Thin Films of Binary Mixture in the Off-critical Case
(Two Layers Laterally Stratified Composition)

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Abstract

The study examines the non-linear behaviour of thin films of binary mixtures, confined by solid walls subjected to periodic boundary conditions and deposited on a solid neutral substrate with surface opened to the air and free to modulate. The Cahn-Hilliard model is used to investigate the problem, and the free surface is modelled as sharp with its own surface tension. The internal interfaces between the two polymers are allowed to diffuse. The study explores the solution bifurcations of the problem varying the parameter of mean film thickness for laterally stratified compositions. The mixture is considered to be off-critical, with a composition mean concentration of $c = 0.65$. The results reveal a rich variety of solutions, providing valuable insights into the structural properties of the film. The study analyses the behaviours of the systems through its bifurcation diagrams presenting a diverse range of static film morphologies.

Keywords: Thin liquid films, binary mixtures, Cahn-Hilliard model, off-critical composition.

1   Introduction

Thin liquid films of binary mixtures on solid substrates with free surfaces have garnered significant interest due to their widespread applications and intriguing behavior. These films, characterized by their nanometer to micrometer thickness, exhibit complex dynamics and phase behavior. Understanding the behavior of thin liquid films in the off-critical case is crucial for various technological applications, including, materials science, microfluidics [1], surface patterning, coating processes and surface engineering [2], Lubrication and Friction Control [3], Optics and Photonics [4].
In particular, when the film thickness is significantly smaller than the characteristic correlation length, the phase separation in the binary mixture is suppressed, leading to a more homogeneous morphology. On the other hand, when the film thickness is significantly larger than the characteristic correlation length, the phase separation in the binary mixture is enhanced, leading to a more segregated morphology, microstructure, adsorption properties, surface free energy changes [5]. The interfacial interactions between the liquid film, the solid substrate, and the surrounding environment also play a crucial role in governing the film's structure and dynamics.

To investigate the behavior of binary thin liquid films in the off-critical case analytically, researchers often employ mathematical models such as the Cahn-Hilliard model. This model describes the phase separation and diffusion processes in binary mixtures [6]. It considers the intermolecular interactions, diffusion, and capillary forces that influence the film's evolution over time. By simulating the dynamics of the film using such a model, researchers can gain insights into

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the stability, morphology, and pattern formation of the liquid film. In these systems, the presence of a free surface introduces additional complexities. The free surface of the film is characterized by its own surface tension, which influences the film's stability and the interfacial properties between the binary liquid film and the surrounding air. The interfacial dynamics between the two polymers in the mixture are also considered, allowing for the study of diffusion-driven processes within the film. In the off-critical case, where the mean composition of the binary mixture deviates from the critical point, the behavior of thin liquid films on solid substrates with free surfaces becomes particularly intriguing. The non-linear interplay between intermolecular forces, phase separation, and film confinement leads to a rich variety of solutions and static film morphologies [7], [8], [9].

This study explores the behaviors of thin liquid films of binary mixtures on solid substrates with free surfaces, concentrating on the off-critical case characterized by solution bifurcations that occur as the film thickness is varied. The study's objective is to gain insights into the structural properties and morphological transitions of these films by examining the effects of film thickness and interfacial phenomena. To achieve this, the study employs mathematical modeling approaches, specifically the model-H, to investigate the complex interfacial dynamics and behavior of binary thin liquid films in the off-critical regime. The findings of this study contribute to the understanding of thin film behavior and have potential applications in various fields.

2   The Implemented model-H

In the isothermal model-H, the transport equation for momentum, specifically for one component of a binary mixture, is described by the Navier-Stokes equations. These equations govern the conservation of momentum and given in non-dimensional form as:

$$Ps\left[\frac{\partial V}{\partial t} + V.\nabla V\right] = -\nabla.\left\{(\nabla c)(\nabla c) + p_{\text{eff}}\underline{I}\right\} + \frac{Ps}{Re}\,\Delta V \qquad (1)$$

where the density of the mixture is assumed independent of the mixture composition implying that continuity gives $\nabla \cdot V = 0$. Here, $V = (u, w)$ is the velocity field, $c = c_1 - c_2 = 2c_1 - 1$ is the concentration difference of c_1 and c_2 for component 1 and component 2, respectively. The effective pressure $p_{\text{eff}} = p - (c + 1)\Delta c - (\Delta c)^2/2$ contains all diagonal terms of the stress tensor where p is the usual pressure, and the dimensionless numbers Ps and Re are the pressure number and the Reynolds number, respectively [8]. Eq. (1) is coupled to a Cahn-Hilliard description [10], [11] of the binary mixture supplemented by a term that describes advective transport with the velocity V.

