Off-critical Composition of Thin Liquid Films of Binary Mixture

Fathi A Bribesh[a*] (iD), **Hamza A Daoub**[b] (iD)

[a,b]*Department of Mathematics, Faculty of Sciences, University of Zawia, Zawia, Libya.*
Corresponding author:
E-mail address: f.bribesh@zu.edu.ly

A B S T R A C T

This study concentrates on the non-linear solutions of bounded films of binary mixtures with free-modulated surfaces, situated on an energetically neutral solid substrate and subject to periodic boundary conditions on the lateral walls. The Cahn-Hilliard model in its static limit is employed to investigate the problem, and the free surface is considered sharp with its own surface tension. The internal interfaces between the two polymers are allowed to diffuse. The problem is explored through its bifurcations varying several parameters, specifically the surface tension γ, film lateral domain size, and the mean film thickness of homogeneous and laterally (and horizontally) stratified compositions of two layers. The mixture is considered in the off-critical composition with $c = 0.4$. The results reveal a rich family of solutions, providing valuable insights into the structural properties of thin films of binary mixtures.

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

المركبات غيرالحرجة لأشرطة السوائل الرقيقة للمزيج الثنائي

فتحي بريبش^a، حمزة داعوب^b

^{a,b}قسم الرياضيات، كلية العلوم، جامعة الزاوية، الزاوية، ليبيا

الملخص

تركز هذه الدراسة على الحلول غير الخطية لأشرطة مقيدة من خليط ثنائي ذو سطح حر ، موضوع على سطح صلب محايد طاقياً وتخضع لشروط حدودية دورية على الجدران الجانبية. يتم استخدام نموذج كان-هيليارد في حدوده الثابتة لاستكشاف المسألة، ويعتبر السطح الحر حادًا بتوتر سطحه. يُسمح للواجهات الداخلية بين البوليمراين بالانتشار. تتم دراسة المشكلة من خلال التفرعات المتغيرة لعدة بارامترات، على وجه الخصوص توتر السط γ ح وحجم مجال الشريط الجانبي، وسمك الشريط المتوسط للتراكيب المتجانسة والتي تتكون من طبقتين متجانستين جانبيًا (أفقيًا وعرضيًا). يُعتبر الخليط في تركيبة غير حرجة بقيمة $c = 0.4$. تكشف النتائج عن مجموعة كبيرة من الحلول، توفر رؤى قيمة حول الخصائص الهيكلية لأشرطة السوائل الرقيقة من خليط ثنائي.

الكلمات المفتاحية: أشرطة السوائل الرقيقة، مزيج ثنائي، نموذج كان-هيليارد، تركيبة غير حرجة.

1. Introduction

Thin liquid films of binary mixtures on solid substrates with free surfaces are an important area of study in various fields, including physics, chemistry, Material Sciences, and biology [1], [2], [3], [4], and [5], these films are widely used in many industrial technologies as a part of major processing techniques related to protective and adhesive coatings [6], dewetting patterns, painting, spraying, and cleaning [7], and [8]. Such films are characterized by their nanoscale thickness which typically ranges from a few nano-meters to several micro-meters.

When a binary mixture consisting of two different liquids is deposited on a solid substrate the interplay

between intermolecular forces and interfacial energies leads to the formation of the film. The construction of the films depends on several factors including the properties of liquids, substrate specification, and the surrounding environment. One critical parameter that influences the film deformation behaviour is the relative concentration of the two liquids in the binary mixture. Different phenomena can occur depending on the concentration, such as face separation dewetting and interfacial instabilities. Phase separation happens when the two liquids in the binary mixture prefer to segregate from each other, resulting in the formation of distinct domains within the film. This behaviour is driven by the differences in intermolecular interactions and miscibility of the two liquids. Phase separation dynamics can be influenced by many factors, such as temperature, time, and the presence of external fields. Also, witting occurs when the thin film ruptures and recurs from the substrate, leaving isolated droplets behind. This phenomenon is typically observed when the intermolecular interactions between the liquid and the substrate are weak, or when there is an imbalance in interfacial energies. However, film thickness viscosity, and surface roughness can affect the dewetting process [7].

Interfacial instabilities refer to the development of patterns or structures at the liquid-liquid or liquid-air interfaces. These instabilities can be driven by a variety of mechanisms including capillary forces Marangoni effects (variation and surface testation), and hydrodynamic flows. The resulting patterns can exhibit complex morphologies such as stripes, droplet formation, or self-organized structure. The presence of a free surface, such as air, introduces additional complicity to the behaviour of the mixture. The liquid-air interface can influence the spreading dynamics, evaporation rates, and stability of the film and it can also affect the interfacial tension and the formation of surface-related structures.

