

Pattern Formation in Monolayer Transfer Systems with Substrate-Mediated Condensation

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The formation of regular stripe patterns during transfer of surfactant monolayers onto solid substrates is investigated. Two coupled differential equations describing the surfactant density and the height profile of the water subphase are derived within the lubrication approximation. If the transfer is carried out in the vicinity of a first order phase transition of the surfactant, the interaction with the substrate plays a key role. This effect is included in the surfactant free-energy functional via a height-dependent external field. Using transfer velocity as a control parameter, a bifurcation from a homogeneous transfer to regular stripe patterns arranged parallel to the contact line is investigated in one and two dimensions. Moreover, in the two-dimensional case, a secondary bifurcation to perpendicular stripes is observed in a certain control parameter range.

Introduction

Self-organized processes in dewetting systems provide effective methods for the controlled fabrication of micro- and nanostructured surfaces. Monolayers of amphiphilic molecules such as pulmonary lung surfactant DPPC (dipalmitoylphosphatidylcholine)^{1–3} and also of metals such as gold and silver⁴ are known to form regular stripe patterns upon transfer onto solid substrates. Typically, these experiments utilize the Langmuir–Blodgett method, where the substrate is withdrawn from a trough filled with water on which a monolayer has been prepared. Furthermore, similar patterns are also observed in controlled evaporation processes.^{4,5} Here, we want to focus on systems with lipid monolayers of surfactants such as DPPC or DMPE (dimyristoylphosphatidylethanolamine). The corresponding experiments are conducted under conditions close to the so-called main transition of the monolayer, that is, the first order phase transition between the liquid-expanded (LE) and the liquid-condensed (LC) phase using the Langmuir–Blodgett method. The observed patterns consist of ordered arrays of LE and LC domains, including regular stripes either parallel or perpendicular to the three-phase contact line as well as a combination of both resulting in a rectangular structure.^{1,2} Remarkably, the monolayer is transferred at a lateral pressure *below* the transition pressure, that is, directly from the pure LE phase. The partial condensation necessary for the formation of the observed patterns is attributed to substrate–monolayer interactions and is usually referred to as substrate-mediated condensation (SMC).^{3,6–9}

The theoretical investigation of dewetting systems with surfactants is typically based on the lubrication approximation which greatly facilitates the description of thin film flow.^{10–12} A model for thin film dynamics with a surfactant phase transition was derived earlier.¹³ It consists of two coupled nonlinear differential equations describing the height profile of the film and the surfactant density. Thermodynamics of the surfactant is incorporated via a Cahn–Hilliard-type free-energy functional which describes a transition between two stable phases of different surfactant density.

Here, we present a theoretical description of the situation where a monolayer is transferred from an evaporating thin liquid film onto a solid substrate. For that purpose, we extend the model¹³ by inclusion of evaporative effects and substrate-mediated condensation. The latter is included in the surfactant free-energy functional via a height-dependent external field. Within a certain range of transfer velocities, we shall find, instead of homogeneous transfer, two types of regular stripe patterns, one arranged parallel and the other perpendicular to the contact line.

Thin Film Flow

To focus on the effect of substrate-mediated condensation, let us look at a simple model system where surfactants are perpetually transferred to a solid substrate. We consider an evaporating thin film of water on a plate which is removed in the negative x -direction from a water reservoir which ensures a constant film height at the right boundary of the system (see Figure 1). A meniscus is then given by the balance of evaporation and the supply of fresh water, which is carried from the reservoir by the moving plate, yielding a contact line moving relatively to the substrate. The water reservoir is assumed to be covered with a surfactant monolayer of constant density, which is then carried by the flow toward the contact line. The liquid film is described by its height profile $h(x,t)$, which indicates the local film thickness,

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(1) Gleiche, M.; Chi, L. F.; Fuchs, H. *Nature* **2000**, *403*, 173–175.
(2) Chen, X.; Lehnert, S.; Hirtz, M.; Lu, N.; Fuchs, H.; Chi, L. F. *Acc. Chem. Res.* **2007**, *40*, 393–401.
(3) Spratte, K.; Chi, L. F.; Riegler, H. *Europhys. Lett.* **1994**, *25*, 211–217.
(4) Huang, J.; Kim, F.; Tao, A. R.; Connor, S.; Yang, P. *Nat. Mater.* **2005**, *4*, 896–900.
(5) H. Yabu, M. S. *Adv. Funct. Mater.* **2005**, *15*, 575–581.
(6) Leporatti, S.; Brezesinski, G.; Möhwald, H. *Colloids Surf., A* **2000**, *161*, 159–171.
(7) Graf, K.; Riegler, H. *Colloids Surf., A* **1998**, *131*, 215–224.
(8) Spratte, K.; Riegler, H. *Langmuir* **1994**, *10*, 3161–3173.
(9) Riegler, H.; Spratte, K. *Thin Solid Films* **1992**, *210–211*, 9–12.