$$\partial_t c + V \cdot \nabla c = -\nabla \cdot \{\nabla[\Delta c - \partial_c f(c)]\}, \qquad (2)$$

It's important to note that the convective Cahn-Hilliard equation, which captures the diffusive dynamics of the binary mixture, is also coupled with the momentum equation in this model. The continuity equation is given by

$$\nabla \cdot V = 0 \qquad (3)$$

The two-dimensional operators are defined as $\nabla = (\partial_x, \partial_z)$ and $\Delta = (\partial_x^2 + \partial_z^2)$. Whereas, $\partial_c f(c)$ is a chemical potential related to the local bulk free energy $f(c)$, that corresponds to the simple quartic potential $f(c) = (c^2 - 1)^2/4$. To obtain the non-dimensional form of the governing equations (Eq. (1) and Eq. (2)), the scales $l = C\sqrt{\sigma_c/E}$, $U = M E/l C^2$, $\tau = l/U = l^2 C^2/(ME)$ and $P = E$ are introduced for length, velocity, time and pressure, respectively [7]. Thereby the length l represents the thickness of the diffuse interface between the two phases of the mixture and is determined from σ_c (interfacial stiffness of the diffuse interface), the energy scale E and the concentration C at the binodal, M is the mass diffusion coefficient or diffusional mobility. The governing equations are supplemented by non-dimensional boundary conditions introduced in [7]. Note that in our study we used Model-H in its static limit.

We characterize the steady states by the normalized L_2-norm of the concentration field

$$||\delta c|| = \sqrt{\frac{1}{L\bar{h}} \int_0^L \int_0^{h(x)} (c(x) - \bar{c})^2 dz\, dx}, \qquad (4)$$

the normalized L_2-norm of the thickness profile

$$||\delta h|| = \sqrt{\frac{1}{L} \int_0^L \left(h(x) - \bar{h}\right)^2 dx}, \qquad (5)$$

and the normalized system energy

$$E = \frac{1}{L}\int_0^L \left\{ a^+ c\sqrt{1 + (\partial_x h)^2} + \int_0^{h(x)} \left[\frac{1}{2}(\nabla c)^2 + f(c)\right] dz \right\} dx - \bar{h}\, f(1). \qquad (6)$$

The function $f(c)$ is the quartic polynomial as defined above [12], [7].

In this way, the surface modulation is measured by $||\delta h||$ and the strength of decomposition by $||\delta c||$. Principally, for the homogeneous state, we have $||\delta c|| = 0$. The energy E measures the difference to a homogeneous film at equilibrium concentration $c = \pm 1$. Film states are further characterized by their (conserved) volume $V = HL$, where H is the mean film height and L is the lateral domain size. Note that the thickness profile $h(x)$ is part of the result as well as the concentration profile $c(x, z)$.

3   Results

In the present work, we treat the case of the off-critical mixture (mean concentration $c \neq 0$) [8]. With positive mean concentration c, one can observe that liquid 2 forms a minority phase in the mixture. This is consistent with creating a droplet or thin strip of liquid 2 in liquid 1 that can be attached to the free surface or the substrate. However, at the pitchfork bifurcation, the droplet spreads completely in a said of liquid 1. The results emphasis on the calculation of bifurcation

diagrams, with a particular emphasis on films composed of laterally stratified two-layer and homogeneous state as a base. The analysis of other structures and their results will be conducted and reported separately in another investigations. Bifurcation diagrams serve as a valuable tool in the study of our system, providing insights into the diverse states and behaviour exhibited by the system as the parameter of mean film thickness is varied. By systematically altering this parameter and examining the resulting bifurcation diagrams, a deeper comprehension of the system's behaviour and the effects of this parameter on the formation and stability of different film structures is gained.

