A Multi-Fluid Model of Membrane Formation by Phase-Inversion

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University of California, Santa Barbara

UCSB

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CNSi Dow AsahiKASEI

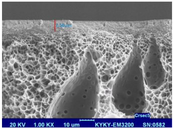
Can we predict the microstructure of polymers?

- Microstructure dictates properties
- Microstructure depends on process history

A very general problem!

Polymer membranes

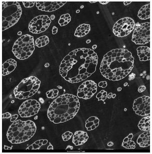
- clean water
- medical filters



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

Polymer Blends

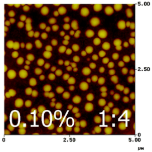
- commodity plastics (e.g. HIPS)
- block polymer thin films



www.leica-microsystems.com

Polymer composites

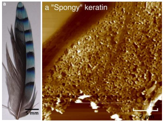
- bulk hetero-junctions
- nano-composites



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

Biological patterning

- Eurasian jay feathers



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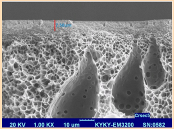

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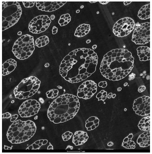

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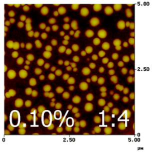

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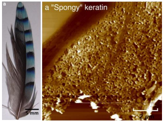

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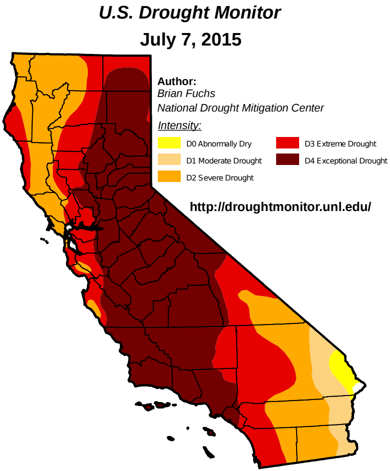
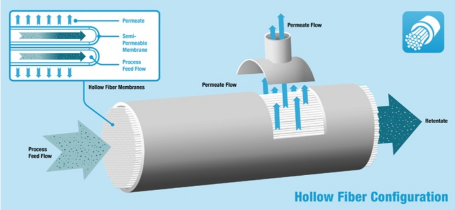
Clean water is a present and growing concern



Why membranes?

- Water is projected to become increasingly scarce.
- Filtration is a key technology for water purification.



http://www.kochmembrane.com/Learning-Center/Configurations/What-are-Hollow-Fiber-Membranes.aspx

Polymer membrane synthesis by immersion precipitation

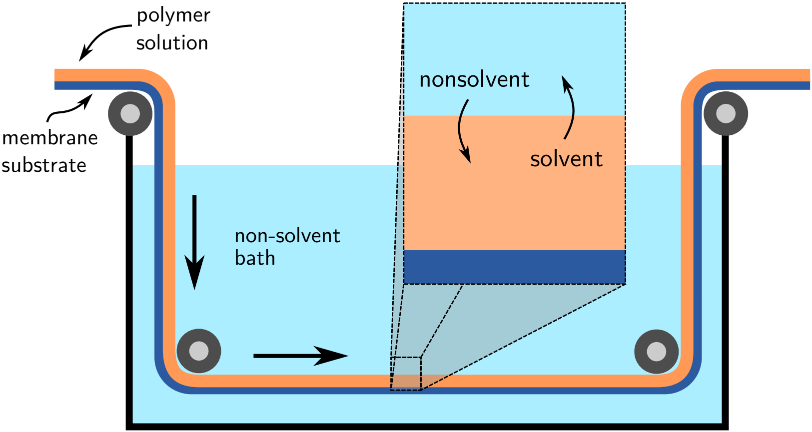
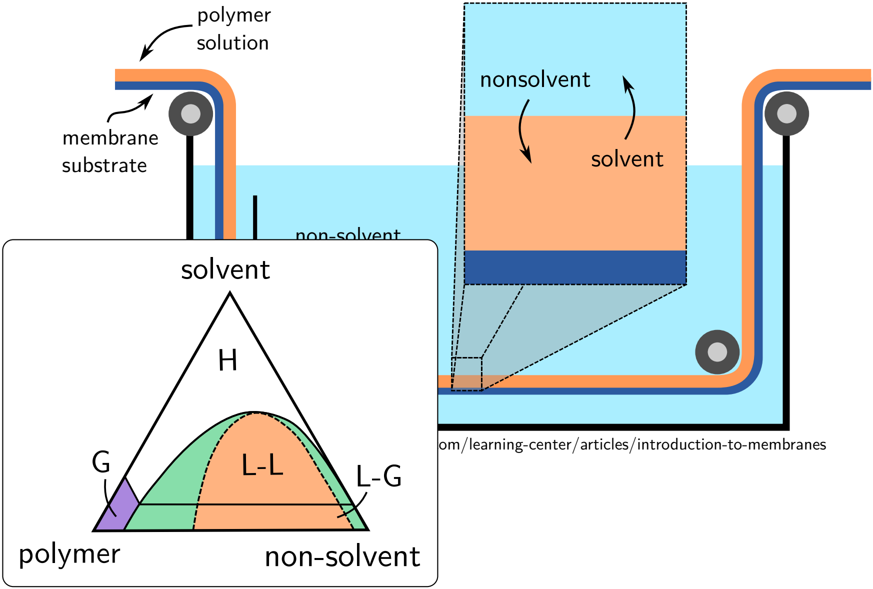


