Photoactivated Langmuir Monolayers as an Active Polar Fluid

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by
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ABSTRACT

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We consider a continuum theoretical description of a Smectic C monolayer made of molecules that can undergo cis-trans isomerization when subject to photo-activation. We use analytical and numerical methods to investigate the dynamics of this system. We show that this system exhibits self-regulation and the existence of propagating solitary waves, central features of an active fluid. Thus we demonstrate that this system can serve as an experimental platform to investigate the physics of this inherently out-of-equilibrium class of materials. The specific results obtained in this study are as follows: a) an equilibrium Smectic C monolayer can exist in one of two states - a homogeneous state and a striped state. b) In the presence of photo-activation the system develops propagating orientation waves. These waves are not a pattern but are rather solitary waves resulting from the self-regulating nature of the dynamics of the system. c) The
properties of these waves are characterized as a function of two system parameters, the strength of spontaneous splay and the relaxation rate for the equilibration process of the molecular isomerization. We find that the speed of propagation increases as a function of both these parameters. c) We localize the activation by illuminating the monolayer using slits of various widths. In this case we find that the localization leads to the formation of a domain wall at the edge of the activated region and propagating waves are set up moving away from this domain wall. In the absence of diffusion, the waves remain confined to the slit of illumination. When diffusion is ramped up, the waves penetrate into the dark regions of the system and hence can potentially serve for controlled pattern generation and stabilization in this liquid crystal system.
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Chapter 1

Introduction

Overview of Liquid Crystal Phases: Liquids are materials that are homogeneous and isotropic, i.e., invariant with respect to all rotations and all translations. Crystalline materials on the other hand are low symmetry phases invariant only under particular space groups. There exists a whole class of materials of intermediate symmetries between these two classes. These mesophase materials are called liquid crystals. Liquid crystals are classified into two groups according to molecules’ positional order and hence the resulting invariance properties, called nematics and smectics respectively. Nematics are materials made of rod-like molecules that have complete translational symmetry, i.e., the centers of gravity of the molecules have no long-range order. But, they tend to align along some common axis $\hat{n}$. They are uniaxial with two fold symmetry about this axis, and they have complete rotational symmetry orthogonal to it. Typically, nematics are composed of the achiral molecules, i.e., do not distinguish between right and left. If they are chiral, the material must be macroscopically racemic (the same amount of right handed and left handed molecules). In a nematic liquid, if a chiral molecule is dissolved (molecules
are different from their mirror image, the structure of the material develops a helical distortion. This state is called a Cholesteric liquid crystal. Cholesterics are also aligned along some axis $\hat{n}$ but unlike in a nematic, $\hat{n}$ is not constant in space, but rather changes periodically. Smectics are materials where molecules are positionally and orientationally ordered. As a consequence, we can see layer structures and well-defined interlayer spacing. Further, smectics can be classified as smectic A and smectic C phases depending on the orientation of the molecules in a layer with respect to the layer normal. In both phases, the centers of gravity show no long-range order inside each layer. While smectics A phase is optically uniaxial and has complete rotational symmetry around this axis, smectic C phase is biaxial and the molecules are aligned tends to align along a direction which is tilted from the normal (Figure 1a). Smectics C phase is composed of racemic mixtures. It is optically inactive since the concentration of right-handed and left-handed molecules are equal. If we add optically active molecules to a smectics C, the structure distorts. It rotates around z-axis and helical configuration is obtained. Finally there exists a phase of smectics referred to as smectic B in which layers show the rigidity of 2D solid. Inside each layer, X-ray reflections are observed. Smectics B phase is the most ordered phase of the three major smectic phases. In terms of the transition temperature for the emergence of each of these phases, we can say that temperature is increasing from solids to isotropic ($T_{\text{solid}} < T_{\text{smectics-B}} < T_{\text{smectics-C}} < T_{\text{smectics-A}} < T_{\text{nematics}} < T_{\text{isotropic}}$), as one would predict based on entropic considerations [1].

**Langmuir monolayers**: Langmuir monolayers are insoluble monomolecular films formed at an air-water interface. These have served as prototypical systems for the study of structure and dynamics of two dimensional liquid crystals have been studied for more than one century.
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Figure 1.1: Schematic illustration of various liquid crystal phases

Langmuir monolayers have been studied in various ways for different purposes. Their interest areas are varying from mathematical applications to biological applications. I will summarize some of them here. Andelman et al.\cite{5} analyzed the effect of the electrostatic interactions by the permanent dipole moment of neutral surfactant molecules and induced dipoles in charged monolayers on phase transitions was studied. Another interesting work on Langmuir monolayer is done by Ma and Allen\cite{6}. Their motivation was to better understand lung surfactant function. They used palmitic acid (PA) and dipalmitoylphosphatidylcholine (DPPC-d62) as the replacement of lung surfactant mixtures. They showed that palmitic acid increases chain ordering of DPPC by decreasing the chain tilt order of DPPC and it leads DPPC to phase separation from the expanded phase to the condensed phase. They also showed that the miscibility of DPPC and PA in the condensed phase cause PA to decrease the collapse pressure on the surface. In monolayers of an azobenzene, it has been shown that ordered domains leads to the point defects and string-like distortions and the dynamics of these point defects were studied by Vallvé et al. They showed that there are two different dynamical regimes where the main driving force
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for the coalescence of point defects is whether defect attraction or line-energy reduction [7]. Watanabe et al. showed that orientational correlation functions of nematic and smectic-C liquid crystals decay algebraically with different exponents 1.9 and 0.2 respectively. These different exponents gives these two phases different optical properties. Nematic monolayer is optically isotropic while the smectic-C monolayer shows anisotropy. Also, they showed that the nematic and smectic-C monolayers can be used as a good model to the ideal two dimensional system with no long-range order [8]. Iglesias et al. analyzed the effect of the bent-core liquid crystals on alignment of Langmuir/Schaefer monolayers [9].

**System at hand:** In this thesis we focus on a particular langmuir monolayer system namely a class of amphiphilic derivatives of azobenzene at air-water interface. this Langmuir monolayer shows a 2 dimensional analog of the smectic C phase. The monolayer consists of trans (rod-like) and cis (crumpled) isomers which undergoes photoisomerization when they are illuminated by visible to ultraviolet light. In the 2D smectic C phase, the continued photoisomerization leads to generation of orientational waves oscillating the azimuthal angle of the tilted molecule [2, 3].

