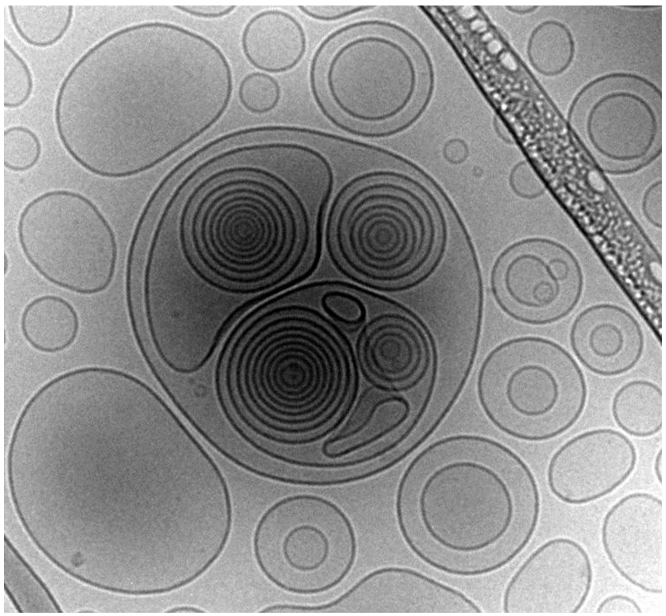
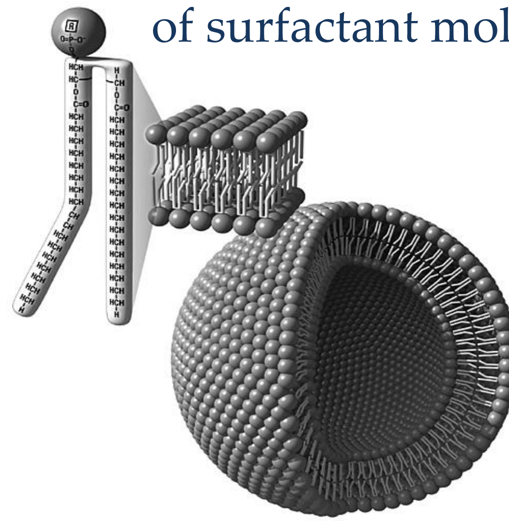
Microstructural Transformations in Concentrated, Charged Vesicle Suspensions



Cryo-TEM image

Vesicles: self-assembled aggregates of surfactant molecules



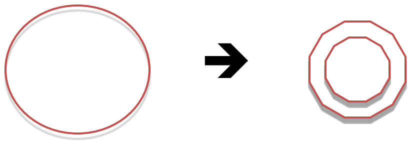
The lipid bilayer is deformable, but also highly permeable to small molecules like H_2O, but impermeable to salts or larger molecules

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



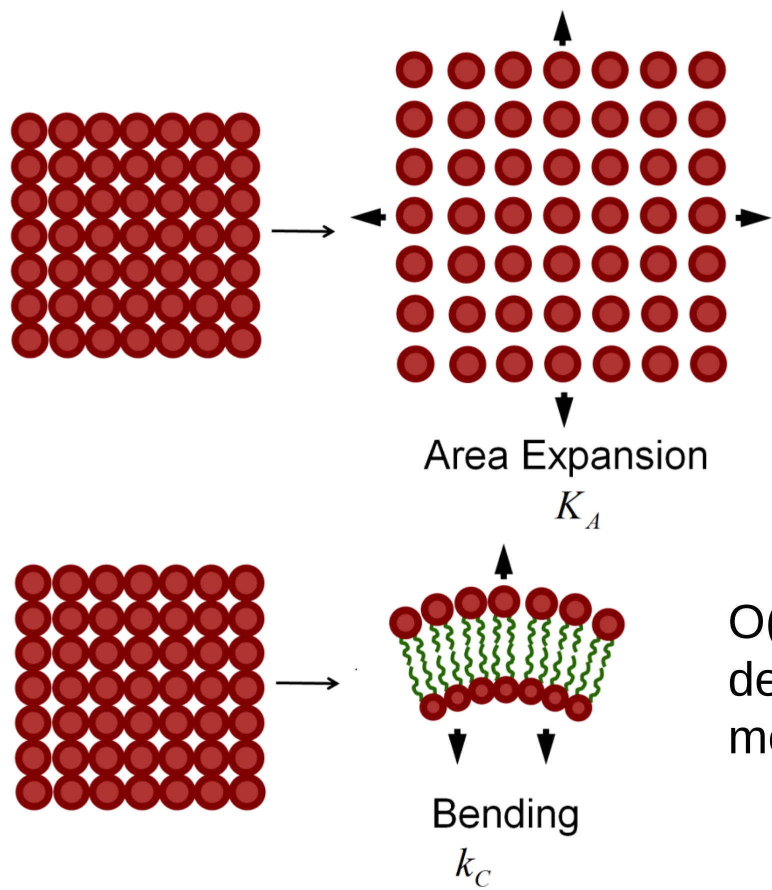
2) If we force a vesicle to deform too quickly, the tension in the membrane may exceed rupture, and the vesicle will burst apart into bilayer fragments, and will reform into a structure that may be very different from its initial structure, though with the same bilayer surface area (multilamellar into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

Key Properties for Suspension Rheology

Bilayer mechanical properties

Volume Fraction

Modes of Membrane Deformation



$K_A >> k_c$
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

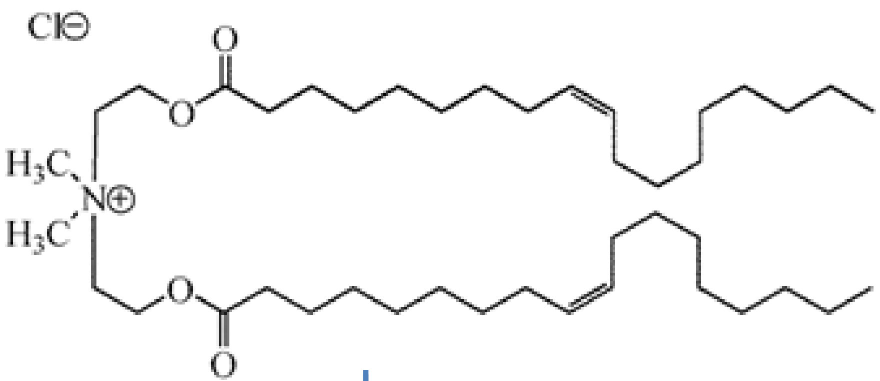
From PhD Thesis of Mansi Seth

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

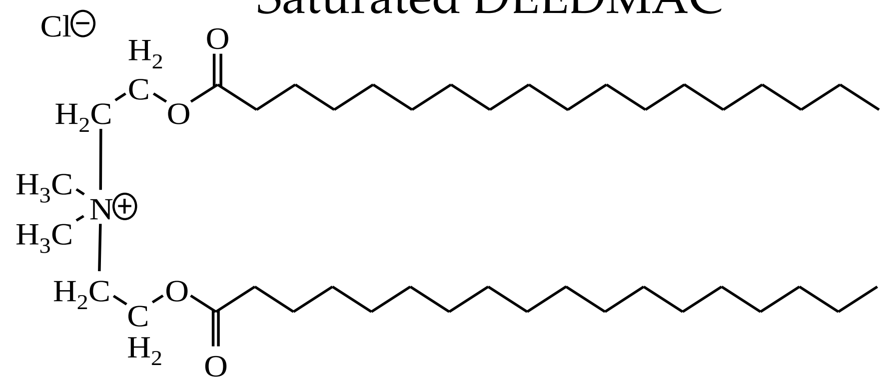
2. Instantaneous formation of cationic vesicle 'gels' (multilamellar to unilamellar transition by extrusion; with an increase in volume fraction to a jammed material)

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(7-8kT) even at room temperature

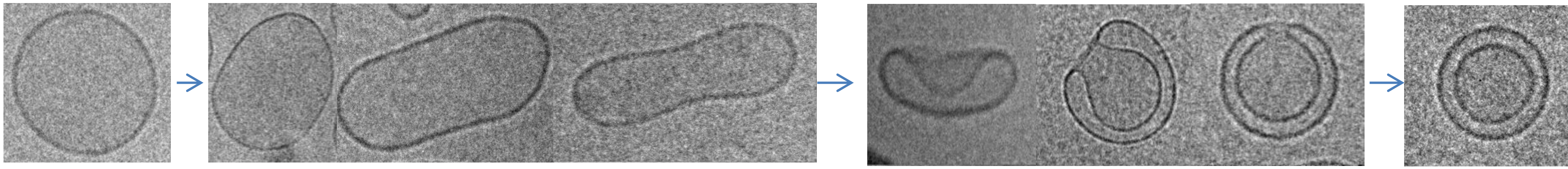
More closely packed,
Much more complex phase behavior in the range from 20-50C (in a fluid state above 55C, in “solid” or gel states below 55C)

1. Spontaneous unilamellar to bilamellar transformations in charged vesicle suspensions: The crowding hypothesis

Ref:. "Origins of Microstructural Transformations in Charged Vesicle Suspensions: The Crowding Hypothesis", M. Seth, A. Ramachandran, L.G. Leal and B.P. Murch, *Langmuir* **30,** 10176-10187 (2014).

