Free surface liquid films of binary mixtures: structuring and stability of stationary solutions.

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We present the steady non-linear solutions of films of confined polymer blends at off-critical concentrations deposited on a solid substrate and with a free evolving surface. The solutions are obtained numerically using a variational form of the Cahn-Hilliard equation in the static limit, which allows for internal diffuse interfaces between the two components of the mixture [1]. Existence of most of the branches of non-linear solutions at off-critical mixture concentrations can be predicted from the knowledge of the non-linear solutions at critical compositions plus the branching points at off-critical compositions derived from a simple linear stability analysis. However, some families of solutions have no correspondence at critical compositions.

We take a surface tension that allows for strong deformations at the sharp free upper surface. Varying the average composition, the size of the films and the surface energy we find a rich morphology of static films in the form of laterally structure films, layered films, droplets on the substrate, droplets on the free surface, and checkerboard structures. We show that laterally structured solutions are energetically favorable over homogeneous and other structured solutions within the whole spinodal region and even close to the absolute stability binodal boundary.

In addition to the transport by diffusion we include the transport by convection through the named model-H, which describes the coupling of momentum transport and diffusion of components in binary mixtures such as polymer blends [2]. We extend the model-H with free surface boundary conditions allowing us to study the combined effect of phase separation within a film of polymer blend and structuring of the surface of the film itself [3]. We apply it to analyze the stability of vertically stratified steady extended films and show that convective transport leads to new mechanisms of instability as compared to the simpler purely diffusive case described by the Cahn-Hilliard model [4]. We carry out this analysis for realistic parameter values corresponding to polymer blends used in experiments with, e.g. PS/PVME mixtures [5, 6].

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[1] F.A.M Bribesh, S. Madruga, and U. Thiele. Two-dimensional steady states in off-critical mixtures with high interface tension. *Eur. Phys. J. Special Topics*, 219:3–12, 2013.

[2] D. M. Anderson, G. B. McFadden, and A. A. Wheeler. Diffuse-interface methods in fluid mechanics. *Ann. Rev. Fluid Mech.*, 30:139–165, 1998.

[3] U. Thiele, S. Madruga, and L. Frastia. Decomposition driven interface evolution for layers of binary mixtures: I. model derivation and base states. *Phys. Fluids*, 19:122106(1–23), 2007.

[4] S. Madruga and U. Thiele. Decomposition driven interface evolution for layers of binary mixtures: II. influence of convective transport on linear stability. *Phys. Fluids*, 21:062104(1–18), 2009.

[5] M. Geoghegan and G. Krausch. Wetting at polymer surfaces and interfaces. *Prog. Polym. Sci.*, 28:261–302, 2003.

[6] K.R. Thomas, N. Clarke, R. Poetes, M. Morariu, and U. Steiner. Wetting induced instabilities in miscible polymer blends. *Soft Matter*, 6:3517–3523, 2010.