(10) Craster, R. V.; Matar, O. K. *Rev. Mod. Phys.* **2009**, *81*, 1131.
(11) Bonn, D.; Eggers, J.; Indekeu, J.; Meunier, J.; Rolley, E. *Rev. Mod. Phys.* **2009**, *81*, 739.
(12) Oron, A.; Davis, S. H.; Bankoff, S. G. *Rev. Mod. Phys.* **1997**, *69*, 931–980.
(13) Köpf, M. H.; Gurevich, S. V.; Friedrich, R. *EPL* **2009**, *86*, 66003.

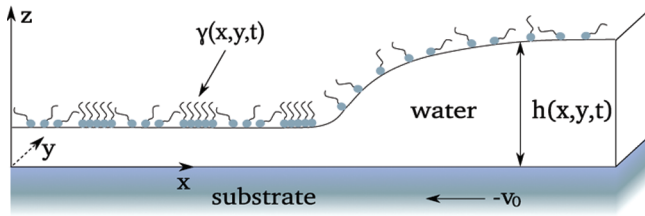


Figure 1. Schematic of a surfactant-laden meniscus. The height profile $h(x,y,t)$ indicates the film thickness at location (x,y) and time t , whereas $\gamma(x,y,t)$ describes the surfactant density at the surface above (x,y) .

whereas the surfactant density at the surface above point $x = (x,y)$ is described by the function $\gamma(x,t)$. Using lubrication approximation, the dimensionless time evolution equations for the height profile $H(X,T)$ and the surfactant density $\Gamma(X,T)$ are obtained as

$$\partial_T H = -\nabla \cdot \left\{ \frac{H^3}{3} \nabla \bar{P} + \frac{H^2}{2} \nabla \hat{\Sigma} - V_0 H \right\} - Ev \Delta \mu \quad (1)$$

$$\partial_T \Gamma = -\nabla \cdot \left\{ \frac{\Gamma H^2}{2} \nabla \bar{P} + \Gamma H \nabla \hat{\Sigma} - V_0 \Gamma \right\} \quad (2)$$

with the generalized pressure $\bar{P} = \varepsilon^3 Ca^{-1} \hat{\sigma} \nabla^2 H - \Pi(H)$ and the scaled surface tension $\hat{\Sigma} = \varepsilon Ca^{-1} \hat{\sigma}$. Here, $\varepsilon = h_0/l_0$ is the ratio of the characteristic height and length scales of the system in question and is assumed to be small in thin film geometries. The inverse capillary number $Ca^{-1} = \sigma_0/(\eta U_0)$ is the surface tension of water σ_0 in the absence of any surfactant, scaled by the dynamic viscosity η and a characteristic velocity U_0 . Generally, the surface tension varies across the surface, depending on the local surfactant density Γ and its spatial derivatives. This dependence is described by the lateral pressure P_{lat} and the relation¹⁴

$$\hat{\sigma} := \frac{\sigma}{\sigma_0} = 1 - P_{lat} \quad (3)$$

and will be discussed in more detail below. The substrate–liquid interaction is described in terms of the disjoining pressure $\Pi(H)$. In the literature, different expressions for $\Pi(H)$ have been considered (see ref 12 and references therein for a discussion of possible choices). Here, we will use $\Pi(H) = A_3 H^{-3} - A_9 H^{-9}$, where $A_3, A_9 > 0$, yielding a precursor height H_p , defined by $\Pi(H_p) = 0$. The transfer velocity, that is, the velocity of substrate withdrawal $V_0 = v_0/U_0$ enters both equations as an advective contribution. In order to model evaporation, we have included a sink term in the evolution equation for H , so that the fluid volume is not conserved. Here $\Delta \mu = \mu_w - \mu_v$ denotes the difference of the chemical potentials of the water film and the ambient vapor phase, whereas $Ev = \eta l_0^2 Q_e/h_0^3$ is the evaporation number with effective rate constant Q_e . The pressure in the vapor above the film is assumed to be close to the saturation pressure, allowing us to identify the chemical potential of the water film with the negative generalized pressure,^{15,16} that is, $\mu_w = -\bar{P}$, $\mu_v = \text{const}$.

