Microstructural Transformations in Concentrated, Charged Vesicle Suspensions

Cryo-TEM image

Vesicles: self-assembled aggregates of surfactant molecules

The lipid bilayer is deformable, but also highly permeable to small molecules like H₂O, but impermeable to salts or larger molecules
Vesicles are a **soft, deformable particle**; always **highly polydisperse**; some people study GUVs, but in practice they are typically **small, O(100nm) or less**

**What is unique about vesicles, viewed as a soft particle?**

*When they deform, they preserve bilayer surface area but not vesicle volume*

1) For a given amount of lipid (i.e. a given area of bilayer) we can have many different volume fractions of particles (unilamellar vs. bilamellar or multilamellar structures)

2) If we force a vesicle to deform too quickly, the tension in the membrane may exceed rupture, and the vesicle will burst apart into bilayer fragments, and will reform into a structure that may be very different from its initial structure, though with the same bilayer surface area (multilamellar into unilamellar, for example) with radically different flow properties
Key Properties for Suspension Rheology

**Bilayer mechanical properties**

**Modes of Membrane Deformation**

- Area Expansion $K_A$
- Bending $k_c$

**Volume Fraction**

$K_A \gg k_c$

O(100) nN/m

O(10-100kT) depending on the membrane phase

Membrane is close to area preserving; bending modulus depends on whether the membrane is in a “fluid” or “solid” phase.
Two Studies Reported Here

From PhD Thesis of Mansi Seth

1. Spontaneous unilamellar to bilamellar vesicle transitions: with a corresponding decrease in volume fraction

2. Instantaneous formation of cationic vesicle ‘gels’ (multilamellar to unilamellar transition by extrusion; with an increase in volume fraction to a jammed material)
Experiments on model cationic vesicle suspensions

di C18:1 DEEDMAC

Saturated DEEDMAC

In ethanol, CaCl$_2$, water

Tends to be relatively loosely packed and mobile (fluid-like) in the bilayer, with bending modulus of $O(7\text{-}8kT)$ even at room temperature

More closely packed, much more complex phase behavior in the range from 20-50$^\circ$C (in a fluid state above 55$^\circ$C, in “solid” or gel states below 55$^\circ$C)
1. Spontaneous unilamellar to bilamellar transformations in charged vesicle suspensions: The crowding hypothesis

Microstructural transformations can affect suspension rheology

Deflation-induced curling of unilamellar vesicles

Such transformations are possible for unsaturated DEEDMAC or for saturated DEEDMAC in the fluid/mobile state where $k_c=6-10kT$

The transformation can be forced:

1. **Addition of hyperosmotic salt solution** [Saveyn et al., (2007)]
   - Leads to loss of water from the vesicle, which and a deflated configuration that is susceptible to curling instability and formation of a doublet

2. **Increase in temperature** [Kas and Sackmann., (1991)]
   - Leads to increase in area of the vesicle

However, our studies of cationic, unsaturated DEEDMAC show that a transformation from unilamellar to bilamellar (with decreased $\phi$) can also occur spontaneously
Spontaneous microstructural transformations of charged vesicle suspensions

What is the driving force for spontaneous deflation, and subsequent transitions in charged vesicle suspensions?

Repulsive (entropic/osmotic) pressure between neighboring vesicles in a suspension above a critical effective volume fraction; sources include Brownian motion, Helfrich undulations and electrostatic repulsion (the latter dominant for charged vesicles)
Crowding Effect in the Formation of a Charged Vesicle Suspension

Dilute Suspension (Low $\phi_{eff}$)

- Not Space Filling
- $C = \text{Salt concentration}$
- $\pi_{in} = Ck_B TN_{av}$
- $\pi_{out} = Ck_B TN_{av}$
- $\pi_{in} = \pi_{out}$
- Osmotic pressure balance satisfied upon vesicle formation

Concentrated Suspension (High $\phi_{eff}$)

