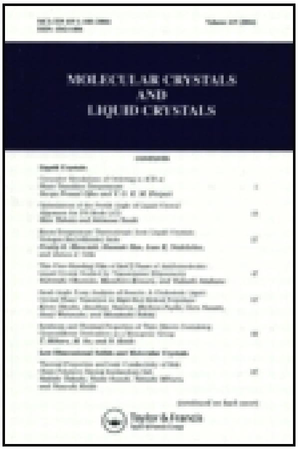

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A Phenomenological Model of Photo-Induced Traveling Waves in Liquid-Crystalline Langmuir Monolayers

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A phenomenological model of photo-induced traveling waves in liquid-crystalline Langmuir monolayers is presented. A linear stability analysis and numerical simulations of this model reveal that there are two oscillatory unstable modes with lower and higher wavenumbers which cause the traveling waves. The unstable mode with the lower wavenumber arises due to an interplay between the spontaneous splay deformation of liquid crystal order and the anisotropic photo-excitation of molecules. The other unstable mode with the higher wavenumber is concerned with the phase separation of the concentration field induced by the spontaneous splay deformation. The numerical simulations also show the coexistence between these two modes for certain parameter values.

Keywords: Langmuir monolayers; nonequilibrium structures; photo-isomerization; traveling waves

INTRODUCTION

A photo-induced traveling wave [1,2] in illuminated liquid-crystalline Langmuir monolayers is one of the most remarkable far-from-equilibrium structures found in soft condensed matter [3]. The

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Langmuir monolayers which consist of certain azobenzene derivatives is known to exhibit a two-dimensional 'smectic-C' phase at moderate surface pressures around 5 mN/m where the constituent rodlike molecules are coherently tilted from the layer normal [4–6]. When the monolayers in smectic-C phase are illuminated with the linearly polarized light, the constituent molecules undergo the trans-cis photo-isomerization converting the molecular conformation from the rod to bent shape, and vice versa and the traveling waves associated with the molecular azimuth ("orientational waves") emerge [2].

In the previous papers [7,8], we have proposed a phenomenological model and demonstrated that our model can well reproduce most of qualitative features of the experimental observations. In our model we take into account the spontaneous splay deformation of the liquid-crystalline order and the anisotropic photo-excitation of molecules, which can lead to the orientational wave propagation even if the uniform state is stable, that is, no 'phase separation' occurs in the absence of illumination. This means that the phase separation related to the concentrations of trans- and cis-isomers is not necessary for the orientational wave propagation. On the other hand, Reigada *et al.* [9,10] have proposed a model of two component Langmuir monolayers in which the phase separation is essential for the wave propagation.

In this paper we show that in our model another oscillatory unstable mode arises for a certain range of parameters where the phase separation occurs in the absence of illumination. This unstable mode appears at a wavenumber which is higher than that of the orientational wave previously studied. Results of one-dimensional numerical simulations show that traveling waves with higher wavenumbers emerge for the large coupling constant of spontaneous splay deformation. We also show that the two modes with higher and lower wavenumbers can coexist forming a domain structure.

MODEL

Here we briefly describe our model [7,8]. Consider a monolayer system that consists of rodlike molecules whose directions are tilted from the layer normal. The local orientation of the molecules can be described by a vector field $\mathbf{c}(\mathbf{r}, t)$ defined as a projection of the three-dimensional vector $\mathbf{n}$ of the molecular direction into the two-dimensional layer plane $\mathbf{r} = (x, y)$ at time t. Introducing a scalar field $\psi(\mathbf{r}, t)$ defined as the local concentration difference between trans- and cis-isomers, we write the free energy F as [4,5,11,12],

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

where the sum is taken over the component c_i $(i = x, y)$ of $\mathbf{c}$ and K, τ, b, D, and χ are positive constants. The coupling term with a coupling constant λ is allowed to enter F because there is no inversion symmetry about $\mathbf{c}$ in this system [13,14]. This term causes the spontaneous splay deformation of liquid crystal order which plays a crucial role in the wave propagation phenomenon.