**Motivation and goals:** The motivation behind this thesis is to demonstrate in principle that photo-activated langmuir monolayers of smectic C materials can serve as a controlled chemical system that contains in its dynamics the key features of a two dimensional active polar fluid and a reaction-diffusion system with local activation and long range inhibition. Active fluids are materials that are driven out of equilibrium at the level of the individual unit and have been the focus of intense investigations both theoretical [10, 11, 12, 13, 14, 15, 16, 17, 18] and in the context of synthetic experimental realizations such as granular rods [19] and colloidal self-diffusophoretic particles [20]. Recently, it was shown that the key feature that
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distinguishes an active polar fluid from an equilibrium polar liquid crystal, which a
Smectic C langmuir monolayer is, is the presence of the mechanism of self regulation
[21]. Self-regulation is the phenomenon of the control parameter of the order-disorder
transition which is the density of particles in effectively controlled by the amount
of order in the system itself. We will show here that, because the photo-activation
occurs at the level of the molecule and depends on the orientation of its azimuth, the
azobenzene system exhibits self-regulation. One consequence of self-regulation is the
existence of propagating solitary waves in the system. We will show that this system
exhibits propagating waves as well, though unlike in the cases studied already in the
literature, these waves are liquid crystal orientation waves. Another widely studied
class of systems are reaction-diffusion systems such as chemical oscillators [22]. The
motivation has been to understand the dynamic emergence of phenomena such as
synchronization and pattern formation [23], relevant to understanding the dynamics
and morphology of living systems. We will show that the langmuir monolayer system
has all the features of a reaction diffusion system and can thereby serve as a physical
prototype that can complement chemical reaction systems widely studied at the
present time.

Layout of the Thesis: In the first section below, we review the existing experimental
and theoretical work on photo-activated langmuir monolayers. Next, we present
the theoretical model of a smectic C monolayer as an active polar fluid. Then, we
carry out a linear stability analysis of the equations of motion associated with this
system and characterize the dynamics of the system for small perturbations. Next,
we numerically integrate the equations of motion and demonstrate the existence, and
characterize the properties of the propagation solitary waves. Then, by using confined
illumination, we show the potential for harnessing this system to study the emergent
consequences of reaction-diffusion dynamics where the activation is localized in space. Finally we conclude with a summary of the primary results and a discussion of the potential future scope of this research.
Chapter 2

Prior Works on Light Activated Monolayers

Introductory remarks: Prior work on this system has been done, experimental and theoretical, within the paradigm of driven liquid crystals. We will first outline experimental work and then the theoretical work.

Experimental Work: In the experiments done by Yuka Tabe and Hiroshi Yokoyama, a single layer of amphiphilic derivatives of azobenzene is spread at the air-water interface. The monolayer is assumed a two-dimensional analog of smectic C phase. The monolayer is kept at temperature 25º and at surface pressure below about 15 mN/m and above which the monolayer can have first order phase transition. As it is seen in Fig 2.1, the excitation light is passes through a filter(480±12nm) is incident normally on the monolayer from below the monolayer. The reflected light is observed with a CCD camera (Fig 2.1).

The experimental founds are in two folds. One is the reorientation of stripe structure and the other one is the traveling orientational waves. Even when there is no
excitation, the Langmuir monolayer forms a static stripe pattern. Illumination on the monolayer with a linearly polarized light at a wavelength 480 nm changes the stripe texture. Molecules changes their orientation toward a light-induced preferred direction. When the illumination is shut off, it takes 10 s the original stripe texture to come back. Traveling orientational waves occurred with continued photoisomerization. The waves travel with 50 µm/s velocity. They also found that the direction of wave propagation is reversed by switching the polarization direction by $\pi/2$.

**Theory 1: Dependence of activation on azimuthal orientation**: According to the model presented by Tabe et al, the dynamics of the system are consisted of two variable. One of them is the projection $c(r,t)$ of the local direction of the rodlike molecules onto the 2D layer surface. And the other one is the local concentration difference between trans and cis isomers $\psi(r,t)$ at position $r = (x,y)$ on the layer surface and at time $t$. In this model, dimensionless free energy $F$ of the system is
\[ F = \int dr \left[ \frac{1}{2} \sum |\nabla c_i|^2 - \frac{\tau}{2} + \frac{u}{4} |c|^4 - \lambda \psi \nabla \cdot c + \frac{D}{2} |\nabla \psi|^4 + \frac{\chi}{2} \psi^2 \right] \] (2.1)

The first term in the above equation stands for the Frank elasticity. The second and third terms correspond to the transition from smectic-A to smectic-C but here, for positive \( \tau \) there is only smectic-C phase only. The spontaneous splay deformation is represented by the forth term. The last two terms are related to scalar order paramaters. With the positive choice of \( \chi \), the tendency to the phase separation in itself is removed. \( \lambda \) that makes this system is in the spatially stable and uniform state in equilibrium is chosen.

In the presence of illumination, reaction terms caused by photoisomerization appear in the kinetic equations. The equation of motion for the order parameters becomes

\[ \frac{\partial \phi}{\partial t} = \nabla^2 \phi + \lambda \left( \sin \phi \frac{\partial \psi}{\partial x} - \cos \phi \frac{\partial \psi}{\partial y} \right) \] (2.2)
\[ \frac{1}{\gamma} \frac{\partial \psi}{\partial t} = 1 - \psi - k \cos^2(\theta - \phi)(1 + \psi) \] (2.3)

where \( \phi \) is the azimuthal angle of molecular direction, \( \theta \) is the angle between polarization of incoming light and molecules on the monolayer, \( \gamma \) and \( k \) are proportional to the intensity of incoming light.

Numerical simulations are done based on Eqns. (2) and (3) for \( k=1, \gamma=0.05 \) and \( \theta=\pi/4 \). Parameters \( \tau \) and \( u \) are fixed to 2 and \( \lambda \) is set to 1. The time step \( \Delta t \) is 0.01. The spatial distributions of the azimuth \( \phi \) defined as \( c=|c|(\cos \phi, \sin \phi) \). In the Fig 2
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Figure 2.2: Spatial distributions of azimuthal angle of molecular direction at time $t=10$ (a), 100(b), 200(c), and 2000(d). (e) shows the spatiotemporal pattern of azimuth $\phi$ along the x-axis. The stripes in orange and green color represent the azimuth of $\phi$ and $-\phi$.

