

Convective instabilities in films of binary mixtures

S. Madruga^{1,2,a} and U. Thiele³

¹ Universidad Politécnica de Madrid, ETSI Aeronáuticos, Plaza Cardenal Cisneros 3, 28040 Madrid, Spain

² Instituto Pluridisciplinar, Universidad Complutense, Paseo Juan XXIII, 1, 28040 Madrid, Spain

³ Department of Mathematical Sciences, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK

Received 21 January 2011 / Received in final form 25 January 2011
Published online 9 March 2011

Abstract. We present a model for the evolution of films of isothermal binary liquid mixtures with a free evolving surface. The model is based on model-H supplemented by appropriate boundary conditions at the free surface and the solid substrate. The equations account for the coupled transport of the concentration of a component (convective Cahn-Hilliard equation) and the momentum (Korteweg-Navier-Stokes equation). The inclusion of convective motion makes surface deflections possible, i.e., the model allows to study couplings between the decomposition of the mixture and the evolving surface corrugations. We present selected steady layered film states for representative polymer mixtures, and show that convective motion favors their destabilization and qualitatively changes the linear instability modes in experimentally accessible ranges of parameters.

1 Introduction

Thin polymer films are increasingly used in advanced technological applications. The use of these films as coatings is often limited by their lack of stability due to their wettability properties on the used substrates. However, the instabilities may be employed to create complex morphologies for polymeric functional layers [1–4]. Furthermore, the development of microfluidics applications such as DNA micro-arrays, thermal control of semiconductor devices, and massively parallel drug screening requires a fundamental understanding of static and dynamic interfacial phenomena at adaptive interfaces and for confined geometries.

A good understanding has been reached for films of simple liquids [5–8]. However, in various technological applications the thin films of interest may be multilayer, multicomponent, evaporating, on structured substrates, or any combination of them. These systems pose interesting fundamental questions that are not yet entirely resolved even for the bulk of the film, and become more challenging as free interfaces

^a e-mail: santiago.madruga@upm.es

and wetting properties are involved. For instance, experiments with films of polymer blends, find that phase separation within the film or phase enrichment at the boundaries may cause the dewetting of the film itself – a dynamical behavior that is not yet well understood [4,9].

The dynamics of binary mixtures, and fluids near the critical point, is described by the so called model-H, which couples momentum transport and diffusion of the components [10]. We adapt this model for films of binary mixtures with a free evolving surface. The resulting model-H with boundary conditions allows to study the combined effect of phase separation in a polymer blend and surface structuring of the film itself. In this work we restrict ourselves to the linear regime. In particular, we study the linear stability of stratified films with respect to lateral perturbations and show that the possibility of convective flow may further destabilize the films and strongly changes the instability modes for realistic parameter values.

2 Evolution equations for films of binary mixtures with a free evolving surface

The Cahn-Hilliard equation describes the evolution of decomposing binary mixtures as driven by diffusive transport. The interface between the two components is diffuse (the interface between two completely immiscible liquids is comparatively very sharp). To include the possibility of convective transport in the mixture one generalizes the Cahn-Hilliard equation with an advective term (see Eq. (2)) and introduces a transport equation for momentum that contains a concentration-gradient contribution to the stress tensor (see Eq. (1)). The resulting set of transport equations is called model-H [10,11].

We consider a film of a binary mixture on a horizontal smooth homogeneous solid substrate. The film is ‘open to the air’, i.e., it has a free upper surface that may be non-flat and may evolve in time. For simplicity, we suppose the system is two-dimensional and infinitely extended in the lateral direction, with the origin of the Cartesian frame fixed at the substrate. The dimensionless governing equations expressing the balance of momentum and concentration, and the continuity equation may be derived employing phenomenological non-equilibrium thermodynamics as discussed in Ref. [12]. They read

$$Ps [\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v}] = -\nabla \cdot \{(\nabla c)(\nabla c) + p_{\text{eff}} \mathbf{I}\} + \frac{Ps}{Re} \Delta \mathbf{v}, \quad (1)$$