The kinetic equations of $\mathbf{c}$ and ψ are written as

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

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

where L and M are the relaxation constant and the mobility, respectively, and $\mathbf{f}(\mathbf{c}, \psi)$ and $g(\mathbf{c}, \psi)$ are the reaction terms due to the photoisomerization which are given by [9,10]

$$\mathbf{f}(\mathbf{c}, \psi) = -\gamma_2 \frac{1 - \psi}{1 + \psi} \mathbf{c}, \tag{4}$$

$$g(\mathbf{c}, \psi) = -(\gamma_1 + \gamma_2)\psi - (\gamma_1 - \gamma_2), \tag{5}$$

where γ_1 and γ_2 are the trans-to-cis and cis-to-trans reaction rates, respectively. The trans-to-cis reaction rate should depend on the relative orientation of $\mathbf{c}$ to the polarization of excitation light. It is reasonable to use the following expression for the anisotropy of the reaction rate,

$$\gamma_1 = \Gamma_0 |\mathbf{c}|^2 + \Gamma_1 (\hat{\mathbf{E}} \cdot \mathbf{c})^2, \tag{6}$$

where Γ_0 and Γ_1 are positive constants and $\hat{\mathbf{E}} \equiv (\cos\theta, \sin\theta)$ with the orientation θ of the polarization of light. Henceforth, we assume $\Gamma_0 = 0$, since we are concerned with a strongly ordered state of liquid-crystalline monolayer system where the isotropic part of γ_1 is negligible.

It is convenient to choose the physical units of length, time, and energy as $(K/b)^{1/2}$, $(Lb)^{-1}$, and K, respectively. Rescaling the Eqs. (2)

and (3) in these units and further rescaling $\mathbf{c}$ by $(\tau/b)^{1/2}$, we obtain the kinetic equations in the dimensionless form as

$$\frac{\partial \mathbf{c}}{\partial t} = \nabla^2 \mathbf{c} + \tau\left(1 - |\mathbf{c}|^2\right)\mathbf{c} - \lambda \nabla \psi + \mathbf{f}, \tag{7}$$

$$\frac{\partial \psi}{\partial t} = M\nabla^2\left(-D\nabla^2\psi + \chi\psi + \nu\psi^3 - \lambda\nabla\cdot\mathbf{c}\right) + g, \tag{8}$$

with

$$\mathbf{f} = -\gamma\frac{1-\psi}{1+\psi}\mathbf{c}, \tag{9}$$

$$g = \gamma\left[1 - \psi - k\left(\hat{\mathbf{E}}\cdot\mathbf{c}\right)^2(1+\psi)\right], \tag{10}$$

where $\gamma \equiv \gamma_2/(Lb)$, $k \equiv \Gamma_1\tau/(\gamma_2 b)$, and the parameters τ, λ, M, D, χ, and ν in Eqs. (7)–(10) have been redefined as τ/b, $\lambda/(K\tau)^{1/2}$, $M\tau/(LK)$, $Db/K\tau$, χ/b, and ν/b, respectively. Note that the parameter γ is proportional to the intensity of excitation light and k is the ratio of the trans-to-cis to the cis-to-trans reaction rates and depends on the wavelength of excitation light.

LINEAR STABILITY ANALYSIS

Here we perform a linear stability analysis of Eqs. (7)–(10). Since we are concerned with the orientational wave propagation, we apply the constant tilt approximation, that is, $|\mathbf{c}| = \text{const}$. For simplicity we put $|\mathbf{c}| = 1$ so that $\mathbf{c} = (\cos\phi, \sin\phi)$ with the azimuthal angle ϕ. Then Eqs. (7) and (8) become

$$\frac{\partial \phi}{\partial t} = \nabla^2\phi - \lambda\hat{\mathbf{c}}\times\nabla\psi, \tag{11}$$

$$\frac{\partial \psi}{\partial t} = M\nabla^2\left(-D\nabla^2\psi + \chi\psi + \nu\psi^3 - \lambda\hat{\mathbf{c}}\times\nabla\phi\right) + g(\phi,\psi), \tag{12}$$

where

$$g(\phi,\psi) \equiv \gamma\left[1 - \psi - k\cos^2(\phi-\theta)(1+\psi)\right], \tag{13}$$

and $\hat{\mathbf{c}}\times\nabla \equiv \cos\phi\,\partial_y - \sin\phi\,\partial_x$ with ∂_x and ∂_y being the partial differential operators with respect to x and y, respectively.

