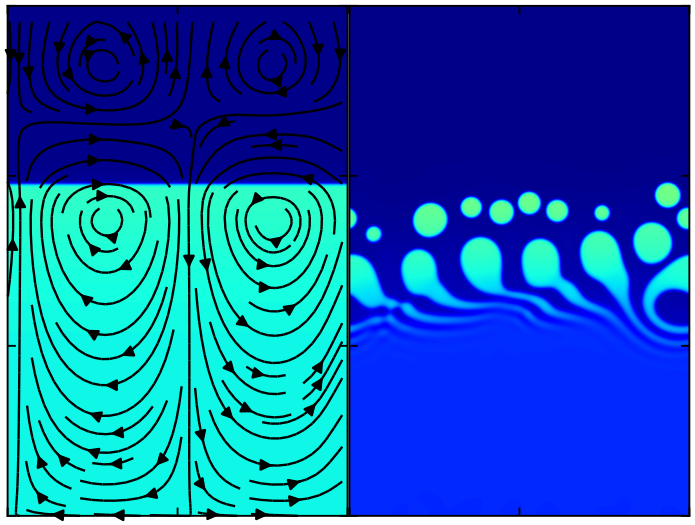
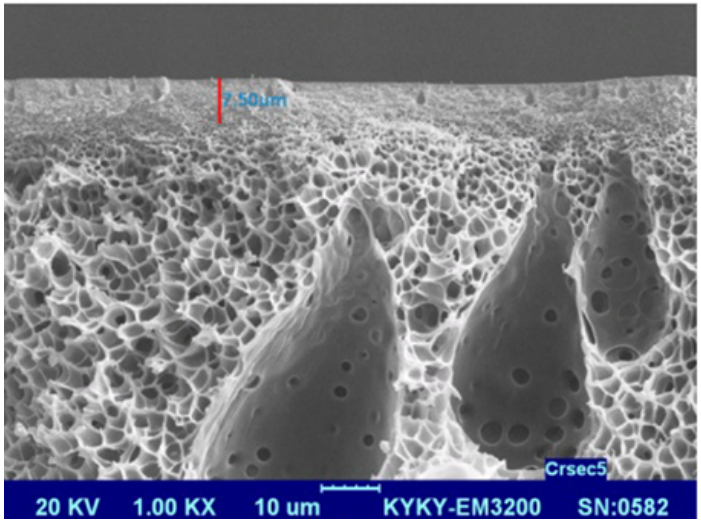
Marangoni instability during NIPS of a ternary polymer solution





Douglas R. Tree[1] and Glenn Fredrickson[2]

[1]Brigham Young University

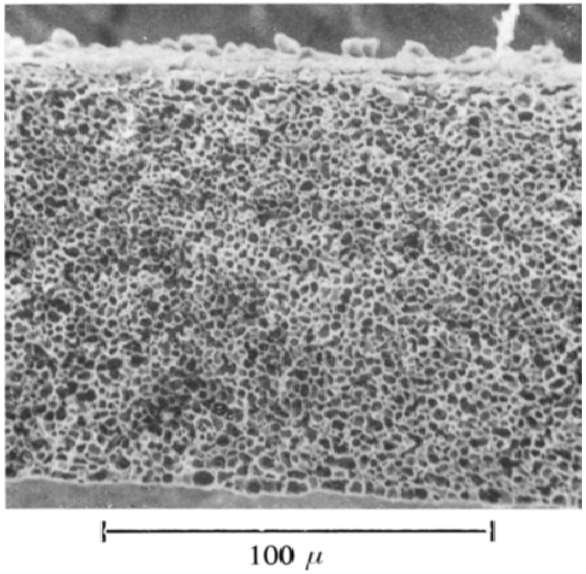
[2]University of California, Santa Barbara

APS March Meeting

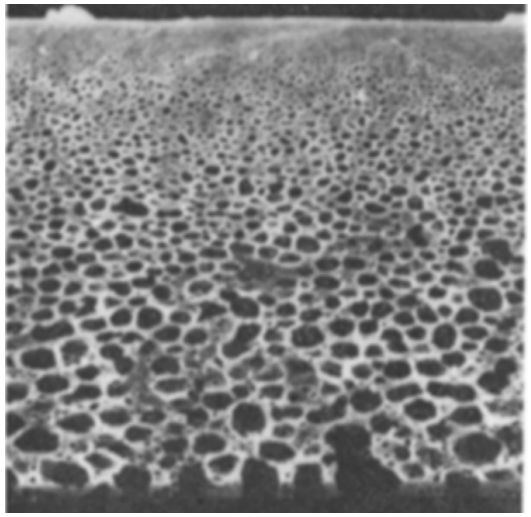
March 6, 2018

Microstructural variety in membranes

Uniform "Sponge"

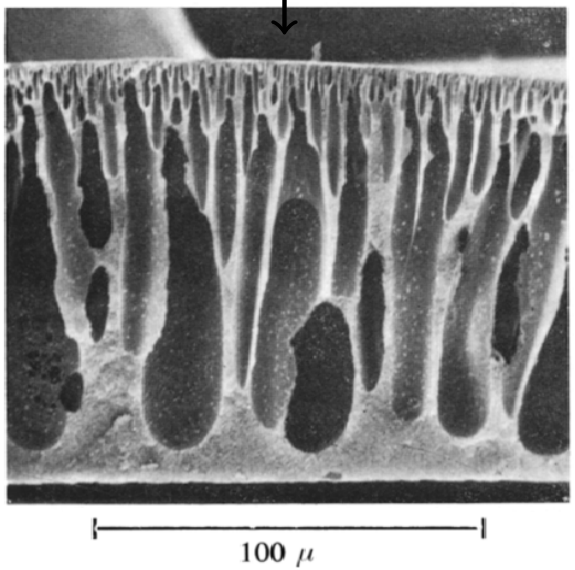


Asymmetric "Sponge"



Skin Layer

Fingers or
Macro-voids



Strathmann et al.
Desalination. (1975)

Polymer membrane synthesis by immersion precipitation

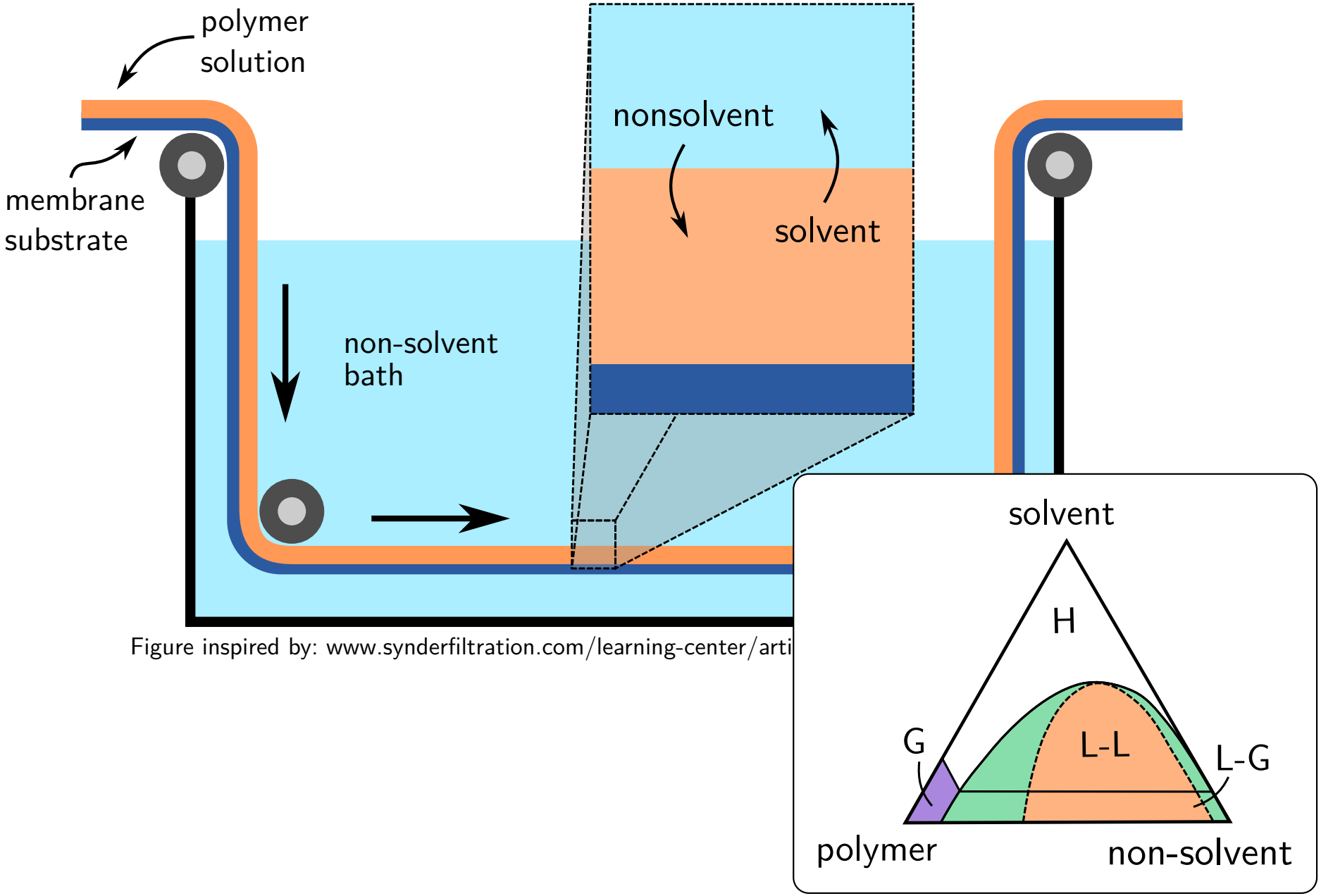


Figure inspired by: www.synderfiltration.com/learning-center/arti

A ternary solution model

$\dot{F}[\{\boldsymbol{v}_i\}]$ free energy

$\Phi[\{\boldsymbol{v}_i\}]$ dissipation

$\lambda G[\{\boldsymbol{v}_i\}]$ constraints

↓

Transport Equations

- Diffusion & Momentum
- Coupled, Non-lin. PDEs

↓

Solve numerically

- Pseudo-spectral on GPUs
- Semi-implicit stabilization

Ternary polymer solution (Flory–Huggins–de Gennes)

$$F = \int d\boldsymbol{r} \left[f(\{\phi_i\}) + \frac{1}{2} \sum_i \kappa_i \left|\nabla \phi_i\right|^2 \right]$$

Newtonian fluid with ϕ-dependent viscosity

$$\Phi = \frac{1}{2} \int d\boldsymbol{r} \left[\sum_i \zeta_i (\boldsymbol{v}_i - \overline{\boldsymbol{v}})^2 + 2\eta(\{\phi_i\}) \boldsymbol{D} : \boldsymbol{D} \right]$$

Incompressibility

$$\lambda G = p \nabla \cdot \overline{\boldsymbol{v}}$$

Tree et al. Soft Matter 13, 3013–3030 (2017)

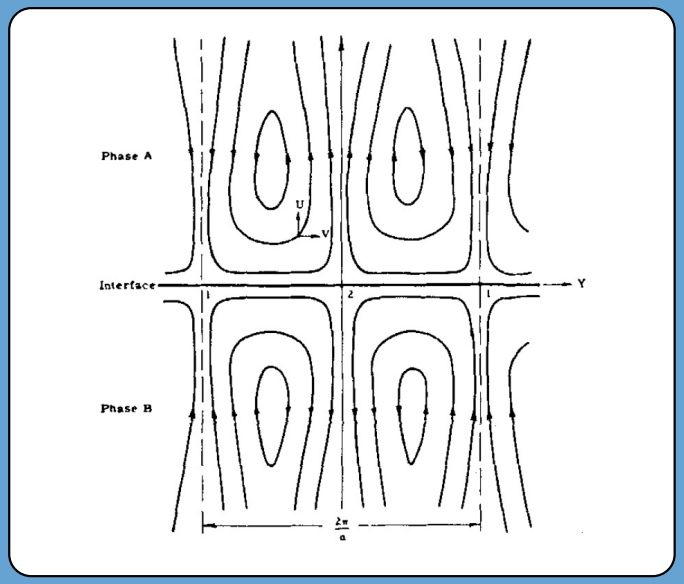
Are macrovoids formed by a hydrodynamic instability?