The study implemented model-H [9] to investigate the challenging physics of binary mixture systems in the presence of surface transitions, in restricted geometry. The phase diagram of bulk binary mixtures is well documented as is the study of various surfaces occurring when the bulk phase is in contact with a wall. The structure of thin films as a function of surface tension, system size, and film thickness is not yet known precisely. In particular the existence and the nature of phase separations in binary mixture. Considerably, from the complexity and richness of experimental results. We focus on the description of the structure and formation developments of thin

liquid films of a binary mixture of two demixing-dewetting liquids [9], [10] , [11]. The mixture is situated on an energetically neutral, horizontal solid substrate with a neutral upper surface open to the ambient air. The free surface is allowed to modulate according to the system situation. The system is described using an evolution equation for the film using Model-H. The governing equations for the problem have been solved by optimizing the energy functional where the domain is discretized using the finite element method as an initial value problem with periodic boundary conditions. We sketch important results when varying different parameters such as surface tension strength γ [9], lateral domain size, and mean film thickness. We investigate the solution structure and its consequences for the system structure, concentrating on thin films of two layers. We focus on results for homogeneous, laterally, and vertically stratified compositions in the off-critical case [12] with $c = 0.4$, varying surface tension, lateral domain size, and film mean thickness. Throughout the investigations of the dependence of the L_2-norms of surface modulation and concentration field as well as the system's total energy on those parameters.

2. The Implemented Model

Isothermal model-H couples the transport equations for momentum, and mass density of one component of the binary mixture (Navier-Stokes equations and the convective Cahn-Hilliard equation). It can be formulated in many ways according to the definition of the pressure. This study pursues the definition applied in [9] and describes model-H according to their notation. The time evolution of a binary fluid mixture in an isothermal situation is often described by model-H [13], which stands for a coupled system of kinetic equations describing the transport of momentum and of some conserved scalar field (concentration) [14]. The Navier-Stokes description of a simple fluid is supplemented by an additional contribution to the stress tensor that depends on Korteweg stress [15].

The non-dimensional form of the transport equation of momentum is given by

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

$$+ \frac{Ps}{Re}\,\Delta V \qquad (1)$$

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 $p_{eff} = p - (c + 1)\Delta c - (\Delta c)^2 / 2$ 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 [16]. Eq. (1) is coupled to a Cahn-Hilliard description [17], and [18] of the binary mixture supplemented by a term that describes advective transport with the velocity V.

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

and 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 [9]. 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 [9]. 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.

$$E = \frac{1}{L} \int_0^L \left\{ a^+ c\sqrt{1 + (\partial_x h)^2} \right.$$

$$+ \int_0^{h(x)} \left[\frac{1}{2}(\nabla c)^2 \right.$$

$$\left. + f(c)\right] dz \left. \right\} dx - \bar{h} f(1) \quad (6)$$

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 $c(x, z)$.

In the present work, we treat the case of the off-critical mixture (mean concentration $c \neq 0$) [16]. 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 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.

3. Results

Our study focuses on the calculation of bifurcation diagrams, with a particular emphasis on films composed of two layers and the homogeneous state as a base. The analysis of other structures and their results will be conducted and reported separately in another investigation. 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 parameters are varied. In this case, the parameters being investigated include surface tension, lateral domain size, and mean film height. By systematically altering these parameters and examining the resulting bifurcation diagrams, a deeper comprehension of the system's behaviour and the effects of these parameters on the formation and stability of different film structures is gained.

We focus specifically on two-layer films and structures related to them, leaving the analysis of other complicated structures for future investigation. The study aims to explore the behaviour and properties of this particular film configuration in greater detail. The decision to investigate other structures separately may be driven by the complexity and diversity of the results obtained, requiring further analysis and interpretation beyond the scope of the current study.
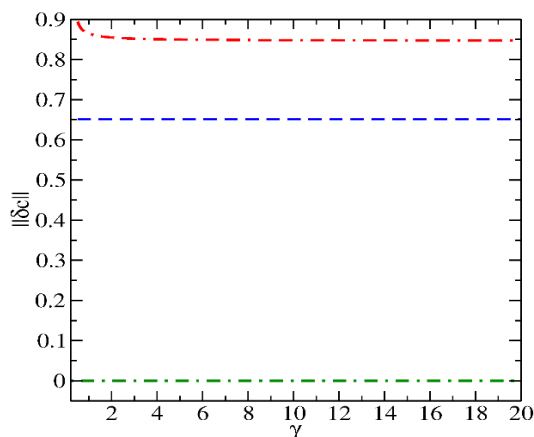
3.1 varying surface tension γ

Surface tension arises due to the cohesive forces between the molecules at the liquid-gas interface. It quantifies the energy required to increase the surface
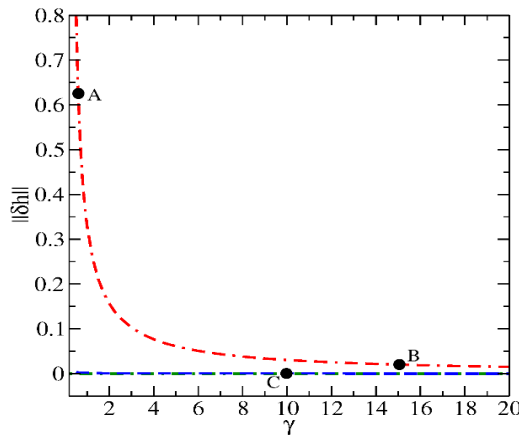
Figure 1. (Colour online) Shown is L_2-norm of surface deflection for the homogeneous and laterally stratified branch (1/2,0) and vertically stratified branch (0,1/2) for energetically neutral film at free surface, varying surface tension γ. The lateral domain size and film mean thickness are fixed at L = 10 and H = 5, respectively.

area of the liquid. In a binary mixture, it depends on the concentration of the components at the liquid-gas interface and can be different from the surface tensions of the pure components. This phenomenon is known as the surface tension deviation. The surface tension of a binary mixture can be influenced by several factors, including the intermolecular interactions between the components, the molecular size and shape, and the temperature. The interactions between the different components can lead to either an increase or a decrease