Figure inspired by: www.synderfiltration.com/learning-center/articles/introduction-to-membranes

Polymer membrane synthesis by immersion precipitation



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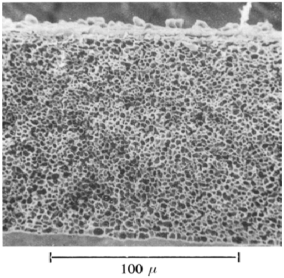
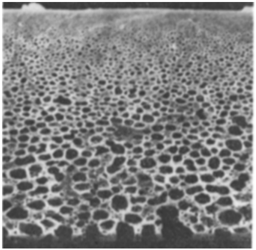
Microstructural variety in membranes

Uniform "Sponge"

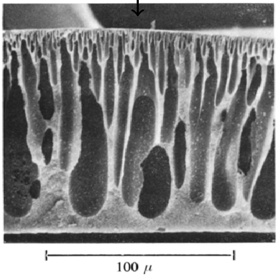


Asymmetric "Sponge"

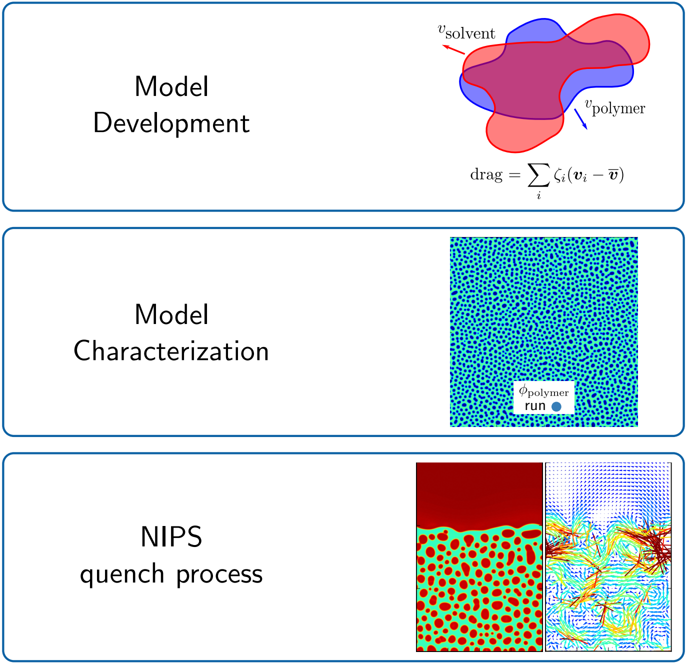


Skin Layer

Fingers or
Macro-voids

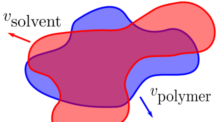


Strathmann et al.
Desalination. (1975)



Model Development
v_{solvent}
v_{polymer}
$\text{drag} = \sum_i \zeta_i(\boldsymbol{v}_i - \overline{\boldsymbol{v}})$
Model Characterization
ϕ_{polymer}
run
NIPS quench process

Model Development



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

Model Characterization

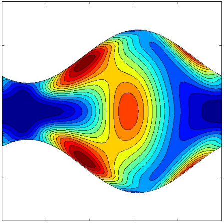
NIPS quench process

How can we model microstructure formation?