In the literature . . .

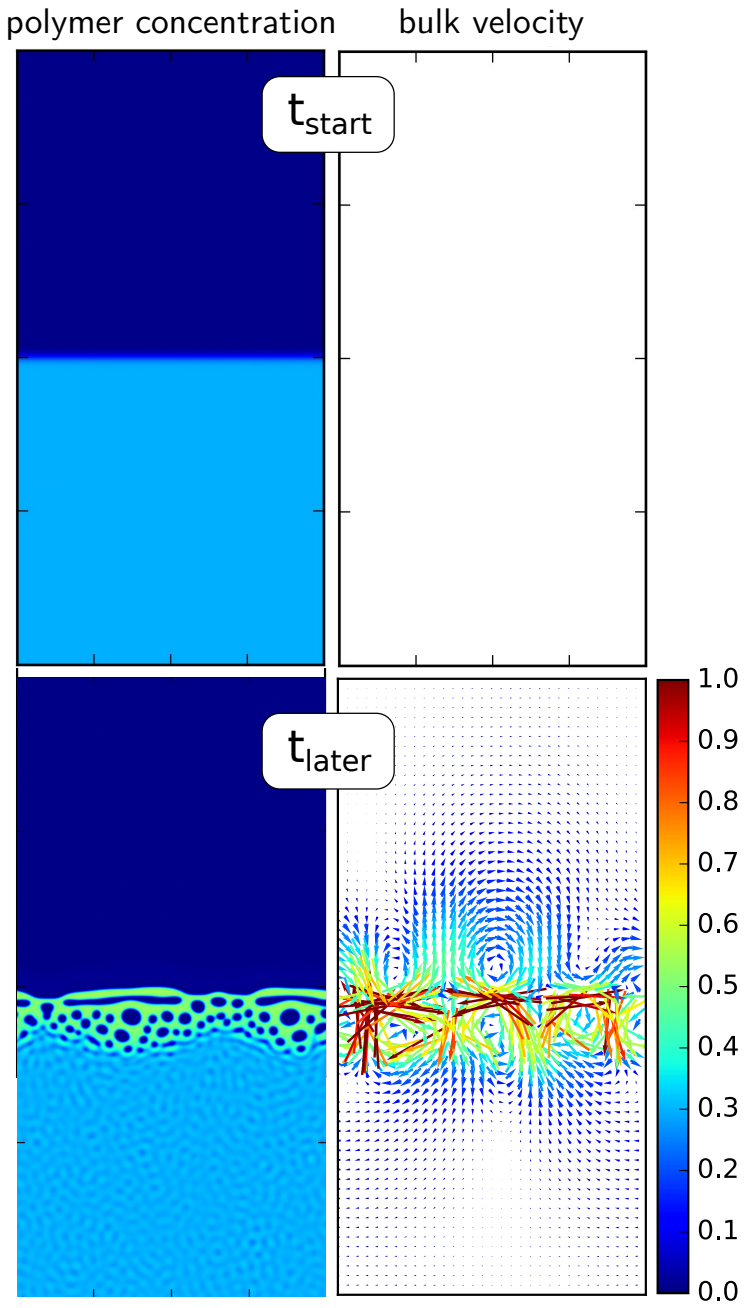
Because the onset of the formation of macrovoids often occurs at the interfacial boundary between the immersed solution film and the coagulation bath, many authors propose that interfacial phenomena cause the initiation of the voids

- Matz [10], Frommer and Messalam [7] and Stevens et al [18] propose that surface tension gradients are the driving forces which account for the initiation of convection cells at the in-

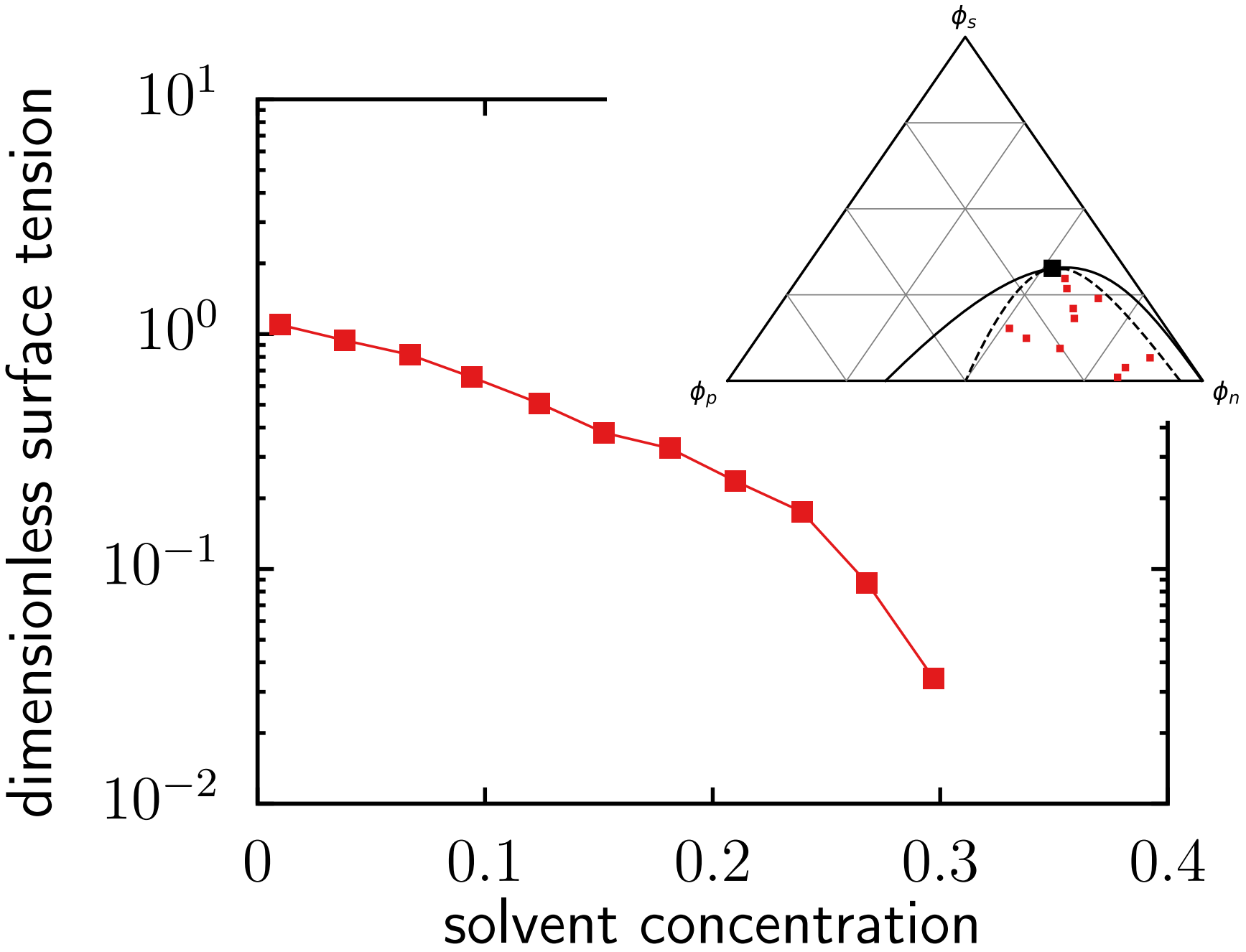
Smolders et al. J. Membr. Sci. (1992).



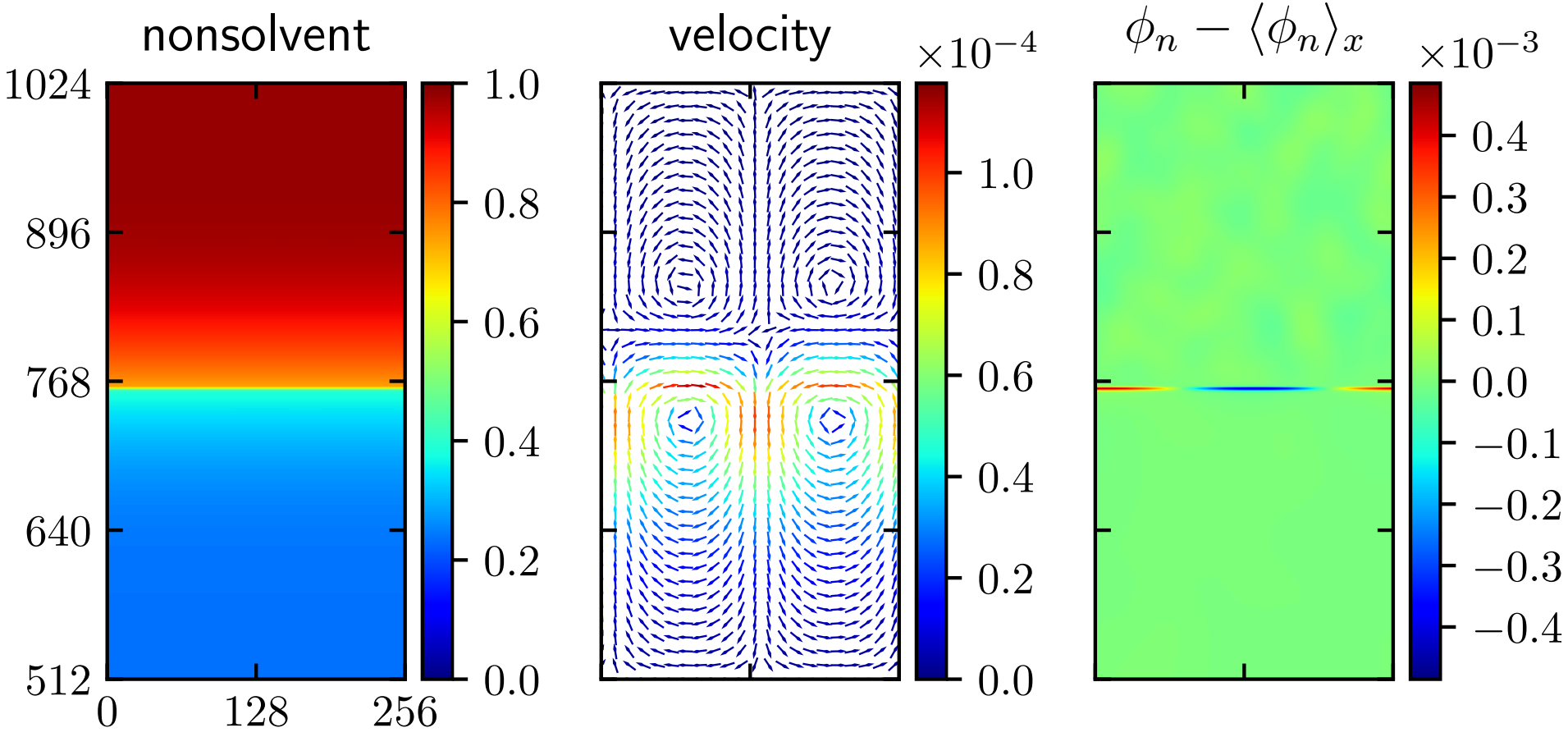
Sternling and Scriven. AICHE J. (1959).