Microstructural transformations can affect suspension rheology

Deflation-induced curling of unilamellar vesicles



Unilamellar Spherical (Singlet) → Unilamellar Deflated → Curled Up Stomatocyte/Invagination → Doublet

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

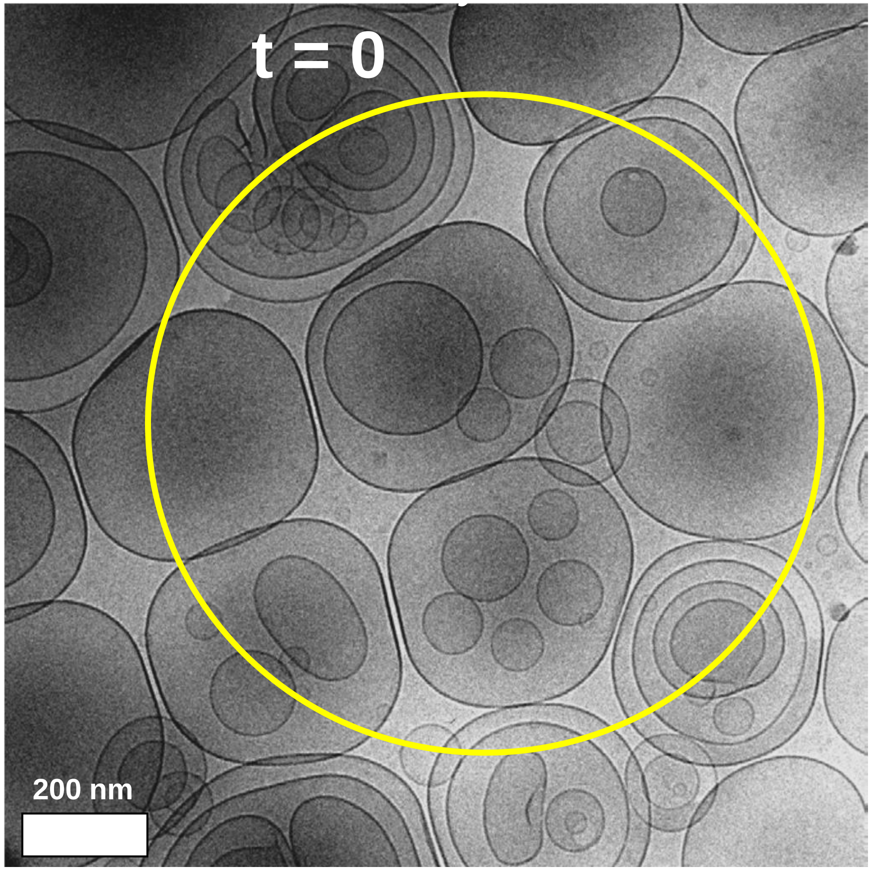
The transformation can be forced:

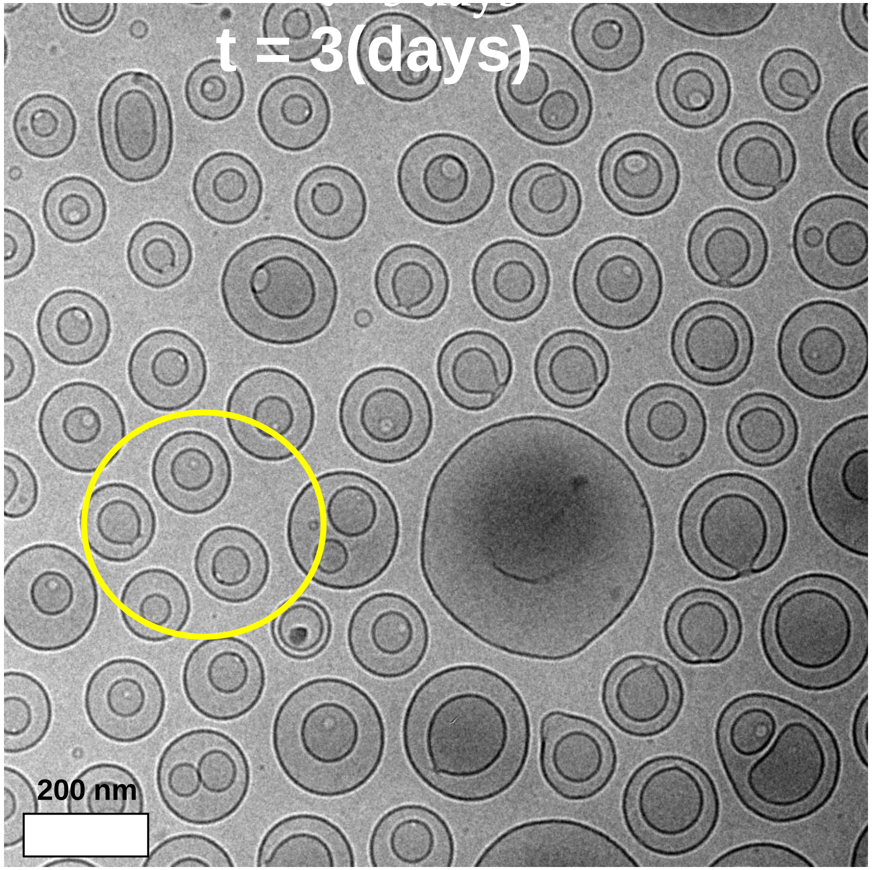
1. Addition of hyperosmotic salt solution [Saveyn et al., (2007)]
   - Leads to loss of water from the vesicle, which and a deflated configuration that is susceptible to curling instability and formation of a doublet

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

However, our studies of cationic, <u>unsaturated</u> DEEDMAC show that a transformation from unilamellar to bilamellar (with decreased ϕ) can also occur spontaneously

Spontaneous microstructural transformations of charged vesicle suspensions



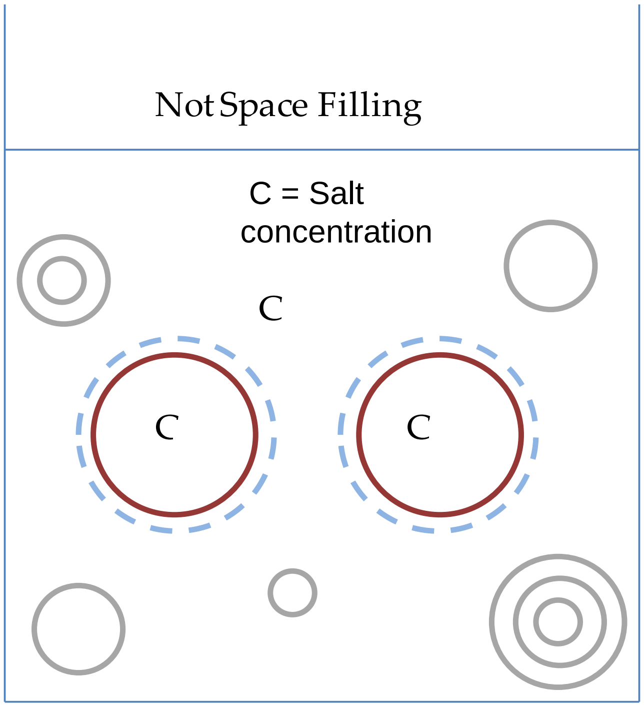


What is the driving force for spontaneous deflation, and subsequent transitions in charged vesicle suspensions?

