_{t\rightarrow c} c_{trans}$$

(6)

with $D_{cis}$ and $D_{trans}$ being the diffusion constants, we anticipate that the scaling relations such as $t \propto I^{1/2}$ and $x \propto I^{1/2}$ should hold. This scaling, which is also compatible with the Ginzburg–Landau equation describing the dynamics of the orientation variables [7], yields that $\lambda \propto I^{-1/2}$, $v \propto I$ and $\nu \propto I^{1/2}$. In comparison with the present observations, this is obviously too weak a dependence on the excitation power, implying the active role played by other factors such as the LC ordering.

3.5. Wave properties: velocity versus temperature

It should be natural to expect that the wave properties be strongly dependent on temperature through the rotational viscosity and rate constants. As shown in figure 8, indeed, even a small temperature rise\(^6\) causes a significant increase of the wave velocity. The activation energy of

\(^6\) Since the monolayer must be deeply inside the smectic-C phase, the temperature cannot be changed much. The temperature region in figure 8 corresponds to the smectic-C phase far from the phase transition temperature.
Figure 8. The temperature dependence of wave velocity. The filled circles are experimental data for illuminated 8ABO5COOH Langmuir by 532 nm wavelength linearly polarized light at 1 mW cm\(^{-2}\). The solid curve indicates the fitted curve based on the equation \(v = C \exp\left(-\frac{E_a}{RT}\right)\) with the parameters of \(C = 6.8 \times 10^{10} \mu\text{m s}^{-1}\) and \(E_a = 56 \text{ kJ mol}^{-1}\).

4. Discussion and conclusion

Recently, Reigada et al [16] formulated a theoretical model to describe the dynamic pattern formation in condensed Langmuir monolayers. Their model is based on the combination of the usual reaction–diffusion equation coupled with the photo-orientational kinetics, and was able to qualitatively reproduce the wave generation inside an appropriate parameter range. The crucial point of the model is the introduction of a new kinetic term taking care of the orientational relaxation after the molecule is transformed from the orientationally disordered cis-form to the ordered trans-form. Although the model appears quite promising, they did not take direct account of the anisotropy of photo-excitation and hence cannot tackle such a significant phenomenon as the reversal of wave propagation in response to 90\(^\circ\) rotation of the polarization. Given the initial success of their model clearly indicating the possibility of wave generation in monolayers, however, we expect that this model should serve as a basis for full description of the travelling waves in the condensed Langmuir monolayers.

In summary, we have described the properties of the photo-induced travelling waves in liquid crystalline Langmuir monolayers of azobenzene derivatives. The waves are associated with the periodic rotation of the molecular azimuth, not accompanied by tilt oscillation. For the waves to propagate over a long distance, the constituent molecules must be dynamically excited to undergo frequent structural changes between the trans and cis states while keeping the average cis ratio at a few per cent. In the determination of the wave direction, the coupling of the excitation anisotropy and the broken symmetry with regard to the film plane should play a principal role, without either of which the embryo of the waves cannot propagate in any
The velocity of the wave shows linear dependence on both the rate constants of the photo-isomerization and the rotational viscosity of the molecular azimuth in the LC monolayer state. In the previous report, we had regarded the isomerization effect as just a perturbation that slightly modified the free energy equation of the system, which could not reproduce the observed dynamics. The result shows that individual molecular motion is directly involved in the wave propagation and therefore the dynamic equation must include the photo-isomerization effect not just as a perturbation but as a direct driving force. Although the gap has not been completely filled between the molecular motion and the macroscopic waves, the recently proposed model of Reigada, Sagués and Mikhailov should be a good starting point for elucidating the whole picture of the dynamic patterns in LC Langmuir monolayers.

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