Is there a surfactant?



A classic Marangoni instability?



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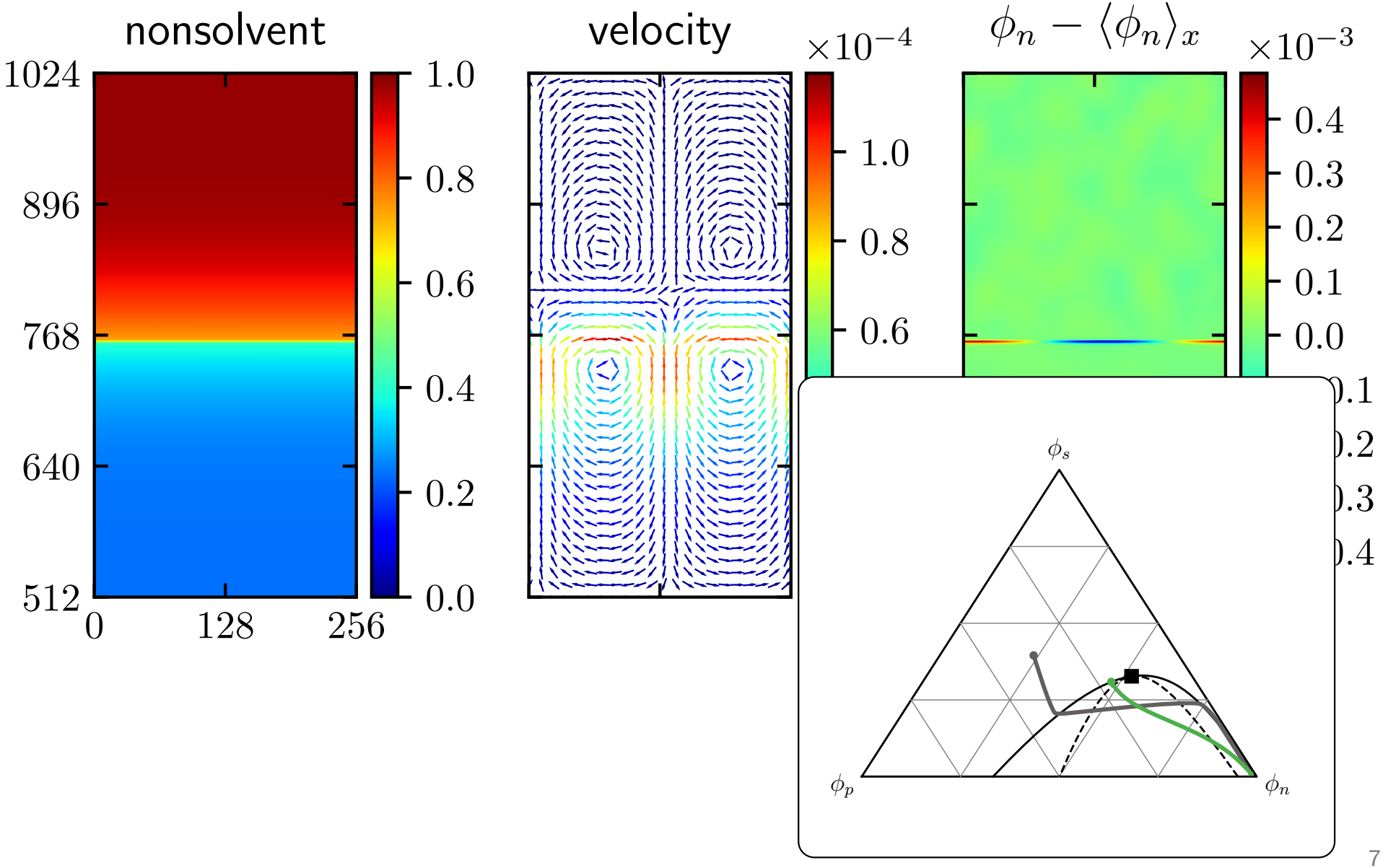
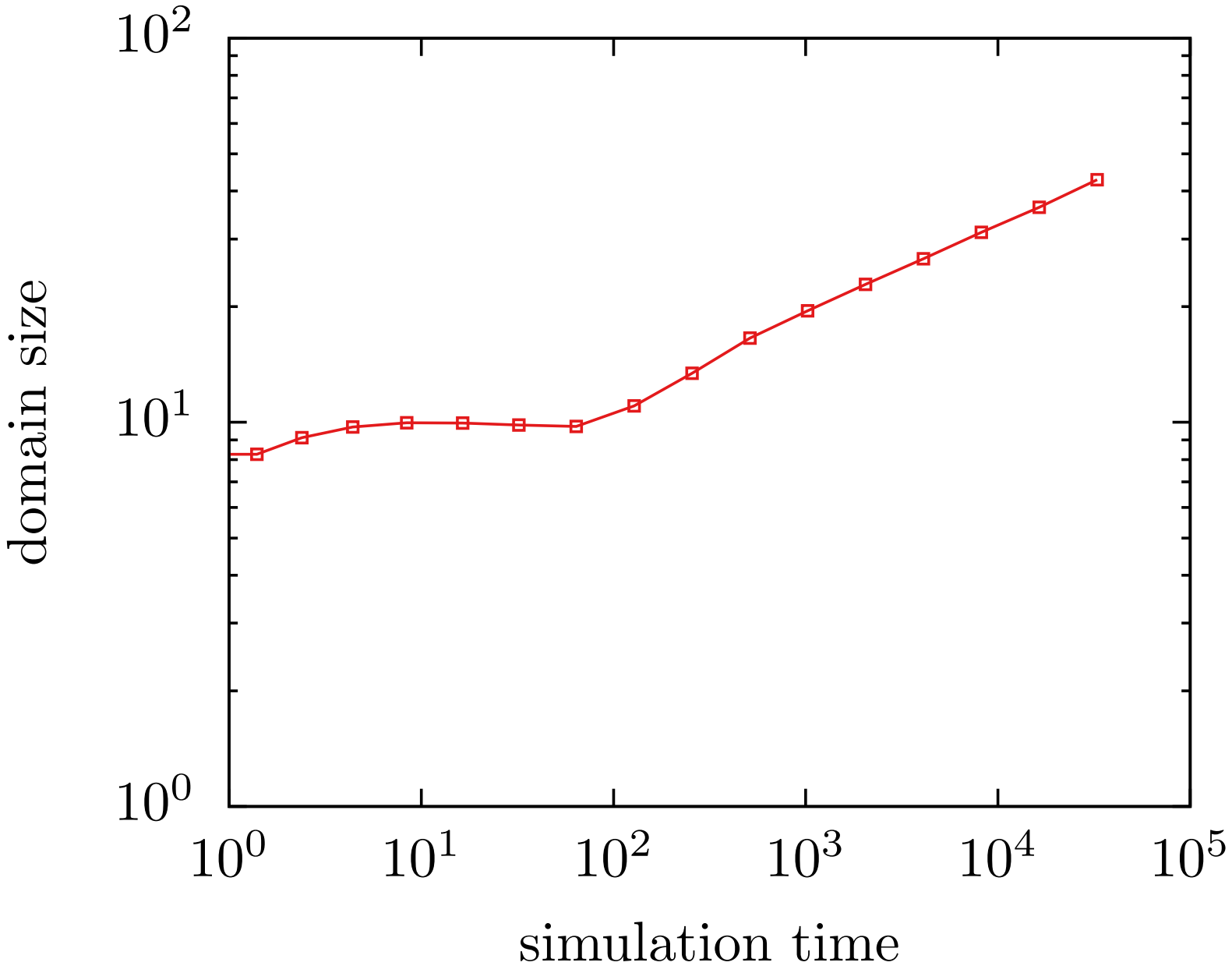
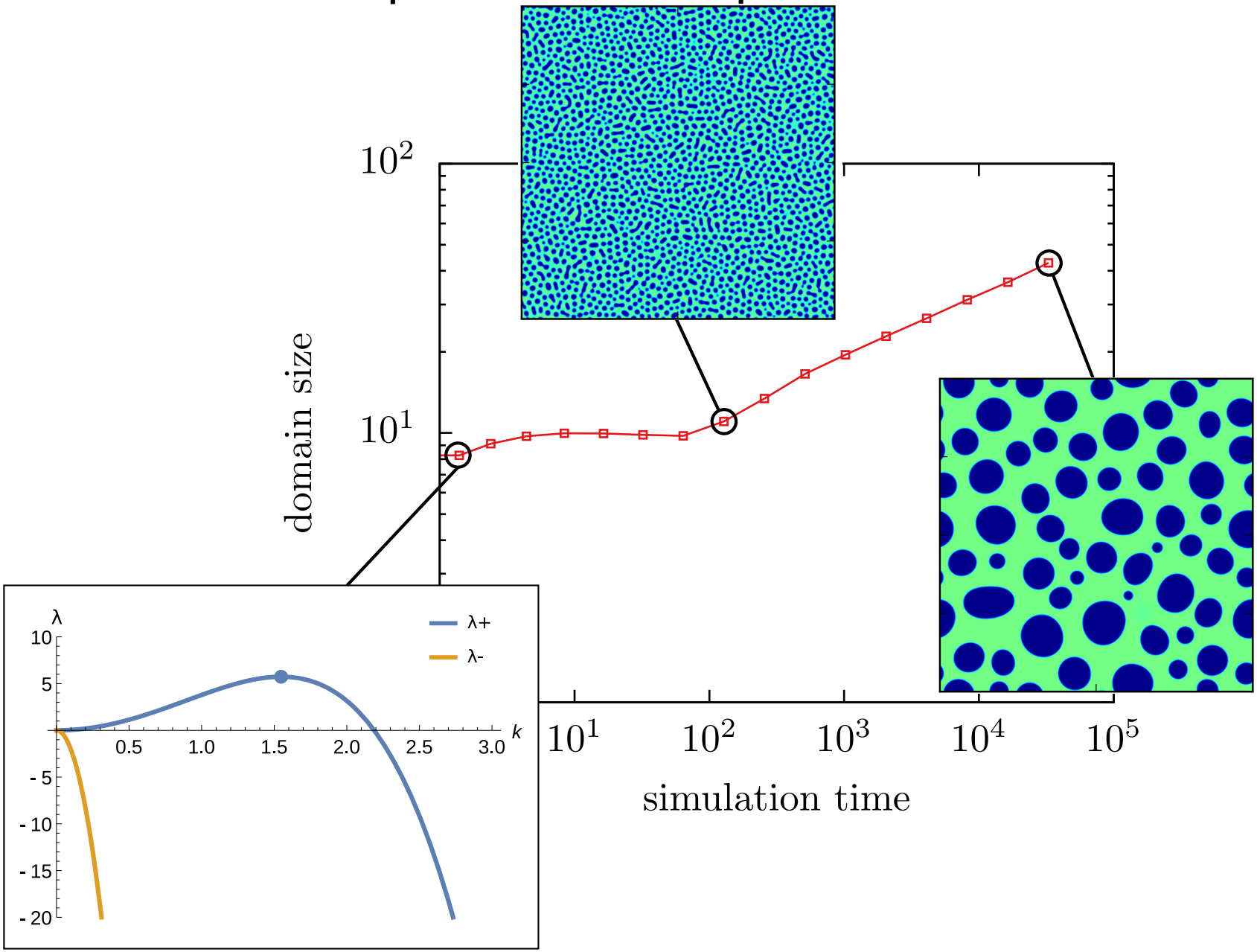