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 φ_{eff})



Non-interacting double layers

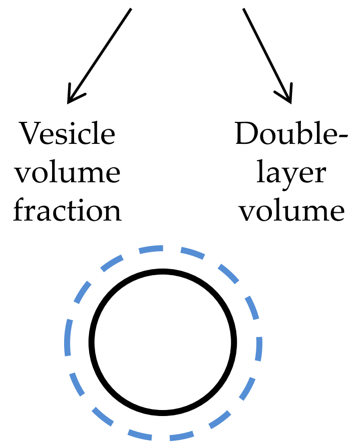
$$\pi_{in} = Ck_BTN_{av} \qquad \pi_{out} = Ck_BTN_{av}$$

$$\pi_{in} = \pi_{out}$$

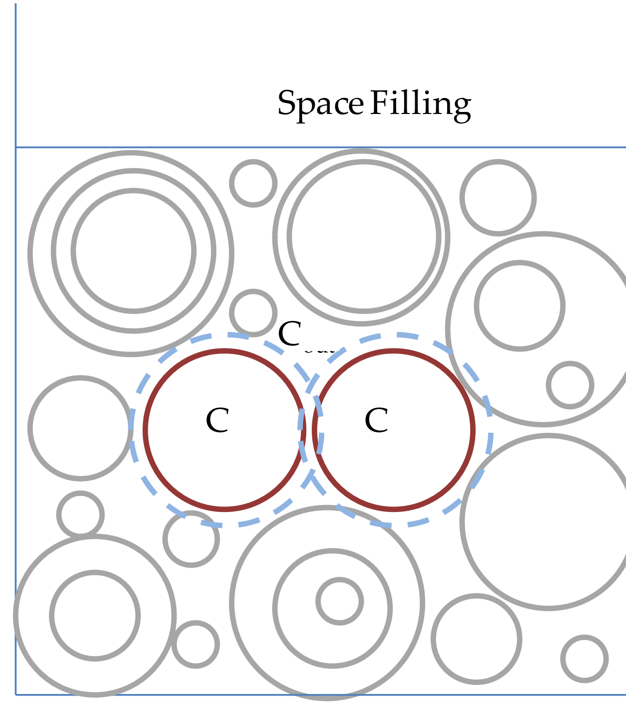
Osmotic pressure balance satisfied upon vesicle formation

Effective volume fraction

$$\phi_{eff} = \phi + \delta\phi$$



Concentrated Suspension (High φ_{eff})



Interacting double layers

$$\pi_{in} = Ck_BTN_{av} \qquad \pi_{out} = Ck_BTN_{av} + \pi_{elec}$$

$$\pi_{in} \neq \pi_{out}$$

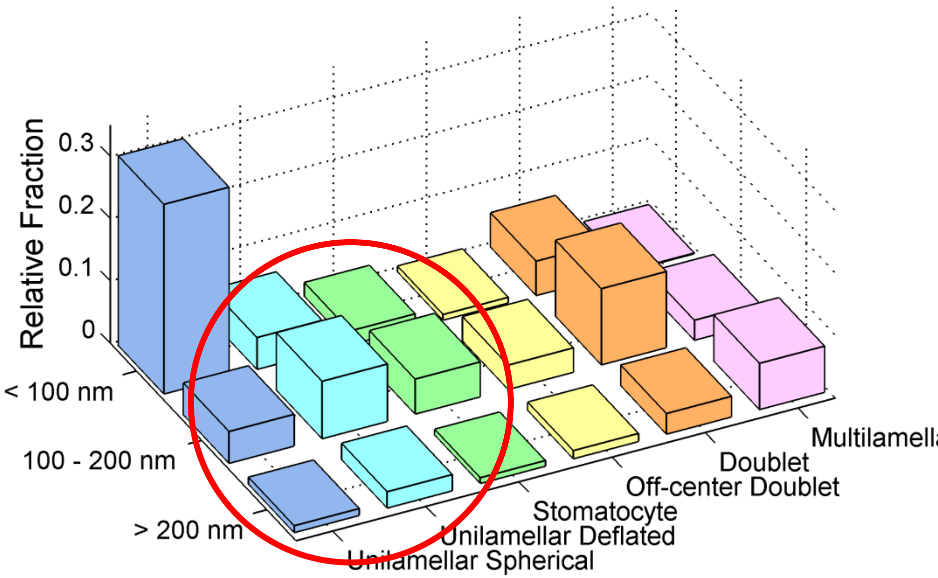
Vesicles can deflate by losing water until $\pi_{in} = \pi_{out}$ (but this is opposed by bending rigidity and tends not to happen for small vesicles(10s of nm); first step in transition to bilamellar vesicles

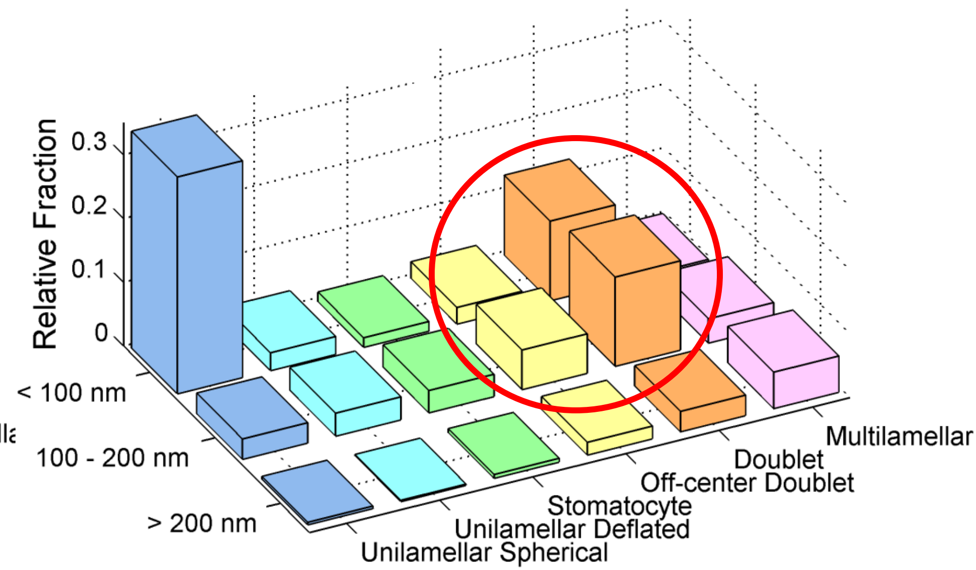
CryoTEM Imaging Summary

35 mg/ml unsaturated DEEDMAC

4.5 mM $CaCl_2$

t = 0 days **t = 3 days**





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

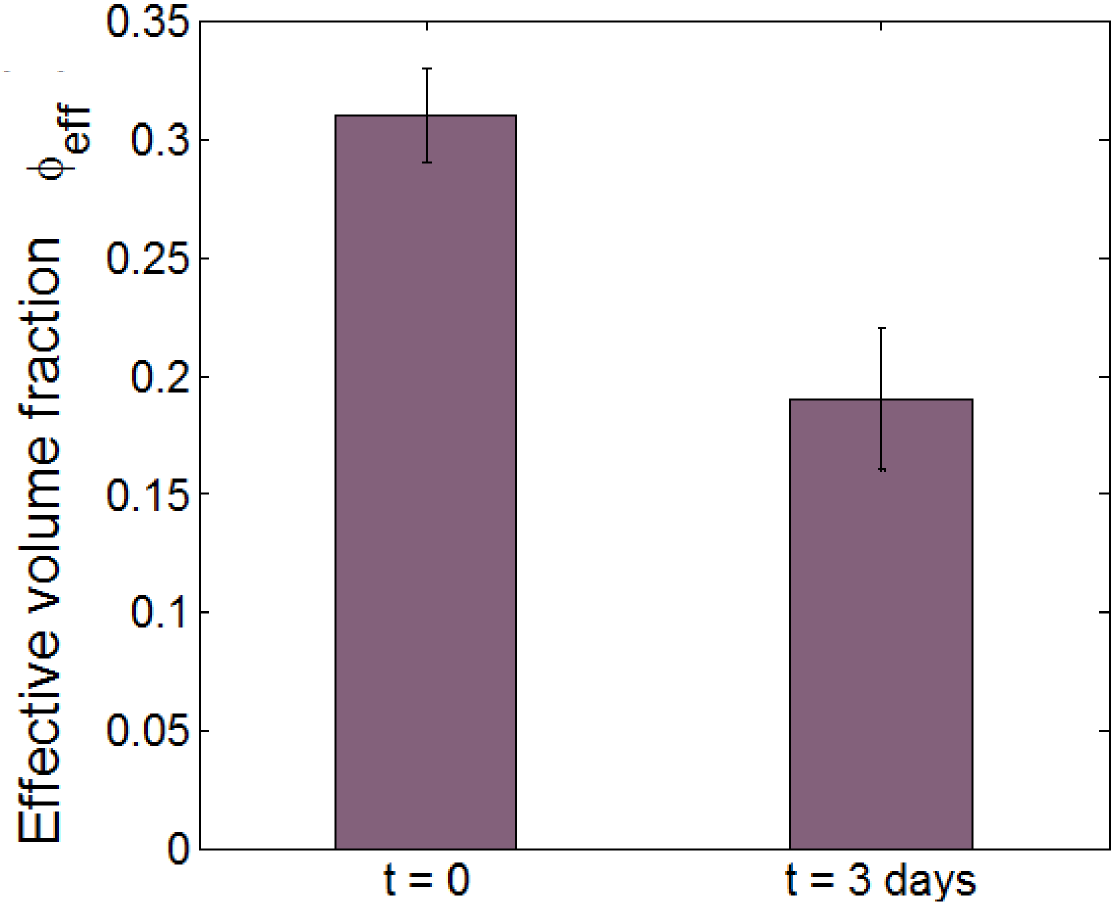
At t = 3 days, there are almost no unilamellar spherical/deflated vesicles – Increase in the number of <100 nm doublets