The film thickness is a critical parameter that can significantly influence the structure of thin films of binary mixtures in various manners. Therefore, understanding the effect of film thickness on the structure of the films is crucial for controlling and optimizing their properties for various applications. Here, we discovered several intriguing results when varying the film thickness, particularly in the context of surface deflection, concentration field, and system energy. Notably, the increase in film thickness provides a means to create a diverse array of structures. In the early stages, when the film thickness is relatively small, only two solutions exist, representing the homogeneous and laterally stratified states. However, as the thickness increases, additional solutions emerge featuring droplets either attached to the free surface or the substrate, thereby resulting in a richer morphology.

Concerning L_2-norm of surface modulations in terms of the film thickness of the binary thin liquid film. In the case of a homogeneous film state, where the film is uniform, there are no detected surface deflections, and the L_2-norm of the surface modulations is zero ($||\delta h|| = 0$).

When a pure mixture is horizontally attached to the free surface of the film, the L_2-norm of the surface modulations is also close to zero ($||\delta h|| \approx 0$), especially for higher film thickness H. This is because the fluid attached to the free surface is pure, representing a single component. This can be represented by the red dotted curve in Figure 1(a), and profile samples shown in Figure 2(c) and Figure 2(n). However, in all other branches that represent states where the fluid-fluid contact line hits the free surface, different surface modulations are observed. The behavior of the surface modulations depends on the concentration of the components in the film. This can be seen in Figure 1 and the corresponding profiles in Figure 2, where the surface modulations vary depending on the component concentration and the interaction between the fluid phases. The presence of different branches or states in a laterally stratified thin liquid film with fixed domain size $L = 10$ and varying mean film height H. These branches exhibit various surface modulations and connect to different solution states.

In the initial stages, the film already exhibits lateral stratification, and its surface deflection shows various modulations, as indicated by the red dotted curve in Figure 1(a). This solution state progresses through multiple stages and eventually connects to a droplet solution where a droplet attached to the substrate. This can be observed in the profile samples shown in Figure 1(a) and the panels presented in Figure 2(a), Figure 2(b), Figure 2(c), and Figure 2(n).

The branch with the highest surface modulation occurs when a pure droplet, representing the minority component of the liquid, is attached to the free surface. This branch is depicted by the magenta dot-dot-dash line in Figure 1(a) and its profile is shown in Figure 2(l). However, as the concentration of the droplet decreases upon hitting the free surface, there is a reduction in surface modulation on the same branch. This can be seen in the profile presented in Figure 2(m).
Another laterally stratified branch exists in the early stages of film thickness development. This branch is characterized by the presence of a weak liquid component representing the minority. Interestingly, this branch continues to exist even for higher film thickness, and it gives rise to the blue dashed and black dotted branches that bifurcate from it. The profiles shown in Figure 2(d), Figure 2(f), and Figure 2(j) represent this behavior.

Additionally, there are other branches that bifurcate from this weak lateral strip branch. In these branches, a weak lateral strip develops a droplet on the side of the film, attached to the lateral confined wall. These branches are represented by the black dotted branches in Figure 1(a), and their profiles can be compared using Figure 2(h), Figure 2(g), and Figure 2(i). The surface modulation varies depending on the branch and the structural behavior of the film, as shown in Figure 1(a) in comparison with the profile samples in Figure 2.

The L_2-norm of the concentration field $\|\delta c\|$ represents the overall concentration variation across the film. It is a measure of the magnitude or intensity of concentration differences between different components or phases in the film. It is calculated by considering the concentration deviations or fluctuations from the average concentration. It provides a quantitative measure of the concentration variations and can help assess the level of mixing or segregation between the components. $\|\delta c\|$ in terms of film thickness is depicted in Figure 1(b). When considering the film thickness, some observations can be made regarding the L_2-norm of the concentration field. For the homogeneous state, where the film is uniform, the L_2-norm of the concentration field remains at $\|\delta c\| = 0$. This indicates that there are no perturbations or variations in the concentration across the film.
However, for all other states, the L_2-norm of the concentration field is non-zero ($\|\delta c\| \neq 0$). This implies that there are concentration variations present in the film.
At thinner films, the laterally stratified solution exhibits the highest perturbation in concentration, with the L_2-norm of the concentration field reaching approximately $\|\delta c\| = 0.65$. This suggests significant variations in concentration across the film in this state.
As the film thickness increases, the L_2-norm of the concentration for the laterally stratified film fluctuates and declines, reaching a minimum of not less than $\|\delta c\| \approx 0.48$ at around $H \approx 4.5$. However, it then increases again to approximately $\|\delta c\| = 0.55$ when $H = 10$. This indicates that the concentration variations decrease initially but then increase again as the film thickness continues to grow. These observations are reflected in the red dotted curve shown in Figure 1(a).