A reminder about spinodal decomposition kinetics

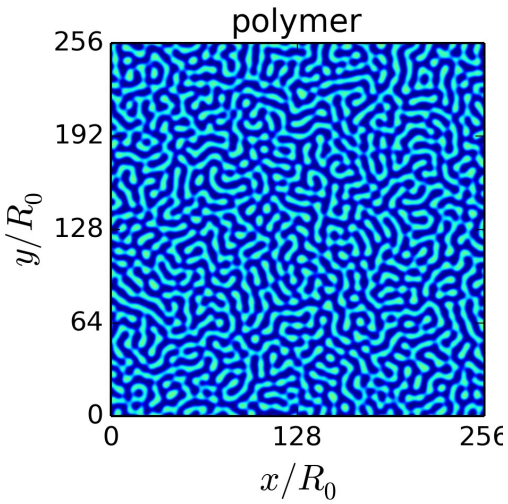


A reminder about spinodal decomposition kinetics

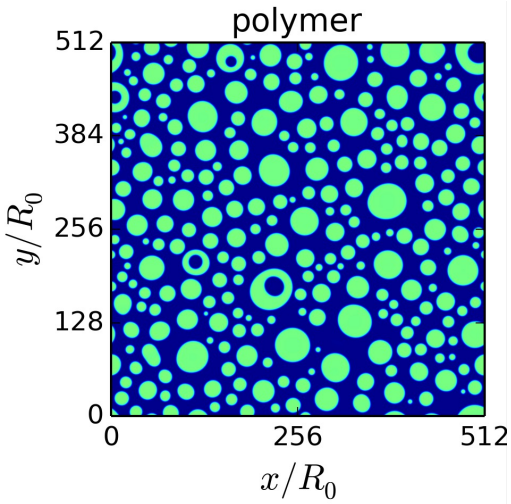


The role of Marangoni flow in bulk coarsening

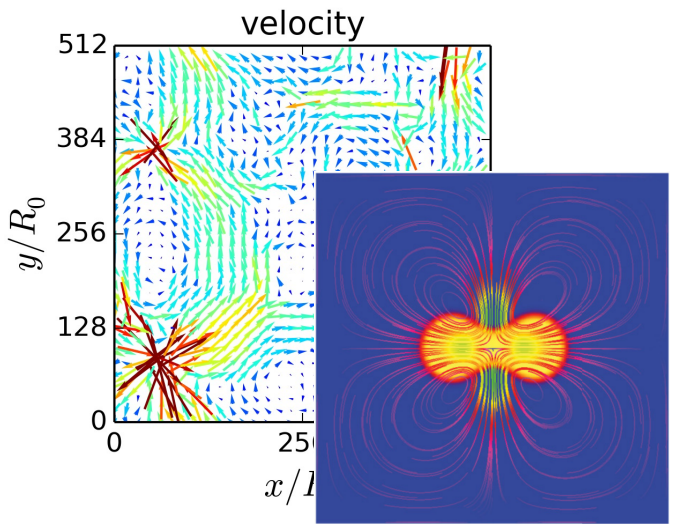
surface diffusion



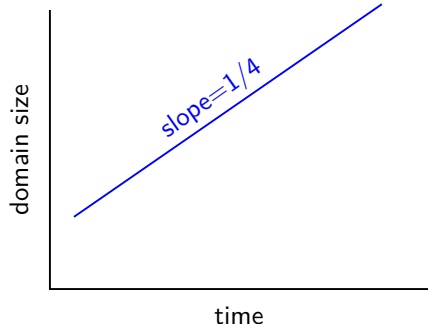
bulk diffusion

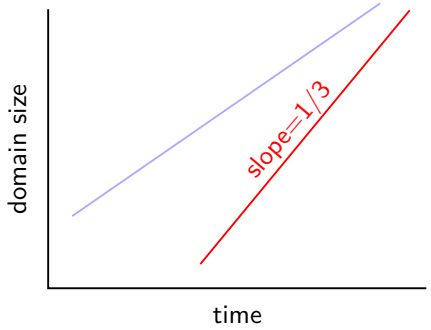


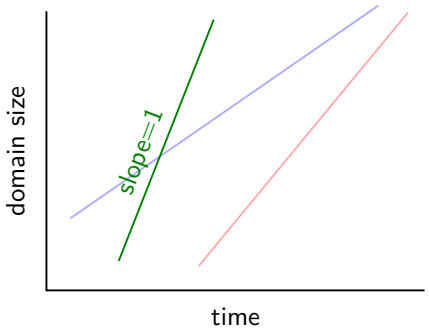
hydrodynamics



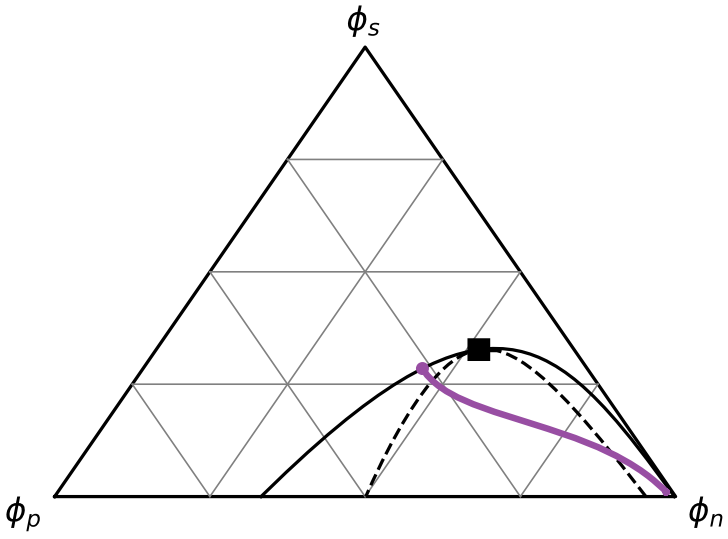
Wang et al. PRE (2012)