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

and

$$\nabla \cdot \mathbf{v} = 0, \quad (3)$$

respectively, with the operators $\nabla = (\partial_x, \partial_z)$, $\Delta = (\partial_x^2 + \partial_z^2)$, and the velocity field $\mathbf{v} = (u, w)$. The composition field $c = c_1 - c_2$ denotes the concentration difference between the two components of the mixture, $p_{\text{eff}} = p - (c + 1)\Delta c - (\Delta c)^2/2$ comprises all diagonal terms of the stress tensor, and p is the mechanical thermodynamical pressure (given by the local Gibbs-Duhem relation). The local bulk free energy is assumed to correspond to the simple quartic potential $f(c) = (c^2 - 1)^2/4$. Two dimensionless numbers appear in the bulk equations, the pressure number $Ps = \rho M^2 E^2 / C^6 \sigma_c$ and the Reynolds number $Re = M E \rho / \eta C^2$, with ρ the density, M the diffusion coefficient, E the energy scale, C the concentration at the binodal, σ_c the coefficient of the gradient energy of the concentration field, and η the dynamic viscosity.

The ratio Re/Ps corresponds to the ratio of the typical velocity of the viscous flow driven by the internal ‘diffuse interface tension’ and the typical velocity of diffusive processes. The ratio Re/Ps is the most important bulk parameter for the extremely slow creeping flow typical for polymer blends.

Boundary conditions are as discussed in Ref. [12]: At the solid substrate ($z = 0$) one has zero diffusive mass flux through the solid-liquid interface and allows for an energetic bias, i.e.,

$$\partial_z [(\partial_{xx} + \partial_{zz})c - \partial_c f(c)] = 0 \quad (4)$$

$$-\partial_z c + S\partial_c f^-(c) = 0 \quad (5)$$

respectively. Similar conditions apply at the (curved) free surface ($z = h(x, t)$), i.e.,

$$[\partial_z - (\partial_x h)\partial_x][(\partial_{xx} + \partial_{zz})c - \partial_c f(c)] = 0 \quad (6)$$

$$[\partial_z - (\partial_x h)\partial_x]c + S\partial_c f^+(c)\sqrt{1 + (\partial_x h)^2} = 0, \quad (7)$$

where $S = \gamma_0/lE$ is the dimensionless surface tension of the liquid-gas interface, and γ_0 is the reference surface tension at $c = 0$. The derivatives of the surface energies have the forms $\partial_c f^\mp(c) = a^\mp$ (not to confuse with the values of $\partial_c f(c)$ at the boundaries) where a^\mp models preferential attachment of one component of the mixture to the substrate ($-$) or free surface ($+$). The linear expressions for f^\mp indicate that there is no change in the interaction between the two species at the interfaces (see [12, 13] for more details).

For the velocity field we request no-slip and no-penetration at the substrate, i.e., $v = w = 0$ at $z = 0$. At the free surface the conditions correspond to the balance of the tangential forces

$$\begin{aligned} & -[\partial_x c + (\partial_x h)\partial_z c][\partial_z c - (\partial_x h)\partial_x c] + \frac{Ps}{Re} [(\partial_z u + \partial_x w)(1 - (\partial_x h)^2) \\ & + 2(\partial_z w - \partial_x u)\partial_x h] = S\sqrt{1 + (\partial_x h)^2} [\partial_x + (\partial_x h)\partial_z] f^+(c), \end{aligned} \quad (8)$$

and the one of the normal forces

$$\begin{aligned} & -\frac{1}{1 + (\partial_x h)^2} [\partial_z c - (\partial_x h)\partial_x c]^2 - p_{\text{eff}} + \frac{Ps}{Re} \frac{2}{1 + (\partial_x h)^2} \\ & \times [\partial_x u(\partial_x h)^2 + \partial_z w - \partial_x h(\partial_z u + \partial_x w)] = Sf^+(c)\partial_x \left[\frac{\partial_x h}{(1 + (\partial_x h)^2)^{1/2}} \right]. \end{aligned} \quad (9)$$

The tangential gradient of $f^+(c)$ corresponds to a solutal Marangoni force. Furthermore, at the free surface one imposes the kinematic condition ensuring that the free surface follows the velocity field $\partial_t h = w - u\partial_x h$.