A difficult challenge

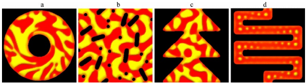
- Complex thermodynamics out of equilibrium
- Spatially inhomogeneous (multi-phase)
- Multiple modes of transport (diffusion & convection)
- Large separation of length/time scales

Continuum fluid dynamics



Teran et al. Phys. Fluid. (2008)

Self-consistent field theory (SCFT)



Fredrickson. J. Chem. Phys. 6810 (2002)
Hall et al. Phys. Rev. Lett. 114501 (2006)

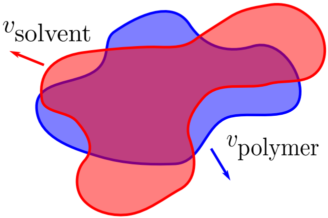
Key idea – cheaper models

Classical density functional theory (CDFT)/"phase field" models

Multi-fluid models

Two-fluid model

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



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de Gennes. J. Chem Phys. (1980)

The Rayleighian

A Lagrangian expression of "least energy dissipation" for overdamped systems ($\mathrm{Re} = 0$).

$$R[\{\boldsymbol{v}_i\}] = \dot{F}[\{\boldsymbol{v}_i\}] \quad \text{free energy}$$
$$+ \Phi[\{\boldsymbol{v}_i\}] \quad \text{dissipation}$$
$$- \lambda G[\{\boldsymbol{v}_i\}] \quad \text{constraints}$$

$$\frac{\delta R}{\delta \boldsymbol{v}_i} \quad \& \quad \frac{\partial \phi_i}{\partial t} = -\nabla \cdot (\phi_i \boldsymbol{v}_i)$$

Transport equations

Doi and Onuki. J Phys (Paris). 1992

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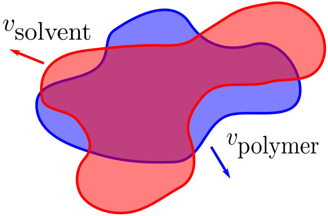

