

Modeling the effects of mass transfer on microstructure formation via NIPS in polymer membranes

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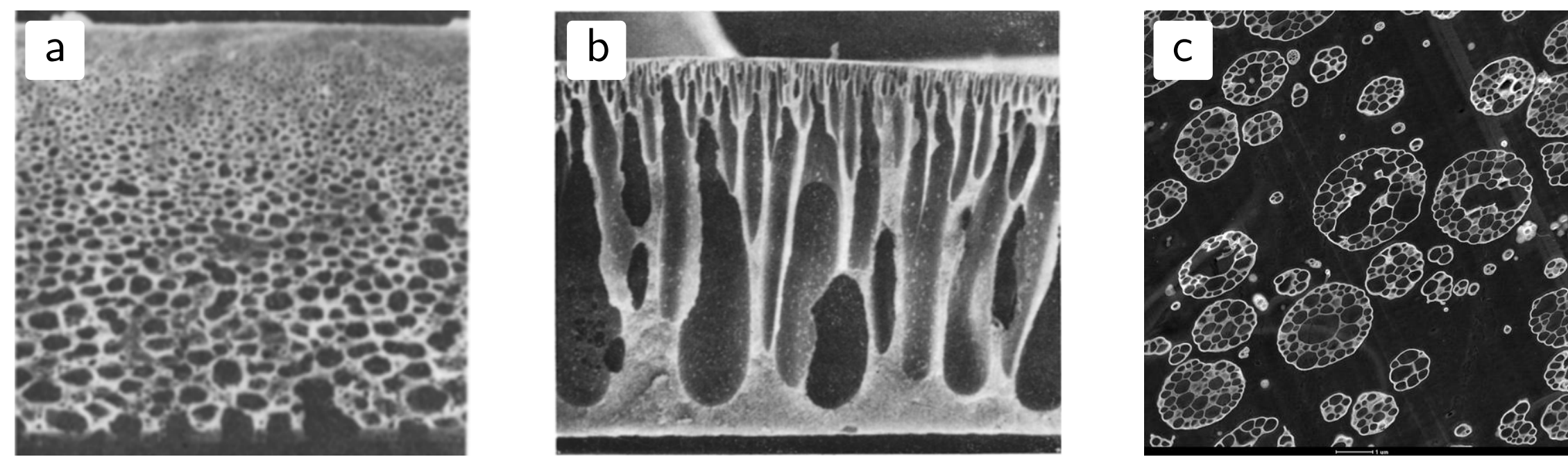


Funding and HPC support:
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Motivation

Microstructure in polymer materials

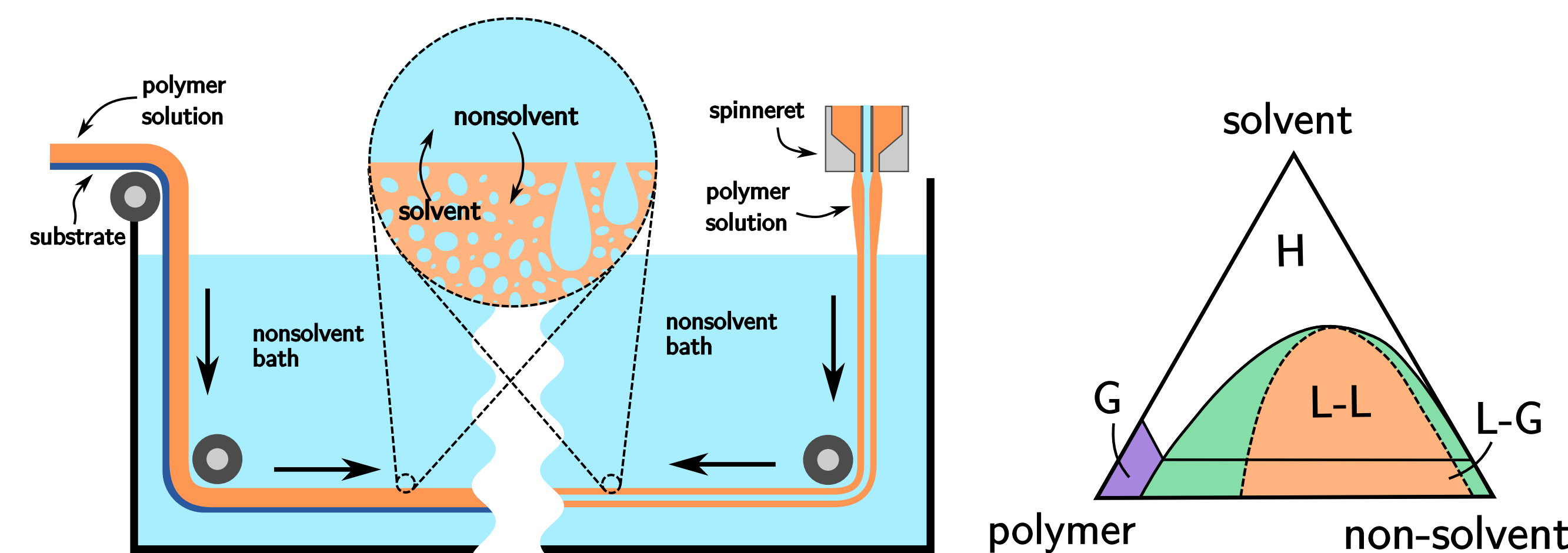
To predict the properties of polymer materials, we need to understand their microstructure. Microstructure is dictated by process history, meaning we must consider process dynamics as well as thermodynamics. In doing so, we are confronted with the challenge of modeling phase separation dynamics and multi-phase flow in polymeric liquids.