(a, b, c, d, e), Tabe et al. observed an orientational wave propagating downward. As time passes, the orientational waves are generated. The wave generation is mainly associated with the azimuth $\phi$. Furthermore, the propagation direction is reversed when the polarization of light switched by $\pi/2$ and the propagation direction is determined by the relation between the projection of the trans molecules onto the 2D layer and the polarization of illumination. The propagation velocity of the traveling waves increases as the power of illumination increases. In addition to this, there is no traveling waves without the anisotropy of $\gamma$.

**Theory 2: Phase separation paradigm:** In this system, Langmuir monolayer is formed by two diffusive molecules. One of them is rod-like molecules and the other one is crumpled molecules. Among these types of molecules, photoinduced isomer-
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ization is considered. The local concentration order parameter $c$ represents the local fraction of the elongated molecules. The other order parameter is the local orientation order $\vec{a}$ which is the projection of the molecular direction of the elongated molecules. The vector $\vec{a}$ is defined as $\vec{a} = \vec{n} \sin \eta$ where $\vec{n}$ is the molecular direction, $\eta$ is the tilt angle and $\phi$ is the azimuthal angle.

The free energy functional $\mathcal{F}$ to describe the system is constructed in terms of the order parameter $c$ and $\vec{a}$ and it will be decomposed into two parts. One of the parts is $\mathcal{F}_c$ depending exclusively on the affinity between two isomers in the monolayer. The other part of the free energy is tail-tail interaction $\mathcal{F}_{or}$ which is both sensitive to $c$ and the orientation of the elongated molecules. $\mathcal{F}_c$ can be written in the following way

$$\mathcal{F}_c = \int dxdy \left[ -\tilde{\chi}_c c^2 + \frac{1}{2} \tilde{\chi}_2 (\vec{\nabla} c)^2 \right]$$

(2.4)

$\mathcal{F}_c$ describes the phase separation due to the lateral interactions between the molecules. The short-range interaction potential is determined by its strength $\chi_o$ and $\chi_2$ can be estimated as $\chi_2 \approx \frac{1}{2} \chi_o r_o^2$, where $r_o$ is the characteristic radius of the lateral interaction.

The free energy related to the orientation of the elongated molecules in the monolayer can be written as

$$\mathcal{F}_{or} = \int dxdy \left[ -\frac{1}{2} \tilde{\rho}(c)a^2 + \frac{1}{4} \tilde{\beta} a^4 + \frac{K_s}{2} (\vec{\nabla} \cdot a)^2 + \frac{K_b}{2} (\vec{\nabla} \times a)^2 + \tilde{\Lambda} c (\vec{\nabla} \cdot \vec{a}) \right]$$

(2.5)

The first two terms are coming from the Landau expansion up to the quadratic term for the modulus of the molecular orientation. The third and forth terms in Eqn. (5) corresponds to the Frank elasticity terms for the splay and bend distortion,
respectively. The fifth term is the lowest order splay contribution \((\vec{\nabla} \times \vec{a})\) which is coupled to the order parameter \(c\). For sufficiently strong coupling, the uniformly oriented phases are destabilized by the linear splay. Additionally, the linear splay term leads the system to the equilibrium nonhomogeneous splayed states.

The two order parameters \(c\) and \(\vec{a}\) are introduced to describe the system. The kinetic equations of \(c\) and the vector \(\vec{a}\) are

\[
\frac{\partial c}{\partial t} = \nabla^2 c + \vec{\nabla} \cdot [c(1-c)\vec{\nabla} \mu] + \kappa (1-2c) \tag{2.6}
\]

\[
\frac{\partial \vec{a}}{\partial t} = p(c)\vec{a} - \beta a^2 \vec{a} + K \nabla^2 \vec{a} + \Lambda \vec{\nabla} c - \kappa \frac{1-c}{c} \vec{a}
\]

where \(\mu = -2\chi_o c - \chi_2 \nabla^2 c + \alpha a^2 + \Lambda \nabla \cdot \vec{a}\) and \(p(c) = \pi_o + 2\alpha (0.5 - c)\). \(\mu\) in the above equation is the chemical potential and it is defined as \(\mu = \frac{\delta F}{\delta c}\).

For the system in nonequilibrium, Reigada et al. [4] chose the same numerical value of the common parameters \(\chi_2 = 0.0052, \chi_o = 2.27, \alpha = 1.5, \beta = 2\) for the numerical analysis.

When there is no splay coupling \((\Lambda = 0)\), the azimuthal orientation is not influenced by variations of the local concentration \(c\) and the local tilt \(\vec{a}\). With parameters \(\pi_o = 1.5, \kappa = 1\) and \(K=0.001\) and with random azimuth distribution as an initial condition, the molecules tend to have parallel orientation because of elastic interactions. This parallel orientation leads to a pattern characterized by a number of orientational defects that remains stationary. In the center of defects the tilt of the molecules are zero. When the molecules are passing around a defect, the azimuthal direction changes by \(2\pi\) (Fig 2.3a). When the linear splay term is included into the system, the Turing-like patterns transformed into travelling waves. With the choice of \(\kappa = 0.5, \pi_o = 1.25\) and \(\Lambda = K = 0.01\) (weak splay constant), the patterns look like
a droplets. The droplet structures of large $c$ and small $a$ form and move following the local molecular orientation path. The pattern of azimuthal orientation is frozen under weak splay coupling. The velocity of the droplet structures is an increasing function of the splay coupling constant $\Lambda$ and the reaction rate $\kappa$. Also, it is noted that the size of travelling structures is affected by the strength of elastic interactions. The larger the $K$ the bigger are the droplets. For large $K$, uniform state becomes stable and no spatial organization is observed (Fig 2.3b). If the reaction rate $\kappa$ is increased further ($\kappa = 1$), the patterns resembles the patterns of traveling waves in absence of splay coupling. The striped patterns move along the direction determined by the local azimuthal orientation of elongated molecules (Fig 2.3c). If $\Lambda$ is increased further (strong splay coupling), the azimuthal orientation of molecules becomes affected by the traveling or stationary patterns. For strong splay coupling $\Lambda = 1$ (also for $K=0.1$, $\kappa=1$ and $\pi_o=1.25$), the system forms striped pattern first, the stripes undergo breakdown and stationary defects formed (Fig 2.3d). If bigger reaction rate constant is chosen, the traveling waves that are accompanied by the azimuthal reorientation of molecules are formed. For splay coupling $\Lambda = 1.5$ and the reaction rate $\kappa = 3.5$, after a short transition from random initial condition, regular striped patterns travelling at constant velocity are formed (Fig 2.3e).