Equations (11)–(13) have a stationary uniform solution $\phi = \phi_0$ and $\psi = \psi_0$ with an arbitrary constant ϕ_0 and $\psi_0 = \left[1 - k\cos^2(\theta - \phi_0)\right]/\left[1 + k\cos^2(\theta - \phi_0)\right]$. Linearizing Eqs. (11) and (12) around this solution and introducing a Fourier mode $\mathbf{U}_q = (\phi_q, \psi_q)^T \equiv \int d\mathbf{r}(\phi - \phi_0, \psi - \psi_0)^T \exp(-i\mathbf{q}\cdot\mathbf{r})$ with a wave vector $\mathbf{q} = (q_x, q_y)$, we obtain the linear equation $d\mathbf{U}_q/dt = L_q\mathbf{U}_q$ with

$$L_q = \begin{pmatrix} -q^2 & -i\lambda\hat{\mathbf{c}}_0 \times \mathbf{q} \\ iM\lambda q^2\hat{\mathbf{c}}_0 \times \mathbf{q} + g_\phi^0 & -Mq^2\left(Dq^2 + \tilde{\chi}\right) + g_\psi^0 \end{pmatrix}, \tag{14}$$

where $\hat{\mathbf{c}}_0 \times \mathbf{q} \equiv q_y \cos\phi_0 - q_x \sin\phi_0$, $g_\phi^0 \equiv -2\gamma k \sin[2(\theta - \phi_0)]/[1 + k\cos^2(\theta - \phi_0)]$, $g_\psi^0 \equiv -\gamma[1 + k\cos^2(\theta - \phi_0)]$, and $\tilde{\chi} \equiv \chi + 3\nu\psi_0^2$.

Since the largest eigenvalue σ_q of L_q gives the (complex) growth rate of the Fourier mode $\mathbf{U}_q$, the stability of the uniform solution is determined by $\max_q \mathrm{Re}\sigma_q$. In the following we examine behavior of σ_q in the parameter space (λ, γ).

In the absence of photo-isomerization ($\gamma = 0$), σ_q is always a real number and $\mathbf{U}_q$ is most unstable for $\mathbf{q} = \pm q\hat{\mathbf{z}} \times \hat{\mathbf{c}}_0$ and $q = q_0 \equiv \left[2(\lambda^2 - \tilde{\chi})/(3D)\right]^{1/2}$ for $\lambda^2 > \tilde{\chi} \equiv \lambda_c^2$, where $\hat{\mathbf{z}}$ is the unit normal to the layer. This unstable mode arises due to the phase separation induced by the spontaneous splay deformation. As a result a stripe pattern corresponding to the unstable Fourier mode will appear. When $\lambda^2 \le \lambda_c^2$, there is no unstable mode with a finite wavenumber, that is, the uniform state is stable.

When the system undergoes the photo-isomerization ($\gamma > 0$), the spontaneous splay deformation can be coupled with the anisotropy of the photo-excitation, giving rise to new unstable modes. It can be shown by the linear analysis that the uniform state is destabilized by increasing λ or decreasing γ and an oscillatory unstable mode arises at a lower wavenumber $q = q_L$ (see Fig. 1). This unstable mode corresponds to the orientational wave observed experimentally. The analysis of this mode has been done in the previous paper [7,8].