- Space Filling
- $\phi_{eff} = \phi + \delta\phi$
- Interacting double layers
- $\pi_{in} = Ck_B TN_{av}$
- $\pi_{out} = Ck_B TN_{av} + \pi_{elec}$
- $\pi_{in} \neq \pi_{out}$
- Vesicles can deflate by losing water until $\pi_{in} = \pi_{out}$ (but this is opposed by bending rigidity and tends not to happen for small vesicles (10s of nm); first step in transition to bilamellar vesicles
CryoTEM Imaging Summary

35 mg/ml unsaturated DEEDMAC

4.5 mM CaCl₂

**t = 0 days**

**t = 3 days**

Several unilamellar deflated and curled up/stomatocyte structures present even at t=0 (generated during the formation process)

At t = 3 days, there are almost no unilamellar spherical/deflated vesicles – Increase in the number of <100 nm doublets

Note: Bending rigidity resists deflation/shape changes; and prohibits such changes for small vesicles
Volume fraction results (measured by an independent technique*)

35 mg/ml unsaturated DEEDMAC

4.5 mM CaCl$_2$

Effective volume fraction reduces from 0.32 to 0.19

Effect of lowering surfactant concentration

Initial volume fraction for 22 mg/ml is similar to the “3 day value” at the higher (35 mg/ml) DEEDMAC concentration.

35 mg/ml unsaturated DEEDMAC

4.5 mM CaCl$_2$

22 mg/ml unsaturated DEEDMAC

4.5 mM CaCl$_2$

Volume fraction unchanged after 7 days
Effect of lowering the surfactant concentration: decrease $\phi$

CryoTEM Imaging Summary

22 mg/ml unsaturated DEEDMAC
4.5 mM CaCl$_2$

$t = 0$ days

$t = 7$ days

Very few unilamellar deflated/curled up structures present at time $t = 0$.

On lowering the concentration of surfactant, there is virtually NO TRANSITION of the suspension micro-structure!
Long time effects?

CryoTEM Imaging Summary

22 mg/ml unsaturated DEEDMAC
4.5 mM CaCl$_2$

t = 0 days  

Microstructure is essentially unchanged over long times ~ O(months)
Effect of increasing the salt concentration
35 mg/ml unsaturated DEEDMAC
27 mM CaCl$_2$

On increasing salt concentration, both electrostatic repulsion and bending modulus are reduced, and effective volume fraction is reduced.

Virtually no transition of suspension microstructure and volume fraction

Fewer unilamellar deflated/curled up structures present at t=0
Lowering salt concentration increases electrostatic repulsion between vesicles, and increases the bending modulus by 2x.

Initial (t=0) Size Distribution

4.5 mM CaCl$_2$

- Almost no unilamellar deflated/stomatocyte vesicles

0.1 mM CaCl$_2$

- Unilamellar deflated and stomatocyte vesicles form ~ 20% of total vesicle population

Initial effective volume fraction increases
Effect of lowering the salt concentration

\[ 22 \text{ mg/mL} \]

\[ 0.1 \text{ mM CaCl}_2 \]

\( t = 0 \text{ days} \)

\( t = 10 \text{ days} \)
By reducing the number of extrusion passes to 4, suspension has higher initial volume fraction, undergoes ‘crowding’ transformation.
1. We can control flow properties of a vesicle suspension when the bilayer is in the liquid phase by forcing a decrease in volume fraction by addition of salt (but the opposite transition has not been observed to date).

2. Vesicles do not like to exist in a crowded (high concentration) state and will spontaneously go to a lower volume fraction if given enough time (we measure in days, but the process is likely much faster); provided the membrane is in the mobile, low bending modulus phase.