If one wants to analyze the origin of the waves, it is obviously seen that this effect is described by $\kappa^{1-c}d^a$. If this term was not in the free energy, the system would have only stationary patterns, not traveling waves.

**Summary:** In experimental work and both theoretical work done by Yuka Tabe et al. and Reigada et al. shows that orientational traveling waves are observed on Langmuir monolayer. Experiments show that traveling waves are formed as stripe patterns associated with azimuth of molecular direction. The direction of the waves
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Figure 2.3: Fig (a) shows the pattern of traveling waves that interact with orientational defects in the absent of splay constant. The concentration and orientation fields in a pattern of flowing droplets with the weak splay coupling is shown in (b). For large $K$, uniform state becomes stable and no spatial organization is observed (b). If reaction rate is increased further, the stripe patterns shown in (c) move along the direction determined by the local azimuthal orientation of elongated molecules. If $\Lambda$ is increased further, the stripes undergo breakdown and stationary defects formed (d). For higher reaction rate, regular striped patterns are formed. The azimuthal angle undergoes $\pi$ rotation from one stripe to another stripe (e).

are reversed, when the polarization of illumination is switched by $\pi/2$. In the systems with wave bifurcation either traveling wave or standing wave can be observed. Standing waves are the superpositions of two waves traveling opposite directions. When the bifurcation is supercritical, it is neccessary to look at the interaction between two modes, representing traveling waves with the opposite propagation directions. The sign and the magnitude of the coefficient of the modes would determine which one of these two modes eventually wins (one traveling wave) or both modes equally exist (one standing wave).
Chapter 3

Theory of Photo-activated Langmuir Monolayers

We want to consider a dynamical description of a collection of molecules that sit at an interface. The molecules can exist in one of two isomerizations, a cis-isomer that is a spherically symmetric configuration of the molecule and a trans-isomer that is elongated and capable of developing orientational ordering when present in sufficiently high concentrations. The orientational ordering is such that the molecules align with a specified tilt to the normal of the interphase. Such a system is characterized, on long length and time scales by three hydrodynamic variables, $\psi_{\text{trans}}$, the concentration of trans-isomers in the system, $\psi_{\text{cis}}$, the concentration of cis-isomers and $P$, a two dimensional vector order parameter associated with the amount of orientational ordering. In detail, it is the mean azimuthal angle obtained by projecting the molecules in the plane of the interface. In the following we outline the theoretic description of the system when it is isothermal (Fig 3.1).

The two dynamical variables $\psi_{\text{cis}}$ and $\psi_{\text{trans}}$ are purely functions of temperature
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Figure 3.1: Rod-like molecules at air-water interface form smectics C phase. \( \mathbf{\hat{z}} \) is the normal of the layer and \( \mathbf{\hat{n}} \) is the molecular direction.

and hence fixed in an isothermal system in the absence of any excitations. In this work we focus on low enough temperatures that the system is dominated by trans-molecules and hence exhibits a high degree of orientational ordering in the absence of photoexcitation. In this limit, one can describe the orientational order in the system using a Ginzburg Landau description for the free energy of the system. This free energy takes the form

\[
F = \int dr \left[ \frac{1}{2} \tau |P|^2 + \frac{1}{2} u |P|^4 - \lambda (\psi_{\text{trans}} + |P|^2) \nabla \cdot \mathbf{P} + \frac{1}{2} K (\nabla P)^2 \right] \tag{3.1}
\]

Clearly, the terms proportional to \( \tau \) and \( u \) control a second order phase transition from a disordered state when \( \tau > 0 \) to an ordered state at \( \tau < 0 \). Also, \( u > 0 \) in order that the extremum of the free energy in the ordered state be a stable one. For simplicity, in the following, we take \( \tau = \left( 1 - \frac{\psi_{\text{trans}}}{\psi_{\text{trans}}^c} \right) \) and \( u = \left( 1 + \frac{\psi_{\text{trans}}}{\psi_{\text{trans}}^c} \right) \) where \( \psi_{\text{trans}}^c \) is some critical density that sets the threshold for the onset of orientational order in the system. Next, the term proportional to \( \lambda \) is called spontaneous splay \cite{24} and is unique to polar liquid crystals and is indicative of the system’s tendency, in the absence of other constraints, to develop splay deformations. The term proportional
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to $K$ is the Frank free energy associated with liquid crystalline order in the one elastic constant approximation $[Π]$. Assuming Euler lagrange dynamics on this free energy landscape, the equations of motion for the orientational order parameter in the absence of any excitation becomes

$$\partial_t \mathbf{P} = -\left(\tau + u |\mathbf{P}|^2\right) \mathbf{P} - \lambda \nabla \psi_{\text{trans}} + \lambda (\mathbf{P} \cdot \mathbf{P} - P_t \mathbf{P}_t) + K \nabla^2 \mathbf{P} \quad (3.2)$$

This is a well established description of ferrofluids in equilibrium for example $[?]$. This is the theoretical description of our system in the absence of photo-excitation.

Next, let us consider the effect of light on the dynamics of the system. As mentioned earlier, we are considering the system at low enough temperatures that the trans-isomer is the ground state. When light of an appropriate frequency is shined on the monolayer, the molecules are excited into the cis-state. We assume that the thermal relaxation back to the ground state is the fastest process in the system. Further, it is known that the rate of photo-excitation depends on the relative orientation of the polarization of the incoming light and the azimuth of the molecule in the monolayer. Based on this, we get the dynamics of the concentration fields to be of the form

$$\partial_t \psi_{\text{trans}} = -\gamma_1 \psi_{\text{trans}} + \gamma_2 \psi_{\text{cis}}$$

$$\partial_t \psi_{\text{cis}} = -\gamma_2 \psi_{\text{cis}} + \gamma_1 \psi_{\text{trans}}$$