Surfactant Thermodynamics and Substrate-Mediated Condensation

Since the surfactant density varies across the surface, its free-energy is given by the functional¹⁷ $\mathcal{F}[\Gamma] = \int d^2X f(X)$ with

(14) Adamson, A. W. *Physical Chemistry of Surfaces*; Wiley Interscience: New York, 1990.

(15) Pismen, L. M. *Phys. Rev. E* **2004**, *70*, 021601.

(16) Thiele, U.; Vancea, I.; Archer, A. J.; Robbins, M. J.; Frastia, L.; Stannard, A.; Pauliac-Vaujour, E.; Martin, C. P.; Blunt, M. O.; Moriarty, P. J. *J. Phys.: Condens. Matter* **2009**, *21*, 264016.

(17) Cahn, J. W.; Hilliard, J. E. *J. Chem. Phys.* **1958**, *28*, 258–267.

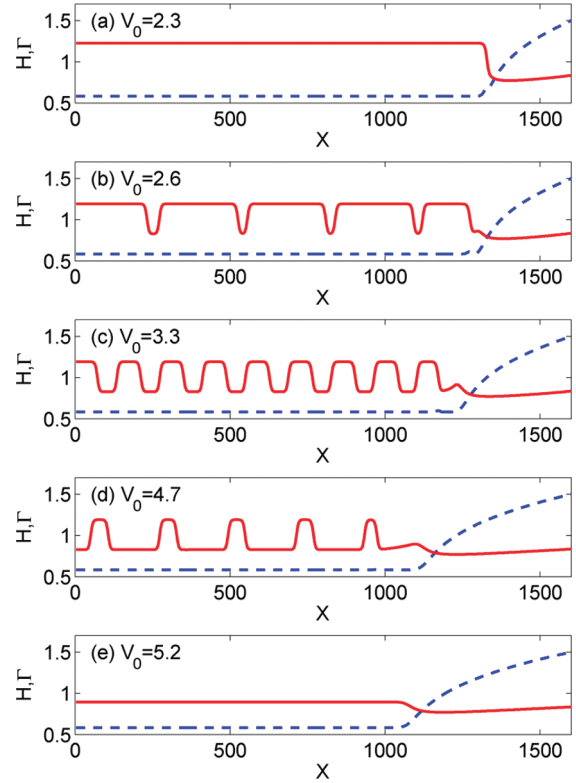


Figure 2. Snapshots of one-dimensional simulations at different transfer velocities V_0 , where the solid red line denotes the surfactant density Γ and the dashed blue line corresponds to the height profile H : (a) homogeneous transfer of LC surfactant, (b) periodic pattern of alternating LE and LC domains, (c, d) periodic patterns with narrower LC domains, and (e) homogeneous transfer of LE surfactant.

the free-energy density

$$f = \varepsilon^2 \frac{K}{2} (\nabla \Gamma)^2 + F_{\text{hom}}(\Gamma) \quad (4)$$

where $K = \kappa \gamma_0^2 / (h_0^2 \sigma_0)$ with characteristic surfactant density γ_0 is the nondimensionalized line tension κ of surfactant phase boundaries. The function F_{hom} represents the free energy of a system with homogeneous surfactant density Γ . In the following, we consider a bistable system where the low- and high-density minima of F_{hom} correspond to the liquid-expanded and the liquid-condensed phase, respectively.