Microstructure of some important polymer materials: (a) asymmetric pores and (b) macrovoids in polymer membranes; (c) high-impact polystyrene. Figures (a) and (b) are reproduced from Strathman et al. *Desalination*, 1974. Figure (c) is reproduced from www.leica-microsystems.com.

Nonsolvent induced phase separation (NIPS)

The nonsolvent induced phase separation (NIPS) process is widely used to induce the formation of microstructure in polymer membranes. During NIPS, a polymer solution is exposed to a nonsolvent, which subsequently exchanges with the good solvent in the polymer solution, and drives a phase separation into polymer-rich and polymer-lean regions. At a high enough polymer concentration, the polymer-rich regions solidify, forming the microstructure of the membrane.



Coupled mass transfer and phase separation

While many elements have been studied in isolation, the coupled processes of solvent/nonsolvent exchange and liquid-liquid phase transition kinetics remain poorly understood, despite their centrality to NIPS. In the present work we seek to understand:

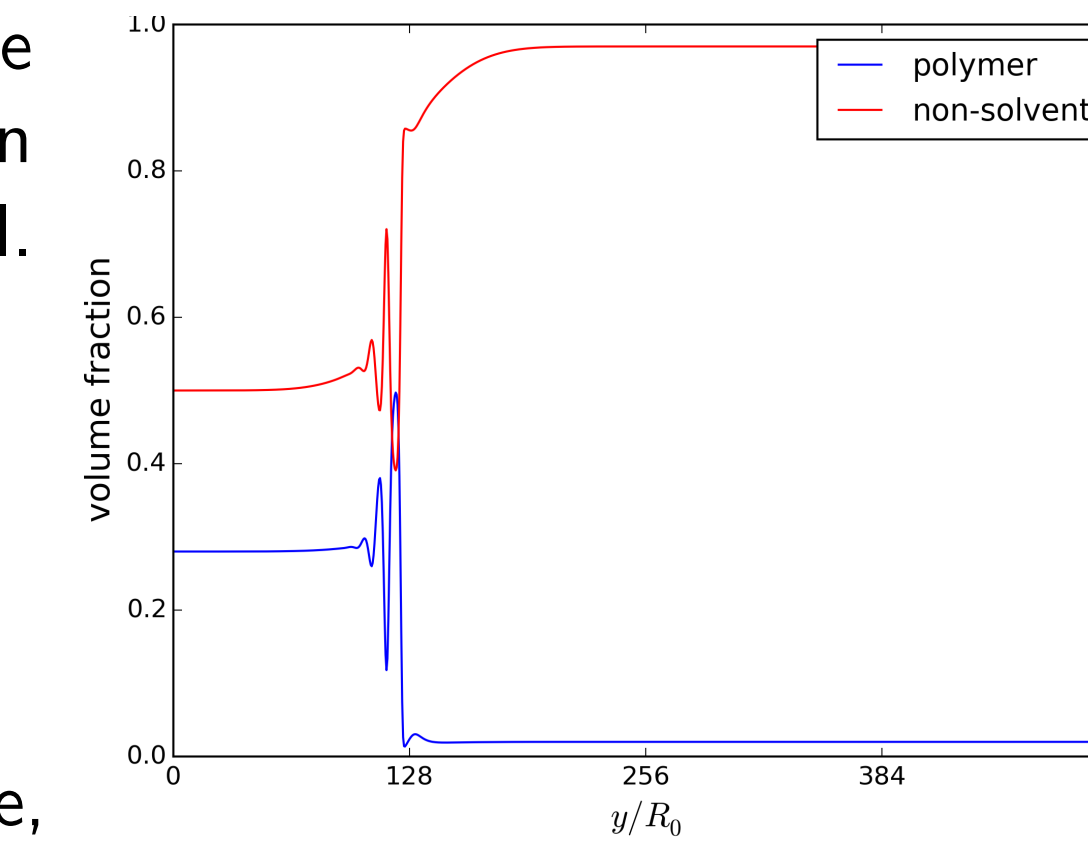
- ▶ What the qualitative regimes of behavior are and how this connects to known theory.
- ▶ What the impact of the initial polymer solution concentration is on kinetics and morphology.
- ▶ How molecular weight, solvent quality, and other parameters affect kinetics and morphology.