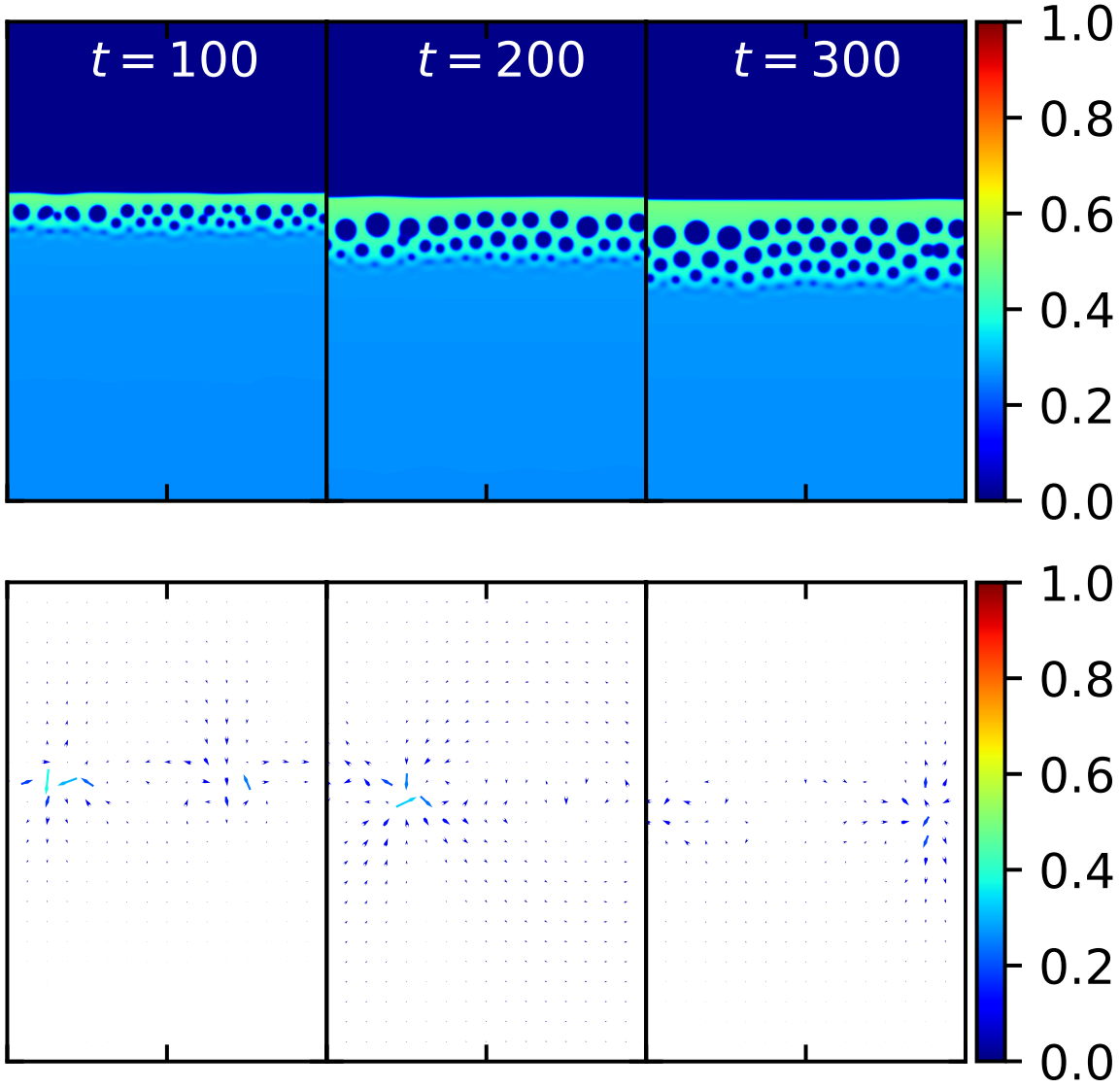






Composition has a dramatic impact on interface stability





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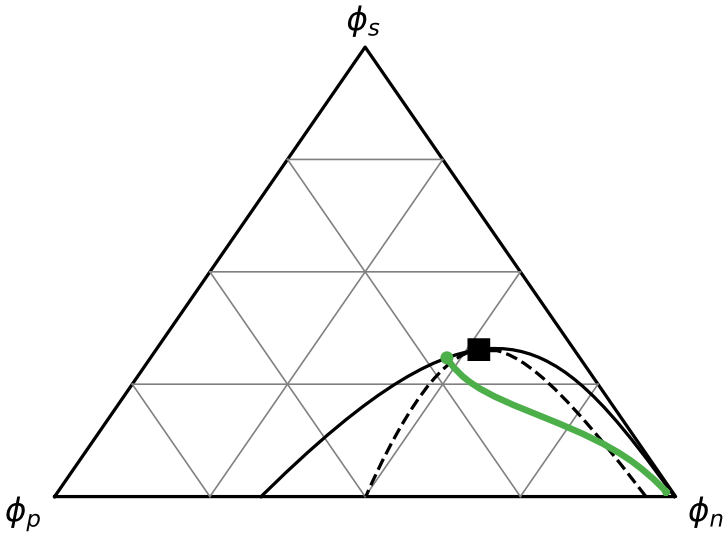