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

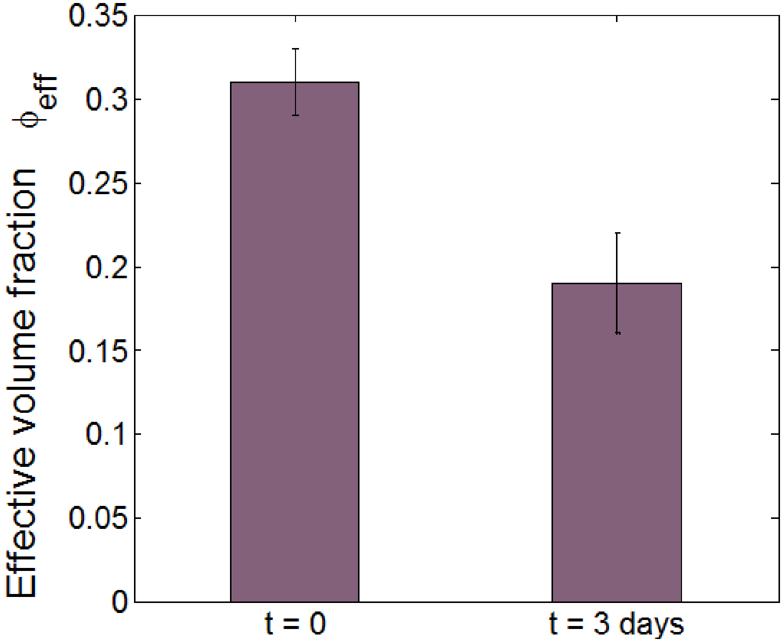
* Seth, Ramachandran and Leal, *Langmuir,* **25,** 15169 (2010)

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

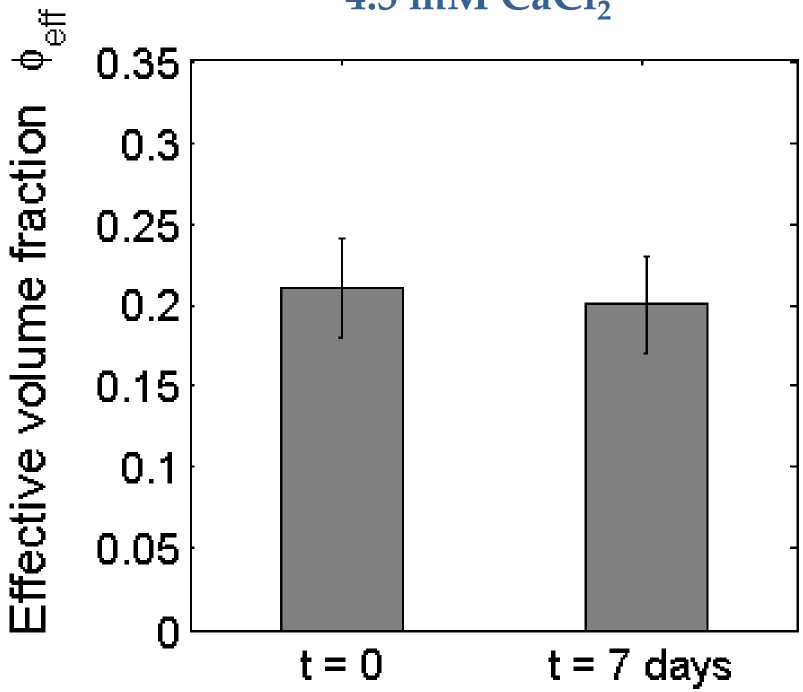
35 mg/ml unsaturated DEEDMAC

4.5 mM $CaCl_2$



22 mg/ml unsaturated DEEDMAC

4.5 mM $CaCl_2$



Volume fraction unchanged after 7 days

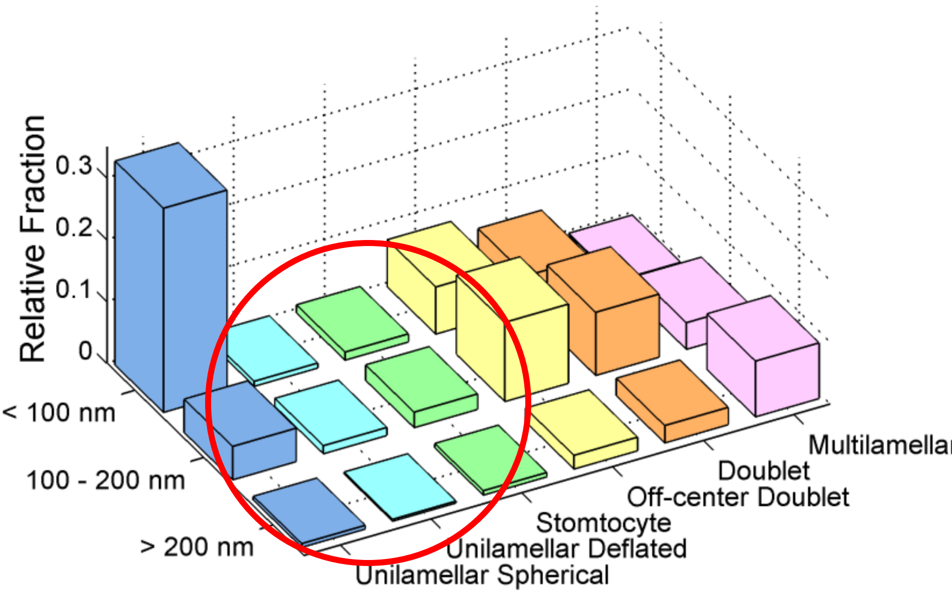
Effect of lowering the surfactant concentration: decrease ϕ

CryoTEM Imaging Summary

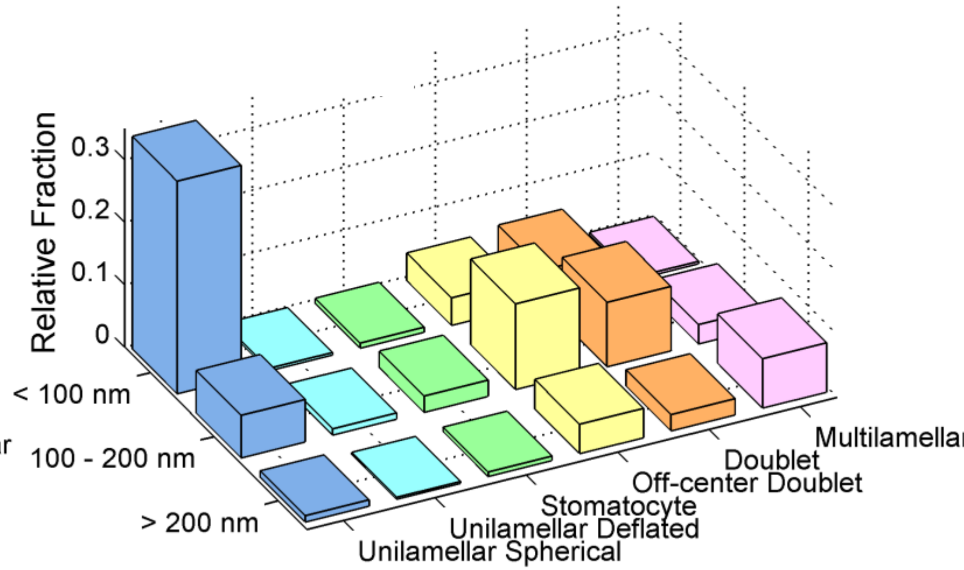
22 mg/ml unsaturated DEEDMAC

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!