Figure 2. (Colour online) Shown is the L_2-norm of the concentration field for the homogeneous and laterally stratified branch (1/2,0) and vertically stratified branch (0,1/2) for energetically neutral film at free surface, varying surface tension γ. The lateral domain size and film mean thickness are fixed at L = 10 and H = 5, respectively. The film is in off-critical case with c = 0.4.

in the surface tension compared to the pure components. It can occur when the intermolecular interactions between the components are weaker than the interactions within each pure component. However, positive deviation from ideal can happen when the intermolecular interactions between the components are stronger than the interactions within each pure component, resulting in a higher surface tension for the binary mixture. This shows the importance of introducing the effect of surface tension on the film decomposition.

We vary surface tension to observe the fluctuations of L_2-norm of surface modulation, L_2-norm for the concentration field and the system energy. As shown
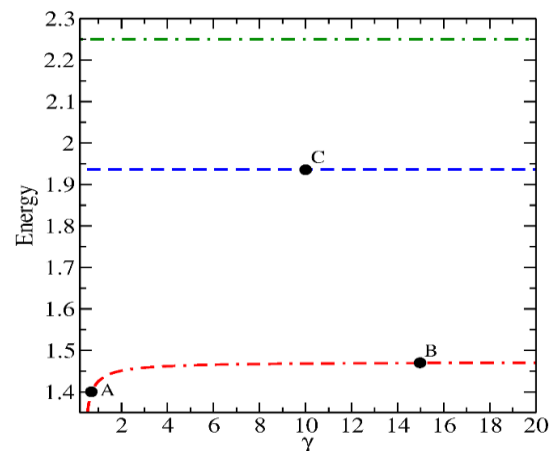

Figure 3. (Colour online) Shown is the energy for the homogeneous and laterally stratified branch (1/2,0) and vertically stratified branch (0,1/2) for energetically neutral film at free surface, varying surface tension γ. The lateral domain size and film mean thickness are fixed at L = 10 and H = 5, respectively. The film is in off-critical case with c = 0.4.

in Figure 1 , and Figure 3 (blue-dashed and green-dash-dot lines), there are no significant changes in the L_2-norms and system energy for homogenous and stratified structures when surface tension γ changes. This result due to the unchanged cohesive forces between the molecules and unchanged concentration for the homogenous (or pure) liquid at the liquid-gas interface, see Figure 4(c). In a homogeneous state film (0,0) [9], the two components of the mixture are uniformly distributed. Hence, the free surface remains flat when varying surface tension γ. This behaviour is indicated by the (green dash-dotted) curve in Figure 1, i.e., $||\delta h|| = 0$. This means that regardless of changes in surface tension, the free surface of the homogeneous state film does not exhibit significant modulations or variations.

In the case of stratified films, specifically the film

(0,1/2) [9], the free surface is occupied by either pure liquid 1 or pure liquid 2. This occurs due to energetic neutralization on both the free surface and the substrate. Since only one component is attached to the free surface, it remains flat as varying the surface tension. This is represented by the (blue dashed) line in Figure 1, and the film profile shown by Figure 4(c).

Furthermore, the laterally structured film (1/2,0) [9] changes at the free surface when the surface tension is varied, it leads to changes in intermolecular forces between the pure components and influences the distribution of the two components across the surface which produce differences in concentration across the

(a)

(b)

(c)
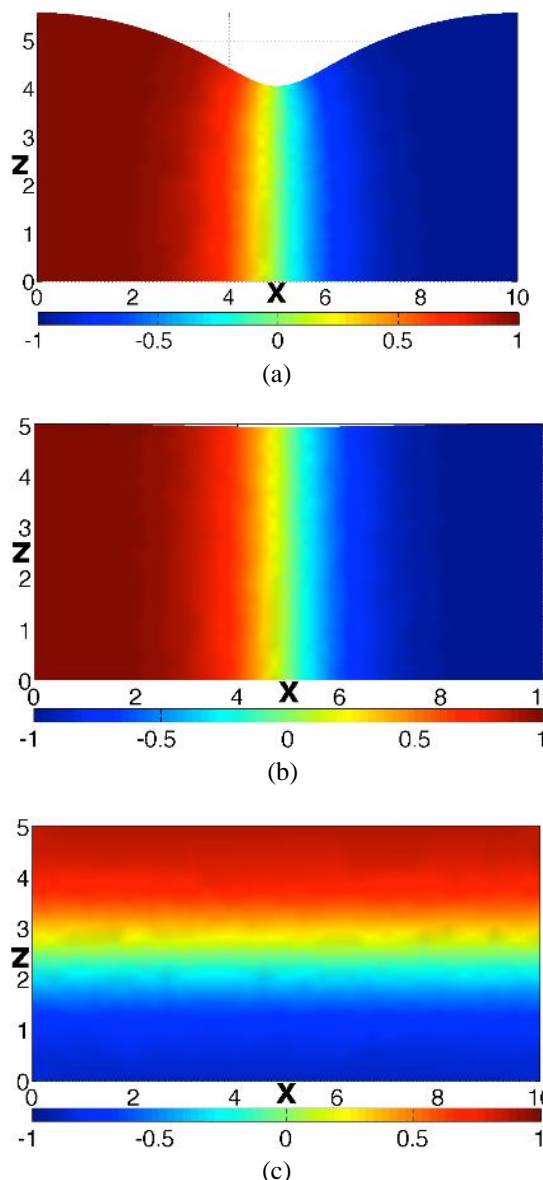
Figure 4. Shown are samples of film profiles for laterally and vertically stratified branches at the corresponding labels in Figure 1. and Figure 3. Panels a, b and c correspond to the labels A, B and C, respectively.