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↘ ↙

Transport equations

Doi and Onuki. J Phys (Paris). 1992

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

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

Transport equations

Model H

Model B

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

Convection-Diffusion

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

Chemical Potential

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

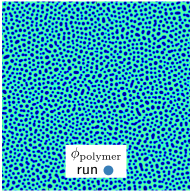
Momentum

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

Incompressibility

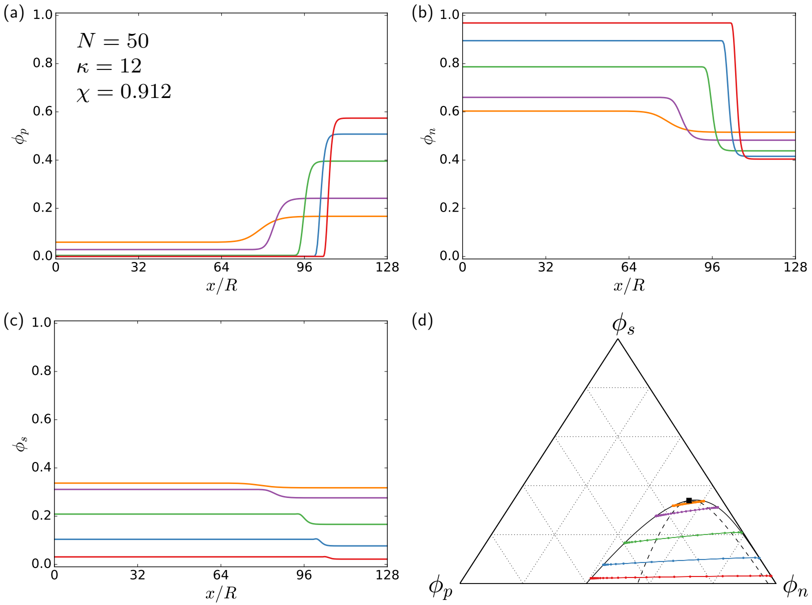
Model
Development

Model
Characterization

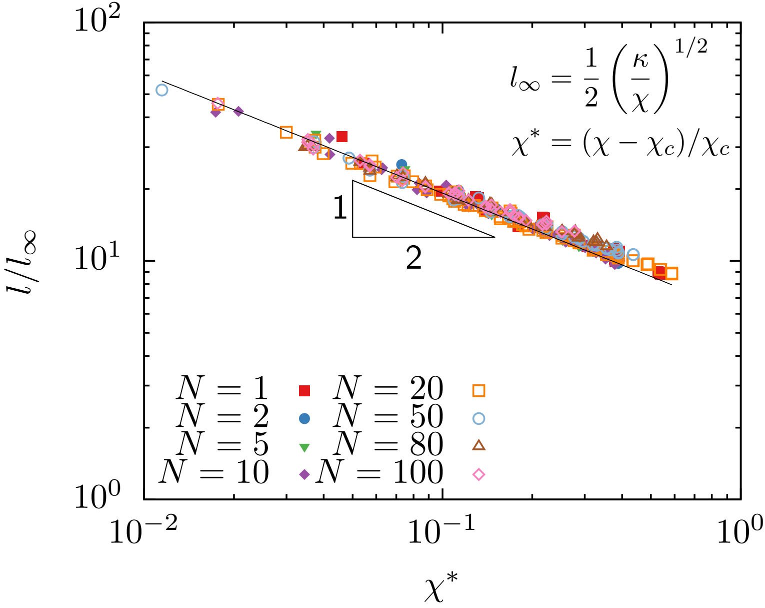


NIPS
quench process

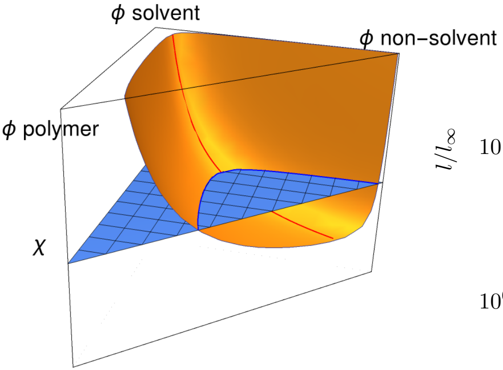
Characterization of model thermodynamics

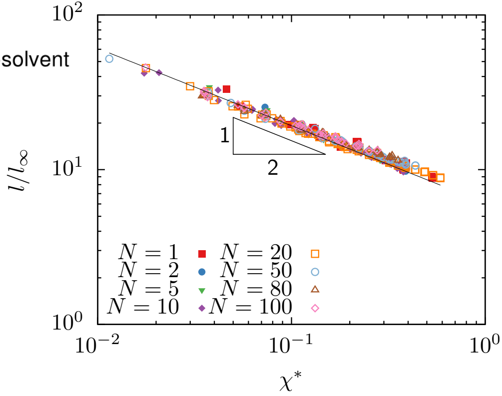


Calculated interface width for many parameters



What explains the interface width data?