In the above $\gamma_1$ is the rate of conversion of trans-to-cis due to photo excitation and hence scales with the intensity of light and depends on the polarization and azimuthal orientation of the molecules. $\gamma_2$ is the thermal relaxation rate that relaxes cis molecules back to their trans isomerization and is just a constant in the context
of our isothermal system. We take the rate $\gamma_1$ to be of the form

$$\gamma_1 = \gamma I \left[ (2|\mathbf{P}|^2 - |\mathbf{P}|) \left( \mathbf{E} \cdot \mathbf{P} \right)^2 + (1 - |\mathbf{P}|^2) \right]$$

where $\mathbf{E}$ is the direction of polarization of incoming light and $I$ is its intensity. This form reflects the fact that when the molecules are orientationally ordered the transition will be induced only by that component of light that has an appropriate polarization. So, in the perfectly ordered state, when $|\mathbf{P}| = 1$, $\gamma_1 \rightarrow \gamma I \left( \mathbf{E} \cdot \mathbf{P} \right)^2$ and in the completely disordered state $\gamma_1 \rightarrow \gamma I$. Since the transition is proportional to the intensity of light, we are precluding spontaneous (thermal) transitions to the cis state, which is a valid assumption for low enough temperatures and can of course be readily relaxes for more general considerations. Finally, we take $\gamma_2 = \gamma$ a constant.

In order to enable further analysis, we define $\psi = \psi_{\text{trans}} - \psi_{\text{cis}}$, the differential concentration of our two isomers and normalize it with the mean concentration of molecules in our system, i.e., $\psi_{\text{trans}} + \psi_{\text{cis}} = 1$. Then the equation of motions we analyze are

$$\partial_t \psi = -(\gamma_1 + \gamma_2) \psi - (\gamma_1 - \gamma_2)$$

and

$$\partial_t \mathbf{P} = -\left( \tau + u |\mathbf{P}|^2 \right) \mathbf{P} - \lambda \nabla \psi + \lambda (\mathbf{P} \nabla \cdot \mathbf{P} - \mathbf{P} \nabla \cdot \mathbf{P}^t) + K \nabla^2 \mathbf{P}$$

These equations are the focus of our study in the following.
3.1 Linear Dynamics 1: In the absence of light

As a first step, let us characterize the base state of our polar fluid in the absence of any photo excitation. Let us set $I = 0$ and assume that we are interested in dynamics on long time scales compared to the thermal relaxation rate $\gamma$, so that the concentration variables have relaxed to their equilibrium values. Given the low temperature of interest we take $\psi_{\text{trans}} = 1$. Further, without loss of generality, we take the direction of polarization to be along the $x$-direction. Let us consider the perturbation of the form

$$ P = P_0 \hat{x} + \delta P (\mathbf{r}, t) \hat{x} + \delta p_\perp (\mathbf{r}, t) \hat{y} $$

(3.5)

In the above, $P_0$ is the equilibrium magnitude of the polar order which we can readily find to be $\sqrt{-\tau}/w$. $\delta P$ represents fluctuations in the magnitude of the liquid crystalline order while $\delta p_\perp$ are fluctuations in the director associated with the orientational ordering. Let us introduce a Fourier transform $\tilde{X}(\mathbf{q}, t) = \int d\mathbf{r} e^{i\mathbf{q} \cdot \mathbf{r}} X(\mathbf{r}, t)$ and component the spatial gradient vector along and orthogonal to direction of broken symmetry, i.e., $q \cos \theta = q_x$. Then, the linearized equation for the dynamics of the system are

$$ \partial_t \delta \tilde{P} = (-\|\tau\| - q^2 K) \delta \tilde{P} - iq \lambda P_0 \sin \theta \delta \tilde{p}_\perp $$

(3.6)

and

$$ \partial_t \delta \tilde{p}_\perp = iq \sin \theta \lambda P_0 \delta \tilde{P} - K q^2 \delta \tilde{p}_\perp $$

(3.7)

Equivalently, writing in matrix notation,

$$ \begin{bmatrix} \partial_t \delta \tilde{P} \\ \partial_t \delta \tilde{p}_\perp \end{bmatrix} = \begin{bmatrix} -\|\tau\| - q^2 K & -iq \lambda P_0 \sin \theta \\ iq \sin \theta \lambda P_0 & -K q^2 \end{bmatrix} \begin{bmatrix} \delta \tilde{P} \\ \delta \tilde{p}_\perp \end{bmatrix} $$

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By looking at the eigenvalues of the above matrix, we can see whether these fluctuations decay or grow. If the real part of the equations are negative, the fluctuations decay and the fluctuations grow if they are positive. One can find the eigenvalues of the above matrix as

$$s_{\pm} = \left( -\frac{\|\tau\|}{2} - q^2 K \right) \pm \frac{1}{2} \sqrt{\|\tau\|^2 + 4q^2 \sin^2 \theta \lambda^2 \left( \frac{\|\tau\|}{u} \right)}$$  \hspace{1cm} (3.8)

In the homogeneous limit, $q = 0$, $s_{\pm}$ becomes $s_+ = 0$ and $s_- = -\|\tau\|$ where $\tau = 1 - \frac{\psi_{\text{trans}}}{\psi_{\text{trans}}}$, giving us the expected result that while the director fluctuations are a truly hydrodynamic mode, a Goldstone mode associated with the broken continuous symmetry, the magnitude fluctuations are overdamped and decay on the effective rotational diffusion time set by $\tau$. Next, let us consider spatial fluctuations along the direction of ordering, i.e., $\theta = 0$. In this case the modes become $s_+ = q^2 K$ and $s_- = -q^2 K - \|\tau\|$. Thus, both modes are diffusive and stable to fluctuations long the direction of broken symmetry.

Next, let us consider fluctuations orthogonal to the direction of broken symmetry, i.e., $\theta = \frac{\pi}{2}$. In the long wavelength limit, the modes take the form

$$s_{\pm} = \left( -\frac{\|\tau\|}{2} - q^2 K \right) \pm \frac{\|\tau\|}{2} \left( 1 + 2q^2 \lambda^2 \left( \frac{1}{u \|\tau\|} \right) \right)$$

and hence $s_+ = -q^2 (K - \lambda^2 \left( \frac{1}{u} \right))$. This mode becomes unstable whenever $\frac{\lambda^2}{u} > K$. Thus, whenever the strength of the spontaneous splay is such that it is able to overcome the Frank Elasticity, the director fluctuations are destabilized. This instability leads to the formation of a striped state where the orientation of the molecules rotate with a characteristic length scale $\frac{20}{u}$. More generally, the onset of
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this instability is determined by the condition

\[
\left( \frac{\|\tau\|}{2} + q^2 K \right) < \frac{\|\tau\|}{2} \left( 1 + q^2 \sin^2 \theta \lambda^2 \left( \frac{1}{u \|\tau\|} \right) \right)^{1/2}
\]

Thus, the base state of our system can be a homogeneous polar state or a striped state characterized by a changing director field in the regime of parameters we are interested in. In the following we will focus on the homogeneous base state and reserve for the discussion at the end of the presentation some comments about the striped phase of our langmuir monolayer.