free surface. The regions with lower surface tension will tend to increase the modulation, while the regions with higher surface tension will tend to contract. see (red dot-dash-dash) curve in Figure 1 and compare to surface modulations in the profiles shown by Figure 4 (a), and Figure4(b). As a result, the surface of the film becomes patterned. Also, changes observed in the L_2-norm of concentration filed and in system energy see (red dot-dash-dash) curve in Figure 2, and Figure 3.

Based on our observation, the behaviour of the films at the free surface depends on whether the mixture is
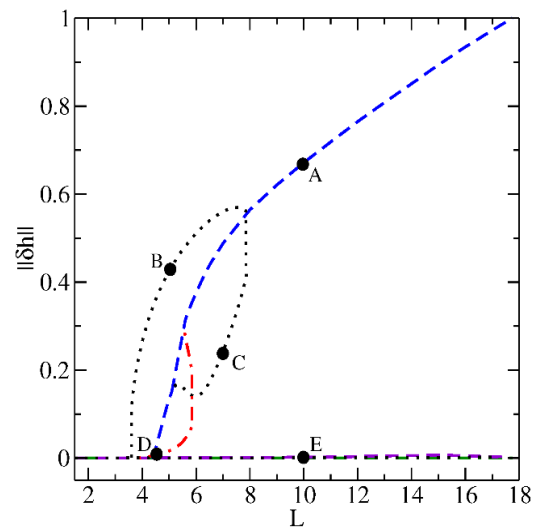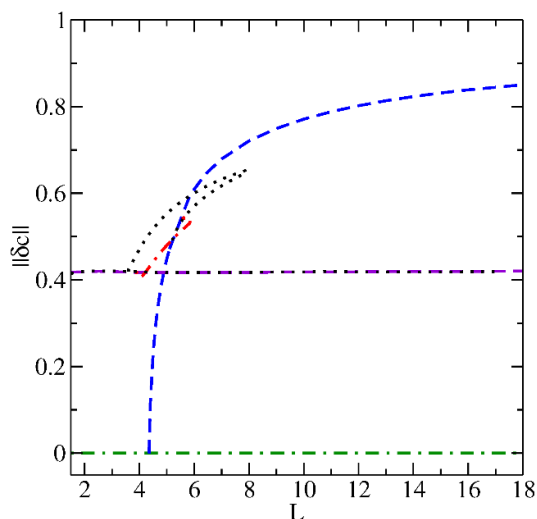

Figure 5. (Colour online) Shown is L_2-norm for surface deflection of the branch $(1/2, 0)$ and related branches for neutral film, varying lateral domain size L. The film mean thickness is fixed at $H = 5$ for off-critical mixture with $c = 0.4$.

homogeneous across the free surface or not, when varying surface tension. However, the free surface of the laterally stratified film (1/2,0) exhibits modulation against surface tension. This modulation is observed in the lateral distribution of the two components within the film. For low surface tension, the free surface of laterally stratified films shows significant modulations, as the surface tension increases the modulations decrease. This behaviour is depicted by the (red dashed) curve in Figure 1, whereas Figure 4(a) and Figure 4(b) represent solution profile samples labelled as A and B in Figure 1 and Figure 3, respectively, which correspond to specific points along the (red dashed) curve in Figure 1. These profiles illustrate the variation in the composition and distribution of the two components within the laterally stratified film in terms of surface tension.

3.2 Varying lateral domain size L

Experimental observations and theoretical models are often employed to study and understand the intricate behaviour of these complex systems. The lateral domain size refers to the length of individual domains within a thin liquid film of a binary mixture. Generally, the lateral domain size can significantly affect the surface morphology of the binary films. When the lateral domain size is large, distinct domains with well-defined boundaries can form on the surface, leading to a patterned or textured appearance. On the other hand, when the lateral domain size is small, the surface may appear more homogeneous and smoother. The specific morphology will depend on the interplay between surface tension, intermolecular forces, and the composition of the binary mixture. Also, the lateral domain size can influence the stability of thin films. Smaller lateral domain sizes contribute to enhanced stability by minimizing the interfacial energy between different domains. This can help prevent the

Figure 6. (Colour online) Shown is L_2-norm for the concentration field of the branch $(1/2, 0)$ and related branches for neutral film, varying lateral domain size L. The film mean thickness is fixed at H = 5 for off-critical mixture with c = 0.4.

coalescence or merging of domains, leading to a more stable film. Larger lateral domain sizes, on the other hand, may be more prone to coalescence and can result in the formation of larger, irregularly shaped domains or a more unstable solution. In binary mixtures that

undergo phase separation, the lateral domain size can influence the kinetics and dynamics of phase separation processes. The formation and growth of domains within the film can be influenced by factors such as domain size, and interfacial tension. The size

and distribution of lateral domains can affect the rates of nucleation, growth, and coarsening of phases, as well as the final equilibrium morphology of the film.

