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Generation, propagation, and switching of orientational waves in photoexcited liquid-crystalline monolayers

Tohru Okuzono,[1] Yuka Tabe,[1,2] and Hiroshi Yokoyama[1,2]
[1]*Yokoyama Nano-structured Liquid Crystal Project, ERATO, Japan Science and Technology Agency, 5-9-9 Tokodai, Tsukuba 300-2635, Japan*
[2]*Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan*
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Photoinduced orientational waves in illuminated liquid-crystalline monolayers is one of the most remarkable far-from-equilibrium phenomena that systems of soft condensed matter exhibit. We model this behavior from a phenomenological point of view, taking the anisotropic photoexcitation of molecules into account. Numerical simulations as well as theoretical analyses of the model reveal that the intricate interplay between the spontaneous splay deformation of the liquid-crystalline order and the anisotropy of the photoexcitation can lead to the generation and propagation of orientational waves. The model can explain all the salient features of the phenomenon—in particular, the anomalous reversal of the propagation direction upon 90° rotation of the polarization direction of illumination, which evaded theoretical explanation for nearly a decade.

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Nonequilibrium structure formation in soft condensed matter is one of the most fascinating problems in a cross-disciplinary field among physics, material science, and biology [1]. The orientational waves discovered in illuminated liquid-crystalline Langmuir monolayers [1–3] are such structures occurring in a system which is physically well characterized and controllable.

Langmuir monolayers are insoluble monomolecular films formed at the air-water interface which exhibit a rich variety of self-organized structures [4]. Certain azobenzene derivatives, indeed, are known to develop two-dimensional (2D) "smectic-*C*" liquid-crystalline Langmuir monolayers at moderate surface pressures of around 5 mN/m, in which the constituent rodlike molecules are coherently tilted from the layer normal [5]. Under illumination with visible to ultraviolet light, the azobenzene derivatives undergo the *trans-cis* photoisomerization reaction that converts the molecular conformation from the rod to bent shape and vice versa. In the 2D smectic-*C* phase, the continued photoisomerization under uniform illumination was found to generate spatiotemporal patterns in the form of orientational waves [2,3], associated with collective oscillation and propagation of the azimuthal angle of the tilted molecule [3]. Remarkable features of this phenomenon are as follows. (i) Only linearly polarized light, neither circularly nor randomly polarized light, can generate the orientational waves. (ii) The propagation direction of the orientational wave is reversed when the polarization of light is switched by 90°. (iii) The traveling waves appear for the lower intensity of the illumination. (iv) The traveling waves appear only when the illumination is done near the visible edge of the optical absorption band. (v) The propagation velocity monotonically increases with the light intensity up to a certain threshold above which the waves disappear.

Our model, phenomenologically taking account of the 2D liquid-crystal order as well as the anisotropic photoexcitation, provides a virtually complete description of all these behaviors of the orientational waves. In contrast to the previous theoretical study by Reigada, Sagués, and Mikhailov [6], which assumes essentially the phase separation of *trans*- and *cis*-isomers, the orientational wave propagation in our model takes place even if there is no tendency of the phase separation of the concentration in itself, which is consistent with experiment. The essential mechanism of wave generation and propagation lies in the interplay between the spontaneous splay deformation of the molecular azimuth and the anisotropy of photoexcitation, mediated by the varying concentration of *cis*-isomers. This anisotropic model forms an entirely new class of pattern-forming systems. By numerical simulations and a linear stability analysis, we show the nature of the rich nonequilibrium dynamics that the model carries.

Equilibrium properties of the system are determined by the free energy functional of gross variables relevant to the phenomenon. Here we take, as such variables, the local direction of the rodlike molecules $\mathbf{c}(\mathbf{r},t)$ defined as a projection of the director $\mathbf{n}$ of the molecules onto the 2D layer surface and the local concentration difference between *trans*- and *cis*-isomers $\psi(\mathbf{r},t)$ at position $\mathbf{r}=(x,y)$ on the layer surface and at time t. Using these variables we can write the free energy F in the dimensionless units [7,5],

$$F = \int d\mathbf{r}\left[\frac{1}{2}\sum_i |\nabla c_i|^2 - \frac{\tau}{2}|\mathbf{c}|^2 + \frac{u}{4}|\mathbf{c}|^4 - \lambda\psi\nabla\cdot\mathbf{c} + \frac{D}{2}|\nabla\psi|^2 + \frac{\chi}{2}\psi^2\right], \tag{1}$$