A consequence of preserving area instead of volume

A qualitative model was developed to predict the volume reduction (i.e. volume decrease) for monodisperse vesicles of different initial size and at different salt concentrations (see Soft Matter paper).
2. Instantaneous formation of ‘jammed’ suspensions via extrusion of a suspension of the saturated DEEDMAC vesicles

Thermotropic phase behavior of saturated DEEDMAC bilayer

3 phases of DEEDMAC

- Liquid phase ($L_\alpha$)
  - Translation and flip-flop motions occur, chain conformational disorder
  - Hydrated head-group

- Gel phase ($L_\beta$)
  - Restricted chain motion, only rotational disorder remains
  - Chains organize in hexagonal 2D lattice
  - Hydrated head-group
  - Higher inter-bilayer repulsion, larger head-group area (compared to $L_c$)
  - Increased bending modulus $\times 10-15$, and decreased permeability

- Coagel phase ($L_c$)
  - Loss of rotational disorder
  - Chains organize in triclinic packing
  - Partially hydrated head-group
  - Higher bilayer density
  - Lower inter-bilayer repulsion, smaller head-group area (compared to $L_\beta$)
  - Smaller effective volume fraction


Another lever to control rheology?
Rheology of unextruded DEEDMAC suspensions

35mg/ml, 4.5 mM CaCl$_2$
Aged at 20° C for 4 days

Pre-transition (coagel to gel)
Main- transition (gel to fluid);

Small amplitude oscillatory shear at 2pi rad/s (1 Hz),
With temp change at 1° C/min

Storage modulus
(Loss Modulus is similar but smaller)

Pre-transition (coagel to gel)
Main- transition (gel to fluid);

Pre-transition (coagel to gel)
Main- transition (gel to fluid);

Large bending modulus
But weak repulsion
Reduced φ
Compared to L$_β$

Small bending modulus

35mg/ml, 4.5 mM CaCl$_2$
Aged at 20° C for 4 days

Small amplitude oscillatory shear at 2pi rad/s (1 Hz),
With temp change at 1° C/min

Storage modulus
(Loss Modulus is similar but smaller)
Rheology of unextruded DEEDMAC suspensions

4.5 mM CaCl$_2$

27 mM CaCl$_2$

Added salt: weaker repulsion, smaller volume fraction, smaller $G', G''$

Note: Control of rheology via temperature, and salt levels for a given amount of surfactant
Liquid-like consistency

Un-Extruded Sample

Actual suspension

Phase contrast microscopy image

Homogenous suspension of big and small multilamellar vesicles (also cryo-TEM)

20 microns
Effect of extrusion – Formation of Vesicle Gel

35mg/ml (50 mM) total surfactant concentration

Vesicle Suspension

Extrude through 800nm pores

60°C

Cools to room temperature at extruder outlet

Instantaneous ‘Gel’ Formation

Note: Original (pre-extruded) suspension retains (low) viscosity upon cooling to room temperature
Effect of extrusion on oscillatory rheology (20°C)

$G', G''$ increase by 3-4 orders of magnitude upon extrusion
Effect of extrusion on ‘steady’ shear rheology

\[ \eta \sim \dot{\gamma}^{-0.8} \]

"Typical multilamellar vesicle suspension"

(Roux. et al. 1994, Wagner et al. 1998)

Instantaneous formation of a yield stress material
Actual suspension

Solid–like

Large, 400nm – 600nm size vesicles
But many smaller monodisperse vesicles too

Extremely ‘jammed’ microstructure
Reminiscent of compressed emulsions/foams
Rheology - strain amplitude sweep

Characteristic of soft, glassy materials

Peak in $G''$ (consistent with the yielding behavior of a jammed microstructure)

Cryo-TEM image

Large, 400nm – 600nm size vesicles

Microstructure is consistent with rheology

Extrusion leads to formation of glassy suspension
What role does Extrusion play?

Vesicle is forced through filter pore due to applied pressure

Outer layers of multilamellar vesicle peeled off as membrane tension exceeds rupture tension i.e.

\[ \Delta P = 2\tau \left( \frac{1}{R_p} - \frac{1}{R_0} \right) \]

For \( \Delta P = 200 \text{ psi} \)

\[ 2R_0 = 1 \mu m \]
\[ 2R_p = 800 \text{ nm}, \quad \tau = 1379 \text{ mN/m} \]

\[ \tau > \tau_{rup} \sim O(10 \text{ mN/m}) \]

Reduces lamellarity and size but increases number density of vesicles

Extrusion leads to the formation of a ‘crowded’ suspension;

Another consequence of preserving bilayer surface area instead of vesicle volume

200 nm
Effect of increasing bending rigidity

At higher bending rigidity, larger vesicles will resist deflation due to bending costs and the suspension is trapped in the crowded state (no relaxation to reduced volume fraction). Leads to formation of ‘jammed’ suspension if temperature drops below $T_m$ before vesicles can escape crowded conditions via the spontaneous change to bilamellar (and multilamellar) vesicles.