In this part, we vary the lateral domain size L and examine L_2-norm of surface modulation, L_2-norm for the concentration field, and the total energy of the system. As both the substrate and free surface are energetically neutral, there are stratified solutions represented by identical two branches $(0, 1/2)_a$ and $(0, 1/2)_b$ [16], see (black dotted) and (purple dashed) curves in Figure 5 - Figure 7. One with liquid 1 attached to the free surface and the other with liquid 1 attached to the substrate [19].

We observe two interesting solutions work as a transition between the laterally stratified and the
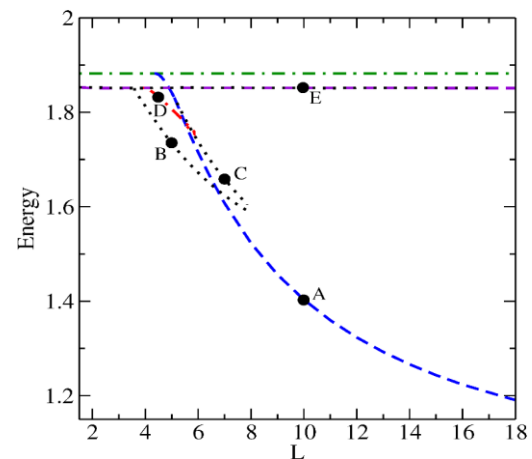
Figure 7. (Colour online) Shown is the energy of the branch $(1/2, 0)$ and related branches for neutral film, varying lateral domain size L. The film mean thickness is fixed at H = 5 for off-critical mixture with c = 0.4.

horizontally stratified branches. One is the branch that represents the transition between the stratified state $(0,1/2)$ and the lateral state $(1/2,0)$ with the creation of a droplet of liquid 2 attached to the free surface. This branch is presented by the (black dotted) curve shown in Figure 5, with samples of its profiles indicated by Figure 8(b), and Figure 8(c). The other one is the solution that represents a transition between the laterally stratified and the horizontally stratified solution with the creation of a droplet of liquid 2 attached to the substrate as shown by the (red dash-dot) curve shown in Figure 5 - Figure 7. These two branches represent the transition between the two laterally and the two duplicated horizontally stratified solutions.

Regarding to L_2-norm of surface modulations, the film surface of the homogenous state remains flat along the

(a)

(b)

(c)

(d)

(e)
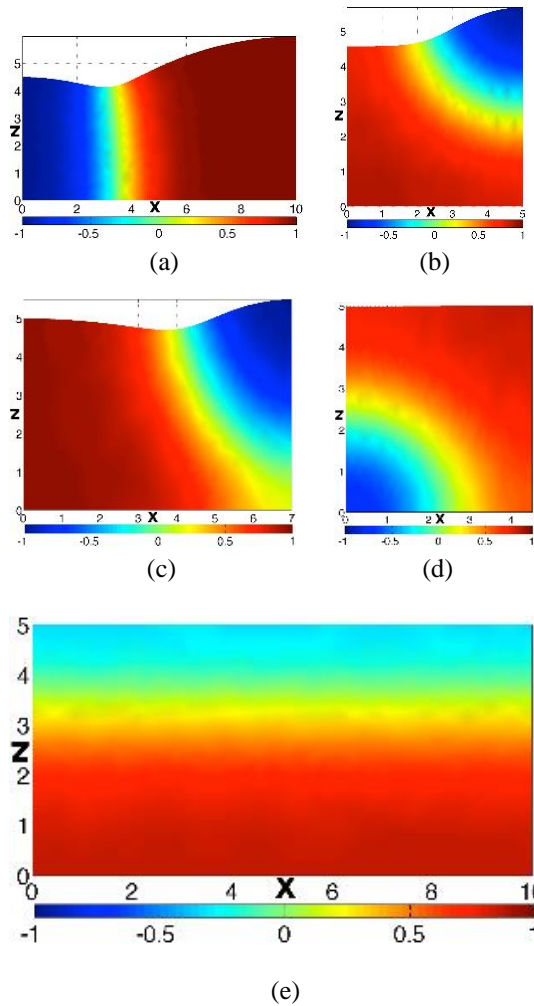
Figure 8. Shown are the film profiles for the branch (1/2,0) and related ones at the corresponding labels in Figure 5. and Figure 7. Panels a, b, c, d and e correspond to the labels A, B, C, D and E, respectively.

branch in terms of lateral domain size see Figure 5. The lateral branch $(1/2, 0)$ bifurcates from the homogenous state with rapid increase to reach a relatively high value of surface deflection $\|\delta h\|$, as compared to the other branches, see the (blue dashed) curve in Figure 5 - Figure 7. This branch is a duplicated branch due to the symmetry of boundary conditions and the absence of energetic bise at both the substrate and free surface. A sample of the film profile is shown by Figure 8(a). The free surface of these solutions also remains flat as varying the lateral domain size L. A sample of the solution profiles is shown by Figure 8(e). However, the L_2-norm of the concentration field of the homogeneous state remains at zero as varying the lateral domain size, see the (green-dash-dot) line in Figure 7. On the other hand, the L_2-norm of concentration field of the stratified