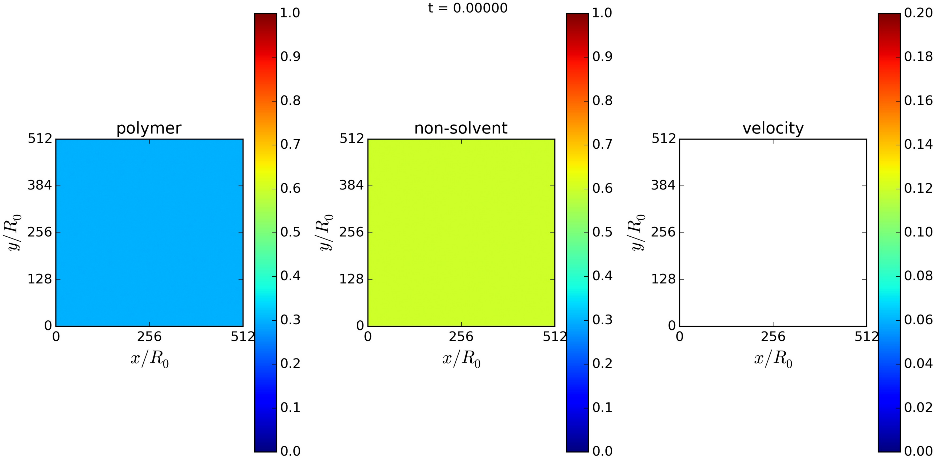


We are near the critical point, χ_c

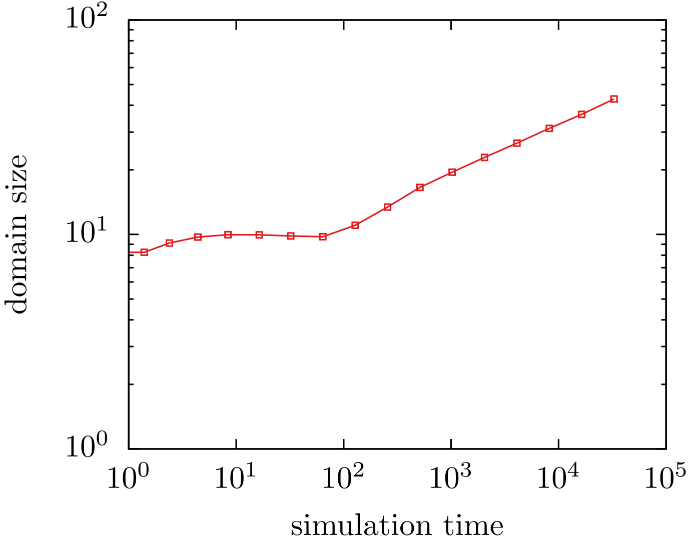
We recover the mean-field critical exponent,

$$l = l_\infty \left(\frac{\chi - \chi_c}{\chi_c} \right)^{-1/2}$$

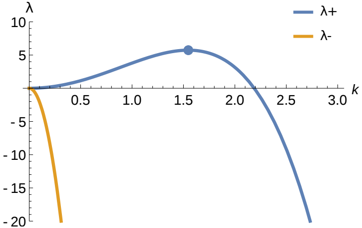
Characterization of phase separation dynamics



There are two dynamic regimes



Early-time regime — initiation of spinodal decomposition



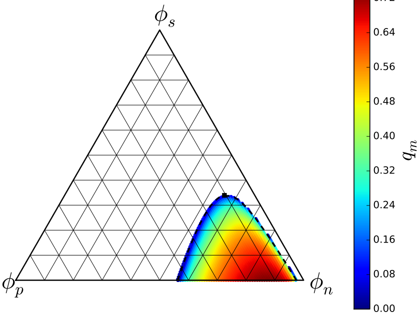
Linear stability analysis

Exponential growth of the fastest growing mode,

$$\delta\psi = \exp[\lambda_+(q)t]$$

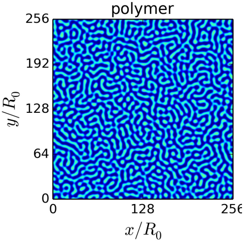
Two key parameters

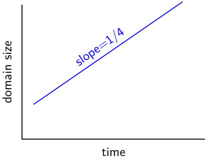
- q_m – fastest growing mode
- λ_m – rate of spinodal decomposition