3 Linearized equations

It is often found experimentally that thin films of a decomposing mixture first stratify vertically on a relatively short time scale and then develop lateral structures on a slower time scale [3]. Therefore we are interested in steady layered films characterized by concentration profiles $c_0(z)$ and $v_0 = w_0 = 0$, and their stability with respect to lateral perturbations. Quiescent profiles $c_0(z)$ are obtained solving the bulk Cahn-Hilliard equation $\partial_{zz}[\partial_{zz}c_0 - \partial_c f(c)|_{c_0}] = 0$ with boundary conditions at $z = 0, h_0$: $\partial_z[\partial_{zz}c_0 - \partial_c f(c)|_{c_0}] = 0$ and $\mp\partial_z c_0 + S\partial_c f^\mp(c)|_{c_0} = 0$.

To analyze the stability of the base states with respect to infinitesimal perturbations, we use the ansatz $\mathbf{v} = \mathbf{v}_0 + \varepsilon\tilde{\mathbf{v}}_1$, $p_{\text{eff}} = p_0 + \varepsilon\tilde{p}_1$, $c = c_0 + \varepsilon\tilde{c}_1$, and $h = h_0 + \varepsilon\tilde{h}_1$, with $\mathbf{v}_0 = 0$ and $p_0 = (\partial_z c_0)^2$. The fields $\varepsilon\tilde{\mathbf{v}}_1$, $\varepsilon\tilde{p}_1$, $\varepsilon\tilde{c}_1$, and $\varepsilon\tilde{h}_1$ denote the infinitesimal perturbations of velocity, pressure, concentration, and thickness fields, respectively. The small parameter ε will be used to order terms in the series expansion. The perturbations are decomposed into a sum of normal modes $(\tilde{\mathbf{v}}_1, \tilde{p}_1, \tilde{c}_1, \tilde{h}_1) = (\mathbf{v}_1(z), p_1(z), c_1(z), h_1) \exp(\beta t + ikx)$, where β is the growth rate and k the lateral wavenumber. Using this ansatz in Eqs. (1) to (9) and eliminating the pressure in the momentum and boundary equations we write the linearized model-H as an eigenvalue problem

$$\partial_{zzzz}c_1 = -(\beta c_1 + w_1 \partial_z c_0) - [(k^4 - 2k^2 \partial_{zz})c_1 - (\partial_{zz} - k^2)(c_1 \partial_{cc} f|_{c_0})], \quad (10)$$

and

$$\begin{aligned} \partial_{zzzz}w_1 &= \beta Re(\partial_{zz} - k^2)w_1 + \frac{Re}{P_s} k^4 c_1 \partial_z c_0 \\ &\quad - \frac{Re}{P_s} 2k^2 \partial_z [(\partial_z c_0)(\partial_z c_1)] + \frac{Re}{P_s} k^2 \partial_{zz}(c_1 \partial_z c_0) + 2k^2 \partial_{zz}w_1 - k^4 w_1 \end{aligned} \quad (11)$$

that is in form similar to the Orr-Sommerfeld equation. For the linearized boundary conditions see [13]. To find numerically the base states and to solve the eigenvalue problem we use the numerical continuation algorithms based on Newton and Chord iterative methods bundled in the package AUTO [14]. In particular, we start from known trivial solutions and find the layered steady states and the growth rates characterizing the linear stability via subsequent continuation in various parameters [13].

4 Linear stability of stratified films

In general, there exist two types of steady state solutions that are laterally uniform: (i) homogeneous flat films characterized by constant concentration c_0 (they only exist for $a^\mp = 0$) and (ii) stratified or layered flat films characterized by a vertical concentration profile $c_0(z)$. Several branches of stratified solutions may exist [12], but here we only consider the branches with minimal free energy as these are the physically more relevant solutions. Branches labeled as $n = 0$ correspond to weak vertical stratifications (homogenous solutions energetically favorable for neutral surfaces and $h \leq \pi$) and $n = 1/2$ to strong stratifications (for neutral surfaces they appear for $h > \pi$). The stability of type (i) solutions is studied for quadratic energy bias at the interfaces in the context of purely diffusive decomposition in a gap between two solid plates [15]. Here, we review selected results of Ref. [13] that discusses the stability of both solution types including diffusive and convective transport. In particular, we present the stability properties of selected stratified base states.

