Dynamics of Inhomogeneous Polymeric Fluids

Douglas R. Tree

Materials Research Laboratory University of California, Santa Barbara



CFDC Meeting February 3, 2016

Can we predict the microstructure of polymers?

- Microstructure dictates properties
- Microstructure depends on process history

A very general problem!



- clean water
- medical filters



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

Polymer composites

- bulk heterojunctions
- nanocomposites
 Hoppe and Saricifici J. Mater. Chem. (2006)

Polymer Blends

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



www.leica-microsystems.com

Biological patterning

 Eurasian jay feathers



Parnell et al. Sci. Rep. (2015)

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

The Rayleighian

A Lagrangian expression of "least energy dissipation" for overdamped systems (Re = 0).



$$\begin{array}{ccc} \frac{\delta R}{\delta \boldsymbol{v}_i} & \& & \frac{\partial \phi_i}{\partial t} = -\nabla \cdot (\phi_i \boldsymbol{v}_i) \\ & \swarrow & \swarrow \\ & & \swarrow \\ & & & \swarrow \\ & & & \text{Transport equations} \end{array}$$

Doi and Onuki. J Phys (Paris). 1992



de Gennes. J. Chem Phys. (1980)

Multi-fluid models

Two-fluid model

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

The Rayleighian

A Lagrangian expression of "least energy dissipation" for overdamped systems (Re = 0).

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

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

Doi and Onuki. J Phys (Paris). 1992



de Gennes. J. Chem Phys. (1980)

PFPD Software

Phase-Field Polymer Dynamics

Efficient, parallelized, object-oriented C++ program for simulating the flow and phase behavior of inhomogeous polymeric fluids.



PFPD Software

Phase-Field Polymer Dynamics

Efficient, parallelized, object-oriented C++ program for simulating the flow and phase behavior of inhomogeous polymeric fluids.



Integration of transport equations



Stable and efficient time integration

Semi-implicit stabilization

- Unconditionally stable for practical use
- Inexpensive relative to fully implicit methods

$$\frac{\phi^{n+1} - \phi^n}{\Delta t} = \nabla \cdot [M(\phi)\nabla\mu_i^n] + m\nabla^2\mu_{\rm lin}^{n+1} - m\nabla^2\mu_{\rm lin}^n$$

Variable time-stepping

- Step-doubling (50% greater cost per step)
- Enables much larger step sizes for slow dynamics



State-of-the-art method for hydrodynamics

Variable- η Stokes equation

- Fixed-point method
- Enhanced efficiency with
 - Anderson mixing
 - 1st order continuation
- Solution for both PS and hybrid discretizations

$$\nabla^2 p = \nabla \nabla : (\Theta^n - \Pi)$$
$$\nabla^2 \hat{\boldsymbol{v}}^{n+1} = \frac{1}{\eta^*} \nabla \cdot (\Theta^n - \Pi - \boldsymbol{I}p)$$

where,

$$\Theta^n = [\eta(\phi) - \eta^*] \left[\nabla \boldsymbol{v}^n + (\nabla \boldsymbol{v}^n)^T \right]$$



$$\begin{split} 0 &= -\nabla p - \nabla \cdot \Pi \\ &+ \nabla \cdot \left[\eta(\phi) \left(\nabla \boldsymbol{v} + \nabla \boldsymbol{v}^T \right) \right] \\ 0 &= \nabla \cdot \boldsymbol{v} \end{split}$$





PFPD Software

Phase-Field Polymer Dynamics

Efficient, parallelized, object-oriented C++ program for simulating the flow and phase behavior of inhomogeous polymeric fluids.



Non-periodic Boundary Conditions

Pseudo-spectral derivatives

$$\frac{\partial f}{\partial x} \approx FFT^{-1}[-ik_x\hat{f}]$$

 periodic or homogeneous BCs only

very good accuracy

Х



Finite differences

$$\frac{\partial f}{\partial x} \approx \frac{f_{i+1} - f_{i-1}}{2\Delta x}$$

- flexible BCs
- accuracy depends on order of FD

A hybrid method

- Periodic BCs in y (PS)
- Arbitrary BCs in x (FD)

Spinodal decomposition example (diffusion only)





PFPD Software

Phase-Field Polymer Dynamics

Efficient, parallelized, object-oriented C++ program for simulating the flow and phase behavior of inhomogeous polymeric fluids.