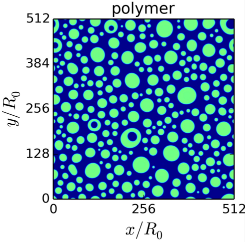
Long-time regime — coarsening

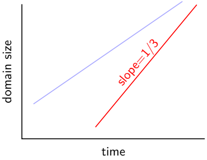
surface diffusion



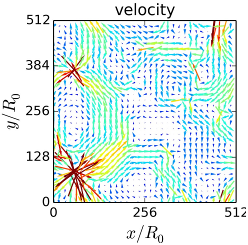


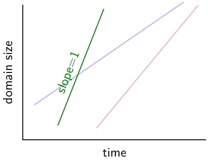
bulk diffusion



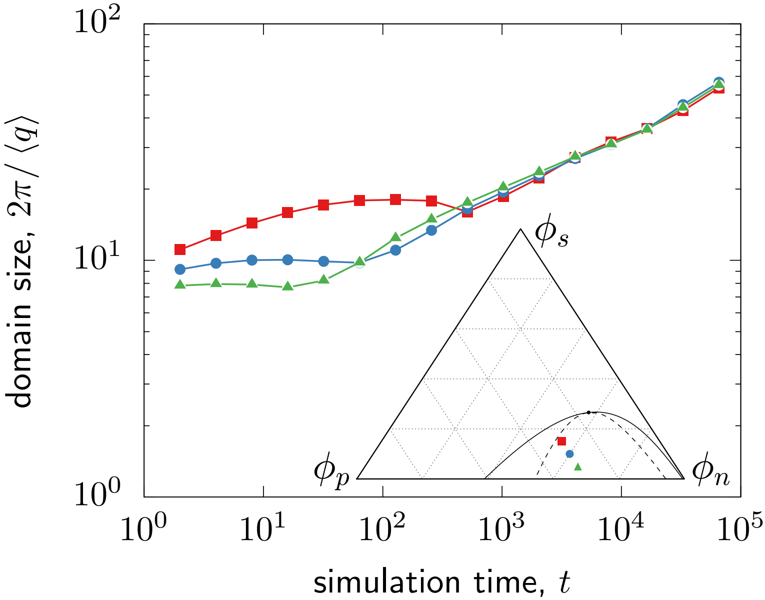


hydrodynamics





Comparing simulations to the LSA



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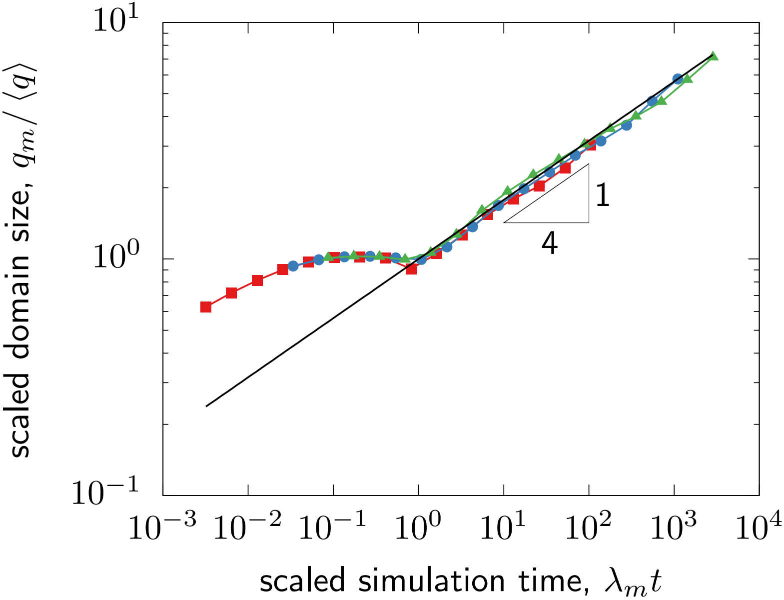
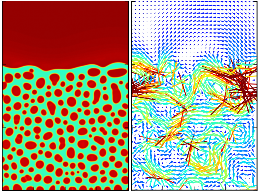


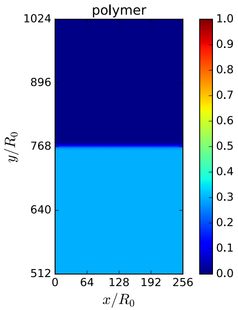
Model
Development

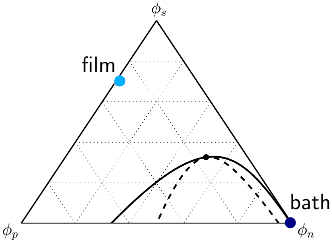
Model
Characterization

NIPS
quench process



How does a quench happen by mass transfer?





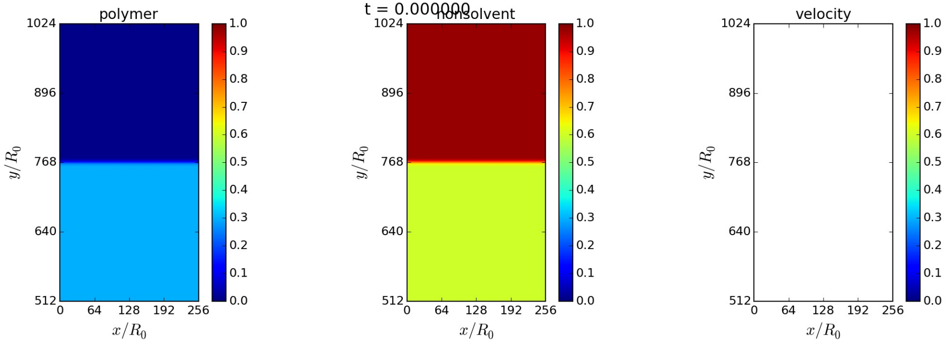
Qualitative features of NIPS (mass-transfer) v. TIPS (temp.)

1. Inherent anisotropy and inhomogeneities
2. Driving force (solvent exchange) and phase separation inseparably linked by mass transfer

Important questions

1. What is the effect of the initial bath/film concentration?
2. What role does film thickness play?
3. How does mass transfer path affect microstructure?