Results and Discussion

Theoretical background

Classic papers on phase transition dynamics give important context to our results. Pego [3] did an asymptotic analysis of a binary Cahn-Hilliard model. He predicts four time scales (by increasing size):

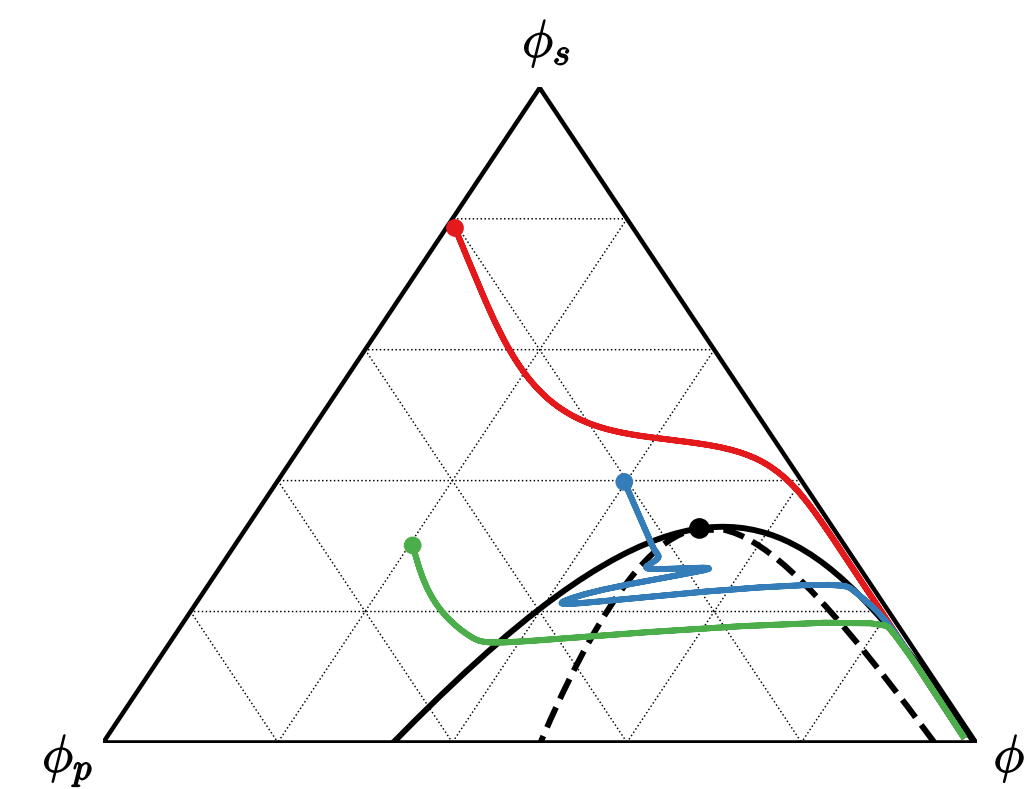
- ▶ Rapid equilibration of the interface,
- ▶ Growth of diffusive boundary layers,
- ▶ Swelling/shrinking film via phase transition, i.e. Stefan diffusion, and
- ▶ Swelling/shrinking film due to interface curvature, i.e. Ostwald ripening/coarsening.