Substrate–monolayer interactions lower the free energy of the surfactant at the three-phase contact line and thus facilitate its condensation onto the substrate.⁶ This effect can be modeled by inclusion of a height-dependent external field in the surfactant free-energy density. Restricting ourselves to free-energy densities that can be approximated sufficiently well by a fourth-order polynomial around the critical surfactant density Γ_{cr} , we obtain

$$\tilde{F}_{\text{hom}}(\tilde{\Gamma}, H) = \sum_{k=0}^4 F_k \tilde{\Gamma}^k + S(H) \tilde{\Gamma} + \mathcal{O}(\tilde{\Gamma}^5) \quad (5)$$

where $\tilde{\Gamma} = \Gamma - \Gamma_{\text{cr}}$, so that we can identify $F_{\text{hom}}(\Gamma, H) = \tilde{F}_{\text{hom}}(\tilde{\Gamma}, H)$. Although $F_{\text{hom}}(\Gamma, H)$ is not necessarily symmetric, it must possess two minima in order to model a phase transition, leading to a restriction in the choice of the coefficients F_k . This means that $F_{\text{hom}}(\Gamma, H)$ is a general double-well potential centered around $\Gamma = \Gamma_{\text{cr}}$ with a height-dependent first-order contribution. However, for the sake of simplicity, in the following, we assume $F_{\text{hom}}(\Gamma, H)$ to be symmetric for vanishing S . It has to

be emphasized that this is no real limitation, since, around the coexistence plateau, a wide range of experimentally obtained pressure–area isotherms can be fitted reasonably well under the assumption of a symmetric F_{hom} . Alas, the exact form of the height dependence $S(H)$ is difficult to obtain experimentally, and so far only the overall strength of the SMC has been measured from a change of lateral pressure in the monolayer when it is transferred from the water onto the substrate.⁸ However, it is clear from the experimental evidence that $S(H)$ goes to a finite negative value for $H \rightarrow H_p$, leading to a tilt of F_{hom} toward its higher density minimum, that is, the LC phase, as the monolayer approaches the substrate. Also, $S(H)$ should vanish quickly for $H \rightarrow \infty$, since the SMC has a measurable effect only very close to the substrate. Although the following results are qualitatively valid for a class of functions $S(H)$ meeting these minimal constraints, without loss of generality we choose $S(H) = \beta\psi(H)$, where $\psi(H) = \int dH \Pi(H)$ with integration constant zero is the potential of the substrate–liquid interaction and β is a positive coupling constant. By this choice, SMC acts on length scales comparable to the substrate–liquid interaction.

With the chemical potential

$$\mu = \frac{\delta \mathcal{F}[\Gamma]}{\delta \Gamma} = -\varepsilon^2 K \nabla^2 \Gamma + \frac{\partial F_{\text{hom}}}{\partial \Gamma}(\Gamma, H) \quad (6)$$

we can write down the lateral pressure in the form

$$P_{\text{lat}} = -f + \Gamma \mu = P_{\text{hom}}(\Gamma) - \varepsilon^2 K \left[\frac{1}{2} (\nabla \Gamma)^2 + \Gamma \nabla^2 \Gamma \right] \quad (7)$$

where the local part of P_{lat} is denoted as $P_{\text{hom}} := -F_{\text{hom}} + \Gamma \partial F_{\text{hom}} / \partial \Gamma$. Inserting eq 5 yields a third-order polynomial in Γ for P_{hom} . For the purpose of numerical calculations, we have estimated the coefficients of the polynomial from a fit to an experimentally obtained pressure–area isotherm of DPPC at 25 °C.¹⁸ The next point to emphasize is that the pressure in inhomogeneous systems of spatially varying density Γ is described by a tensor \mathbf{P} with the components $P_{ij} = P_{\text{lat}} \delta_{ij} + \varepsilon^2 K (\partial_i \Gamma) (\partial_j \Gamma)$.^{19,20} Since ε is assumed to be small, all terms of order ε^5 in eqs 1 and 2 can be safely ignored. Therefore, the lateral pressure enters the equations only in the form of $\nabla \cdot \mathbf{P} = \nabla (P_{\text{lat}} + \varepsilon^2 K (\nabla \Gamma)^2)$, so that one can simply use the *scalar* pressure $P = P_{\text{lat}} + \varepsilon^2 K (\nabla \Gamma)^2$ throughout all calculations.