By examining the L_2-norm fluctuations for the different branches shown in Figure 1(b) along with the corresponding concentration profiles in Figure 2, we can gain insights into the concentration dynamics, mixing behavior, and phase separation tendencies within the system. The fluctuations

provide a quantitative measure of the concentration variations and can help identify the dominant states or configurations with significant concentration differences. A higher value of $\|\delta c\|$ indicates larger concentration differences or fluctuations, suggesting a more pronounced variation in the distribution of the components within the film. Conversely, a lower value of $\|\delta c\|$ implies relatively uniform or smooth concentration profiles, indicating a more homogenous distribution of the components.

By analyzing the L_2-norm of the concentration field, one can gain insights into the degree of mixing, segregation, or phase separation occurring in the binary thin liquid films. This information is valuable for understanding the behavior and dynamics of such systems and can have implications in various fields.
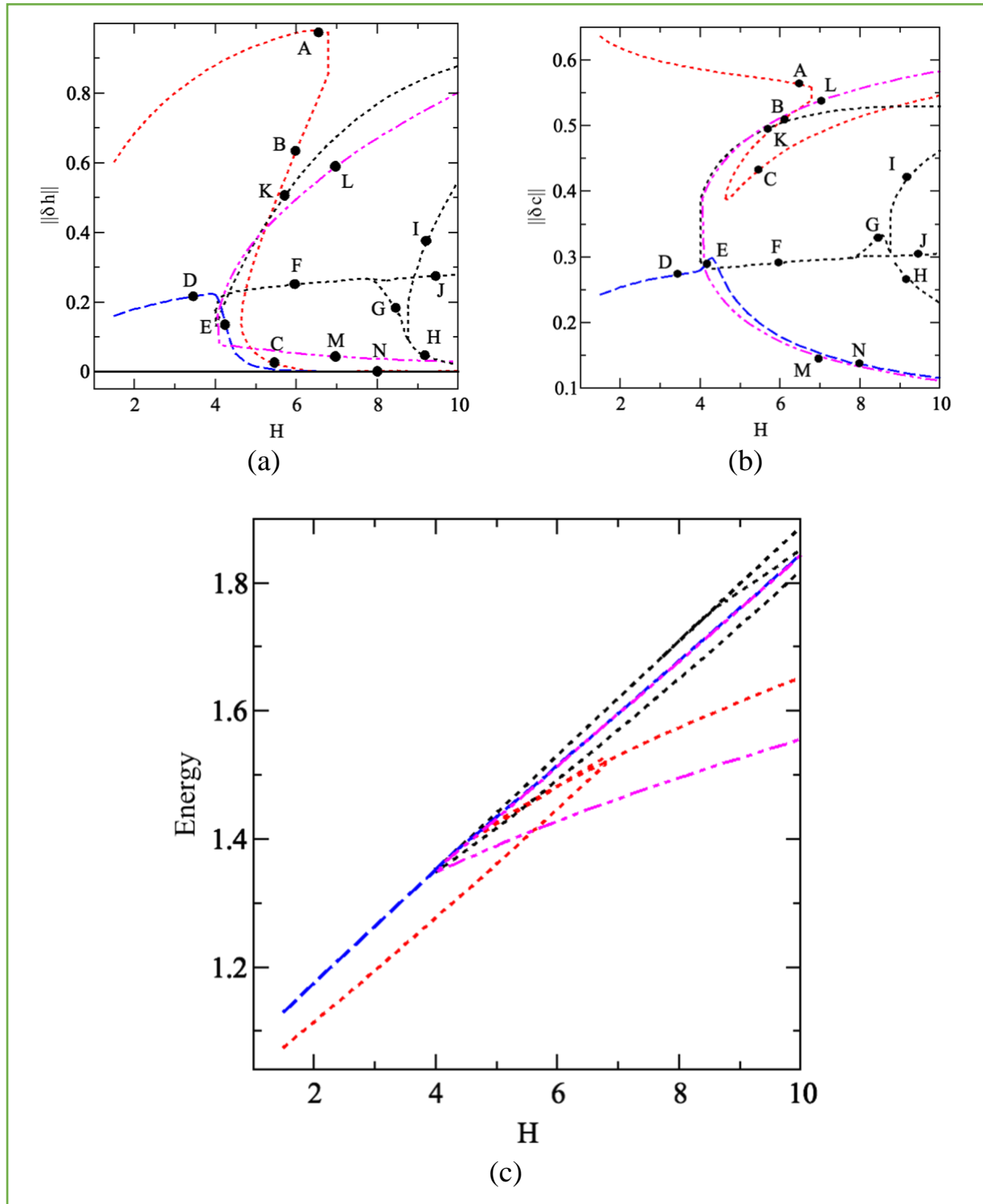
Error! Reference source not found.: *(colour online) Shown are, panel (a) L_2-norm of surface deflection, panel (b) L_2-norm of the concentration field, and panel (c) the energy for laterally stratified branch* $(1/2,0)$ *and related branches varying film thickness H.*
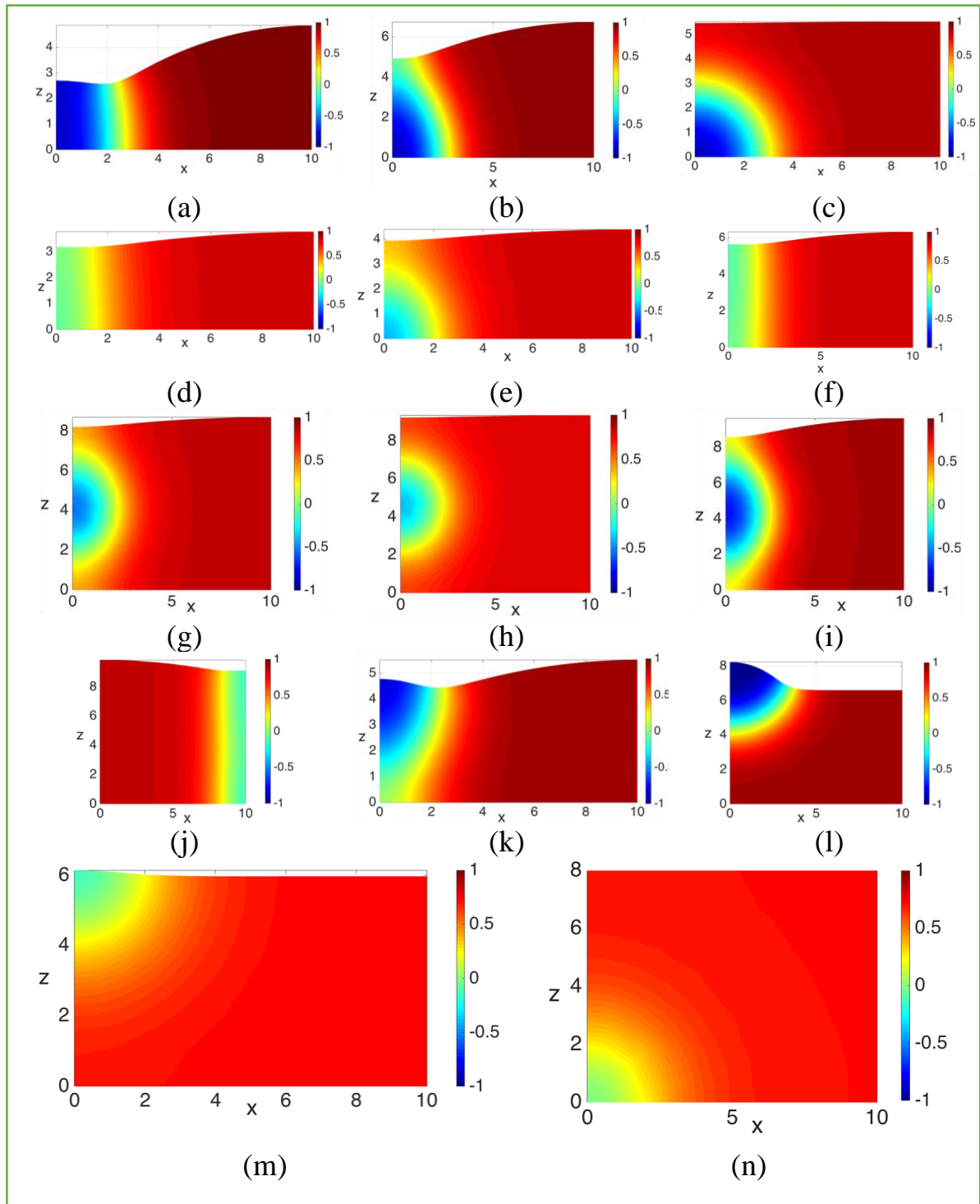
Error! Reference source not found.: *Shown are samples of film profiles for laterally stratified branch a
nd related branches at the corresponding labels in* **Error! Reference source not found.***(a) and* **Error!
Reference source not found.***(b). Panels a, b, c, d, e, f, g, h, i, j, k, l, m and n correspond to*