Ball and Essery [4] (and others) showed that when symmetry is broken by a surface spinodal decomposition is *surface-directed*. As shown above, instead of proceeding isotropically, phase separation starts at the surface and propagates into the bulk.

In contrast with these theories, our model has a finite film. Consequently, the relative size of the boundary layer to the film thickness gives rise to two different regimes.

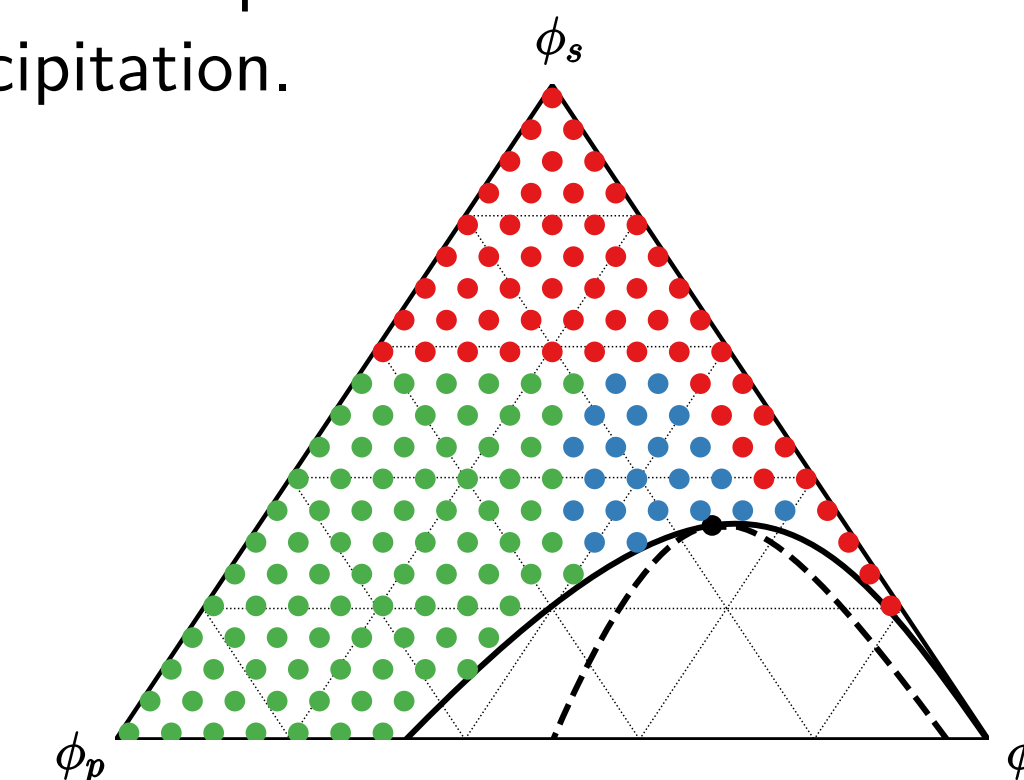
Early-time regime – Instantaneous precipitation



At early times, before the boundary layer reaches the wall, one obtains a stationary mass transfer path. We observe three types behavior:

- ▶ No phase separation (red)
- ▶ Stable phase separation (green),
- ▶ Spinodal decomposition (blue).

The latter corresponds to experimental observations of instantaneous precipitation.