Neutral surfaces. Figure 1(a) shows for a rather thin film of $h_0 = 3.5$ the concentration profile $c_0(z)$ of the base state (solid line) for neutral surfaces ($a^\mp = 0$) and the perturbation concentration field $c_1(z)$ (dashed line). The concentration c_0 decreases monotonically with thickness, i.e., it corresponds to a two-layer configuration with the component two enriched near the free surface. The concentration eigenmode c_1 shows nearly an up-down symmetry (cf. Fig. 1(a)) and has its maximal amplitude at the center of the film. The corresponding perturbation eigenmode for the vertical velocity component is shown in Fig. 1(b). Although the convective motion is mainly driven by the gradients of c_0 , i.e., driving is strongest around $z \approx 0.5$ the velocity perturbation itself shows a strong up-down asymmetry due to the possibility of liquid motion at the free surface but not at the substrate where $w_1 = 0$. Note also that the velocity is crossing zero at about $z \approx 0.6$.

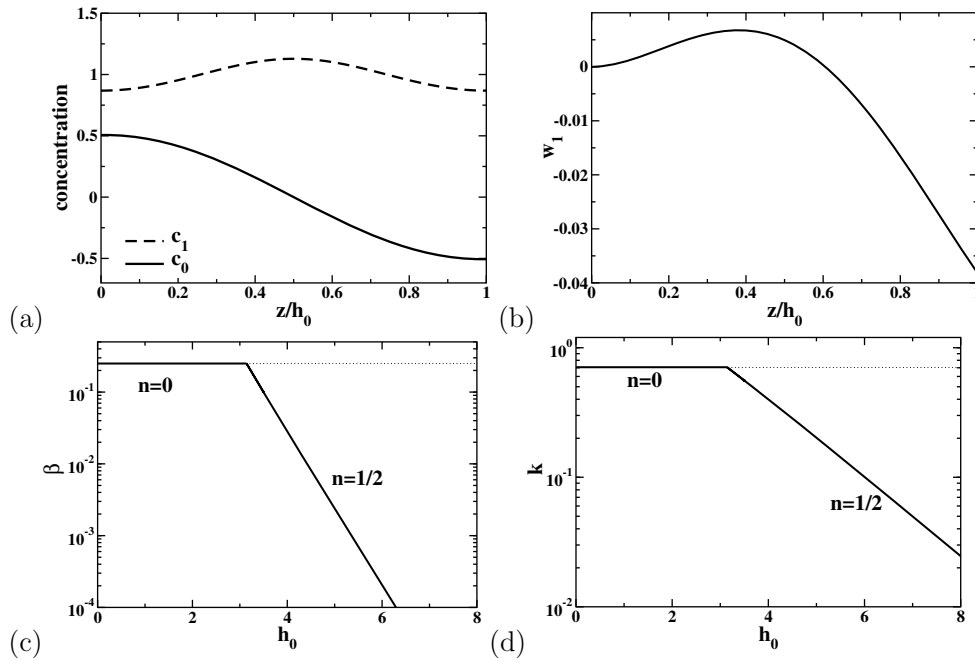


Fig. 1. Characteristics of the lateral instability modes of a free surface film of a binary mixture in the case of energetically neutral boundaries ($a^\mp = 0$). (a) Concentration profile (solid line) and perturbation profile of the concentration field (dashed line) for a stratified film with $h_0 = 3.5$, (b) perturbation velocity field for $h_0 = 3.5$, (c) maximum growth rate, and (d) associated wavenumber as a function of the film thickness for $n = 0$ and $n = 1/2$ base states (cf. Figs. 9 and 10 of Ref. [12]). Remaining parameters are $S = 1$, $Re = 0$ and $Ps/Re = 1$.

Figures 1(c) and 1(d) show the maximal growth rate and associated lateral wave number as a function of the film thickness. There are two regimes: for $0 < h_0 < \pi$ the base states correspond to a homogeneous film. For $h_0 > \pi$ a layered base state exists whose vertical profile is shown in Fig. 1(a). The layered film is unstable with respect to lateral perturbations, however, its growth rate and associated wave number decrease exponentially with increasing film thickness. Therefore one expects that sufficiently thick films appear to be stable on typical experimental time scales.