Here we discuss behavior of σ_q in the strong coupling regime ($\lambda > \lambda_c$) for $\gamma \neq 0$ where the phase separation should be involved in the non-equilibrium pattern formation. In Figure 1 we show q-dependence of the eigenvalue σ_q near the point $(\lambda_c, 0)$ in the parameter space. In this figure the real and the imaginary parts of σ_q as functions of q are plotted for $(\lambda, \gamma) = (1.4, 0.002)$ (other parameters are fixed at $k = D = \chi = \nu = 1$, $M = 0.1$, and $\theta = \pi/4$). We find four peaks of $\mathrm{Re}\sigma_q > 0$ at $q = \pm q_H$ and $\pm q_L$ ($q_H > q_L > 0$). The unstable mode with $q = q_H$ coincides with the mode ($q = q_0$) discussed above in the absence of photo-isomerization but is now accompanied with an oscillation for $\gamma > 0$ since $\mathrm{Im}\sigma_{q_H} \neq 0$. This implies traveling waves induced by phase

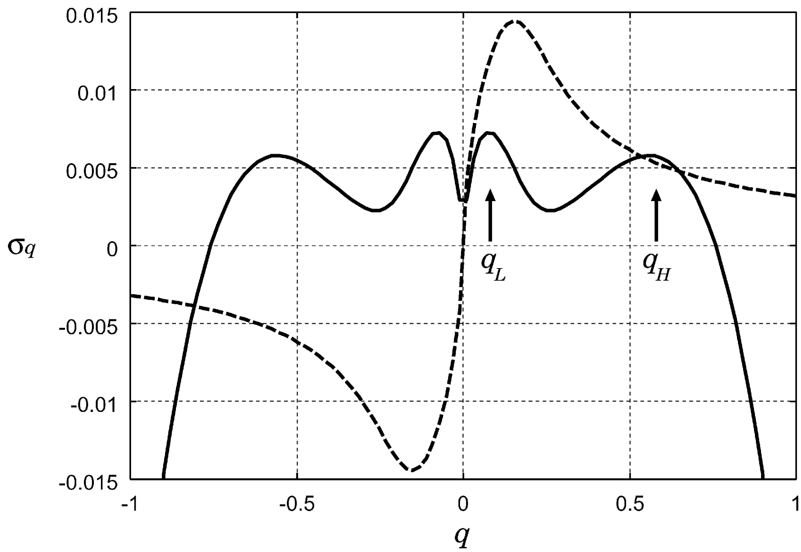

FIGURE 1 The q-dependence of the eigenvalue σ_q. The real and imaginary part of σ_q as functions of q are plotted by solid and dashed lines, respectively, for $(\lambda, \gamma) = (1.4, 0.002)$. There are two peaks of $\mathrm{Re}\sigma_q$ at $q = q_L$ and q_H for $q > 0$.

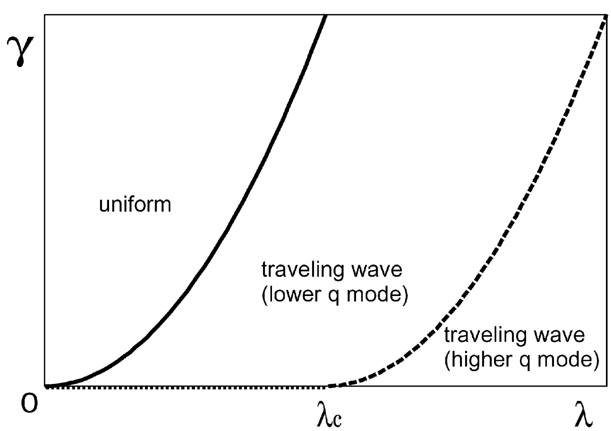

FIGURE 2 A schematic phase diagram in the parameter space (λ, γ). The solid line is the linear stability line below which (and $\gamma > 0$) the uniform stationary solution $(\phi, \psi) = (\phi_0, \psi_0)$ is oscillatory unstable and the traveling waves with $q = q_L$ emerge. The dashed line is the secondary instability line below which (and $\gamma > 0$) the traveling waves with $q = q_H$ emerge. On the λ-axis $(\gamma = 0)$ the uniform solution is stable for $\lambda \leq \lambda_c$ (dotted line), otherwise the stationary periodic structures with $q = q_0$ appear.

separation to exist. Indeed, the traveling waves are observed in numerical simulations for large values of λ presented in the next section. Although the stability analysis shown above is only valid for the primary instability of the lower q mode, we conjecture that traveling waves with $q = q_L$ become unstable as increasing λ and those with $q = q_H$ emerge. In other words, there is a secondary instability line (dashed line in Fig. 2) which ends at $(\lambda, \gamma) = (\lambda_c, 0)$ in the parameter space (λ, γ). A schematic phase diagram is shown in Figure 2.