3.2 Dynamics in the presence of light - Self regulation

As stated above, the order disorder transition of our Langmuir monolayer is assumed to be described by a Ginzburg Landau form associated with a second order phase transition. But, in the presence of photo activation, the control parameter associated with this phase transition is itself controlled by the activity which in turn depends on the magnitude of order in the system. This phenomenon we call dynamical self-regulation and is a characteristic feature of all active liquid crystals and we will focus on this aspect of the dynamics of the system in this section.

In order to do so, let us begin by considering the coupled homogeneous equations controlling the variables \( P(t) \), the magnitude of polar ordering and \( \psi(t) \) the differential concentration of trans isomers. These are

\[
\partial_t \psi = -\gamma \left( \left[ P(2P - 1) \cos^2 \phi + \left( 1 - P^2 \right) \right] + 1 \right) \psi - \gamma \left( \left[ P(2P - 1) \cos^2 \phi + \left( 1 - P^2 \right) \right] - 1 \right)
\]
\[ \partial_t P = - \left( -\psi + (2 + \psi) P^2 \right) P \]

where we have introduced the notation \( \hat{E} \cdot \hat{P} = \cos \phi \) and assumed that \( \psi_{\text{trans}} = 1/2 \). Let us first solve for the steady state admitted by these equations. This gives

\[ \psi = - \frac{(I [P (2P - 1) \cos^2 \phi + (1 - P^2)] - 1)}{(I [P (2P - 1) \cos^2 \phi + (1 - P^2)] + 1)} \]

and

\[ \left( \frac{(I [P (2P - 1) \cos^2 \phi + (1 - P^2)] - 1)}{(I [P (2P - 1) \cos^2 \phi + (1 - P^2)] + 1)} \right) + \left( \frac{(I [P (2P - 1) \cos^2 \phi + (1 - P^2)] + 3)}{(I [P (2P - 1) \cos^2 \phi + (1 - P^2)] + 1)} \right) P^2 = 0 \]

Simplifying the above equations by using the fact that \( P << 1 \), to get

\[ \left( (-I \cos^2 \phi) + (-IP \cos^2 \phi + 4) P \right) = 0 \]

\[ P = 2 \left[ \frac{1 \pm \sqrt{1 + I \cos^2 \phi}}{I \cos^2 \phi} \right] \]

More generally, the consequence of self-regulation is better unfolded numerically integrating up the homogeneous equations above. These findings are summarized in Fig 3.2.

### 3.3 Linear Dynamics 2: In the Presence of Light

We do the same linear stability analysis for the case when \( \gamma \neq 0 \). We have the perturbation \( P = P_0 \hat{x} + \delta P (r, t) \hat{x} + \delta p_\perp (r, t) \hat{y} \) for the molecular direction and \( \psi = \psi_o + \delta \psi \) for the concentration order parameters. \( \psi_o \) can be found from the steady
Figure 3.2: (a) shows that molecular direction increases with time and reaches its steady state value after $t=500$. The molecular concentration decreases in time (b).

state of the equation $\partial_t \psi$ as

$$\psi_0 = -\frac{\gamma[(2P_0^2 - 1)\cos^2\phi - P_0^2]}{\gamma[(2P_0^2 - 1)\cos^2\phi + 2 - P_0^2]}$$

(3.10)

We linearize the non-linear equations by substituting the perturbations into the equations of motion for the order parameters and keeping the terms up to first order fluctuation terms. In the existence of light, the linearized equations are

$$\partial_t \delta \tilde{P} = (2\tau - q^2K)\delta \tilde{P} - iq\lambda P_0 \sin \theta \delta \tilde{p}_{\perp} + iq\lambda \cos \theta \delta \tilde{\psi}$$

(3.11)

$$\partial_t \delta \tilde{p}_{\perp} = iq \sin \theta \lambda P_0 \delta \tilde{P} - K q^2 \delta \tilde{p}_{\perp} + iq \sin \theta \delta \tilde{\psi}$$

(3.12)

$$\partial_t \delta \tilde{\psi} = -\gamma 2P_0(\cos^2\phi - 1)$$

$$\frac{(2P_0^2 - 1)\cos^2\phi + 2 - P_0^2}{\gamma 2\phi(2P_0 - \frac{1}{P_0})} \delta \tilde{P} - \frac{\gamma 2\sin 2\phi(2P_0 - \frac{1}{P_0})}{(2P_0^2 - 1)\cos^2\phi + 2 - P_0^2} \delta \tilde{p}_{\perp}$$

$$-\gamma[(2P_0^2 - 1)\cos^2\phi + 2 - P_0]\delta \tilde{\psi}$$

(3.13)
Let us simplify the above equations by making different choices for the fluctuations and by setting various parameters to different values to understand the system better. When $\delta P$ is overdamped, from the equation $\partial_t \delta \tilde{P} = (2\tau - q^2 K) \delta \tilde{P}$, we can find $\delta \tilde{P}$ as $e^{2\tau t} \delta P(0)$ and $\delta \tilde{P}$ goes to zero eventually since $\tau$ is negative. We take $\delta \tilde{P} = 0$ and $P_o \approx 1$ and by substituting these into the equations for $\delta \tilde{p}_\perp$ and $\delta \tilde{P}$. The linearized equations becomes

$$\partial_t \delta \tilde{p}_\perp = -q^2 K \delta \tilde{p}_\perp + iq\lambda^2 \sin \theta \delta \tilde{\psi} \quad (3.14)$$

$$\partial_t \delta \tilde{\psi} = \frac{2 \sin 2\phi}{\cos^2 \phi + 1} \delta \tilde{p}_\perp - \gamma [\cos^2 \phi + 1] \delta \tilde{\psi} \quad (3.15)$$