Numerical Simulation

We discretize eqs 1 and 2 using 384 and 384×384 gridpoints in one and two dimensions, respectively. Derivatives are approximated by second-order finite differences, and an embedded adaptive Runge–Kutta scheme of order 4 (5) is employed for time stepping.²¹ The simulations for our choice of parameters¹⁸ are performed on a domain of length L in one dimension and on a square domain of size $L \times L$ in two dimensions, where $L = 1600$. Our goal is to simulate the substrate withdrawal from a water

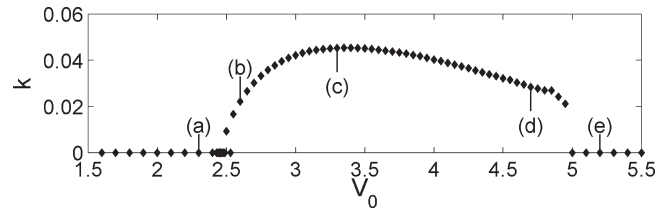


Figure 3. Wavenumbers of the observed patterns against transfer velocity. The letters (a)–(e) mark the wavenumbers corresponding to the velocity values used in Figure 2.

reservoir which is covered with surfactant in the liquid-expanded phase. Therefore, the following boundary conditions hold:

$$\Gamma(L) = \Gamma_L, \quad \partial_X^2 \Gamma(L) = 0 = \partial_X \Gamma(0) = \partial_X^2 \Gamma(0)$$

$$H(L) = H_L, \quad \partial_X^2 H(L) = 0 = \partial_X H(0) = \partial_X^2 H(0)$$

where we choose $\Gamma_L = 0.835$, which is the density of the LE phase, and $H_L = 1.5$. In two-dimensional simulations, periodic boundary conditions in the Y -direction are used. As initial conditions, we use a kinklike function going from the density of the pure LC phase to Γ_L for Γ and a Gaussian drop centered at $X = L$ for H . Random noise of amplitude 0.1 is added to both $\Gamma(X,0)$ and $H(X,0)$. Note that the choice of the initial conditions has no influence on the long-time evolution of the system, since after very short simulation time, the film profile H evolves into a stationary meniscus, as shown in Figure 2a. Its shape is determined by the balance of evaporation and the supply of fresh water, which is carried from the water bath into the integration domain by the moving substrate.

Using the transfer velocity V_0 as a control parameter, different operation regimes of the system eq 1/eq 2 are found: for small values of V_0 , the transfer is homogeneous and the substrate is coated with a monolayer in the LC phase (see Figure 2a). However, if we increase the velocity to some critical value $V_{\text{cr},l} \approx 2.4$, the system bifurcates, exhibiting a periodic spatiotemporal pattern, consisting of alternating domains of surfactant in the LE and the LC phase (see Figure 2b). These domains are created at the contact line and then advected by the flow. The creation of a new domain goes along with a small bump in the height profile, which quickly evaporates. Upon further increase of the control parameter, the initially broad LC domains get narrower, while the LE stripes grow (see Figure 2c and d). Finally, the transfer again becomes homogeneous for velocities $V_0 \gtrsim V_{\text{cr},u} = 4.8$, and the substrate is coated with a pure LE monolayer (see Figure 2e). Figure 3 displays the bifurcation diagram showing the wavenumber $k = 2\pi/\lambda$, where λ is the period length of the observed structures, as a function of the transfer velocity, and can be compared qualitatively to similar bifurcation diagrams obtained from experiments.^{2,22} All aforementioned patterns have analoga in the two-dimensional case, where stripes parallel to the contact line correspond to the alternating domains of the one-dimensional simulations (see Figure 4a). However, the formation of these stripes is not stable for velocities close to the upper and lower bounds $V_{\text{cr},u}$ and $V_{\text{cr},l}$: After a few stripes are produced, the regularity breaks down and disordered domains are created (see Figure 4b). Nevertheless, there exists a velocity range $2.58 \lesssim V_0 \lesssim 3.10$, where this disordered state is only transient and marks a transition from parallel to perpendicular stripes (see Figure 4c–f).

(18) The coefficients $F_0 = -0.1$, $F_1 = F_3 = 0$, $F_2 = -0.04$, $F_4 = 0.6$, $\Gamma_{\text{cr}} = 1$ were obtained from a fit to experimental data provided by M. Hirtz (private communication), and Γ was scaled so that $\Gamma_{\text{cr}} = 1$. SMC parameter $\beta = 0.2$, domain interface tension $K = 162.8$, and evaporation parameters $\text{Ev} = 0.05$, $\mu_{\text{vapor}} = 0.01$ had to be estimated. Hamaker constant $A_3 = 0.265$ results from scaling of a typical value $a_3 = 0.5/(12\pi) \times 10^{-20}$ J; A_9 is chosen to yield a precursor height ≈ 5.8 nm. The ratio of length and height scales $\varepsilon = 0.1$. Inverse capillary number $\text{Ca}^{-1} = 72750$ corresponds to water.