NUMERICAL SIMULATION

Here we carry out numerical simulations of our model in one spatial dimension. We take y as the spatial coordinate for the initial state $\mathbf{c} = (1, 0)$ and $\psi = \psi_0$ with small random perturbations. We numerically solve Eqs. (7)–(10) on a one-dimensional lattice (with 256 lattice points) using a simple finite difference Euler scheme with a lattice spacing $\Delta x = 0.5$ and a time step $\Delta t = 0.01$ under the periodic boundary conditions. The parameters $\tau = 2$, $k = D = \chi = \nu = 1$, $M = 0.1$, and $\theta = \pi/4$ are fixed.

Figure 3(a) shows a snapshot of profiles of ϕ (thick line), $|\mathbf{c}|^2$ (thin line), and ψ (dashed line) at $t = 5000$ for $(\lambda, \gamma) = (1.9, 0.05)$. All of these profiles propagate with a constant speed to the left as shown by the arrow in the figure. The traveling wave in this figure is formed after the lower q mode instability discussed in the previous section.

For the parameter $(\lambda, \gamma) = (2.1, 0.05)$ we observe a traveling wave with a higher wavenumber corresponding to the higher q unstable mode (Fig. 3(b)). The propagation speed of the waves in Figure 3(b) is slower than that in Figure 3(a). We see that the wave amplitude of $|\mathbf{c}|^2$ in Figure 3(b) is larger than that in Figure 3(a) and the profile of ψ in Figure 3(b) is almost symmetric whereas that in Figure 3(a) is strongly asymmetric.

If we appropriately tune the parameter λ, we can observe a quite interesting pattern in which the two modes with $q = q_L$ and q_H coexist forming a domain structure. Figure 3(c) shows the coexisting pattern obtained numerically for $(\lambda, \gamma) = (2.0, 0.05)$. In this figure both two wave patterns inside the domains propagate to the left and the domains slowly move to the right. A spatio-temporal plot of ϕ for this simulation is shown in Figure 4. The two-mode coexistence is observed only for precisely tuned parameters which should form the dashed line in Figure 2. Near these parameters the domains are formed, but they shrink or expand and eventually disappear (one-mode pattern arises).

The numerical simulations presented here are carried out for the quenched systems from the uniform system with small random