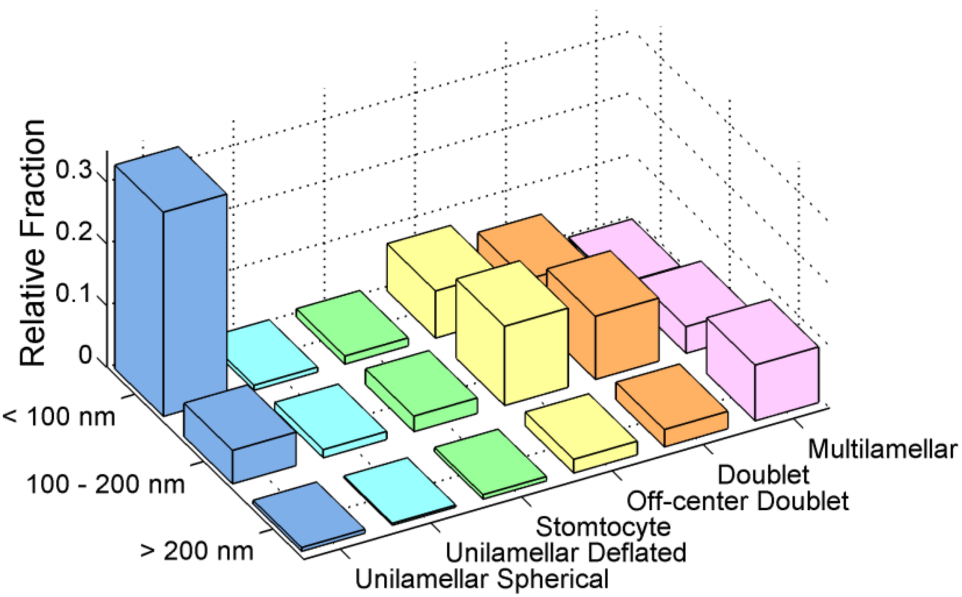
Long time effects?

CryoTEM Imaging Summary

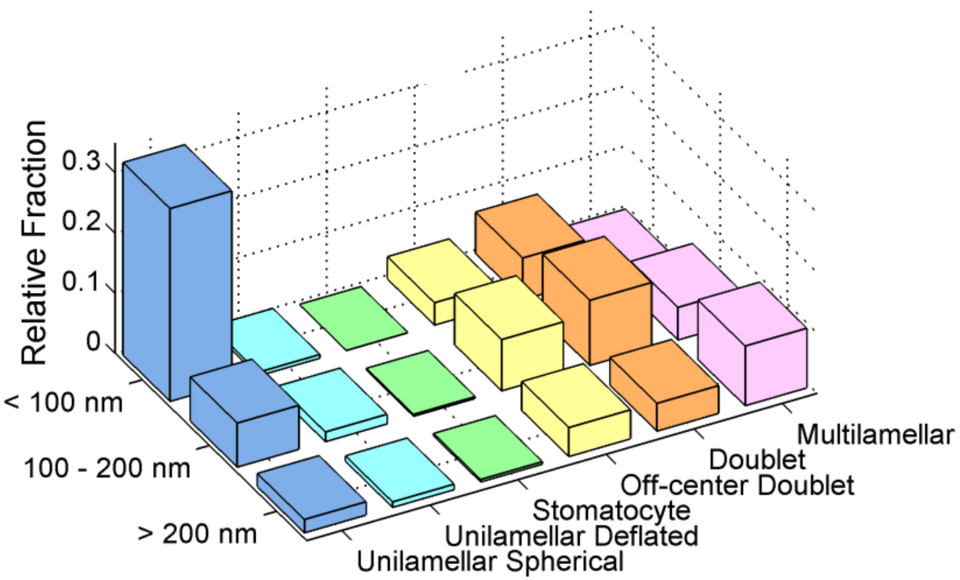
22 mg/ml unsaturated DEEDMAC

4.5 mM $CaCl_2$

t = 0 days



t = 1.5 months



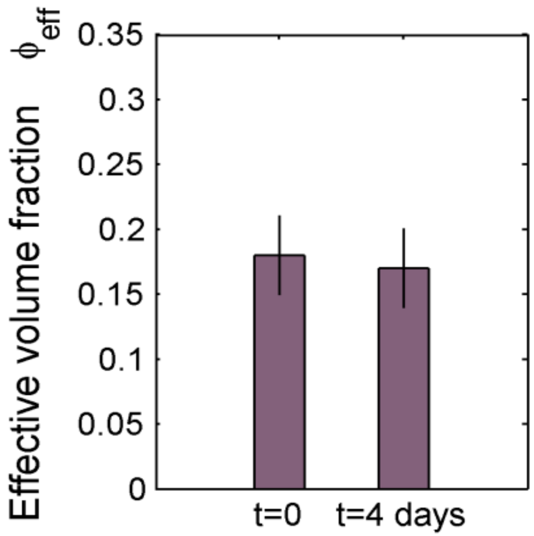
Microstructure is essentially unchanged over long times ~ O(months)

Effect of increasing the salt concentration

35 mg/ml unsaturated DEEDMAC

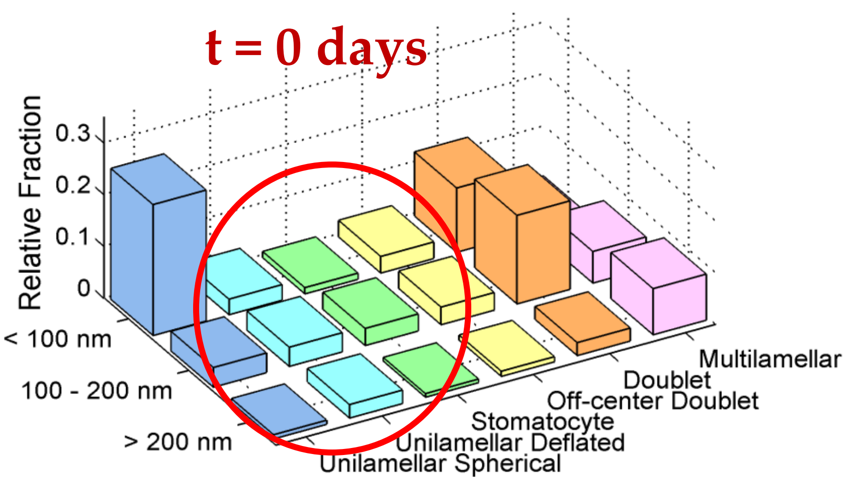
27 mM $CaCl_2$

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



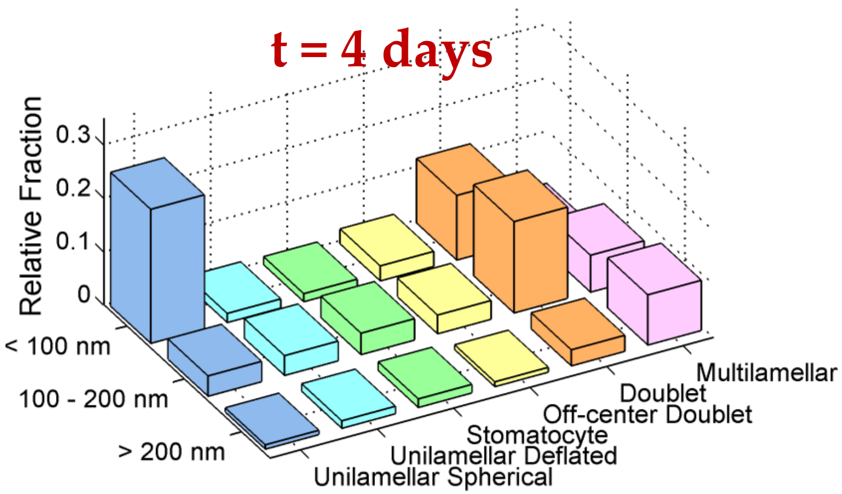
Virtually no transition of suspension microstructure and volume fraction