Asymmetrically biased surfaces. As second example we present in Fig. 2 results for a realistic situation of asymmetric energetic bias. We chose $a^- = 0$, i.e., the substrate does not prefer any of the two components and $a^+ = 0.1$, i.e., the free surface has a small preference for component two of the mixture. We compare stability results for the purely diffusive case (dashed lines in (d) and (e)) with the case where convective transport is included, i.e., the free surface can evolve (solid lines in (d) and (e)). Up to $h_0 \simeq 5$ the stability of the two cases is very similar. As the thickness is increased above $h_0 \simeq 5$, the film becomes much more unstable when convection is included. Most importantly, for $h_0 > 6.5$ the film becomes linearly stable if only transport by diffusion is considered. In contrast, the inclusion of the transport by convection, and the additional degrees of freedom it provides, makes the film unstable for a wide range of thicknesses. This instability is entirely due to the convective modes of the system. The growth rate and wavenumber of the most unstable mode decreases roughly exponentially with increasing film thickness.

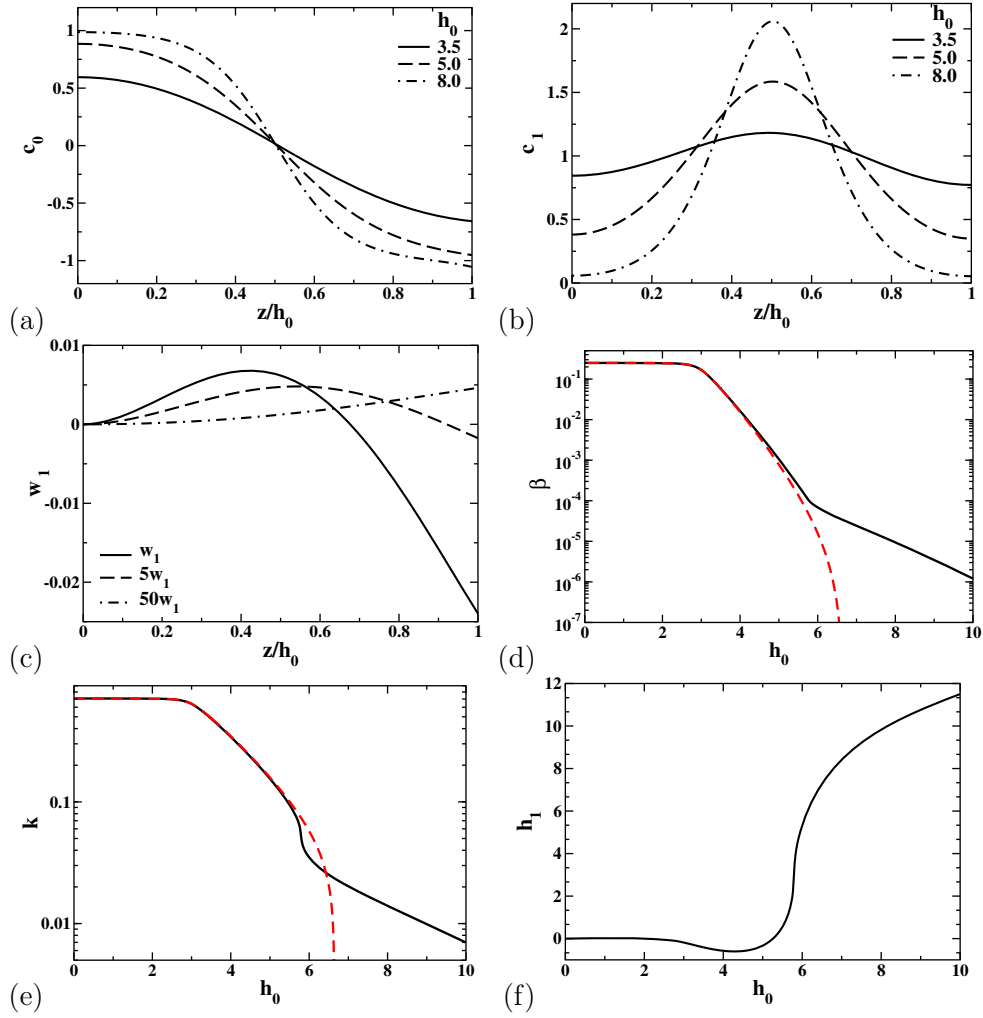


Fig. 2. Characteristics of the lateral instability modes of a binary mixture with free surface and energetically asymmetric boundary conditions ($a^+ = 0.1$, $a^- = 0$). Shown are (a) the concentration profile $c_0(z)$ for the $n = 1/2$ (layered) base state at film thicknesses h_0 as given in the legend, the corresponding perturbations of (b) concentration $c_1(z)$ and (c) vertical velocity $w_1(z)$. Note that for $h_0 = 5.0$ and $h_0 = 8.0$ in (c) we have