As temperature drops below $T_m$, membrane solidifies

Bending rigidity increases

At higher bending rigidity, larger vesicles will resist deflation due to bending costs and the suspension is trapped in the crowded state (no relaxation to reduced volume fraction)

Leads to formation of ‘jammed’ suspension if temperature drops below $T_m$ before vesicles can escape crowded conditions via the spontaneous change to bilamellar (and multilamellar) vesicles.
Effect of surfactant concentration on rheology

At lower surfactant concentration, volume fraction is lower leading to formation of a weaker glassy system. At 8.75 mg/ml, extrusion does not lead to a glassy suspension.

Finally, if we extrude a higher temperature, vesicles are able to relax the crowded suspension conditions prior to cooling below 56°C at the extruder outlet, and again the transition to the glassy state is avoided.
The End of Discussion of Vesicles

**Key properties:** preserve bilayer surface area rather than vesicle volume

Surface (bilayer) properties can be fluid-like or solid-like depending on the nature of the surfactant and the temperature.
Topic #2: Flow induced spatial inhomogeneities in polymeric liquids

PhD Research Of Joe Peterson

(Our focus is non-dilute, entangled systems, where there is an analogy with concentrated suspensions)
**Suspensions:** even single particles can migrate across streamlines. Although not possible for a rigid particle in a Newtonian fluid at $Re=0$.

if we include even tiny departures:

a) **Inertia** (In simple shear to midplane between walls; in pressure driven flow to 0.6R (Segre-Siberberg effect)

b) **non-Newtonian Suspending Fluid** (Rigid sphere migrates down $N_1$ gradients in a viscoelastic fluid-no migration in simple shear, migration toward the centerline in pressure driven flow; and toward outer cylinder in Couette flow); **But in the opposite direction for weakly elastic, shear thinning fluids**

c) **Deformable Drops**; (complex results, but direction of migration is not necessarily in the direction that would minimize shape deformation; for viscosity ratios between 0.1 and 10 goes in the “wrong” direction.)

d) Other cases have been analyzed; vesicles, capsules, drops in non-Newtonian fluids, non-Newtonian drops etc.
**Dilute Suspensions**

If we have a suspension of particles, these migration effects lead to concentration non-uniformities (opposed by Brownian diffusion if the particles are small enough, and by hydrodynamic interactions between particles as the local concentration increases); although these mechanisms persist under non-dilute conditions, they are often dominated by other effects.

**Concentrated Suspensions**

Shear induced gradients of concentration can be generated even for rigid spherical particles at zero Reynolds number due to the fact that particle interactions produce irreversible dynamics either due to N (>3) body hydrodynamic interactions, or irreversible 2-body interactions due to roughness (or more generally deformation, inertia etc).

Most modern analyses of these effects utilize the suspension balance model (really a “two-fluid” model) with migration required to maintain particle pressure (or normal stress) uniform across a inhomogeneous shear:

There is a strong analogy between these models and the approach we have taken to modeling flow-induced inhomogeneities in entangled polymer fluids; And so, perhaps, something to be learned even for the suspension problem?
Two-Fluid Models for Polymer Melts and Solutions

Part 1: Formalising the quasi-thermodynamic approach
Part 2: Flow-induced demixing in polydisperse blends

Joseph D. Peterson, Glenn H. Fredrickson, L. Gary Leal
03/21/18
Semi-dilute entangled polymer solutions

The Two-Fluid Model

\[ \mathbf{u}_P - \mathbf{u}_S = \frac{1}{\zeta} \nabla \cdot (\mathbf{\sigma} - \mathbf{\pi}) \]


Similar equations exist for dry grains and dense suspensions
Flow-induced migration in a two-fluid model

Centerline: polymers are isotropic

Walls: polymers are compressed in the flow gradient direction

Migration up stress gradients:

$$\mathbf{u}_P - \mathbf{u}_S = \frac{1}{\zeta} \nabla \cdot (\mathbf{\sigma} - \mathbf{\pi})$$

Migration Velocity
Flow-induced demixing in a two-fluid model

High concentration (Right) leads to higher effective viscosity, lower shear rates, and more isotropic configurations.