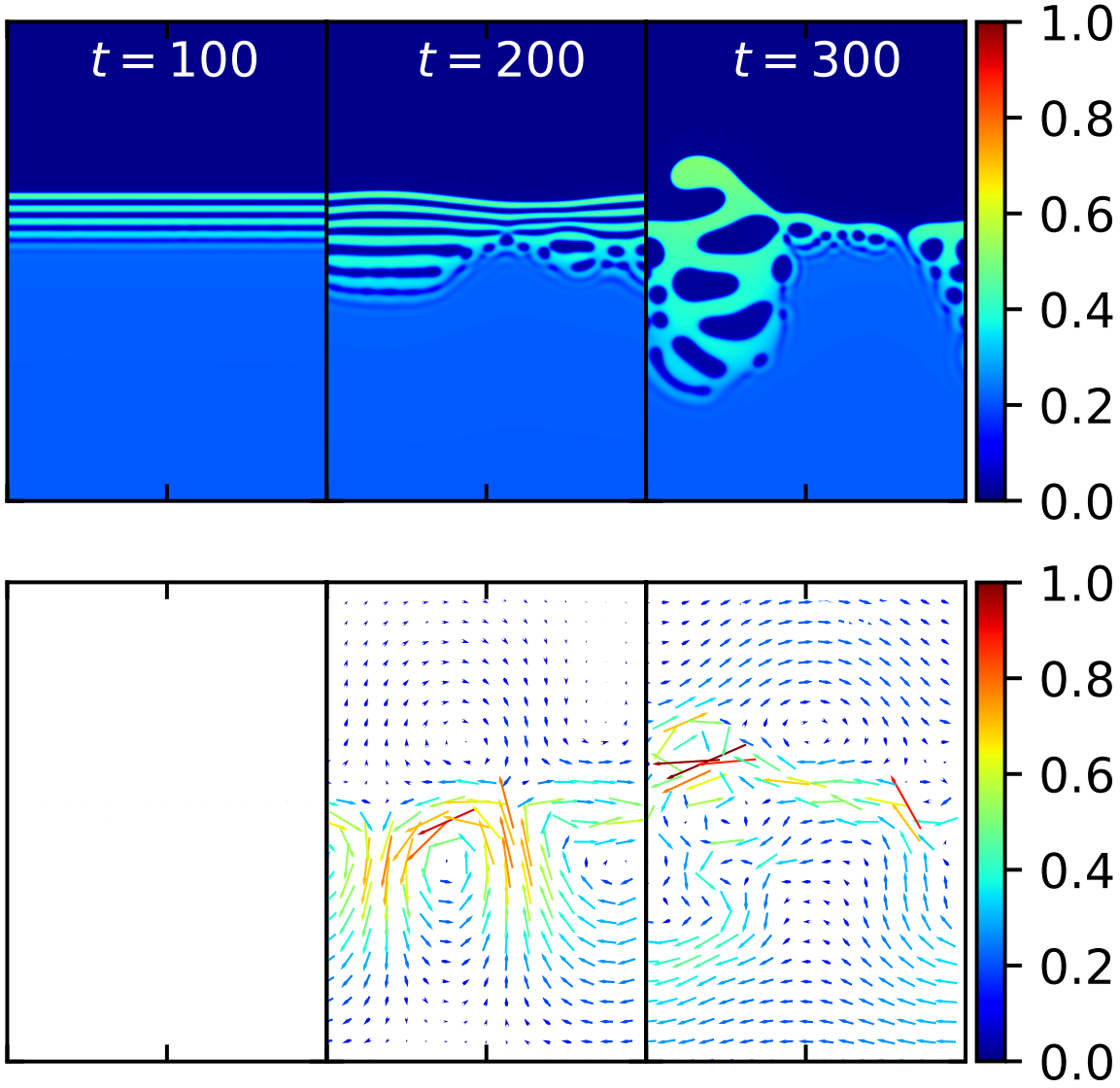

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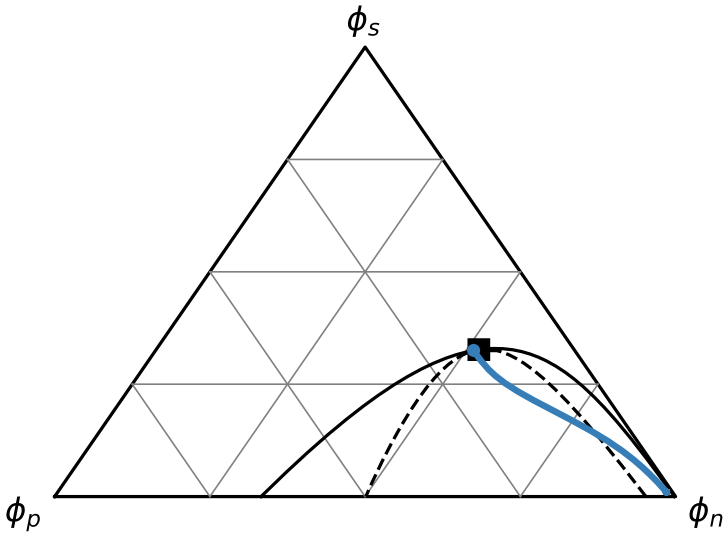
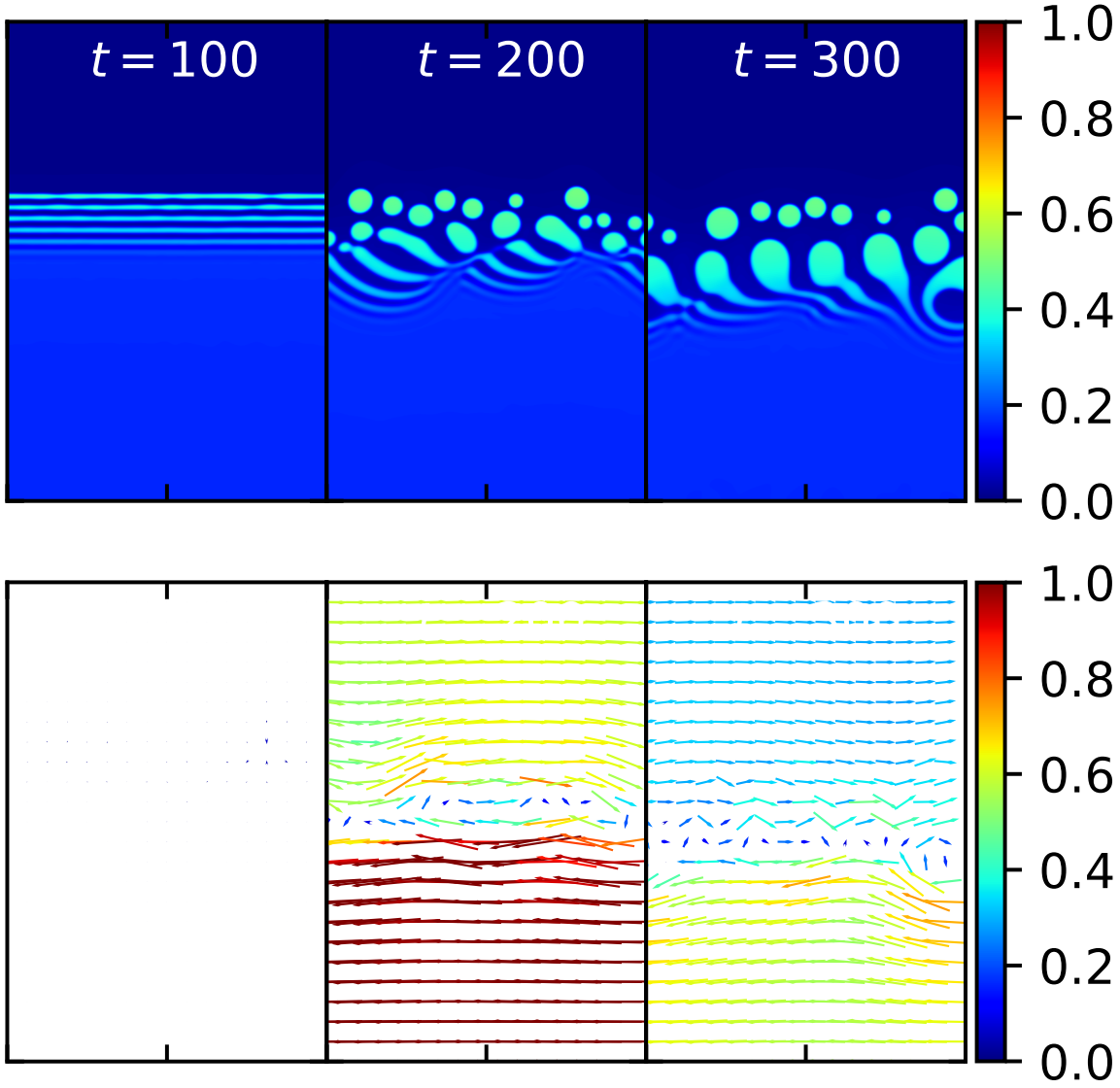
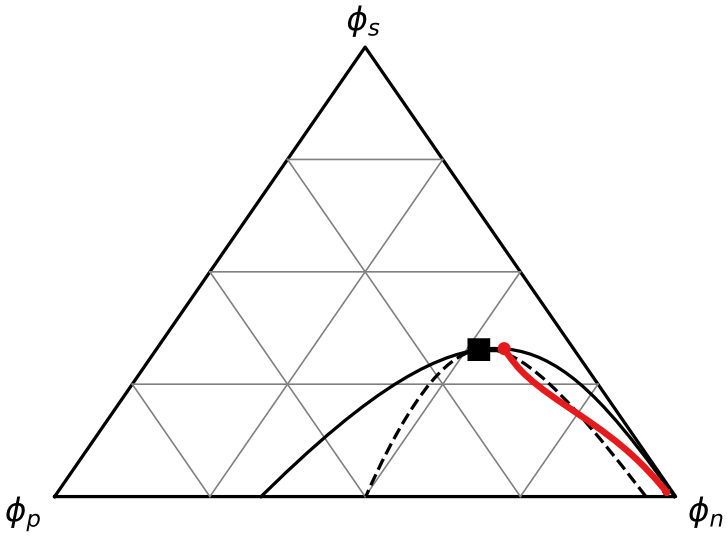
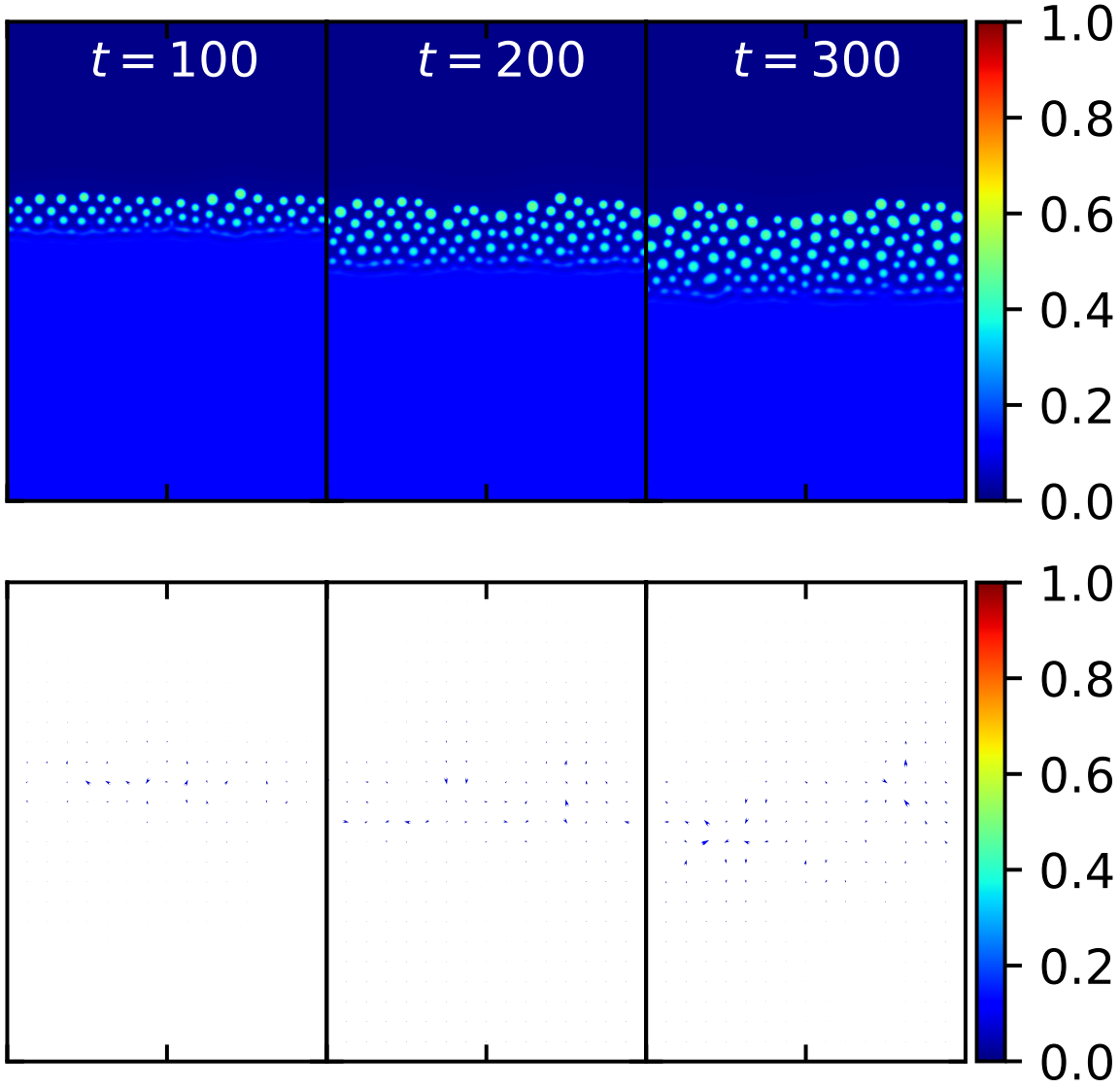




Composition has a dramatic impact on interface stability





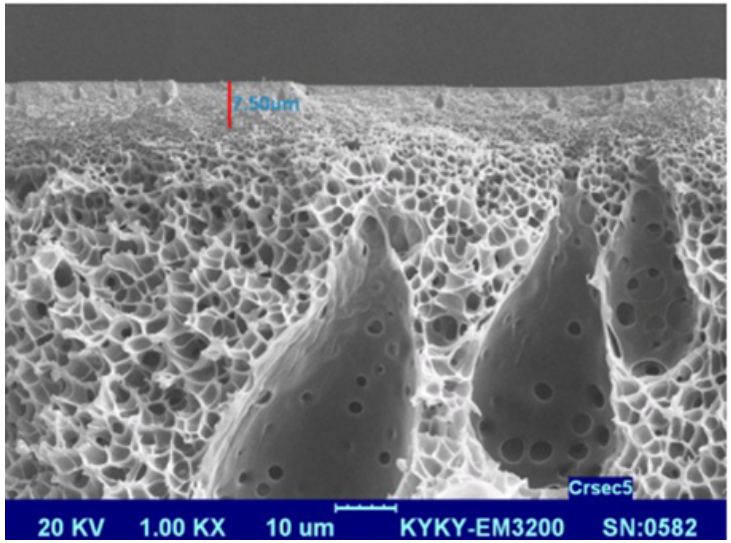
Conclusions

Does Marangoni flow cause macrovoid formation?

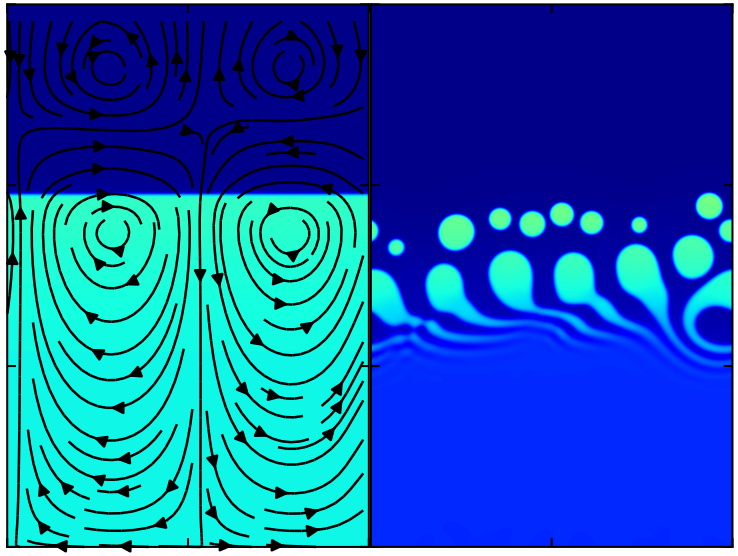
- We don't know yet.
- A weak classic Marangoni instability may exist, but does not distrub the interface.
- Coarsening near the critical composition significantly disturbs the interface.

Related work

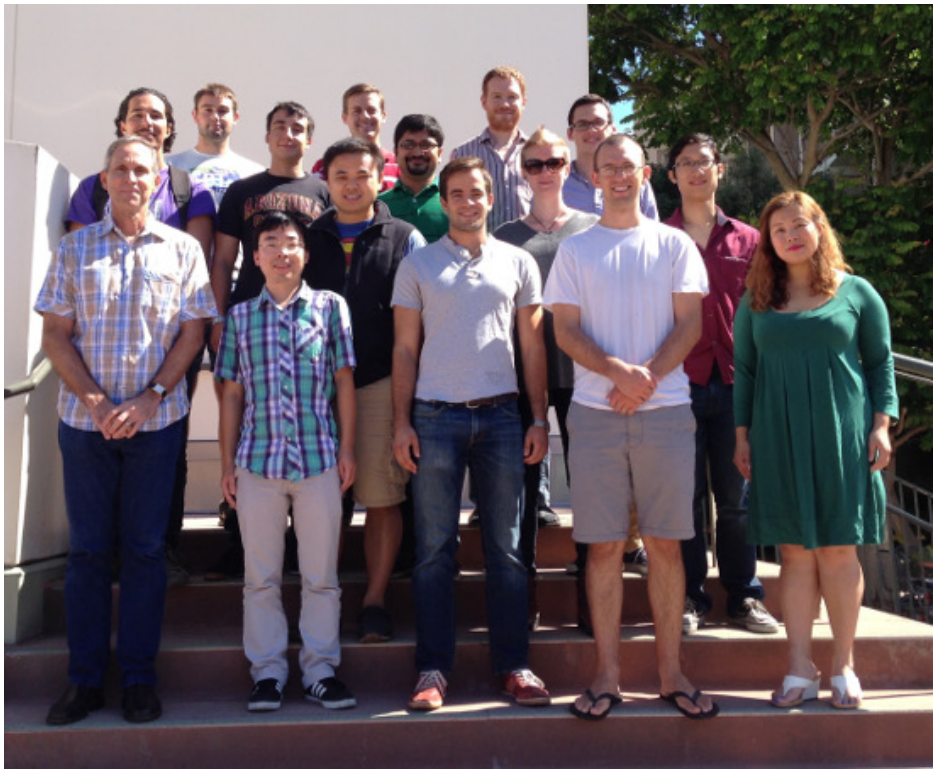
- *Jan Garcia* – Coarsening Kinetics of Ternary Polymer Solutions with Mobility and Viscosity Contrast
- E53 – Fluid Mechanics for Soft Matter I: Flows
- Today, 10:24 – 10:36 AM, LACC 513



Saedi et al. Can. J. Chem. Eng. (2014)



Acknowledgements



- Jan Garcia
- Dr. Kris T. Delaney
- Prof. Hector D. Ceniceros
- Lucas Francisco dos Santos
- Dr. Tatsuhiro Iwama (Asahi Kasei)
- Dr. Jeffrey Weinhold (Dow)

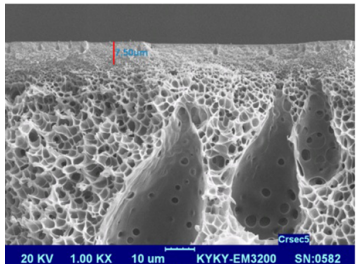
Can we predict the microstructure of polymer materials?

