Interplay of elastic and chemical driving forces for phase separation in biphasic media at large strains

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Abstract

Various polymeric structures, such as microporous membranes, thin films, hydrogels and electrospun fibers, can be engineered through phase separation into solvent and polymer-rich domains under suitable physical and chemical conditions. Tuning the microarchitecture of these structures through the adjustment of material and process parameters allows their use in a wide variety of applications (1). Lately, computational models simulating phase separation induced by different stimuli have been used to avoid or at least supplement extensive combinatorial trial-and-error experimental investigations, as they enable the tracking of microstructure formation in silico (2).
In chemoelastic polymer solutions and gels, the mechanical behavior of the constituent phases significantly influences the microstructural evolution and thus the macroscopic mechanical behavior of the system. In general, phase mixing and separation are associated with deformations of the solution and the evolving phases. When these deformations lead to non-negligible mechanical work, the latter can alter the free energy landscape, shift the binodal points of the phase diagram, and hence affect the phase separation process (3). In the present contribution, we investigate the role of these mechanical effects, focusing on cases involving large deformations, such as drastic volume loss due to external mechanical loads or solvent evaporation. Notably, in solvent evaporation scenarios, traditional models often rely on a rescaling approach rather than explicitly coupling with deformation mechanics (4). We show that the associated changes in geometry can lead to local alterations in composition that trigger and govern microstructure formation.

To this end, a chemomechanical, coupled theory based on the phase-field approach was developed (5), where the mixture is modelled as a single continuous body with diffusing liquid components (6, 7). Within this theory, the chemical (interfacial and mixing) energetic contributions of the original Cahn-Hilliard and Flory-Huggins theories, respectively, were consistently reformulated to account for large deformations in a Lagrangean framework. Special attention is given to the interfacial energy representation, where the fully consistent form implies strong non-linear dependence on deformation, distinct from the common model in literature (c.f. (6, 8)). The governing equations were numerically implemented using FEniCSx and assessed with regard to their predictions of microstructure formation. Through two and three-dimensional simulations, we highlight the importance of the constitutive model specifying the free energy density associated with the formation of interfaces in the geometrically non-linear regime. Finally, the model is used to explore the influence of

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the different material and process parameters on the predicted morphology.

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