Low concentration (Left) leads to lower effective viscosity, higher shear rates, and more compression in the flow gradient direction.

Migration up stress gradients favors demixing.

\[ \mathbf{u}_P - \mathbf{u}_S = \frac{1}{\zeta} \nabla \cdot (\sigma - \pi) \]
Flow-Induced Demixing in Polymer Solutions

Conditions for Shear Induced Demixing

(1) Elastic stresses are large enough to compete with osmotic stresses
(2) Changes in shear rate effect normal stress more than shear stresses

Stress plateau: most unstable at $W_i \approx 5$

$E = \text{elastic/osmotic modulus}$

<table>
<thead>
<tr>
<th>Dimensionless Group</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E = 0.15$</td>
<td>moderate mixing forces</td>
</tr>
<tr>
<td>$\theta = 120$</td>
<td>strongly entangled</td>
</tr>
<tr>
<td>$\eta_s = 10^{-5}$</td>
<td>weak solvent contribution</td>
</tr>
<tr>
<td>$\xi = 0.3$</td>
<td>large coupling friction</td>
</tr>
<tr>
<td>$\overline{H} = 10$</td>
<td>moderate gap size</td>
</tr>
</tbody>
</table>
Shear Induced Demixing (SID) vs Cahn Hilliard

Cahn-Hilliard Demixing

SID in two-fluid model

\[ E = 0.15, \theta = 120, \xi = 0.10, \bar{H} = 10, \Sigma_0 = 0.6225 \]

Does flow somehow ‘shift’ an underlying phase diagram?

Implications for coarsening dynamics, nucleation phenomena, local/global stability analysis, and more

Could turn ‘active areas of research’ into ‘previously solved problems’
Does flow shift the phase diagram?

Can we map a two-fluid model onto a Cahn Hilliard Model?

Consider long-time dynamics in the limit of high coupling friction

- Migration is much slower than stress relaxation
- Start-up transients do not matter
- Polymer stress tensor determined quasi-statically based on shear rate

\[ v_p - v_s = -\frac{1}{\zeta} \frac{\partial}{\partial y} \pi^{\text{eff}}(\phi, \Sigma) \]

\[ \pi^{\text{eff}}(\phi, \Sigma) = \pi(\phi) - \sigma_y^{\text{eff}}(\phi, \Sigma) \]

Concentration equation looks like Cahn Hilliard

\[ \frac{\partial \phi}{\partial t} = \frac{\partial}{\partial y} \left[ M \frac{\partial}{\partial y} \pi^{\text{eff}}(\phi, \Sigma) \right] \]

What is the effective free energy?
Define an ‘effective’ free energy, $\mathcal{L}$, as the free energy of mixing, $F^{mix}$, plus a correction with free energy density $\Delta f$:

$$\mathcal{L} = F^{mix} + \int dV \Delta f(\phi, \Sigma)$$

If $\mathcal{L}$ is the Liapunov functional for $\phi$ (such that thermodynamic intuitions regarding the dynamics are valid) then it follows that $\Delta f$ must satisfy:

$$\frac{\partial}{\partial \phi} \sigma_{yy}(\phi, \Sigma) = \phi \frac{\partial}{\partial \phi} \Delta f(\phi, \Sigma)$$