The behavior of the system energy as a function of film thickness illustrated in Figure 1(c). For film thicknesses below 5.5, the lowest energetically favored state is the lateral branch, as indicated by the red dotted curve in Figure 1(c) and profile sample shown in Figure 2(a). This suggests that for thinner films, the system tends to stabilize in a laterally stratified state with surface modulations. However, for thicker films, the energetically favored state changes. The lowest energetically favored state is the film where a pure droplet of the minority liquid is attached to the free surface, see the profile shown in Figure 2(l). This indicates that as the film thickness increases, the system tends to stabilize in a state where a droplet of the minority component is present on the film surface. The energy level associated with this state is lower than that of the lateral branch for thicker films. For film thicknesses less than 4.5, the highest energetic state is the lateral film with weaker concentration. This means that the system has a higher energy when it exhibits lateral stratification and weaker concentration gradients. The specific details of this state can be observed in the profile shown in Figure 2(k). Nevertheless, for thicker films, the highest energetically favored state is the transition state, as depicted by the profile in Figure 2(k). This indicates that as the film thickness increases beyond 4.5, the system undergoes a transition where the energy associated with this particular state becomes the highest compared to other configurations.

The observations shown in Figure 1(c) provide insight into the energy behavior of the system and how it varies with film thickness. The energy levels of different states determine the stability and preferred configurations of the thin liquid film.

It's important to note that the specific energy values and their variations depend on several factors, including the specific properties of the liquid components, surface tension, and other system parameters. The energy behavior and the preferred states can be influenced by these factors.

Inclusively, As the film thickness increases, other energy contributions become more significant. In particular, the energy associated with the presence of a pure droplet of the minority liquid attached to the free surface becomes dominant. This can be attributed to the interfacial energy between the droplet and the surrounding film, which is lower than the energy associated with lateral modulations. For thicker films, the system prefers the state where a pure droplet of the minority liquid is attached to the free surface because it provides a lower overall energy configuration.

4 Conclusion

Our study has focused on determining the bifurcation diagrams of film perturbations, concentration profiles and the total energy for a two-dimensional system for films of binary mixtures of immiscible liquids in the two-phase region. The modulation of the free surface and the concentration field are coupled through a pair of non-linear evolution equations using model-H. The problem describes the phase separation of a binary liquid mixture or a liquid-gas mixture. Although the study obtained a considerable number of solutions, our investigations were intentionally limited to films of only two-layers of laterally stratified and few others related to

them. The results indicated that the interfacial surface tension gradients with concentration have a significant effect on the surface modulations of the films, modulations in the concentration field, and system energy.

Overall, the study provides valuable insights into the bifurcation behaviour of two-layer films under varying surface tension, lateral domain size, and mean film height. The results obtained contribute to the understanding of the system's dynamics and lay the foundation for future investigations into other film structures.

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