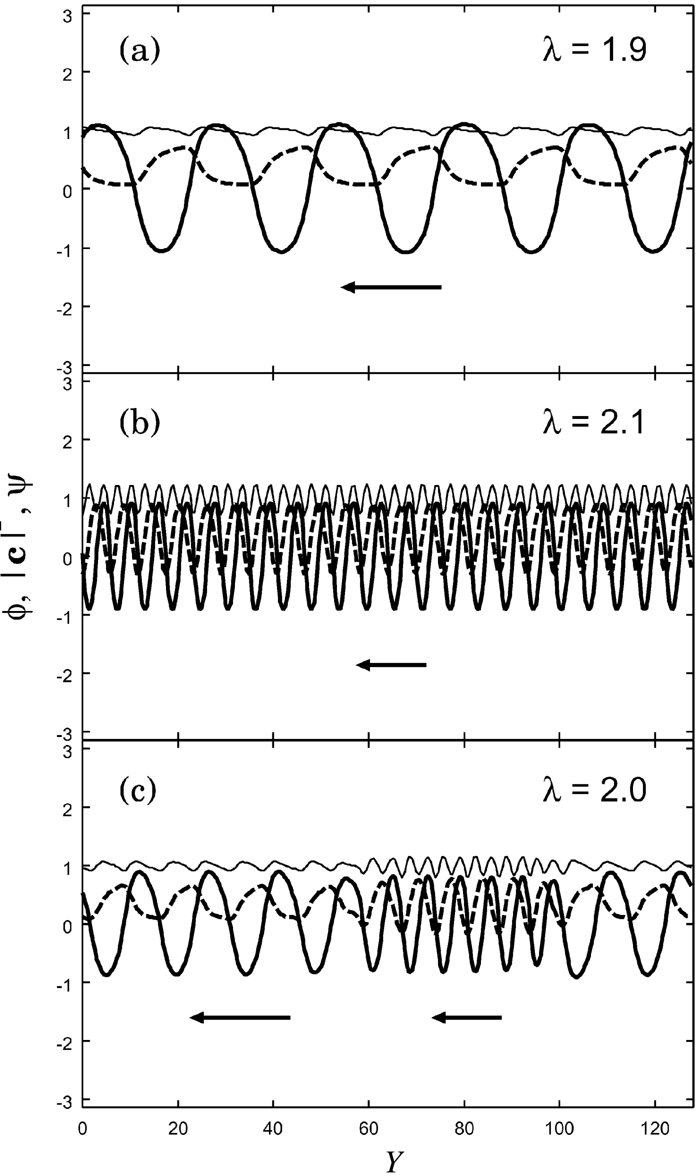

FIGURE 3 Snapshots of the profiles of ϕ (thick line), $|\mathbf{c}|^2$ (thin line), and ψ (dashed line) for $\lambda = 1.9$ (a), 2.1 (b), and 2.0 (c) ($\gamma = 0.05$ is fixed) at $t = 5000$. The waves with $q = q_L$ (a) and q_H (b) propagate to the left as shown by the arrows. For $\lambda = 2.0$ the two propagating modes coexist forming a domain structure which is slowly moving to the right (see Fig. 4).

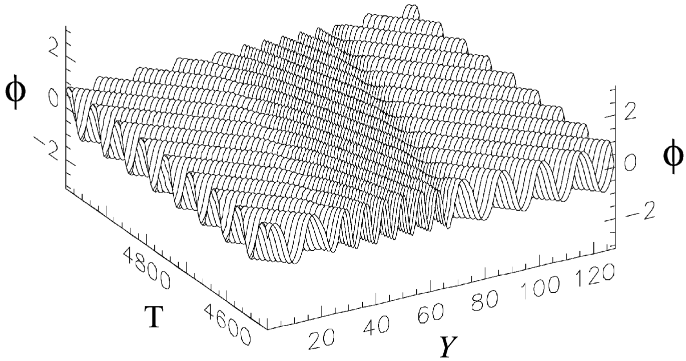

FIGURE 4 Spatio-temporal plot of ϕ for $(\lambda, \gamma) = (2.0, 0.05)$. The coexisting patterns (Fig. 3(c)) for $4500 < t < 5000$ are plotted.

perturbations. If we carry out numerical simulations varying stepwise the parameters in time, we observe a strong hysteresis. A further analysis is necessary for this point, but it is beyond the scope of this paper.

SUMMARY

In this paper we have performed the linear stability analysis of our model taking the phase separation into account. We have shown that there are two oscillatory unstable modes with the lower and higher wavenumbers. The lower q mode instability originates from an interplay between the spontaneous splay deformation and the anisotropy of photo-excitation and causes the orientational wave propagation observed experimentally. On the other hand, the higher q mode instability occurs due to the phase separation induced by the spontaneous splay deformation. It has been confirmed in the numerical simulations of our model that the traveling waves associated with these two modes appear depending on the coupling constant λ. We have also shown in the numerical simulations that these two modes can coexist forming domain structures.

The orientational waves observed experimentally correspond to the traveling waves associated with the lower q mode in our model. Properties of this mode well explain the experimental observations [7,8], while our model also predicts the existence of traveling waves associated with the higher q mode. They are, however, not observed yet experimentally, since it is difficult to control the coupling constant λ. We hope that experiments will be done to examine our theoretical prediction in future.

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