How can we model the free energy?

Field theory simulations (SCFT/CL)

Analytical approximations to a field theory Numerical approximations to a field theory







How can we model the free energy?

Field theory simulations (SCFT/CL) Analytical approximations to a field theory Numerical approximations to a field theory







Deriving free energy functionals



* Other approximations are possible, e.g. slow gradient expansion

G.H. Fredrickson. The Equilibrium Theory of Inhomogeneous Polymers. Oxford (2006).

Square-gradient (Cahn-Hilliard) models

For a simple mixture the RPA (or gradient expansion) simplifies to:

$$F[\phi] = \int dm{r} \left[f_0(\phi) + rac{1}{2}\kappa(\phi) \left|
abla \phi
ight|^2
ight]$$

Flory-Huggins-de Gennes

Ginzburg–Landau

$$f_0(\phi) = \sum_{i=1}^2 \frac{\phi_i}{N_i} \ln \phi_i + \chi_{12} \phi_1 \phi_2$$

$$\kappa(\phi) = b^2 \left(\frac{1}{18\phi_1 \phi_2} - \chi\right)$$

P.G. de Gennes. J. Chem. Phys. (1980).

$$f_0(\phi) = a(\phi)^2 + b\phi^4$$
$$\kappa(\phi) = \kappa$$

Cahn and Hilliard. J. Chem. Phys. (1958).

Stability is a challenge at strong segregation



polymer

non-solvent

-G



Why is it hard? Accuracy

Small w and small $\Delta \phi$ means we need a fine grid (small Δx) and accurate time integration (small Δt).

solvent

Interaction between small w and small $\Delta\phi$



Regularizing the free energy

Modified Flory-Huggins

$$f(\phi) = \frac{\phi}{N} \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi (1 - \phi) + A \exp(-\phi/\delta)$$



Effect of regularization on the phase diagram





What about inhomogeneous polymer models?



Ohta-Kawasaki proof of principle

$$\begin{split} F[\phi] &= \int d\boldsymbol{r} \left[f(\{\phi_i\}) + \sum_i \frac{\kappa_i}{2} |\nabla \phi_i|^2 \right. \\ &\left. + \frac{1}{2} \sum_i \xi_i \int d\boldsymbol{r} \int d\boldsymbol{r}' \, G(\boldsymbol{r}, \boldsymbol{r}') \delta \phi_i(\boldsymbol{r}) \delta \phi_i(\boldsymbol{r}') \right] \end{split}$$





How can we model the free energy?

Field theory simulations (SCFT/CL) Analytical approximations to a field theory Numerical approximations to a field theory







Force matching free energy functionals

A generic functional

Assume $F[\phi]$ can be written as a linear combination,

$$F[\phi] = \sum_{i} c_i f_i[\phi]$$

e.g. (Ohta-Kawasaki)

$$F[\phi] = \int dm{r} \left\{ c_2 \phi(m{r})^2 + c_3 \phi(m{r})^3 + c_4 \phi(m{r})^4 + c_5 |
abla \phi(m{r})|^2 + c_7 \int dm{r}' \, G(m{r} - m{r}') \phi(m{r}) \phi(m{r}) \phi(m{r}')
ight\}$$

Force matching to SCFT

$$\Psi = \frac{1}{V} \int d\boldsymbol{r} \left[\frac{\delta F[\phi]}{\delta \phi(\boldsymbol{r})} \right|_{\phi^*} - \frac{\delta F_{\rm SCFT}[\phi]}{\delta \phi(\boldsymbol{r})} \right|_{\phi^*} \right]^2$$

Outlook of current and future capabilities

World-class software for the dynamics of polymeric liquids

- Parallel (GPU, MPI/OMP)
- Efficient, stable time-integration
- Flexible boundary conditions
- Extensible models (free energy, mobility, etc.)