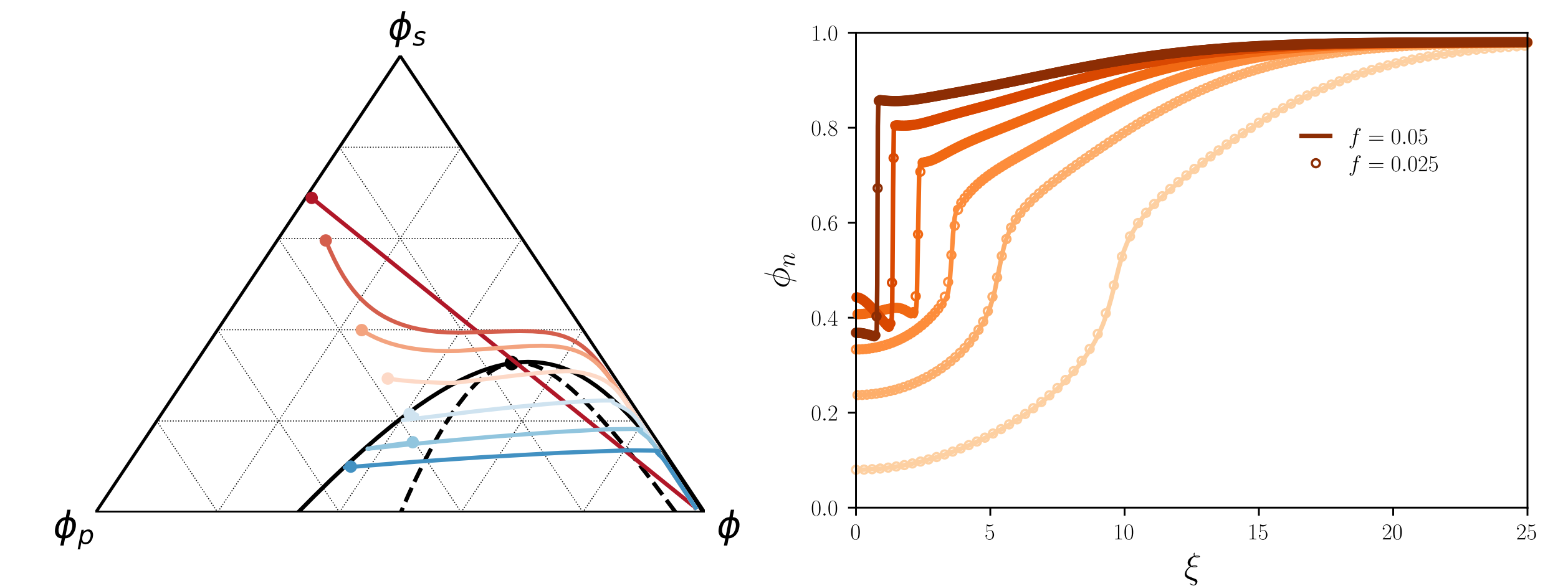
Polymer molecular weight and the solvent quality

- ▶ alter the location of the phase envelope, and
- ▶ change the mutual diffusion coefficient.

In general, increasing molecular weight and the solvent/nonsolvent Flory parameter increases the size of the phase envelope and decreases diffusivity.

Long-time regime – Delayed precipitation

At long times, the mass transfer path is no longer stationary but changes in time. Even if there is no instantaneous precipitation event, a delayed phase separation can occur depending on the initial concentrations, the location of phase envelope and the mutual diffusion coefficient.