Solve to obtain $\Delta f$:

$$\Delta f(\phi, \Sigma) = -\phi \int_{\phi_{ref}}^{\phi} d\phi' \left( \frac{\sigma_{yy}(\phi', \Sigma) - \sigma_{yy}(\phi_{ref}, \Sigma)}{\phi'^2} \right)$$
Example 1: Identifying metastable states
\[ \theta = 120,\ E = 0.15,\ \eta_S = 10^{-4},\ \Sigma = 0.59\quad \bar{\xi}/\bar{H} \ll 1 \]

\[ f^{\text{mix}} + \Delta f \]
Nucleating a Shear Band

$$\theta = 120, E = 0.15, \eta_s = 10^{-4}, \tilde{\xi} = 10^{-2}, \bar{H}/\tilde{\xi} = 100, \Sigma = 0.59$$
What about LAOS?

Consider long-time dynamics in the limit of high coupling friction

- Migration is much slower than stress relaxation and oscillation.
- Assess long-time migration via method of multiple scales.
- Oscillations averaged out: polymer stress tensor determined by limit cycle solution for fixed $\phi$

$$v_P - v_S = -\frac{1}{\zeta} \frac{\partial}{\partial y} \langle \pi^{eff} \rangle$$

$$\langle \pi^{eff} \rangle(t) = 2\pi\omega \int_{0}^{[2\pi\omega]^{-1}} \pi_{LC}^{eff}(t, \phi(\tau))$$

Concentration equation looks like Cahn Hilliard

$$\frac{\partial \phi}{\partial \tau} = \frac{\partial}{\partial y} \left[ M \frac{\partial}{\partial y} \langle \pi^{eff} \rangle \right]$$

Only works for linear stability analysis! Nonlinear dynamics can be very different!
Sidebar: linear stability boundaries

Floquet Stability Analysis, LAOStress

\[ \theta = 100, E = 0.15, \eta_s = 10^{-4} \]

\[ \omega / 2\pi = 2 \]

\[ \Sigma = \Sigma_C - 10^{-3} \]

\[ \Sigma = \Sigma_C + 10^{-3} \]
Examples: Unusual nonlinear dynamics

Lack of coarsening after demixing (seeded from random noise)

Interface is non-monotone in $\phi$ (seeded with macroscopic inhomogeneity)

The culprits:
(1) Diffusion forces an interfacial length-scale
(2) Migration-induced interfacial stresses

$$\theta = 120, E = 0.15, \eta_s = 10^{-4}, \bar{\xi} = 10^{-2}$$

$$2\pi \omega = 0.5, \Sigma = 0.67$$

$$\bar{H} = 1 \text{ (left)} \quad \bar{H} = 16 \text{ (above)}$$
Shear Induced Demixing in Polymer Blends

**Experimental Observations:** There have been extensive studies of the effects of shear on both mixing and demixing, in solutions and blends, starting as far back as the 1950s

Demixing in PS/PVME
(Mani/Winter et. al. early 1990s)

**Theoretical Studies (based on two-fluid approx. for bidisperse systems)**
- Linear flow regime: Doi and Onuki, 1992
- Onset of mixing/demixing ("DE-DR"): Clarke and McLeish 1998
- Full 2D studies of shear induced demixing ("JS-DR", "RP-DR"): Yuan etal, 2002, 2014

**What do we hope to contribute?**
- Improvements in constitutive modelling
- A better grasp on the role of polydispersity
- A focus on ideal blends (i.e. blends of one species with different MWs)
Back of the Envelope Estimations

• $Z_S \ll Z_L$, short chains become solvent-like: **Polydispersity is stabilizing**

\[
E = \frac{G}{K} = \left[ \frac{1}{Z_L \phi_L} + \frac{1}{Z_S \phi_S} \right]^{-1} \approx Z_S \phi_S
\]

• $Z_S \rightarrow Z_L$, vanishing contrast between chains: **Polydispersity is destabilizing**

\[
\frac{k_B T}{b^3 N_e} \left[ \frac{Z_L - Z_S}{Z} \right]^2 \sim \frac{k_B T}{b^3} \left[ \frac{1}{N_L \phi_L} + \frac{1}{N_S \phi_S} \right]
\]

\[
I_P - 1 \sim \frac{1}{Z}
\]