- Microstructure dictates properties
- Microstructure depends on process history

A very general problem!

Polymer membranes

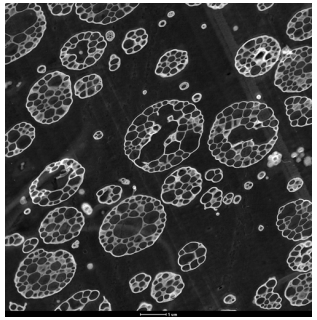
- clean water
- medical filters



Saedi et al. Can. J. Chem. Eng. (2014)

Polymer Blends

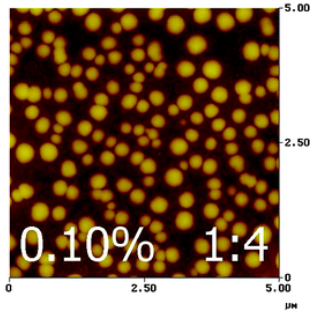
- commodity plastics (e.g. HIPS)
- block polymer thin films



www.leica-microsystems.com

Polymer composites

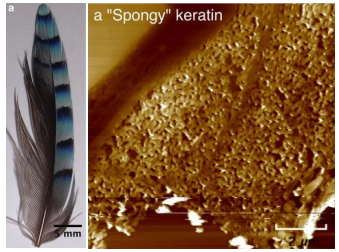
- bulk hetero-junctions
- nano-composites



Hoppe and Sariciftci J. Mater. Chem. (2006)

Biological patterning

- Eurasian jay feathers



Parnell et al. Sci. Rep. (2015)

How can we model microstructure formation?

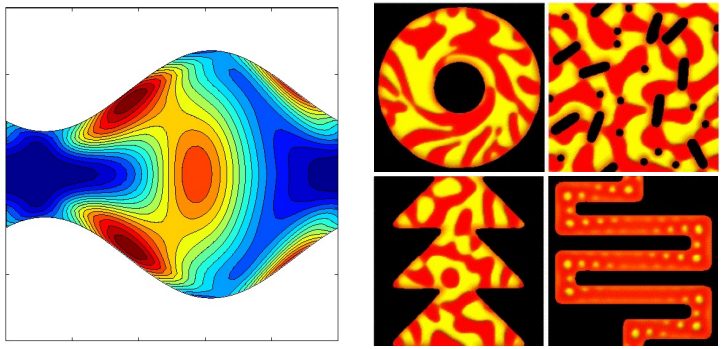
Challenges

- Spatially inhomogeneous
- Multiple transport modes
- Separation of scales

~~Continuum Fluids + SCFT~~

(Too expensive)

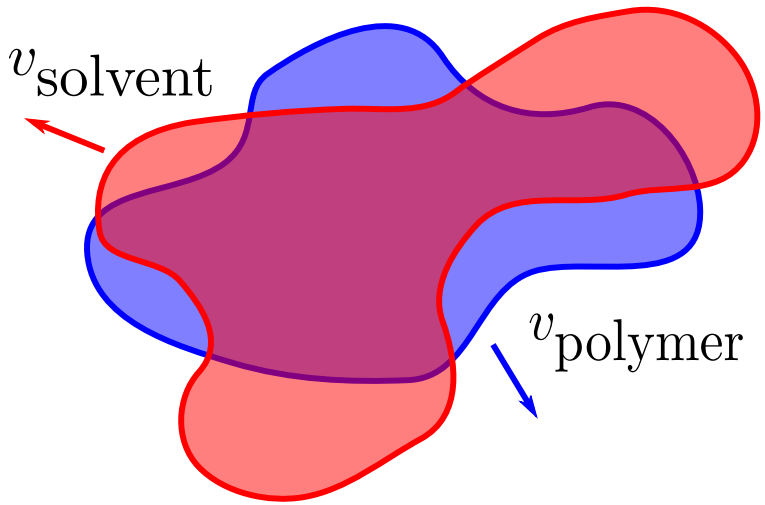
Continuum Fluids + Phase Field



Teran et al. Phys. Fluid. (2008)
Fredrickson. J. Chem. Phys. (2002)
Hall et al. Phys. Rev. Lett. (2006)

Two-fluid model

- Momentum equation for each species
- Large drag enforces cons. of momentum



$$\text{drag} = \sum_i \zeta_i (\boldsymbol{v}_i - \overline{\boldsymbol{v}})$$

de Gennes. J. Chem. Phys. (1980)
Doi and Onuki. J Phys (Paris). 1992

Transport equations

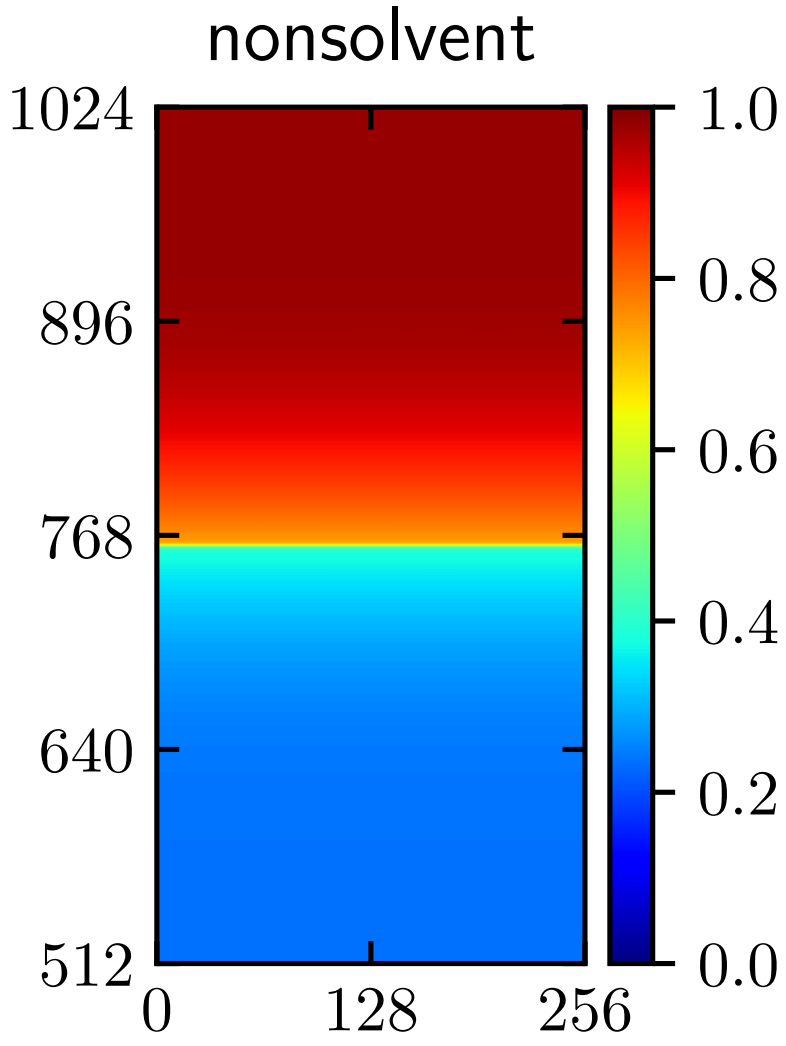
$$\frac{\partial \phi_i}{\partial t} + \boldsymbol{v} \cdot \nabla \phi_i = \nabla \cdot \left(\sum_j M_{ij}(\{\phi\}) \nabla \mu_j \right)$$ Convection-Diffusion

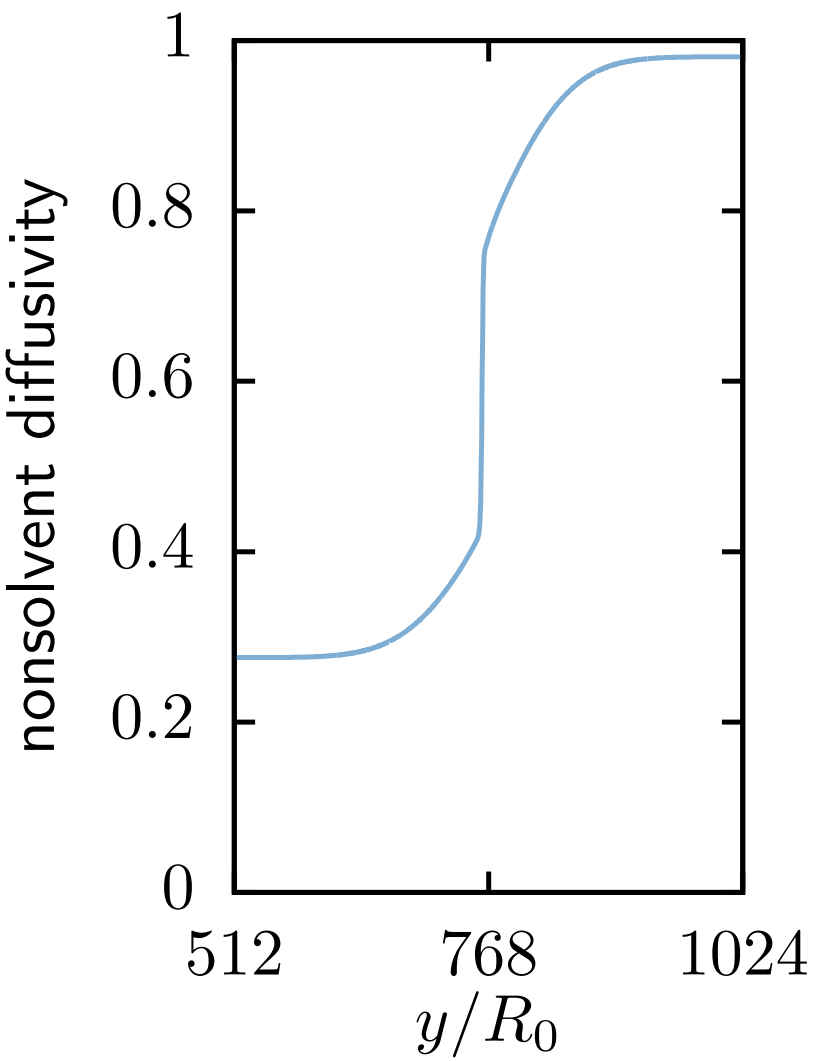
$$\mu_i = \frac{\delta F[\{\phi_i\}]}{\delta \phi_i}$$ Chemical Potential

$$0 = -\nabla p + \nabla \cdot \left[\eta(\{\phi\})(\nabla \boldsymbol{v} + \nabla \boldsymbol{v}^T) \right] - \sum_{i=0}^{N-1} \phi_i \nabla \mu_i$$ Momentum