where the sum is taken over the component c_i $(i=x,y)$ of $\mathbf{c}$ and τ, u, D, and χ are positive constants. The first term on the right hand side of Eq. (1) corresponds to the Frank elastic energy and the second and third terms describe the smectic-A to smectic-C transition [8]. Hereafter, we consider the smectic-C phase only—that is, $\tau>0$. The coupling term with a constant λ which gives a spontaneous splay deforma-

tion is allowed to exist in F because there is no inversion symmetry about $\mathbf{c}$ in this system [7,9–12]. The last two terms are related to the scalar order parameter. Here we assume $\chi > 0$; that is, the concentration field does not tend to phase-separate in itself. It should be noted that the free energy of this type leads to spatially nonuniform equilibrium patterns such as stripes or squares depending on the parameter λ [7]. In this paper, however, we are concerned only with a uniform state, since orientational waves are experimentally observed to propagate in the uniform states [3]. Henceforth, we restrict the value of λ to a region where the spatially uniform state is stable in equilibrium.

In the absence of photoisomerization, the system evolves toward an equilibrium state which minimizes the free energy F. In this case $\mathbf{c}$ and ψ obey the purely dissipative kinetic equations for the nonconserved and conserved order parameters, respectively [13]. The presence of photoisomerization gives rise to reaction terms in the kinetic equations which take the form

$$\frac{\partial \mathbf{c}}{\partial t} = -\frac{\delta F}{\delta \mathbf{c}} + \mathbf{f}, \tag{2}$$

$$\frac{\partial \psi}{\partial t} = M\nabla^2 \frac{\delta F}{\delta \psi} + g, \tag{3}$$

with the reaction terms $\mathbf{f} \equiv -\gamma_2 \mathbf{c}(1-\psi)/(1+\psi)$ and $g \equiv -(\gamma_1 + \gamma_2)\psi - (\gamma_1 - \gamma_2)$, where M is the mobility and γ_1 and γ_2 are the *trans*-to-*cis* and *cis*-to-*trans* reaction rates, respectively. The reaction terms $\mathbf{f}$ and g are derived as a simple extension of those used for the rate equations of the concentration and the tilt order in the two-component reactive Langmuir monolayers by Reigada *et al.* [6].

Since the *trans*-to-*cis* reaction rate should depend on the relative orientation of $\mathbf{c}$ to the polarization of illumination, we take the anisotropy of the reaction rate into account by using the expression $\gamma_1 = \Gamma_0 |\mathbf{c}|^2 + \Gamma_1 (\hat{\mathbf{E}} \cdot \mathbf{c})^2$, where $\hat{\mathbf{E}} \equiv (\cos\theta, \sin\theta)$ with the direction θ of the polarization of illumination. According to a simple molecular theory, both coefficients Γ_0 and Γ_1 are proportional to the intensity of illumination and depend on the orientational order of *trans*-molecules. Since we are concerned with a strongly ordered state, the isotropic part of γ_1 should be small. Hence we assume $\Gamma_0 = 0$ and Γ_1 is a positive constant for simplicity. The *cis*-to-*trans* reaction rate γ_2 should be independent of the orientation of polarization. We hereafter use the parameters $k \equiv \Gamma_1/\gamma_2$ and $\gamma \equiv \gamma_2$ instead of Γ_1 and γ_2 so that γ is proportional to the power of illumination which is experimentally controllable. Henceforth, we put $M = 0$, assuming that the molecular diffusion is very slow compared with the photo-induced reaction rates [14].