By dividing both sides by $\gamma$ and setting $K/\gamma=1$ and $\lambda/\gamma=\lambda^*$, we will end up with the following equations

$$\frac{1}{\gamma} \partial_t \delta \tilde{p}_\perp = -q^2 \delta \tilde{p}_\perp + iq\lambda^* \sin \theta \delta \tilde{\psi} \quad (3.16)$$

$$\frac{1}{\gamma} \partial_t \delta \tilde{\psi} = \frac{2 \sin 2\phi}{\cos^2 \phi + 1} \delta \tilde{p}_\perp - [\cos^2 \phi + 1] \delta \tilde{\psi} \quad (3.17)$$

The below matrix $L$ describes the system of the above equations

$$L = \begin{bmatrix} -q^2 & iq\lambda^* \sin \theta \\ \frac{2 \sin 2\phi}{\cos^2 \phi + 1} & -[\cos^2 \phi + 1] \end{bmatrix}$$

First column corresponds to $\delta \tilde{p}_\perp$ and the second one corresponds to $\delta \tilde{\psi}$. If we look at the above matrix, we can guess that there is nothing interesting at $\phi = 0$ and $\phi = \pi/2$. One can easily say that $\phi$ must be an angle between 0 and $\pi/2$. To verify
our prediction, we look at the modes of the above matrix and see where the real part changes its sign and where the imaginary part is non-zero. Eigenvalues of the above matrix

\[
s_\pm = -\frac{q^2 K - \cos^2 \phi - 1}{2} \pm \frac{1}{2} \sqrt{(-q^2 + (\cos^2 \phi + 1))^2 - \frac{i q^2 \lambda^* \sin \theta \sin \phi}{\cos^2 \phi + 1}}
\]

With the choice of \( \phi = 0 \), unstable modes, that is \( \text{Re}(s) > 0 \) and \( \text{Im}(s) \neq 0 \) for \( q \neq 0 \), leads traveling waves\(^2\).

\[
s_+ = -\frac{q^2 K - q^2}{2} + i \frac{\sqrt{2} \lambda^* \sin 2\phi}{(\cos^2 \phi + 1)} (1 - \cos^2 \phi + \cos^4 \phi)q
\]

\[
s_- = -\frac{q^2 K + q^2}{2} - (\cos^2 \phi + 1) - i \frac{\sqrt{2} \lambda^* \sin 2\phi}{(\cos^2 \phi + 1)} (1 - \cos^2 \phi + \cos^4 \phi)q
\]

With the choice of \( \phi = \pi/4 \), unstable modes, that is \( \text{Re}(s) > 0 \) and \( \text{Im}(s) \neq 0 \) for \( q \neq 0 \), leads traveling waves\(^2\). For another case, we take \( \delta \tilde{\psi} \) is overdamped. We take the limit of that \( \delta \tilde{\psi} \) goes to zero and solve for \( \delta \tilde{\psi} \) and plug it into the equation for \( \delta \tilde{p}_\perp \). We get the following

\[
\partial_t \delta \tilde{p}_\perp = [-q^2 K + \frac{i q^2 \lambda^* \sin \theta \sin 2\phi}{(\cos^2 \phi + 1)^2}] \delta \tilde{p}_\perp
\]

From this equation, we can say that the velocity of the traveling waves \( u \approx \frac{2 \lambda \sin \theta \sin 2\phi}{(\cos^2 \phi + 1)^2} \). Our theoretical predictions verify the experimental results done by Yuka Tabe et al\(^2\). When we switch the angle \( \phi \) between illumination and the wave propagation by \( \pi/2 \), the propagation directions of the waves are reserved or if we take \( -\phi \) instead of
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φ, the wave propagation will be in the opposite direction of the one when the angle is φ.

In summary, we have identified the existence of propagating modes in certain parameter regimes of this system. Note that our dynamics is overdamped. The existence of such propagating solutions is due to the active driving of the system using light and the consequent emergence of self-regulation.
Chapter 4

Numerical Analysis

4.1 Equations and Methods

In this section, we want to use numerical methods to unfold the physics of the propagating modes found earlier. We want to focus on the photo excitation of the homogeneous state of the Langmuir monolayer. For this purpose, we will focus on the regime in which the magnitude of the ordering is saturated, i.e., $P = 1$ and when the intensity of light is set equal to 1. Further, we assume that spatial relaxation due to diffusive processes occurs on a fast time scale and therefore neglect for the most parts, second spatial derivatives in the dynamics. Introducing the angle $\phi$ to denote the orientation of the director in the plane of the interphase, the equations of interest become

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

(4.1)

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

(4.2)
Figure 4.1: Two different visualization of the phase diagram in $\gamma - \lambda$ plane. For large values of $\gamma$ or small values of $\lambda$, there is no propagating waves.

These are the equations we study as a function of three parameters, the strength of spontaneous splay $\lambda$, the relaxation rate for thermal equilibration of cis to trans isomers, $\gamma$ and finally the relative orientation of the polarization of incoming light with the in-plane orientational order.

The numerical study is carried out by implementing a forward Euler discretization of the above equations on MATLAB. For most studies, we used a $256 \times 256$ two-dimensional square lattice by using the explicit first order Euler time stepper with a time step $\Delta t = 0.01$ and the lattice spacing $\Delta x = \Delta y = 256/(80\pi) \approx 1$ with periodic boundary conditions at the domain edges so as to mimic a thermodynamic system.

### 4.2 Uniform Illumination

In the system under uniform illumination, as an initial condition, we took the local concentration difference between trans and cis isomers $\psi$ as 1 everywhere on 2-D
square lattice and the azimuthal orientation of the molecules as 0 everywhere except at the center of the lattice. We took the perturbation of $\phi=\pi/2$ at the center. Based on the simulations, we observed that there is certain threshold for $\lambda$ and $\gamma$ values.

Blue region indicates that there is no traveling waves at small lambda and even if lambda value is high enough to form traveling waves, after $\gamma=1$ we could not observe traveling waves. Gray region is the region where traveling waves barely occurred but not with well-defined stripes. We observed that there is wave propagation with a well defined stripes in the pink region in the chart shown in (Fig 4.1). After this analysis, we switch our interest to analyze the speed of traveling wave which occur in the pink region.