solutions remains constant at about $\|\delta c\| = 0.41$, as varying the lateral domain size L. The laterally stratified solution characterized by its rapid increase near the bifurcation point and then becomes the highest L_2-norm of concentration field, particularly for higher lateral domain size. The transition solutions fluctuate between $\|\delta c\| \approx 0.4$ and $\|\delta c\| \approx 0.65$, see the (black dotted) curve, and (red dash-dot) curve in Figure 6 Energetically, the homogenous solution is higher than other solutions at about 1.88, see (green dash-dot) curve shown in Figure 7. The energy of the stratified is at about 1.85 and it is also remained constant when varying the lateral domain size. The energy of the laterally stratified film is rapidly decreased near the bifurcation point (the transition) and then it becomes the lowest energetically. The energy of the transitional solutions fluctuates between 1.6 and 1.85 as depicted in Figure 7.
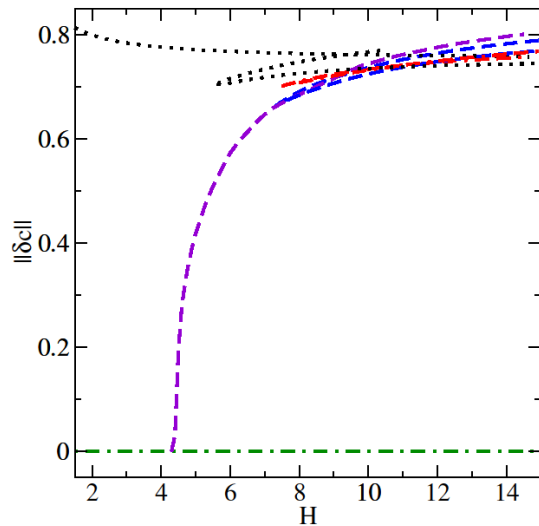
3.3 Varying mean film thickness H

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
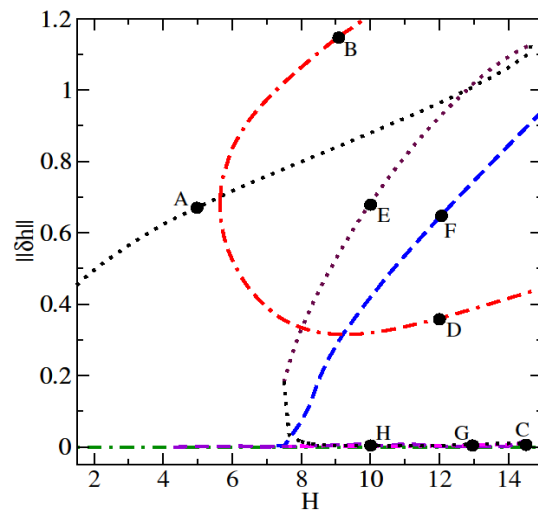
Figure 9. (Colour online) Shown is L_2-norm for surface deflection of the branch $(1/2, 0)$ and related branches for neutral film, varying mean film thickness H. The lateral domain size is at $L = 10$ for off-critical mixture with $c = 0.4$.

structure of these 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 lateral domain size, which is relatively inclusive. 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.

Figure 10. (Colour online) Shown is L_2-norm for the concentration field of the branch $(1/2, 0)$ and related branches for neutral film, varying mean film thickness H. The lateral domain size is at $L = 10$ for off-critical mixture with $c = 0.4$.

Concerning L_2-norm of surface modulations, no surface deflections detected for the homogeneous film state, see (green dash-dot) curve in Figure 9, as well as the horizontally stratified film, where the fluid attached to the free surface and the substrate is of one kind, see the (purple dashed) curve in Figure 9, represented by the profile sample shown by Figure 12(c). However, surface modulation is observed in all films of other states that have the fluid-fluid contact line hitting the free surface or the substrate.

The laterally stratified film already existed for the fixed domain size at $L = 10$, even for small values of film height H and its surface deflection demonstrates various modulations, see (black dotted) curve shown in Figure 9. This solution state is connected interestingly to the droplet solution when the droplet is attached to the substrate, see profile samples shown in Figure 12(a), Figure 12(e), and Figure 12(g).

The horizontally stratified film bifurcates from the homogenous state at about $H = 4.15$ with a flat surface, see the profile sample shown by Figure 12(c). The film surface remains flat for all values of H, see

(purple-dash) curve in Figure 9. This film branch is a duplicated branch due to the solution energetical symmetries of liquid 1 and liquid 2 attached to the free surface or the substrate.

The (red dash-dash-dot) curve represents the solution of the droplet attached to the free surface; The solution sample is depicted by the profile shown by Figure 12(b), which appeared at about $H = 5.6$, and displays the highest L_2-norm of surface modulation. This solution is not connected to any other solution at least in the domain of film height in the scope of our study. The solutions characterized by a flat droplet that is attached to the free surface or the substrate are bifurcated from the stratified state. The branch with a flat droplet attached to the substrate bifurcates at about
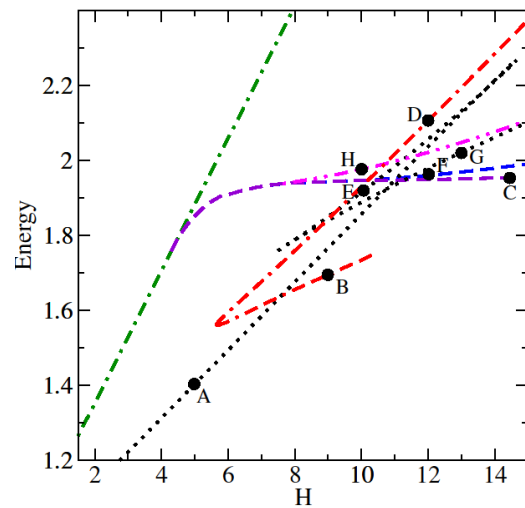
Figure 11. (Colour online) Shown is the energy for the branch $(1/2, 0)$ and related branches for neutral film, varying mean film thickness H. The lateral domain size is at $L = 10$ for off-critical mixture with $c = 0.4$.