multiplied w_1 by a factor of 5 and 50, respectively. Panel (d) gives the maximum growth rate, and (e) the associated wavenumber as a function of the film thickness for $n = 0$ and $n = 1/2$ base states (see Figs. 9 and 10 of Ref. [12]). The dashed lines in panels (d) and (e) correspond to transport by diffusion only while the solid lines correspond to transport by convection and diffusion. Finally (f) gives the maximal deflection of the upper free surface as a function of the thickness. Remaining parameters are $S = 1$, $Re = 0$ and $Ps/Re = 1$.

Therefore the addition of convective transport to the dynamics of the mixture allows the film to realize a different class of solutions, characterized by modulations in the concentration field (Fig. 2(b)) and of the film thickness. The thickness modulations are illustrated in Fig. 2(f) where its perturbation h_1 is given. Up to $h_0 \simeq 5$ the dynamics is ruled mainly by the diffusive transport and the deflection is very small and roughly independent of the thickness. For larger thickness h_0 , however, convective

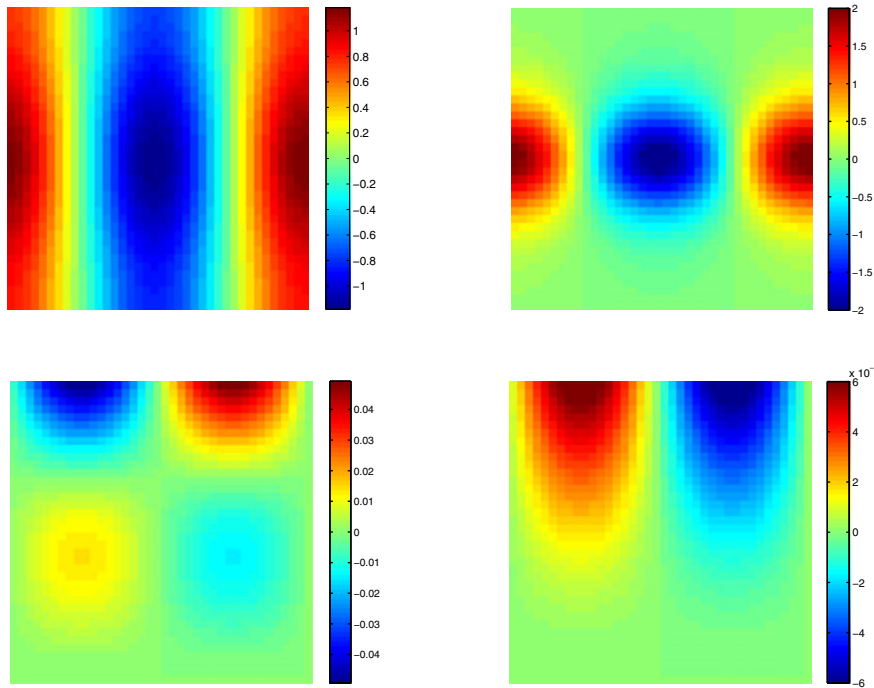


Fig. 3. Top panels: perturbation concentration field $\tilde{c}_1(x, z)$. Bottom panels: corresponding perturbation stream functions. Left panels: $h_0 = 3.5$, $k = 0.483$. Right panels: $h_0 = 8$, $k = 0.01399$. Branch $n = 1/2$, $a^+ = 0.1$, $a^- = 0$. Remaining parameters $S = 1$, $Re = 0$ and $Ps/Re = 1$.

transport becomes important and leads to a strong increase of the surface deflection which also varies strongly with the thickness. These perturbations of the thickness in the linear stage are the seed of dewetting and rupture phenomena in the non-linear stage.