Figures 1(a)–1(d) show a time evolution of the system obtained by the numerical simulation based on Eqs. (2) and (3) for $k = 1$, $\gamma = 0.05$, and $\theta = \pi/4$, starting from the uniform state with a localized perturbation at the center of simulation box. Hereafter we fix the parameters $\tau = u = 2$ and $\lambda = 1$. The numerical calculations were carried out on a 256×256 two-dimensional square lattice using a finite difference Euler scheme with a time step $\Delta t = 0.01$ and a lattice spacing $\Delta x = 1$ under Neumann boundary conditions. The spatial distributions of the azimuth ϕ defined as $\mathbf{c} = |\mathbf{c}|(\cos\phi, \sin\phi)$ at $t = 10$ (a), 100 (b), 200 (c), and 2000 (d) are displayed in Fig. 1 using the color map shown in the upper right of the figure. We observe an orientational wave propagating downward in these figures or, more clearly, in Fig. 1(e), which shows the spatiotemporal pattern of ϕ. Although ψ and the tilt order $|\mathbf{c}|$ also propagate in a similar manner to ϕ, the amplitude of wave in $|\mathbf{c}|$ is much smaller than those in ϕ and ψ. This strongly implies that the wave propagation is mainly associated with the azimuth ϕ as observed in the experiment.

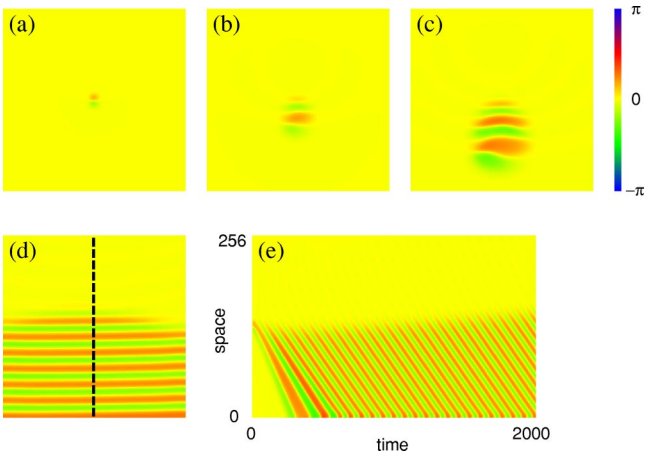

FIG. 1. (Color) Spatial distributions of azimuth ϕ at $t = 10$ (a), 100 (b), 200 (c), and 2000 (d) obtained by the numerical simulation of our model. (e) shows the spatiotemporal pattern of ϕ along the line $x = \text{const}$ indicated by the dashed line in figure (d).

Next, we switch the polarization of light by 90°, namely, $\theta = -\pi/4$ at $t = 200$ [Fig. 1(c)]. In Fig. 2 snapshots of ϕ at $t = 250$ (a), 300 (b), and 350 (c) after the switching are shown. We can see in Figs. 2(a)–2(c) and in the spatiotemporal pattern in Fig. 2(d) that the direction of propagation is reversed after the switching of θ. We also carried out simulations

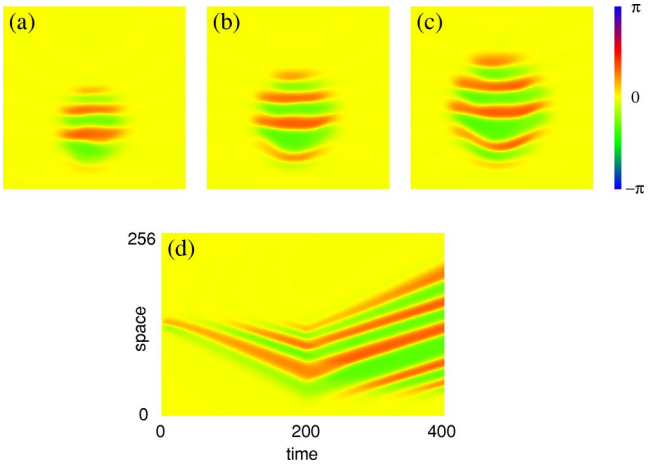

FIG. 2. (Color) Spatial distributions of azimuth ϕ at $t = 250$ (a), 300 (b), and 350 (c) after switching θ by $\pi/2$ at $t = 200$. (d) shows the spatiotemporal pattern of ϕ along the line $x = \text{const}$ indicated by the dashed line in Fig. 1(d).