t = 0 days



Fewer unilamellar deflated/curled up structures present at t=0

t = 4 days

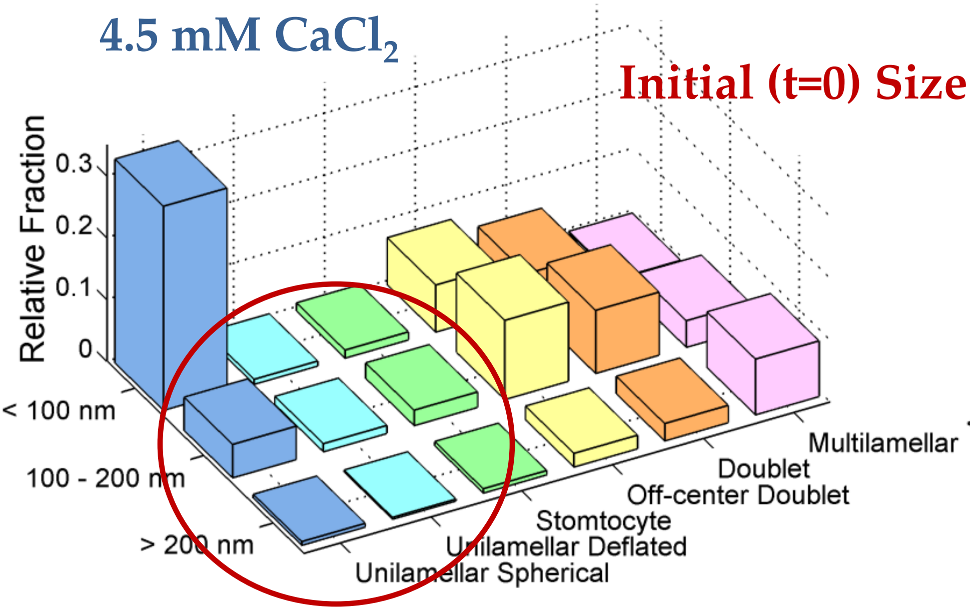


Effect of decreasing the salt concentration

22 mg/ml

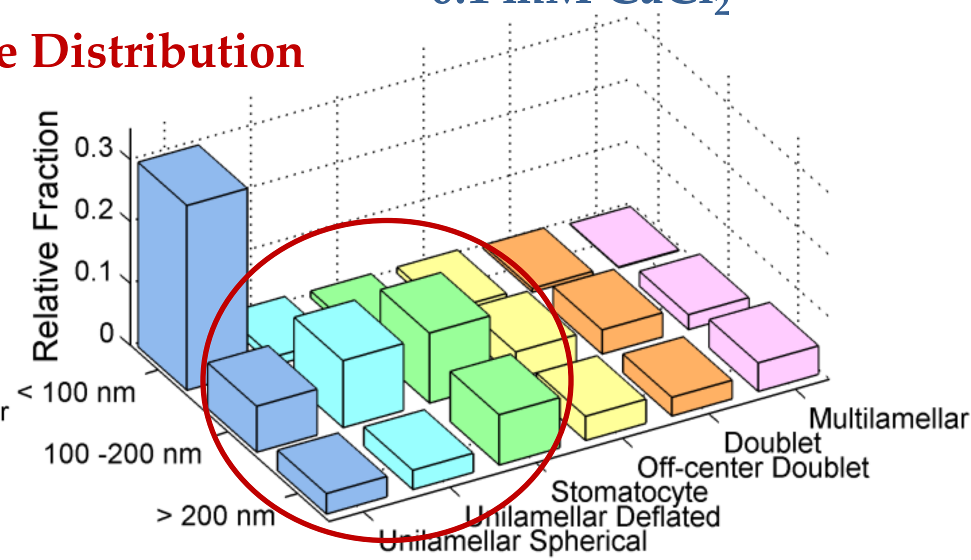
Initial (t=0) Size Distribution

4.5 mM $CaCl_2$



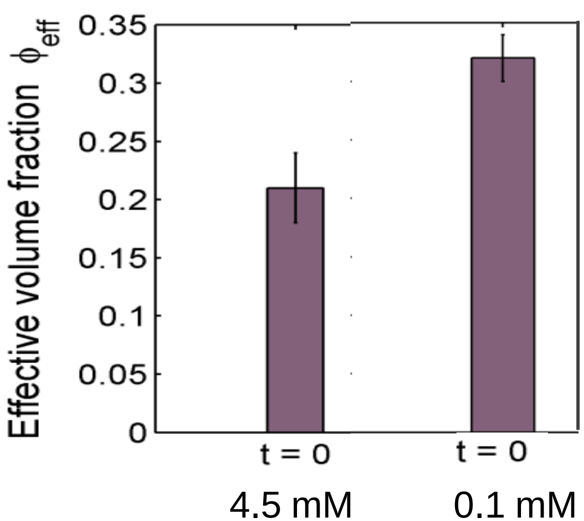
Almost no unilamellar deflated/stomatocyte vesicles

0.1 mM $CaCl_2$



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

Lowering salt concentration increases electrostatic repulsion between vesicles, and increases the bending modulus by 2x



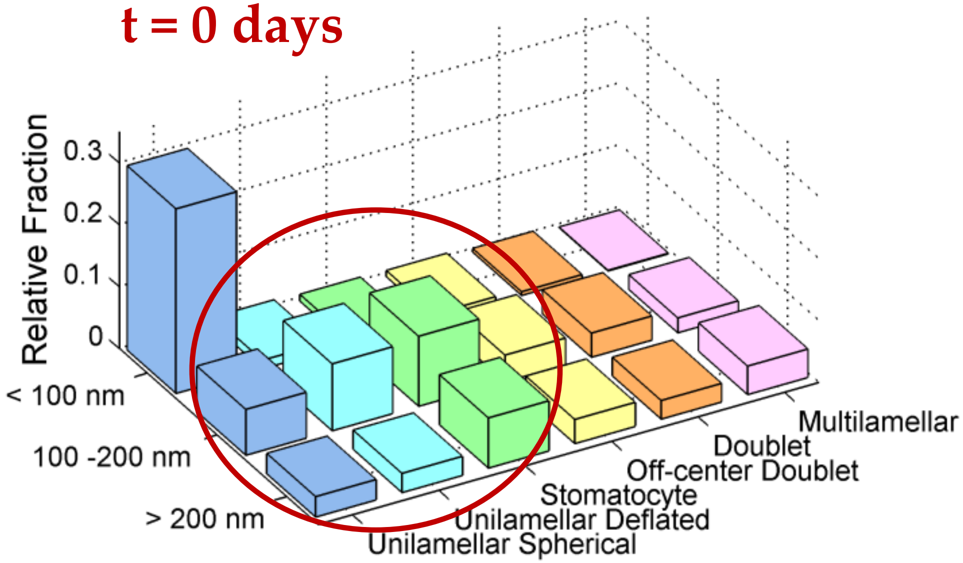
Initial effective volume fraction increases