This qualitative change is as well reflected in a change of the character of the perturbation velocity profile w_1 (cf. Fig. 2(c) and Fig. 3). At $h_0 = 3.5$ it shows non-monotonic behavior that indicates driving from the diffuse interface inside the film (left panels of Fig. 3). This results in two pair of convection cells. However, at larger thicknesses (shown for $h_0 = 8.0$) the w_1 profile increases monotonically with the z coordinate. The driving comes from the vicinity of the free surface resulting in one pair of convection cells (right panels of Fig. 3). The change from $h_0 = 3.5$ to $h_0 = 8.0$ corresponds to a transition from bulk Korteweg driving to driving from the surface that is similar to a solutal Marangoni effect.

5 Conclusion

We have briefly reviewed model-H in its application to the evolution of films of isothermal binary liquid mixtures with a free surface. The model has been used to study steady homogeneous and stratified film states and their linear lateral stability in time. It has been shown that convective transport allows the film to modulate its surface profile and therefore renders the film more unstable. For an alternative linear theory that does not account for an energetic bias for the concentration field although it incorporates a solutocapillary effect see [16]. Note that we are not

aware of any literature results for the fully non-linear time evolution of such a film. However, the static limit of a similar model is employed to determine final steady states that show strong thickness modulations *and* a concentration profile inside the film [17]. Work for asymmetric energetic bias is under way.

S.M. acknowledges support by the EU via a FP7 Marie Curie Reintegration Grant (PERG04-GA-2008-234384). U.T. acknowledges support by the EU via the ITN MULTIFLOW (PITN-GA-2008-214919).

References

1. G. Reiter, A. Sharma, Phys. Rev. Lett. **87**, 166103 (2001)
2. L. Rockford, Y. Liu, P. Mansky, T.P. Russell, M. Yoon, S.G.J. Mochrie, Phys. Rev. Lett. **82**, 2602 (1999)
3. M. Geoghegan, G. Krausch, Prog. Polym. Sci. **28**, 261 (2003)
4. K.R. Thomas, N. Clarke, R. Poetes, M. Morariu, U. Steiner, Soft Matter **6**, 3517 (2010)
5. A. Sharma, R. Khanna, Phys. Rev. Lett. **81**, 3463 (1998)
6. S. Kalliadasis, U. Thiele (eds.), *Thin Films of Soft Matter* (Springer, Wien, 2007)
7. U. Thiele, J. Phys.: Condens. Matter **22**, 084019 (2010)
8. D. Bonn, J. Eggers, J. Indekeu, J. Meunier, E. Rolley, Rev. Mod. Phys. **81**, 739 (2009)
9. R. Yerushalmi-Rozen, T. Kerle, J. Klein, Science **285**, 1254 (1999)
10. D.M. Anderson, G.B. McFadden, A.A. Wheeler, Ann. Rev. Fluid Mech. **30**, 139 (1998)
11. P.C. Hohenberg, B.I. Halperin, Rev. Mod. Phys. **49**, 435 (1977)
12. U. Thiele, S. Madruga, L. Frastia, Phys. Fluids **19**, 122106 (2007)
13. S. Madruga, U. Thiele, Phys. Fluids **21**, 062104 (2009)
14. E.J. Doedel, R.C. Paffenroth, A.R. Champneys, T.F. Fairgrieve, Y.A. Kuznetsov, B.E. Oldeman, B. Sandstede, X.J. Wang, *AUTO2000: Continuation and bifurcation software for ordinary differential equations* (Concordia University, Montreal, 1997)
15. H.P. Fischer, P. Maass, W. Dieterich, **42**, 49 (1998)
16. O.A. Frolovskaya, A.A. Nepomnyashchy, A. Oron, A.A. Golovin, Phys. Fluids **20**, 112105 (2008)
17. L. Frastia, U. Thiele, L.M. Pismen, *Mathematical Modelling of Natural Phenomena* (2010) (in press)