(19) Davis, H. T.; Scriven, L. E. *Adv. Chem. Phys.* **1982**, *49*, 357–454.

(20) Evans, R. *Adv. Phys.* **1979**, *28*, 143–200.

(21) Press, W. H. *Numerical Recipes in C*; University Press: Cambridge, 1999.

(22) Lenhart, S.; Gleiche, M.; Fuchs, H.; Chi, L. *ChemPhysChem* **2005**, *6*, 2495–2498.

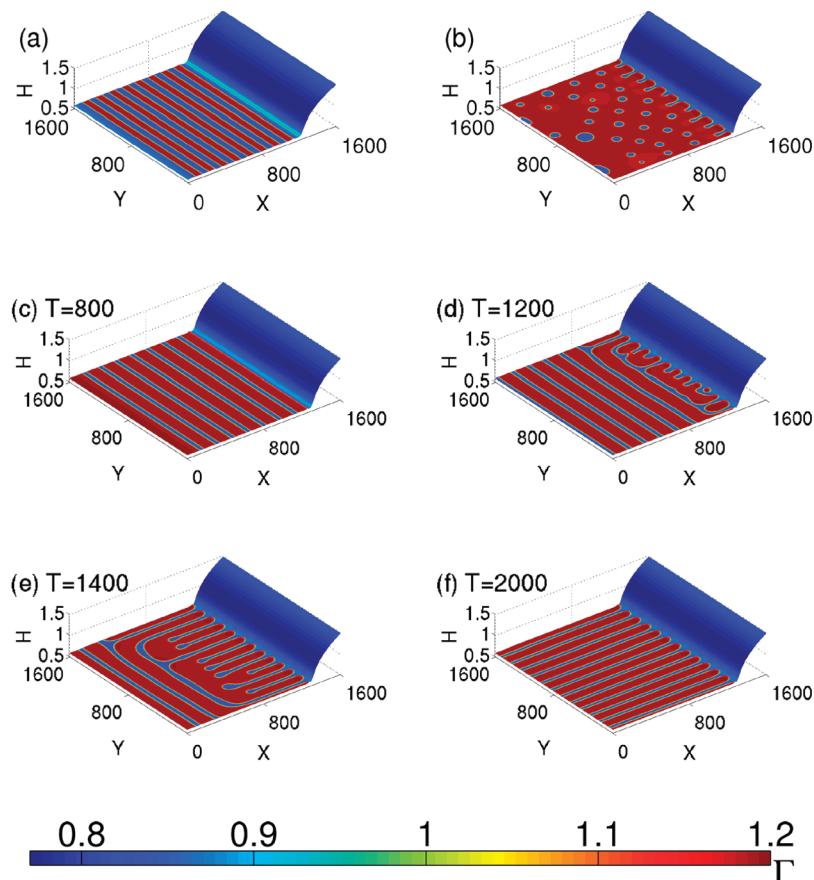


Figure 4. Patterns obtained in two-dimensional simulations, where the height information corresponds to the profile H , while the surfactant density is color-coded: (a) stable stripe pattern obtained for $V_0 = 3.3$ and (b) irregular domains found at $V_0 = 2.55$ as well as a time-sequence (c–f) of a system with $V_0 = 2.9$, where a transition from parallel to perpendicular stripes is observed.

Conclusions and Outlook

Using the lubrication approximation, we have developed a theoretical description for surfactant monolayers which exhibit substrate-mediated condensation during transfer onto a solid. For that purpose, we have incorporated a height-dependent external field in the surfactant free-energy functional. A first investigation of the control parameter space has been presented, showing a bifurcation from homogeneous transfer to regular stripe patterns parallel to the contact line as well as a secondary bifurcation to perpendicular stripes. Our model correctly predicts the existence of the four basic operation regimes known from experiments, going from transfer of a homogeneous LC monolayer

first to perpendicular stripes, then to parallel stripes, and finally to a homogeneous LE layer. From these first results, we expect the system to have a rich phase space and bifurcation behavior. To analyze the bifurcation scenario in detail, it is now necessary to perform a linear stability analysis of the nonhomogeneous stationary solutions of eqs 1 and 2 leading to a nontrivial eigenvalue problem with a space-dependent linearization operator. This problem will be the subject of future investigation.

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