Effect of lowering the salt concentration

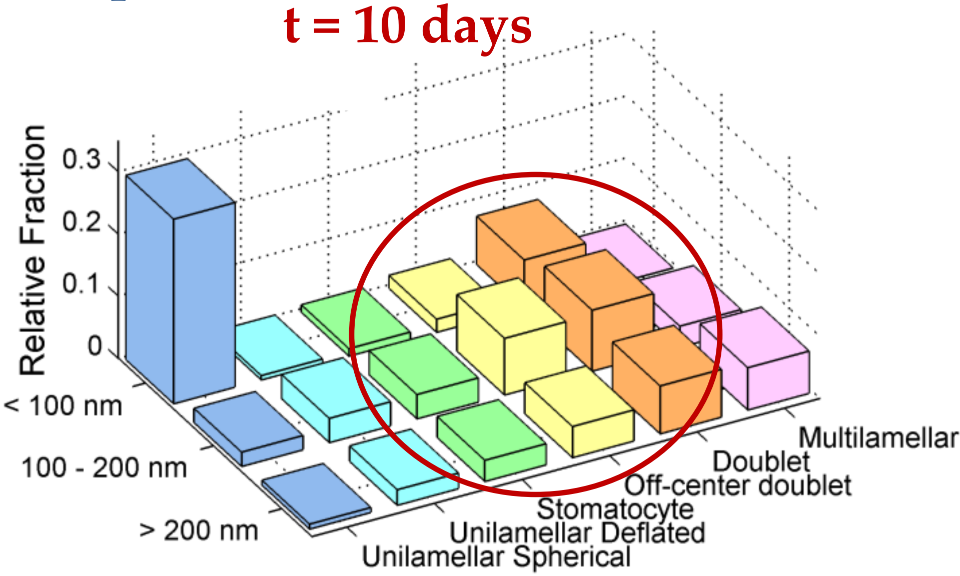
22 mg/mL

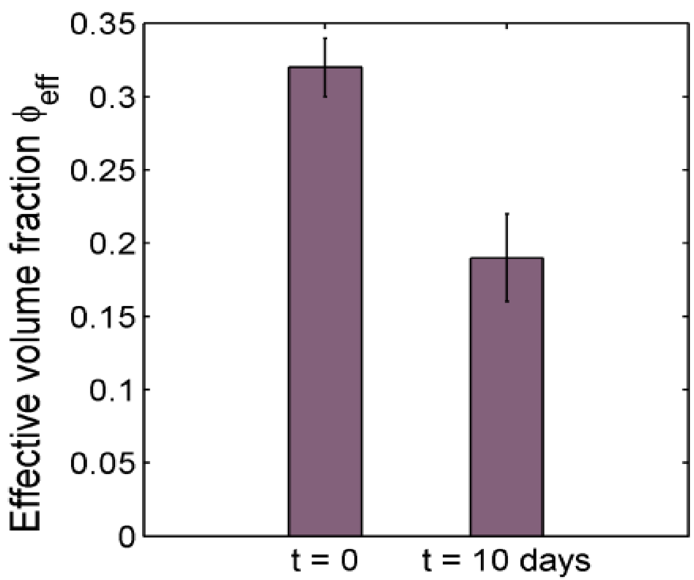
0.1 mM $CaCl_2$

t = 0 days



t = 10 days



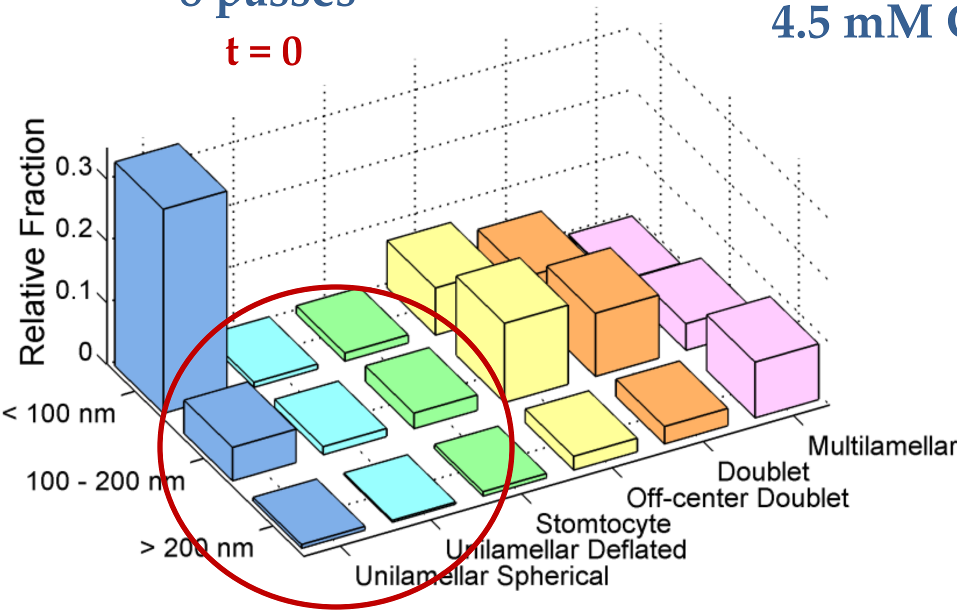


Effect of number of extrusion passes

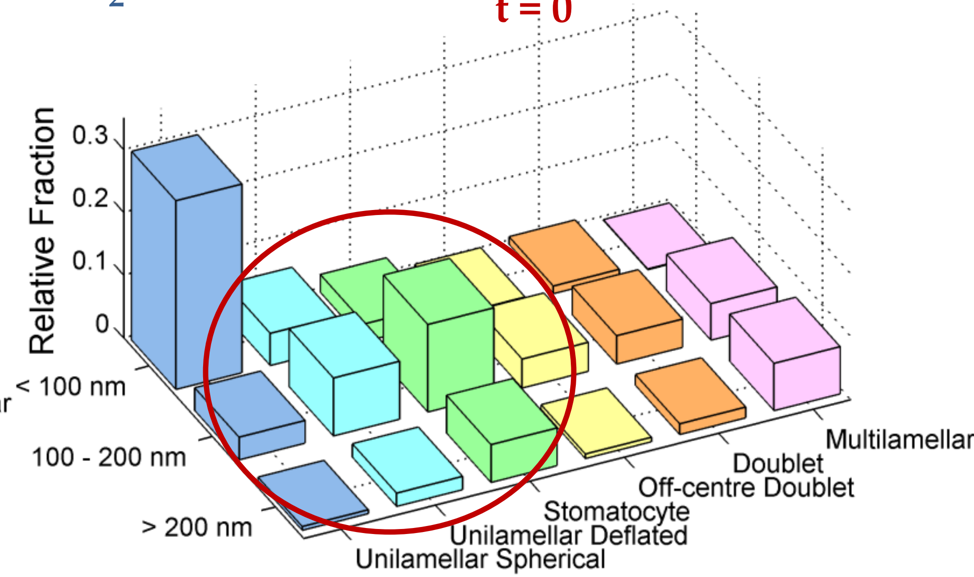
22 mg/ml

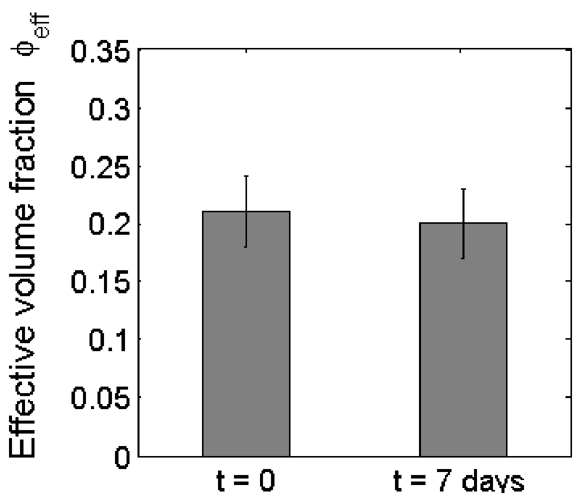
4.5 mM $CaCl_2$

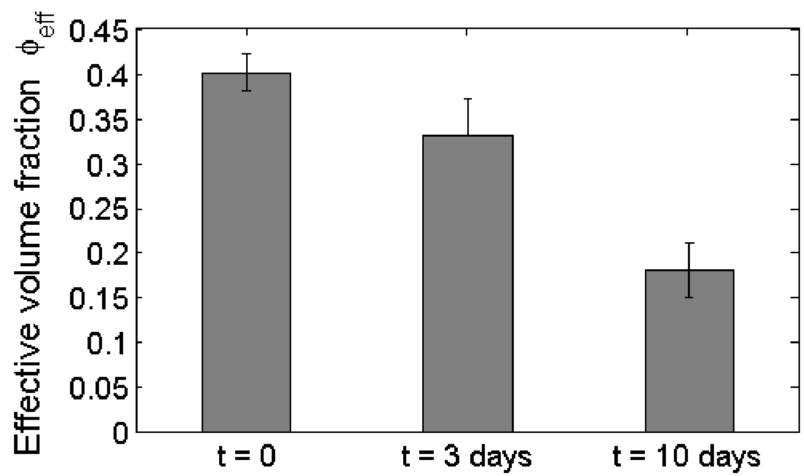
8 passes — t = 0



4 passes — t = 0







By reducing the number of extrusion passes to 4, suspension has higher initial volume fraction, undergoes 'crowding' transformation