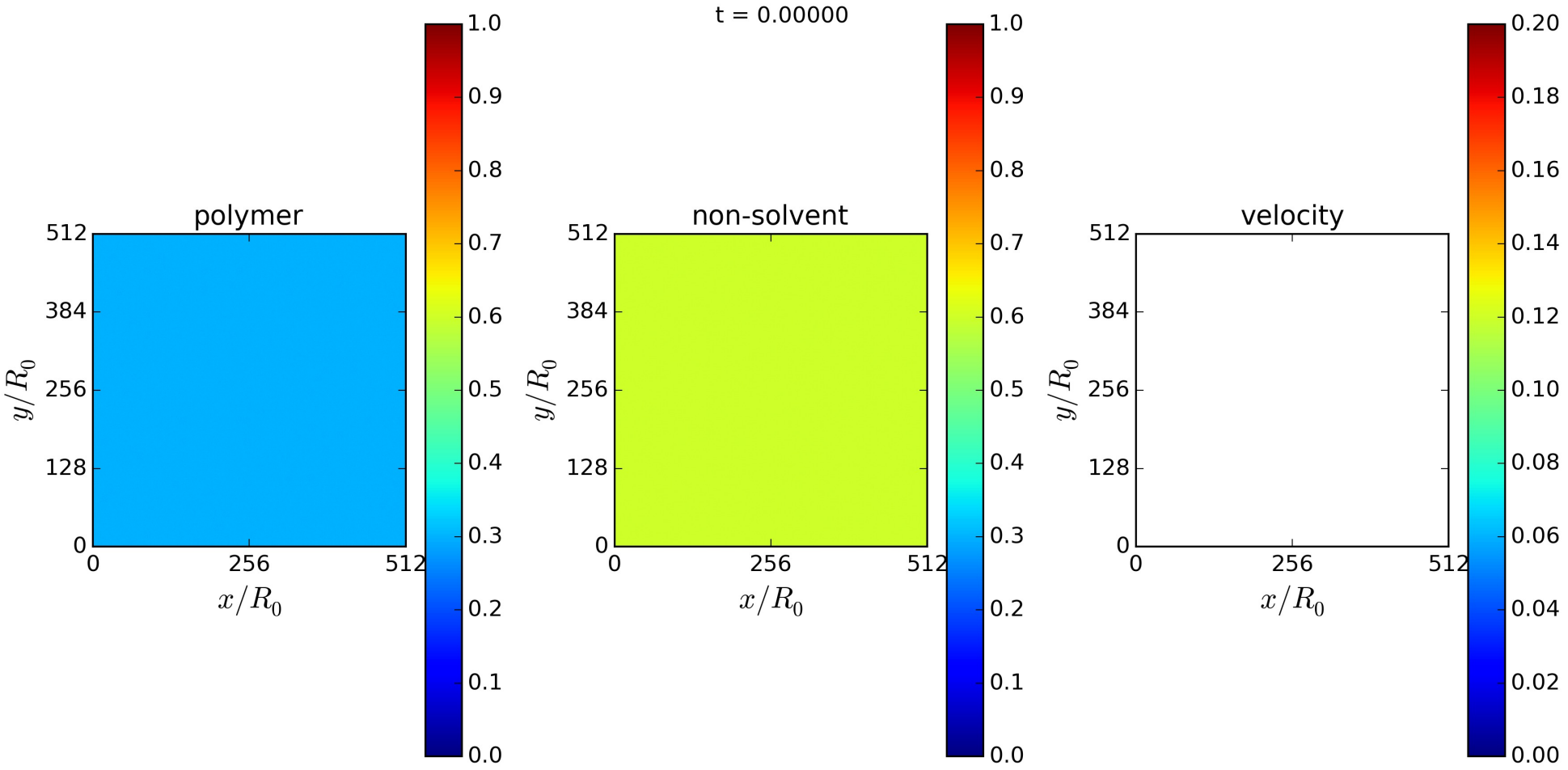
$$0 = \nabla \cdot \boldsymbol{v}$$ Incompressibility

Asymmetric transport between phases?

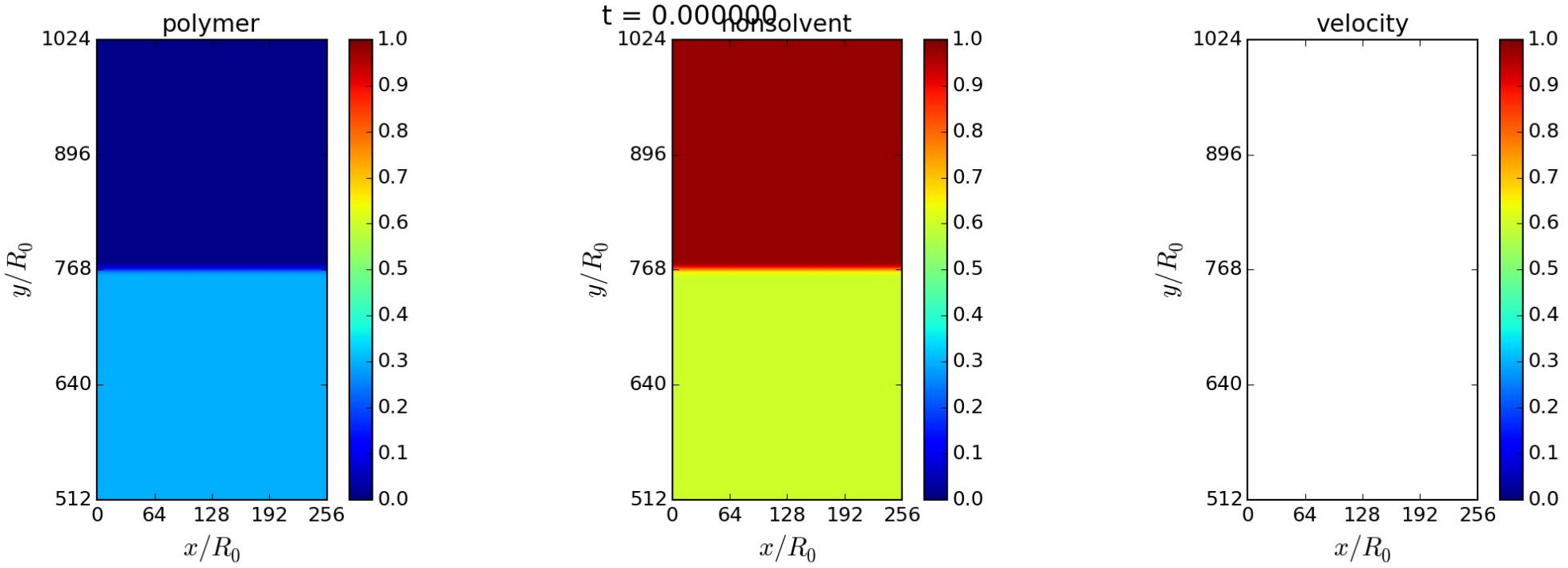




Characterization of phase separation dynamics



Anisotropic quench

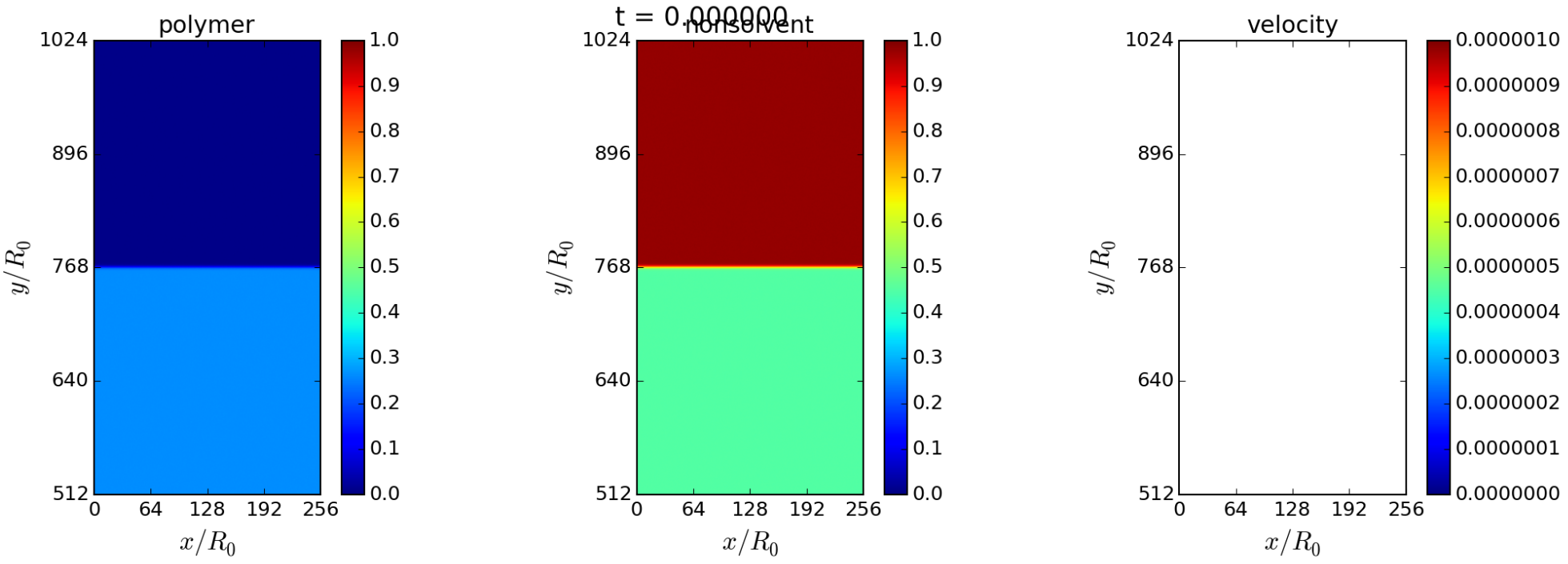


The bath interface gives rise to:

- Surface-directed spinodal decomposition
- Surface hydrodynamic instabilities

Ball and Essery. J. Phys.-Condens. Mat. 2, 10303 (1990)

Marangoni flows also impact coarsening near the interface



(Aside) The bath interface also gives rise to a surface-directed spinodal decomposition process.

Ball and Essery. J. Phys.-Condens. Mat. 2, 10303 (1990)