Anisotropic quench



The bath interface gives rise to:

- Surface-directed spinodal decomposition
- Surface hydrodynamic instabilities

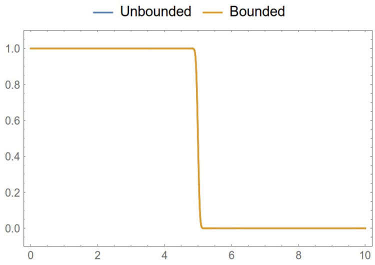
Ball and Essery. J. Phys.-Condens. Mat. 2, 10303 (1990)

Early-time behavior – the infinite film limit

Key concept – time scales

- Phase separation is faster than solvent exchange
- At short times we can neglect the role of film thickness.

Pego. P. Roy. Soc. A-Math. Phy. 422, 261 (1989)



Simple diffusion from a initial step

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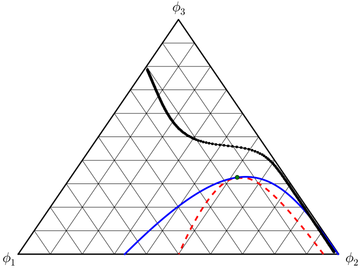

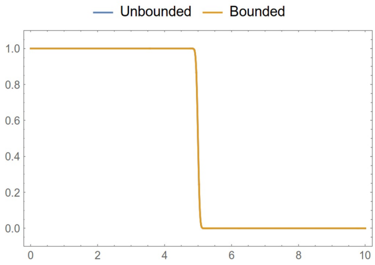

Simple diffusion from a initial step

Three possible cases

1. No phase separation, just diffusion (steady)

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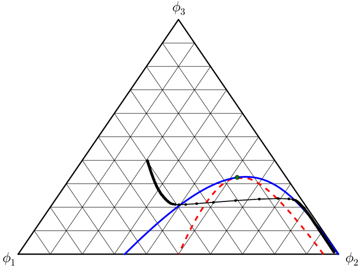

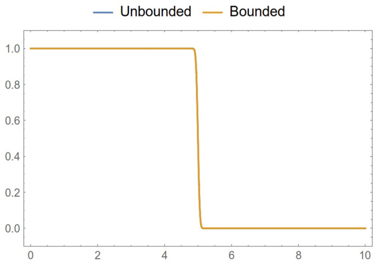

Simple diffusion from a initial step

Three possible cases

1. No phase separation, just diffusion (steady)
2. Phase separation, single domain film (steady)

Early-time behavior – the infinite film limit

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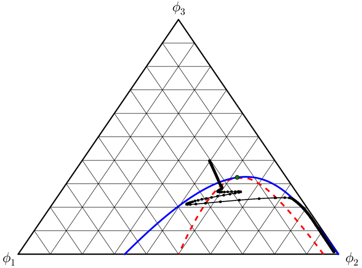

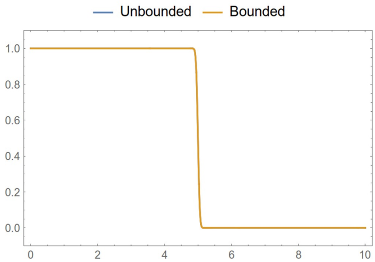

Simple diffusion from a initial step

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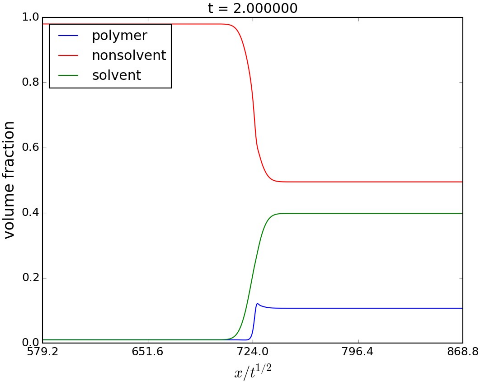
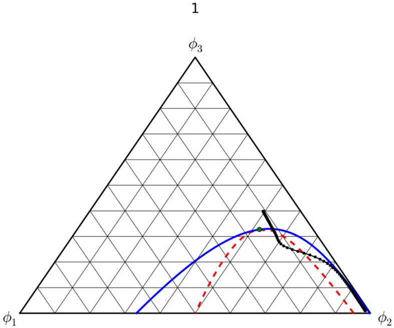
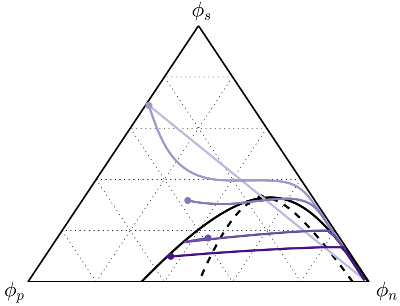
2. Phase separation, single domain film (steady)
3. Phase separation, multiple domain film (unsteady)