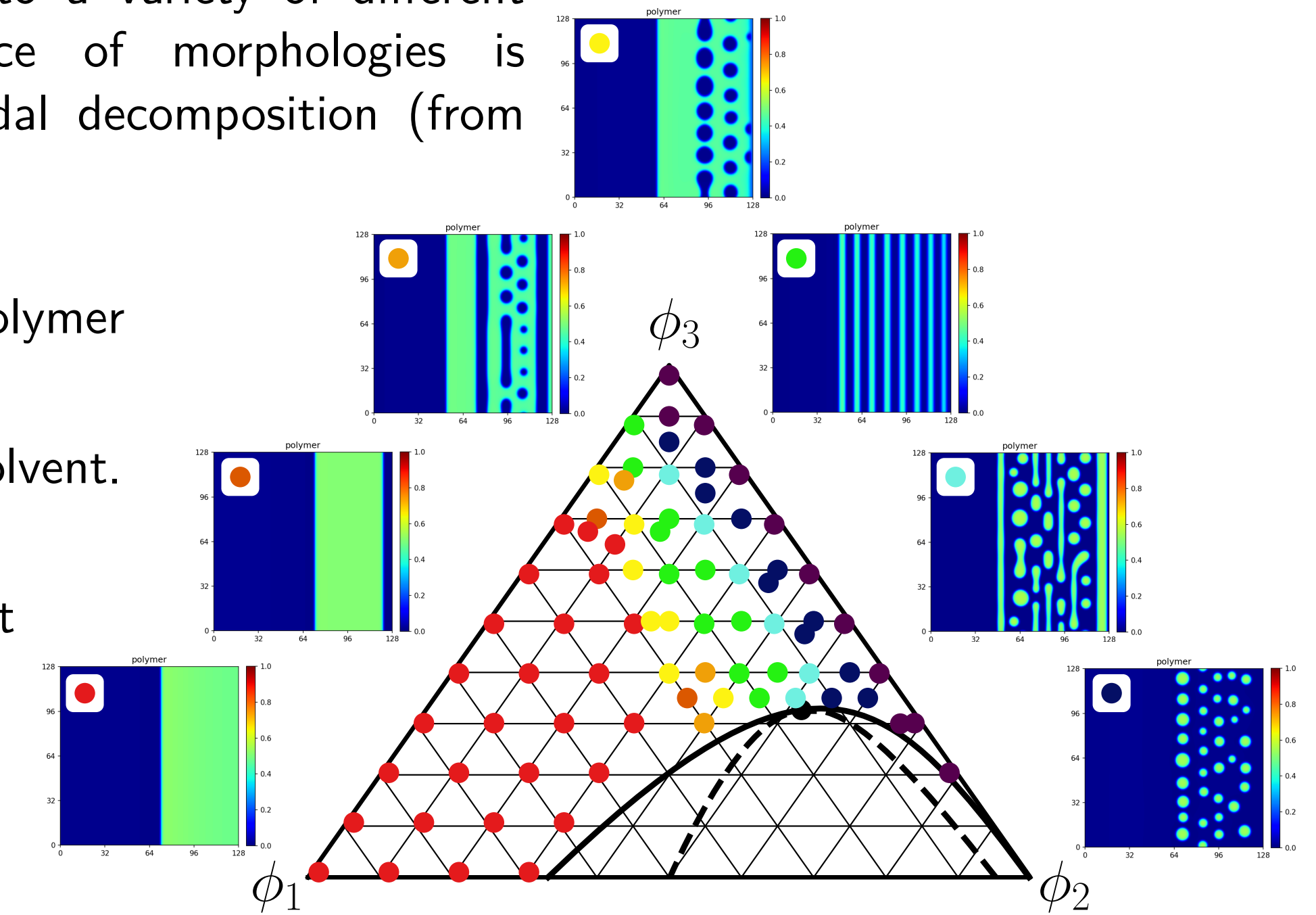


Interestingly, 1D profiles of phase separating films of different initial thicknesses collapse with a similarity variable. Theory only predicts self-similarity or collapse at short times.

Delayed precipitation leads to a variety of different morphologies. The sequence of morphologies is similar to equilibrium spinodal decomposition (from left to right):

- ▶ polymer-only
- ▶ non-solvent droplets in polymer
- ▶ bi-continuous
- ▶ polymer droplets in nonsolvent.

However, unlike the equilibrium case, a nonsolvent gradient is present during precipitation, which results in microstructures with *mixed morphologies*.



Model and Methods

Simulations of the mesoscale physics in NIPS are not trivial. We recently developed a multi-fluid phase field model and accompanying simulation software that allow for efficient, large-scale simulations of NIPS membranes [1,2]. The principle object in the model is a Rayleighian, which consists of a free energy functional, a dissipation functional and constraints.

$$R[\{v_i\}] = \underbrace{\dot{F}[\{v_i\}]}_{\text{free energy}} + \underbrace{\Phi[\{v_i\}]}_{\text{dissipation}} - \underbrace{\lambda G[\{v_i\}]}_{\text{constraints}}$$

Taking variational derivative gives equations of motion, which for the present system consist of a diffusion equation for independent species, a momentum equation and an incompressibility constraint:

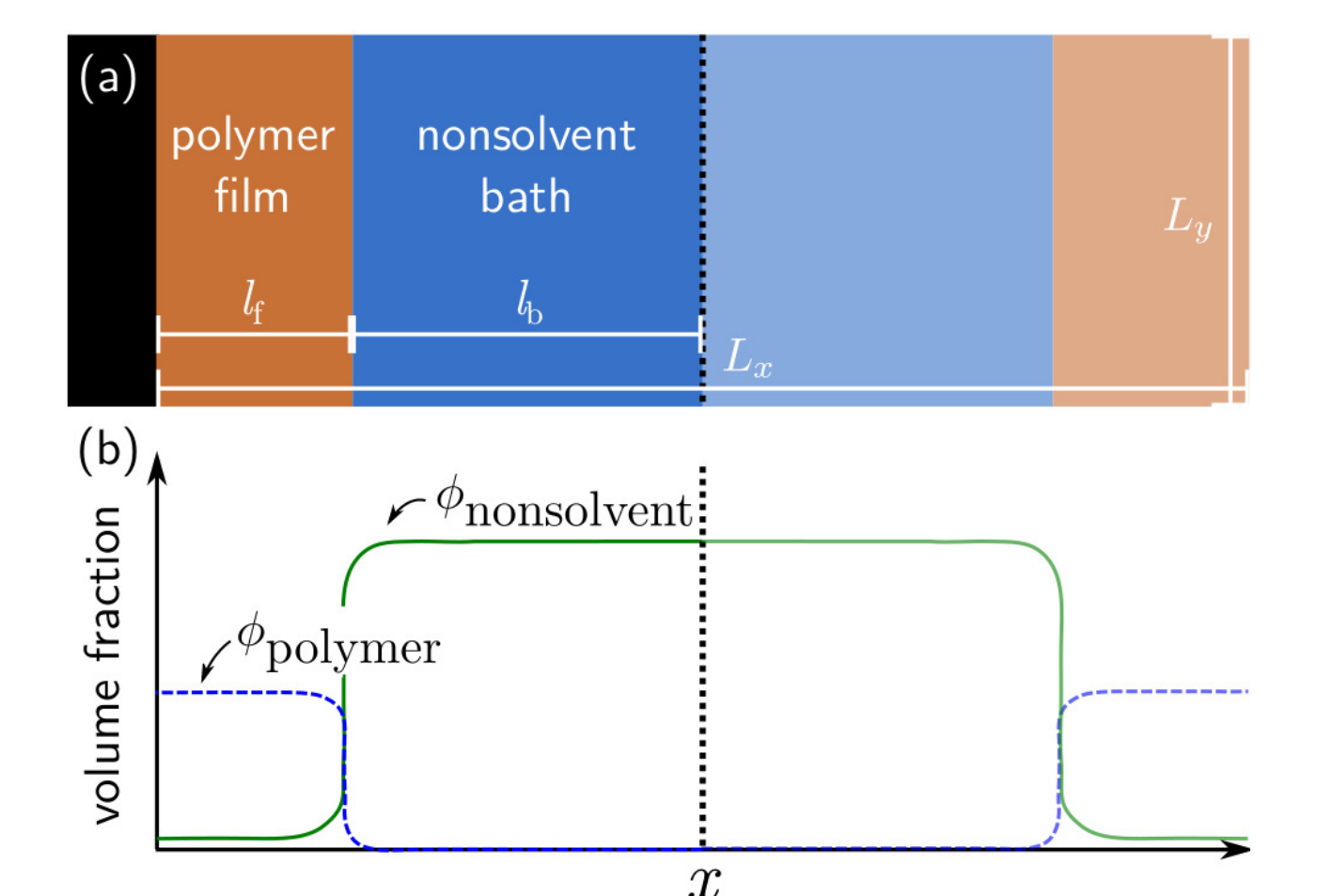
$$\frac{\partial \phi_i}{\partial t} + \mathbf{v} \cdot \nabla \phi_i = \nabla \cdot \left[\sum_j^{p,n} M_{ij} \nabla \mu_j \right]$$

$$0 = -\nabla p + \nabla \cdot [\eta(\nabla \mathbf{v} + \nabla \mathbf{v}^T)] - \nabla \cdot \mathbf{\Pi}$$

$$\nabla \cdot \mathbf{v} = 0$$

We perform two different simulations with this model:

- ▶ **1D large bath simulations.** Using periodic BCs and a pseudo-spectral algorithm, we are able to study a nearly infinite bath at long times.
- ▶ **2D/3D simulations with time dependent BCs.** Using a hybrid pseudo-spectral/finite difference method, we can leverage our 1D data to examine the microstructure.



- [1] D. R. Tree, K. T. Delaney, H. D. Cenicerros, T. Iwama, G. H. Fredrickson. *Soft Matter* 13, 3013–3030 (2017).
- [2] D. R. Tree, T. Iwama, K. T. Delaney, J. Lee, G. H. Fredrickson. *ACS Macro. Lett.* 7, 582–586 (2018)
- [3] Pego. *Proc. Royal Soc. A.* 422, 261–278 (1989).
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