MORPHOLOGY AND STABILITY OF FREE SURFACE FILMS OF POLYMER BLENDS

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Summary We present an extended version of the model-H that allows to study the combined evolution of phase separation and film thickness in free surface films of binary mixtures, such as polymer blends. We apply it to analyze the stability of vertically stratified base states of polymer blends on solid substrates and show that convective transport leads to new mechanisms of instability as compared to diffusive transport. In addition, we study the effect of off-critical compositions and energetic bias on the vertical and lateral structuring and stability of thin polymer blends by means of a variational model.

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, 2, 3]. 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. 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 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 [4].

Within the vast field of complex fluids binary mixtures, such as polymer blends, are specially interesting since they are one of the simplest systems with known evolution equations to explore novel features in complex fluids.

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Influence of convective transport

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 [5]. We have adapted this model for films of binary mixtures with a free evolving surface [6]. 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 [7, 8].

We present some relevant results on the linear stability of stratified films with respect to lateral perturbations and show that the possibility of convective flow leads to new instability mechanisms as compared to the simpler diffusive case. We carry out this analysis for flat films for realistic parameters of polymer blends used in experimental setups such as PS/PVME.

Influence of average composition

Real world mixtures are rarely critical -same average composition of the two components- since i) having a balanced overall composition of the two components is not frequent, ii) the evolution of phase separation leads to strong shifts of compositions, ii) active energetic surfaces can attract preferentially one of the components enhancing bulk differences on average composition of the species. This makes relevant the study of off-critical films of binary mixtures.

In this work we present the bifurcation diagrams of off-critical films of polymer blends with free surfaces, by studying their free energy, and the L2-norms of surface deflection and the concentration field, as a function of lateral domain size and mean composition. We study specific film thicknesses and energetic biases and compare their bifurcation diagrams. Simultaneously, we look at spatial dependence profiles of the height and concentration. To treat the problem of films with arbitrary surface deflections our calculations are based on minimizing the free energy functional at given composition and geometric constraints using a variational approach based on the Cahn-Hilliard equation. The problem is solved numerically using the finite element method (FEM).

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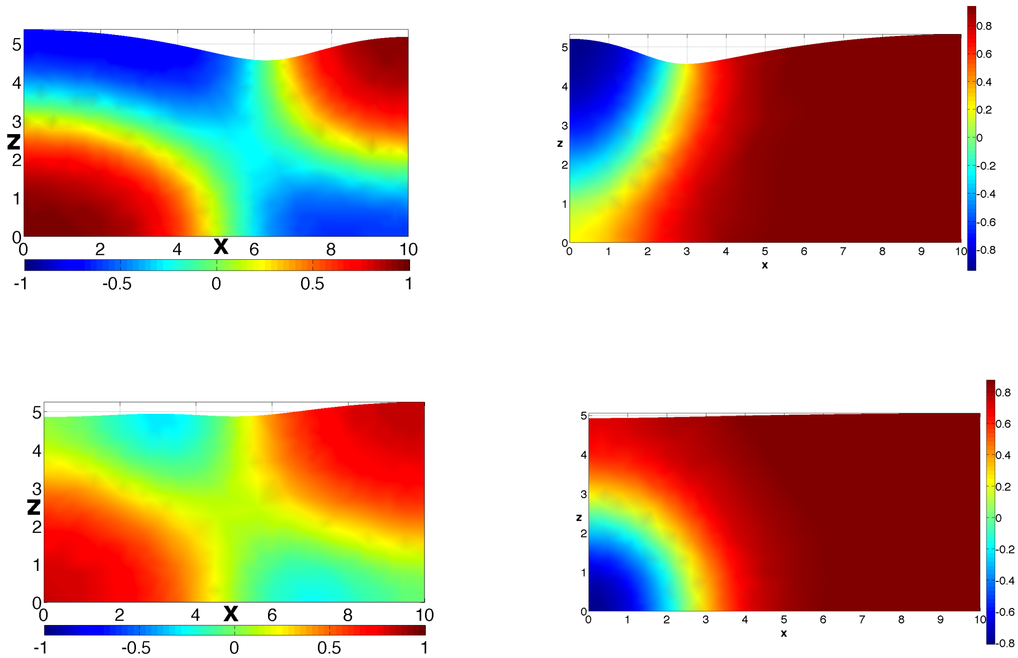

(a)

Figure 1: Profiles for laterally bounded off-critical films of binary mixtures with free evolving surfaces at different average compositions. Figures at the left correspond to the same branch with two superposed vertical and lateral modes, giving rise to a checker-board structure. Figures at the right correspond to the profiles of two off-critical compositions created from a lateral mode branch. Details of parameters can be found in References [8, 9].

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