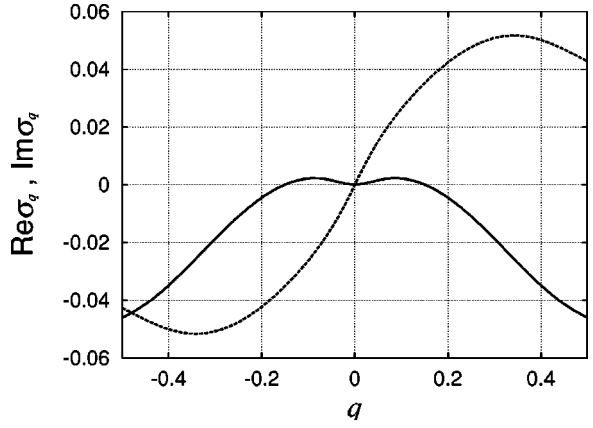

FIG. 3. The q dependence of the largest eigenvalue σ_q. The real and imaginary parts of σ_q as functions of q are plotted by solid and dashed lines, respectively, for $\gamma=0.05$, $k=0.2$, and $\theta=\pi/4$.

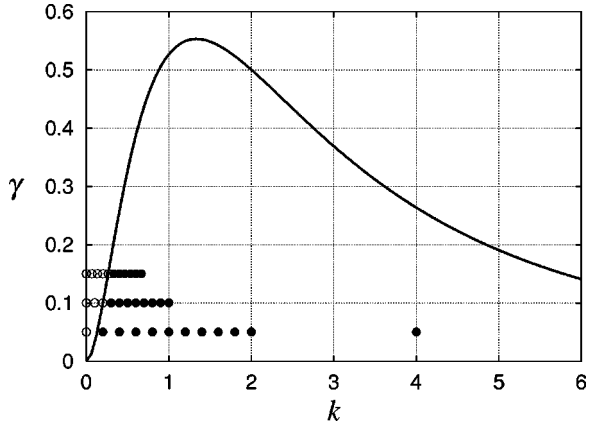

FIG. 4. The linear stability diagram of the uniform equilibrium solution. Below the solid line and $\gamma>0$ the equilibrium solution is unstable and traveling waves emerge; otherwise, it is stable. For the parameters shown by solid or open circles, traveling waves or no patterns are observed, respectively, in the numerical simulations with the uniform initial condition.

without the anisotropy of γ_1 and observed no traveling waves. These results are consistent with the experimental facts listed in the second paragraph.

To understand the mechanism of the wave propagation, we perform a theoretical analysis of Eqs. (2) and (3) using the approximation that the tilt order $|\mathbf{c}|$ is constant, since the spatial variation of the tilt order is small compared with those of other variables as mentioned above. For simplicity we take $|\boldsymbol{c}|=1$ so that $\boldsymbol{c}=(\cos\phi,\sin\phi)$. Then Eqs. (2) and (3) with $M=0$ become

$$\frac{\partial\phi}{\partial t}=\nabla^2\phi+\lambda\left(\sin\phi\frac{\partial\psi}{\partial x}-\cos\phi\frac{\partial\psi}{\partial y}\right), \tag{4}$$

$$\frac{1}{\gamma}\frac{\partial\psi}{\partial t}=1-\psi-k\cos^2(\theta-\phi)(1+\psi). \tag{5}$$

These simplified equations have a uniform equilibrium solution with an arbitrary constant ϕ_0 which corresponds to the azimuthal angle of molecular direction in the uniform state. A linear stability analysis of Eqs. (4) and (5) around this equilibrium solution with $\phi_0=0$ gives the growth rate σ_q of the eigenmode for the perturbation proportional to $\exp(iqy+\sigma_q t)$ with wave number q as a solution of the equation

$$\sigma_q^2-s\sigma_q+d=0, \tag{6}$$

with

$$s=-q^2-\gamma(1+k\cos^2\theta), \tag{7}$$

$$d=q^2\gamma(1+k\cos^2\theta)-iq\frac{2\lambda k\gamma\sin(2\theta)}{1+k\cos^2\theta}. \tag{8}$$

The q dependence of the largest eigenvalue σ_q is shown in Fig. 3. The real and imaginary parts of σ_q as functions of q are plotted by solid and dashed lines, respectively, for $\gamma=0.05$, $k=0.2$, and $\theta=\pi/4$. In this figure we find oscillatory unstable modes at finite wave numbers—that is, Re $\sigma_q>0$ and Im $\sigma_q\neq 0$ for $q\neq 0$—which may cause traveling waves [15,16]. This instability is due to the appearance of the last term in Eq. (8) which comes from the spontaneous splay term in Eq. (1) and the anisotropy of the reaction rate γ_1.