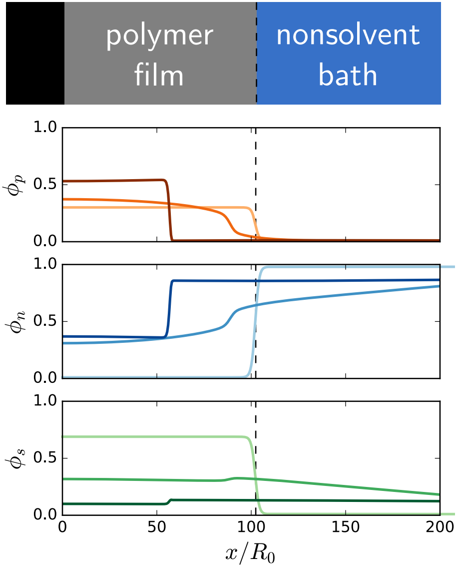
Immediate spinodal decomposition into multi-domain films





A finite-sized film can exhibit delayed phase-separation

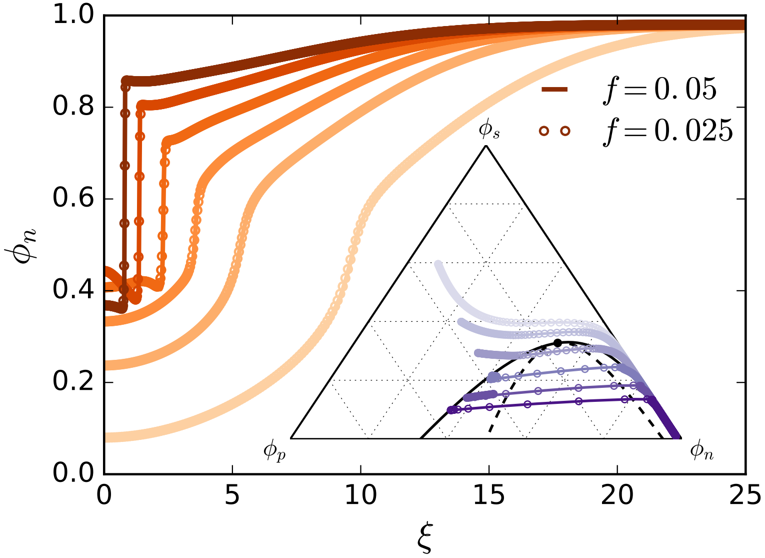




Depending on parameters and initial conditions, a delayed phase separation produces either

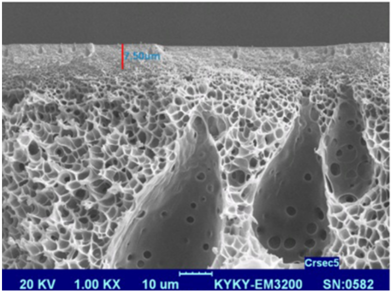
- single domain films (shown)
- multiple domain films

Finite-film data collapse with a similarity variable



Conclusions (1D)

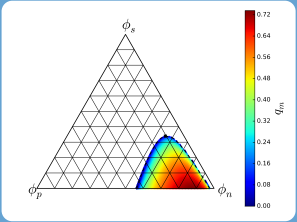
1. Inherent anisotropy?
   - SDSD-like wave
2. Film thickness?
   - Short v. long-time
   - Scales with $xt^{-1/2}$
3. Initial conditions?
   - No PS, single/multiple domains
   - Instantaneous v. delayed PS



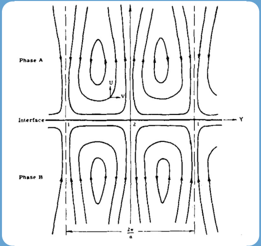
Saedi et al. Can. J. Chem. Eng. (2014)

Future: microstructure (2D)

- Pore gradients



- Macrovoids



Sternling and Scriven. AICHE J. (1959)