$H = 7.5$. Its solution profile sample is shown by Figure 12(h). This solution has a flat surface for the domain of film thickness H, see (Magenta dash-dot-dot) curve shown in Figure 9. Also, the solution state shown by profile Figure 12(f) is bifurcated from the horizontally stratified state at $H = 7.3$. This solution is characterized by its flat droplet attached to the free surface with rapid changes in its surface modulation, see (blue dashed) curve in Figure 9. For this case, the L_2-norm of the concentration field $\|\delta c\|$ is represented by Figure 10. In terms of film thickness, we note that

(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)
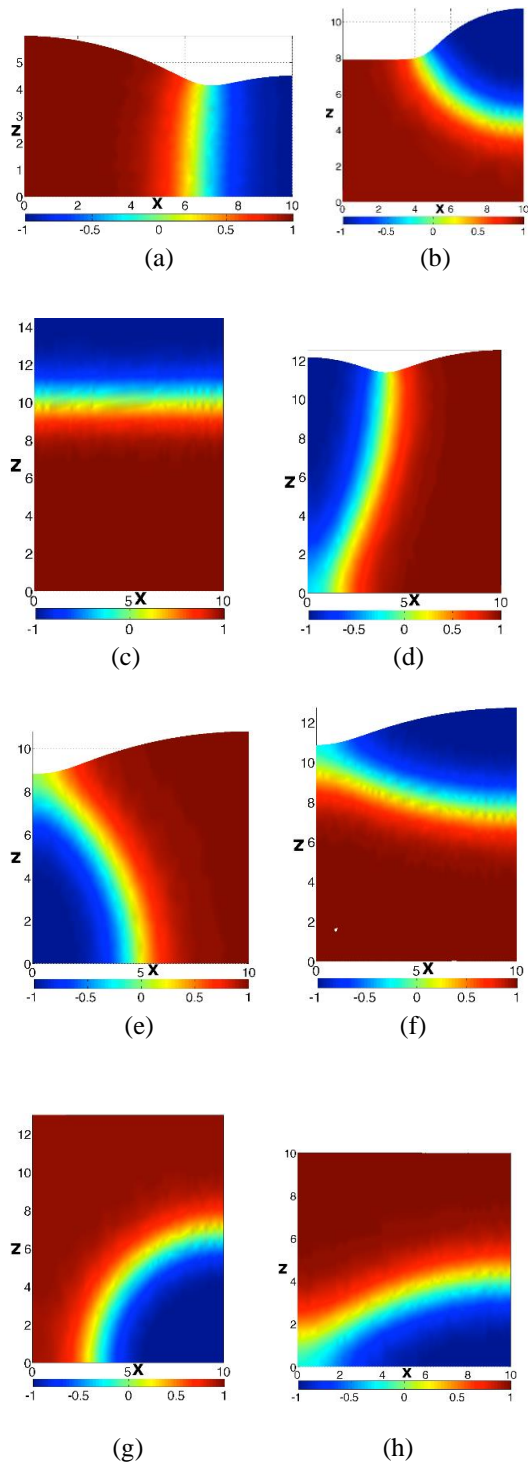
Figure 12. Shown are the film profiles for the branches $(1/2,0)$ and related ones at the corresponding labels Figure 9. and Figure 11. Panels a, b, c, d, e, f, g and h correspond to the labels A, B, C, D, E, F, G and H, respectively.

the L_2-norm for the homogenous state remains at $\|\delta c\| = 0$. However, all other states have $\|\delta c\| \neq 0$. At thinner films, we observe the highest perturbation in concentration is gained by the laterally stratified solution at $\|\delta c\| \approx 0.8$. With more increase in film

thickness, the horizontally stratified film bifurcates at about $H = 4.2$ with a rapid increase in concentration perturbations see the (purple dashed) curve in Figure 10. For higher film thickness that has been considered in this study, the concentration perturbations fluctuate between $\|\delta c\| \approx 0.67$ and $\|\delta c\| \approx 0.8$ for all the resulted film states, see Figure 10.

The system energy behaviour is illustrated in Figure 11 and shows the energy levels of various states as a function of film thickness. The homogeneous base state has the highest energetically, see (green dash-dotted) curve. The lowest energetically for film thicknesses less than 7.5 is the laterally stratified state $(1/2,0)$, illustrated by the (black dotted) curve in Figure 11. This state has a film with a droplet attached to the free surface represented by the profile shown by Figure 12(a). However, for thicker films, the total energy for solutions with the droplet of one component rises over the other and becomes the lowest. This is due to the reduction in interfacial energy between the two components, as one can compare between Figure 12(b) and Figure 12(d). Since the energy associated with the interface between two immiscible liquids measures the strength of the interactions between the molecules at the interface, for higher thickness the solution with droplet attached to free surface represented by (red dash-dash-dot) curve in Figure 11 is the lowest energetically. This branch has been terminated due to convergence issues.