In Fig. 4 we show the linear stability diagram of the uniform equilibrium solution of the simplified equation for $\theta=\pi/4$ obtained by the small-q expansion of σ_q. Below the solid line and $\gamma>0$ in Fig. 4, the equilibrium solution is unstable and traveling waves emerge; otherwise, it is stable [17]. We also show in Fig. 4 the results of numerical simulation of Eqs. (2) and (3) for various values of (k,γ) with the uniform initial condition—that is, $\mathbf{c}(\mathbf{r},0)=(1,0)$ and $\psi(\mathbf{r},0)=0$ with small random perturbations. Traveling waves or no pattern are observed for (k,γ) shown by solid or open circles in Fig. 4, respectively, in agreement with the linear stability argument. As observed in the experiments [2,3], we see in Fig. 4 that the instability occurs in the lower γ region.

The experimental observations show that the emergence of traveling waves depends on not only the intensity but also the wavelength of the excitation light. The latter is related to the parameter k in our model, and $k\approx 1$ is realized only near the visible edge of the optical absorption band where the fractions of *cis*- and *trans*-isomers are comparable. At this wavelength of excitation light the traveling waves are observed as mentioned in the second paragraph. This agrees with our theoretical result that the linear stability line $\gamma=\gamma(k)$ in Fig. 4 has a single peak at $k\approx 1.3$ where the equilibrium state is destabilized first as γ decreases.

Our theoretical analysis also predicts the experimental observation that the propagation directions of waves are reversed when θ is switched by $\pi/2$. We find that the imaginary part of σ_q for some value of θ has opposite sign to that for $\theta+\pi/2$. Hence it is expected that the propagation direction is reversed by the switching $\theta\rightarrow\theta+\pi/2$ if the system is still in the unstable region after the switching. It should be, however, noted that the above argument is based on the linear stability analysis for the uniform solution, whereas the system after the switching is no longer uniform. Actually, the propagation direction is determined by the direction of po-

larization and the spatial distribution of molecular direction. Further discussion is needed why the prediction by the linear stability analysis is correct in this case. This is, however, beyond the scope of this paper.

Tabe *et al.* [3] reported that the propagation velocity of the traveling wave monotonically increases as the power of illumination increases. To obtain the γ dependence of the propagation velocity we carried out numerical simulations of Eqs. (2) and (3) for $k=1$ and $\theta=\pi/4$ in one spatial dimension. In Fig. 5 we plot the propagation velocity of the traveling wave obtained by the one-dimensional simulation as a function of γ which is proportional to the power of illumination. From this figure we find that the velocity monotonically increases with γ and appears to be proportional to γ^{ν} with $\nu \approx 1/2$ in agreement with the recent experimental observations.

In the present study we have limited the parameter λ to the regime for which uniform equilibrium states are thermodynamically stable. However, if we allow λ beyond that limit, the model predicts another oscillatory instability to appear at a distinctly higher wave number on top of the unstable mode studied here, generating qualitatively new spatiotemporal patterns simultaneously comprized of these two modes. This behavior may be examined in future experiments and should serve as a further independent test of the present model. The details will be described in future publications.

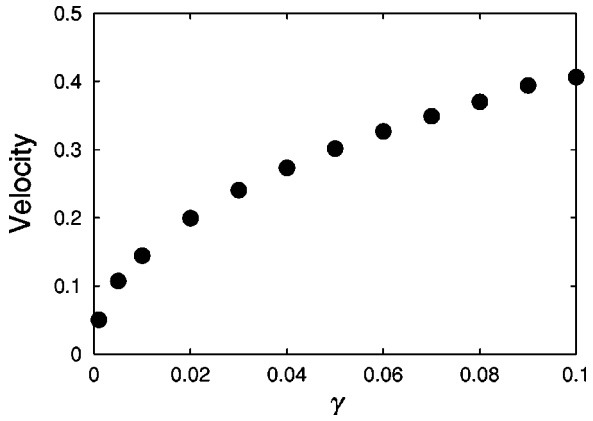

FIG. 5. γ dependence of the propagation velocity obtained by one-dimensional simulations for $k=1$ and $\theta=\pi/4$.

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[17] The equilibrium solution is always stable for $\theta=n\pi/2$ (n is integer) and hereafter we perform the analysis for fixed $\theta \neq n\pi/2$.