![Wave Speed vs Gamma](image1)

(a)

![Wave Speed vs Lambda](image2)

(b)

Figure 4.2: Fig (a) shows the speed of traveling waves with respect to $\gamma$ for different values of $\lambda$. For small $\lambda$ and $\gamma$, the speed of traveling waves is very low. As $\lambda$ increases, the speed of the waves increases. Fig (b) shows the speed of waves are increasing up to a certain value of $\gamma$, then the waves move with constant speed.

In Fig (4.2a), for $\lambda=0.1$, we see that there is no increase in the speed of the traveling waves as $\gamma$ increases. This is below of the threshold value of $\lambda$ for the wave formation. For $\lambda=1$, there is a bump characterizes the speed of the waves. The speed increases until it reaches a threshold value for $\gamma$ which is around 0.2. After this $\gamma$
Figure 4.3: The speed of waves versus $\theta$ is plotted. The waves reach their maximum values when the angle of polarization is integer multiple of $\pi/4$, while their speed is minimum when the direction of illumination and molecules are orthogonal to each other. Then, the maximum speed of the waves are plotted with respect to $\lambda$.

value the speed decreases until the waves flow with a constant speed. After certain threshold, the speed of waves increases (Fig 4.2a).

In the Fig 4.3a, we can see the speed of waves are increasing with increasing $\lambda$, it saturates eventually, has constant values. When we look at the wave speed as a function of $\theta$, we observe that it has peak value at $\theta=\pi/4, 3\pi/4$ and $5\pi/4$. Then we wanted to analyze maximum velocity that the wave can take its maximum value as a function of $\lambda$.

There are certain differences in width with respect to $\lambda$ values. As $\lambda$ increases the width of the stripes are decreases (Fig 4.4).
Figure 4.4: We see that the waves are not of constant width indicative of the fact that they are solitary waves. Fig. (a), (b), (c), (d) shows the width of the waves for $\lambda = 0.5, 1, 3$ and 5, respectively. The width of the stripes are decreasing with increasing $\lambda$ value.

### 4.3 Single Slit and Double Slit Illumination

In addition to uniform illumination with the perturbation $\phi = \pi/2$ at center, we also used the random initial condition for $\phi$ everywhere. Initially, there are differences in pattern formation under the uniform illumination with both initial conditions for $\phi$. After long enough time, both simulations show us approximately the same patterns. In Fig. 4.5a and 4.5b we see that striped patterns are spread through the square lattice and tend to align horizontally. Travelling waves moves downward. Also, we enlighten Langmuir monolayer partially to see the effect of position dependence of illumina-
CHAPTER 4. NUMERICAL ANALYSIS

tion on the direction of propagating waves. We put illumination between x=120 and x=140. Traveling waves moves in positive x-direction and the waves are limited by the boundary of illumination. We observe that a stationary pattern is formed at a position before the illumination starts (Fig 4.5c). When we add diffusion to the system, we see that the molecules are diffusing through the opposite direction of propagation of waves (Fig 4.5d). Under double slit illumination, the traveling waves occurred between the position where illumination starts and ends. Now, there are two stationary patterns at the beginning the illuminations. The molecules remain unchanged where there is no reaction (Fig 4.5e). Fig 4.5f shows the system with the opposite choice of the polarization of illumination for each slit. We reversed the direction of illumination at the second illumination and see the stationary pattern changes its place to the end of the slit where traveling waves start to propagate. Traveling waves switched their propagation direction by 180° with changing the polarization of illumination.

Next, we use different diffusion constant to see the effect of diffusion on the system. As diffusion constant D increases, the region of molecules with 180° azimuth expanding and the width of stripes increases (Fig 4.6).
Figure 4.5: This panel shows the differences between various illumination types. (a) We used uniform illumination with a perturbation of $\phi = \pi/2$ at center. We added some small randomness to $\phi = \pi/2$ as an initial condition in (b). Patterns are spread all through the square grid with uniform illumination. The traveling waves occurs between wall of single slit illumination begins and ends. We see that there is a stationary pattern where the single slit illumination starts (c). When we there is diffusion in the system, Figure (d) shows that patterns are diffusing from the limit of illumination. With double slit illumination, we see that there is no reaction between two slits but inside the illumination limits. The stationary patterns are at the position of where illuminations start (e). When we reverse polarization of incoming light in the second slit, traveling waves switch the propagation waves and stationary pattern also changes its position with changing direction of illumination (f).
Figure 4.6: Traveling waves are illuminated as a single slit between $x=80$ and $x=180$. (a) Stripes are formed when there is no diffusion in the system. (b) With diffusion constant $D=1$, we see that stripes are getting wider and the region at the left outside of the illumination (colored by red) is expanded. With $D=10$, Red region is wider with increasing diffusion constant $D$. 
Chapter 5

Summary and Outlook

In this work we have investigated the dynamics of a photoactivated Smectic C Langmuir monolayer. First, we show that in the absence of photo-activation, a smectic C monolayer can exist in one of two states, namely a homogeneous state and a striped state. Then, we considered the effect of photoexcitation on the homogeneous state. We found that the magnitude of ordering is non-trivially modified by the presence of light and hence its induced cis-trans isomerization dynamics. Further, we showed that the presence of light sets up propagating orientation waves in the system. We characterized the properties of these propagating waves as a function of the strength of the spontaneous splay and the relaxation rate associated with the cis-trans process. Next, by considering localized excitations set up using illuminations confined to slits of various widths, we showed that the effect of diffusion can be capitalized to convert this system into one that can support Turing-like patterns.

The primary consequence of this work is the proof of principle demonstration that a photo-activated langmuir monolayer is a chemical realization of an active polar fluid. The primary features of active polar fluids, namely the existence of self regulation and
the presence of propagating solitary waves in an overdamped system are both present in this system. Active fluids are materials driven out of equilibrium by energy input at the scale of the individual units. Here, the photons absorbed by the molecules serve as the activity and is indeed a drive at the microscale. Self regulation comes about when the control parameter of ordering in the system is influenced by the amount of order itself. This physics is manifest here due to the fact that the trans-to-cis transition rate is controlled by the orientation of the molecule with respect to the polarization of the light source. Hence this system can serve as a controlled experimental platform to explore the physics of active polar fluids that are widely relevant for diverse systems ranging from cytoskeletal dynamics to bacterial suspensions and biofilm formation.
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