As presented in the bifurcation diagram of the system energy, it is observed that the horizontally stratified solution is lower energetically than its branches, which are characterized by flat droplets either at the free surface or at the substrate. The (purple dashed) branch and its two branches, see Figure 11 are higher energetically than their base state. Samples of their profiles are represented by Figures 12(c), Figure 12(f), and Figure 12(h). Essentially, the energy associated with the interface between two immiscible liquids is a measure of the strength of the interactions between the molecules at the interface.

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. The mixture components are characterised by their concentration

gradient. Although the study obtained a considerable number of solutions, our investigations were intentionally limited to films of only two layers 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.

References

[1] V. Cristini, X. Li, J. S. Lowengrub and S. M. Wise, "Nonlinear simulations of solid tumor growth using a mixture model: invasion and branching," *Journal of mathematical biology,* vol. 58, no. 4, pp. 723-763, 2009.

[2] S. M. Wise, J. S. Lowengrub, H. B. Frieboes and V. Cristini, "Three-dimensional multispecies nonlinear tumor growth—I: model and numerical method," *Journal of theoretical biology,* vol. 253, no. 3, pp. 524-543, 2008.

[3] T. Zhang, N. G. Cogan and Q. Wang, "Phase field models for biofilms. I. Theory and one-dimensional simulations," *SIAM Journal on Applied Mathematics,* vol. 69, no. 3, pp. 641-669, 2008.

[4] A. Sharma, R. Khanna and G. Reiter, "A thin film analog of the corneal mucus layer of the tear film: an enigmatic long range non-classical DLVO interaction in the breakup of thin polymer films," *Colloids and Surfaces B: Biointerfaces,* vol. 14, no. 1-4, pp. 223-235, 1999.

[5] J. Heier, J. Groenewold, S. Huber, F. Nüesch and R. Hany, "Nanoscale structuring of semiconducting molecular blend films in the presence of mobile counterions," *Langmuir,* vol. 24, no. 14, pp. 7316-7322, 2008.

[6] S. J. Weinstein and K. J. Ruschak, "Coating flows," *Annual Review of Fluid Mechanics,* vol. 36, 2004.

[7] L. W. Schwartz, R. V. Roy, R. R. Eley and S. Petrash, "Dewetting patterns in a drying liquid film," *Journal of colloid and interface science,* vol. 234, no. 2, pp. 363-374, 2001.

[8] R. Seemann, S. Herminghaus and K. Jacobs, "Gaining control of pattern formation of dewetting liquid films," *Journal of Physics:* *Condensed Matter,* vol. 13, no. 21, p. 4925, 2001.

[9] U. Thiele, S. Madruga and L. Frastia, "Decomposition driven interface evolution for layers of binary mixtures. I. Model derivation and stratified base states," *Physics of Fluids,* vol. 19, no. 12, p. 122106, 2007.

[10] S. Madruga and U. Thiele, "Decomposition driven interface evolution for layers of binary mixtures. II. Influence of convective transport on linear stability," *Physics of Fluids,* vol. 21, no. 6, p. 062104, 2009.

[11] S. Madruga and U. Thiele, "Convective instabilities in films of binary mixtures," *The European Physical Journal Special Topics,* vol. 192, no. 1, pp. 101-108, 2011.

[12] H. Wang and R. J. Composto, "Thin film polymer blends undergoing phase separation and wetting: Identification of early, intermediate, and late stages," *The Journal of Chemical Physics,* vol. 113, no. 22, pp. 10386-10397, 2000.

[13] P. C. Hohenberg and B. I. Halperin, "Theory of dynamic critical phenomena," *Reviews of Modern Physics,* vol. 49, no. 3, p. 435, 1977.

[14] D. M. Anderson, G. B. McFadden and A. A. Wheeler, "Diffuse-interface methods in fluid mechanics," *Annual review of fluid mechanics,* vol. 30, no. 1, pp. 139-165, 1998.

[15] D. J. Korteweg, "Sur la forme que prennent les' equations du mouvements des fluides si l'on tient compte des forces capillaires caus'ees par des variations de densit'e consid'erables mais connues et sur la th'eorie de la capillarit'e dans l'hypoth'ese," *Archives N 'eerlandaises des Sciences exactes et naturelles,* vol. 6, pp. 1-24, 1901.

[16] F. A. Bribesh, L. Frastia and U. Thiele, "Decomposition driven interface evolution for layers of binary mixtures. III. Two-dimensional steady films with flat and modulated surfaces," *Physics of Fluids,* vol. 24, no. 6, p. 062109, 2012.

[17] M. Burger, L. He and C.-B. Schonlieb, "Cahn-Hilliard inpainting and a generalization for grayvalue images," *SIAM Journal on Imaging Sciences,* vol. 2, no. 4, pp. 1129-1167, 2009.

[18] J. W. Cahn and J. E. Hilliard, "Free energy of a nonuniform system. I. Interfacial free energy," *The Journal of chemical physics,* vol. 28, no. 2, pp. 258-267, 1958.

[19] F. A. M. Bribesh, S. Madruga and U. Thiele, "Two-dimensional steady states in off-critical mixtures with high interface tension," *The European Physical Journal Special Topics,* vol. 219, no. 1, pp. 3-12, 2013.