Ongoing studies

- 1. NIPS model and methods (in review)
- 2. Mass transfer (in prep.)
- 3. Coarsening (Jan Garcia)
- 4. Hydrodynamic instabilities (macrovoids)

Low-hanging fruit

- 1. NIPS in flowing systems - Jets
- 2. Alternative formulations for NIPS
 - Multiple solvents
 - Block polymer additives
- 3. Reactive blending

Can we predict the microstructure of polymers?

- Microstructure dictates properties
- Microstructure depends on process history

A very general problem!



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.



 $\label{eq:http://www.kochmembrane.com/Learning-Center/Configurations/What-are-Hollow-Fiber-Membranes.aspx$

Polymer membrane synthesis by immersion precipitation



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

Polymer membrane synthesis by immersion precipitation



Microstructural variety in membranes



Microstructural variety in membranes



A ternary solution model



Ternary polymer solution (Flory–Huggins–de Gennes)

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

Newtonian fluid with ϕ -dependent viscosity

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

Characterization of model thermodynamics



Measured interface width for many parameters



What explains the interface width data?



We recover the mean-field critical

exponent,

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

Microstructural variety in membranes



100 μ

Strathmann et al. Desalination. (1975)

Quench-depth gradient theory



Isotropic spinodal decomposition



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



Increasing the quench-depth



Increasing the quench-depth



Comparing to LSA



The quench-depth graident theory is too simple



Microstructural variety in membranes



Fingers or Macro-voids



Strathmann et al. Desalination. (1975)

Microstructural variety in membranes



Strathmann et al. Desalination. (1975)

100 μ

How does a quench happen by mass transfer?

The kinetics of a mass-transfer-driven quench are inherently different than a temperature-driven quench.



Important questions

- 1. How does mass-transfer initiate the quench?
- 2. How does the initial film concentration affect the quench?
- 3. What role does film thickness play?

Key concept – time scales

Phase separation happens much faster than bulk mass transfer.

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

A simplifying assumption At short times we can neglect the role of film thickness.

Example:



Simple diffusion from a step function initial condition

A simplifying assumption At short times we can neglect the role of film thickness.

Example:



Simple diffusion from a step function initial condition



Three possible cases

1. No phase separation, just diffusion

A simplifying assumption At short times we can neglect the role of film thickness.

Example:



Simple diffusion from a step function initial condition



Three possible cases

- 1. No phase separation, just diffusion
- 2. Phase separation, single domain film

A simplifying assumption At short times we can neglect the role of film thickness.

Example:



Simple diffusion from a step function initial condition



Three possible cases

- 1. No phase separation, just diffusion
- 2. Phase separation, single domain film
- 3. Phase separation, multiple domain film

Ternary plot of immediate SDSD



Real-space plot of immediate SDSD



A finite-sized film can exhibit a delayed phase-separation



The delayed phase separation can produce either single or multiple domains in the thin film, depending on parameters and initial conditions.



Finite-film data collapse with a similarity variable



A comment about macrovoids



What do we know so far about a mass-transfer driven quench?

Important questions

- 1. How does mass-transfer initiate the quench?
- 2. How does the initial film concentration affect the quench?
- 3. What role does film thickness play?

Pego. P. Roy. Soc. A-Math. Phy. 422, 261 (1989) Ball and Essery. J. Phys.-Condens. Mat. 2, 10303 (1990)

(1) Initiation

- Early-time or late-time are qualitatively different
- Single domain films or multiple domain films can form

(2) Initial film concentration

 Imporant influence on whether phase-separation is instantaneous or delayed

(3) Role of film thicknessSets diffusion time-scale

Conclusions

Software development

- Stable, efficient methods and an extensible framework
- NIPS with flow & formulations are promising avenues for future research

Scripts and plotting tools		
Operators - Pseudospectral - Hybrid (FD) BCs	Models - Ternary FHG - Block polymers	Time Int. - Model B - Model H
Field vector/matrix operations		
Field library (KTD)		

Polymer membranes

- Characterized the model and spinodal decomp. kinetics
- Ongoing work:
 - Mass transfer
 - Coarsening and arrest
 - Macrovoids



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

Acknowledgements



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



Effect of hydrodynamics