What happens to polydisperse blends in flow?
**Two Fluid Modelling of Bi-Disperse Polymer Blends**

**Two-Fluid Approximation**
Superimposable Continuum Fluids, deformed by Brochard tube velocity
Coupled by: Friction, incompressibility of volume average velocity
Elastic free energy explicitly included (compare to Doi and Onuki, 1992)

**Constitutive Theory: Double Reptation Rolie-Poly**
Temporary network model with tube-based kinetics
Highly successful, but a subject for another talk, unfortunately
Consistency Check: Transition to Solvent-like Short Chains (rheology)

Homogeneous Rheology

Polymer Blend
$Z_L = 625, Z_S = 5$
$\phi_L = 0.10$

Polymer Solution
$Z = 62.5, \quad \omega = 7 \cdot 10^{-5}$

$J_e^0 \sigma_{xy}$

--- Solution Model
--- Blend Model

\[ J_e^0 = \frac{\lambda_0}{\eta_0} = \lim_{\omega \to 0} \left[ \frac{G'}{G''^2} \right] \quad \text{(creep compliance to normalize for differences in modulus)} \]
Consistency Check: Transition to Solvent-like Short Chains (demixing)

Polymer Blend

\[ Z_L = 625, Z_S = 5, \phi_L = 0.10 \]

Modeled as a “Polymer Solution”

\[ Z = 62.5, E = 4.1, \varpi = 7 \cdot 10^{-5} \]
A Broader Range of Blends

\[ 0 \geq \zeta - \zeta = \zeta \]

Dimensionless Growth Rate

\[ \hat{\sigma}(Wi) = \lim_{k \to 0} \frac{1}{k^2} \left[ -\frac{\sigma(Wi, k)}{\sigma(0, k)} \right] \]

Polydispersity-induced Contrast, \( \chi_D \)

\[ \chi_D = \frac{(\hat{\sigma} + 1)}{\bar{Z} m_2} \quad m_2 = \phi_L \phi_S \left[ \frac{Z_L - Z_S}{\bar{Z}} \right]^2 \]
Non-linear evolution of Demixing

\[ Z_L = 250, Z_S = 150, \phi_L = 0.50, R_g = 0.11, Wi = 0.36 \]
What about continuum polydispersity?

Examples: lognormal MW distribution

Estimating $\chi_D$
Asymptotic Limit: $I_P - 1 \ll 1$, $\bar{Z} \gg 1$

Predicting $\delta \phi(Z)$

$I_P = 1.05$, $\bar{Z} = 100$, $Wi = 0.3$ → unstable

Shear thinning enhances mixing

Demixing possible at low, high $Wi$
Summary and Conclusions

**Polymer Solutions**
- High coupling friction is a useful asymptotic limit for studying migration dynamics
- Simple shear flow: Determine an effective free energy shift
- LAOSTress flow: Thermodynamic analogy doesn’t apply for non-linear dynamics

**Polymer blends**
- Polydispersity is stabilizing for $Z_S \ll Z_L$, destabilizing for $Z_S \sim Z_L$
- Osmotic stresses are virtually insignificant relative to elastic stresses
- Shear thinning favors demixing in solutions, mixing in monodisperse blends
- Effect of continuum polydispersity can be predicted from bi-disperse model results (at least for nearly monodisperse blends)
Thanks and Considerations

Advisors and Committee Members
- L. Gary Leal, Glenn Fredrickson
- Matt Helgeson, Hector Ceniceros

Funding Sources
- NSF
- UCSB

Colleagues
- Dr. Chandi Sasmal
- Dr. Doug Tree
- Dr. Nino Ruocco
- Peng Cheng
- Patrick Corona
- Mike Burroughs

Others
- My wife (Emily) and kids, for keeping me sane
- God, for making a world worth studying
Polymer Migration in Flow: Earliest Ideas

Streamline Curvature
Schafer, Laiken, and Zimm (1974)

Hydrodynamics
? (1974)

Thermodynamics
?(1974)

Migration Velocity