CONCLUDE

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

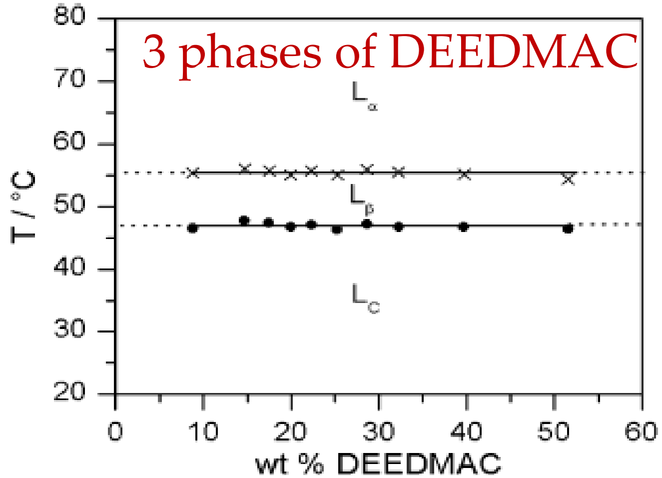
A consequence of preserving area instead of volume

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)

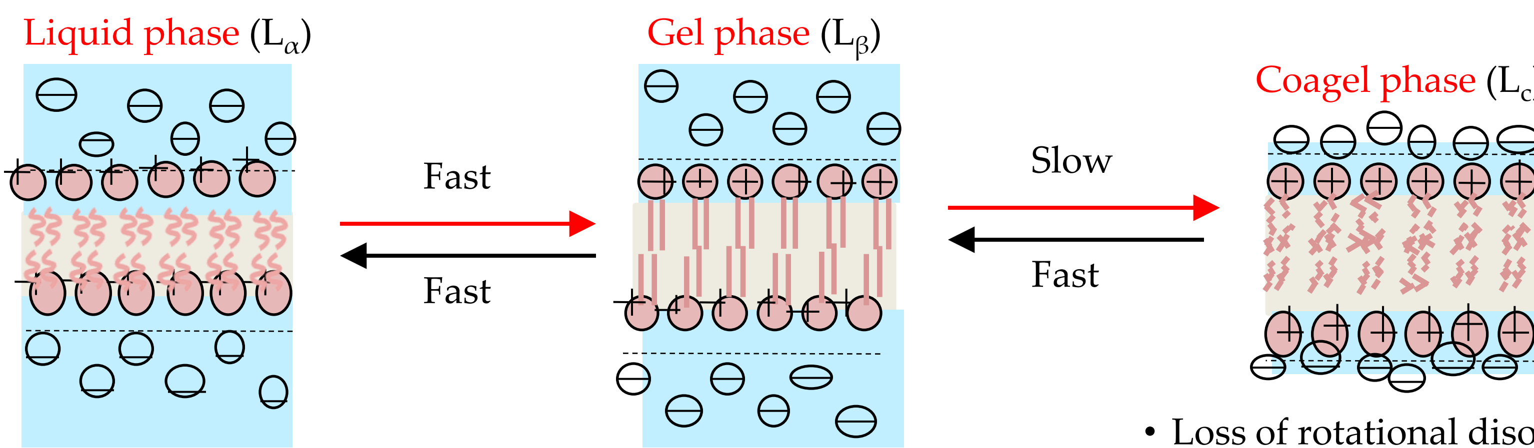
2. Instantaneous formation of 'jammed' suspensions via extrusion of a suspension of the saturated DEEDMAC vesicles

Ref: "Rheological studies of thermotropic phase transitions in cationic vesicle suspensions: Instantaneous 'jamming' and aging behavior", Mansi Seth and L. Gary Leal, *Journal of Rheology,* **58**, 1619 (2014).

Thermotropic phase behavior of saturated DEEDMAC bilayer



Another lever
to control rheology?



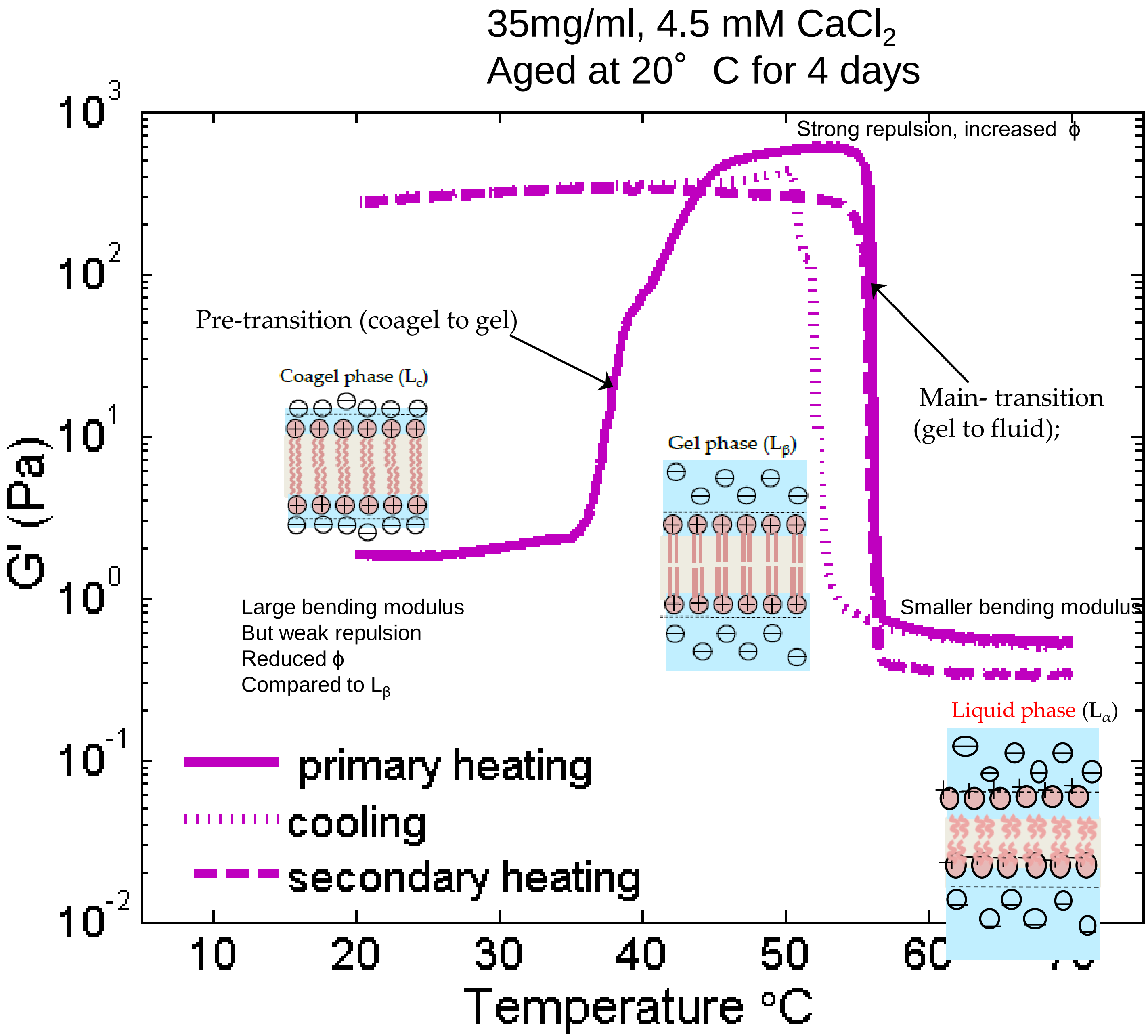
- Translation and flip-flop motions occur, chain conformational disorder
- Hydrated head-group

- 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 x10-15,and decreased permeability

- 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_β)
- Smaller effective volume fraction

[Saveyn et.al., *Soft Matter* (2009), Wu et. al, *Langmuir*, (2011), Tsuchiya et. al., *J.Phys. Chem*. (1994)]

Rheology of unextruded DEEDMAC suspensions

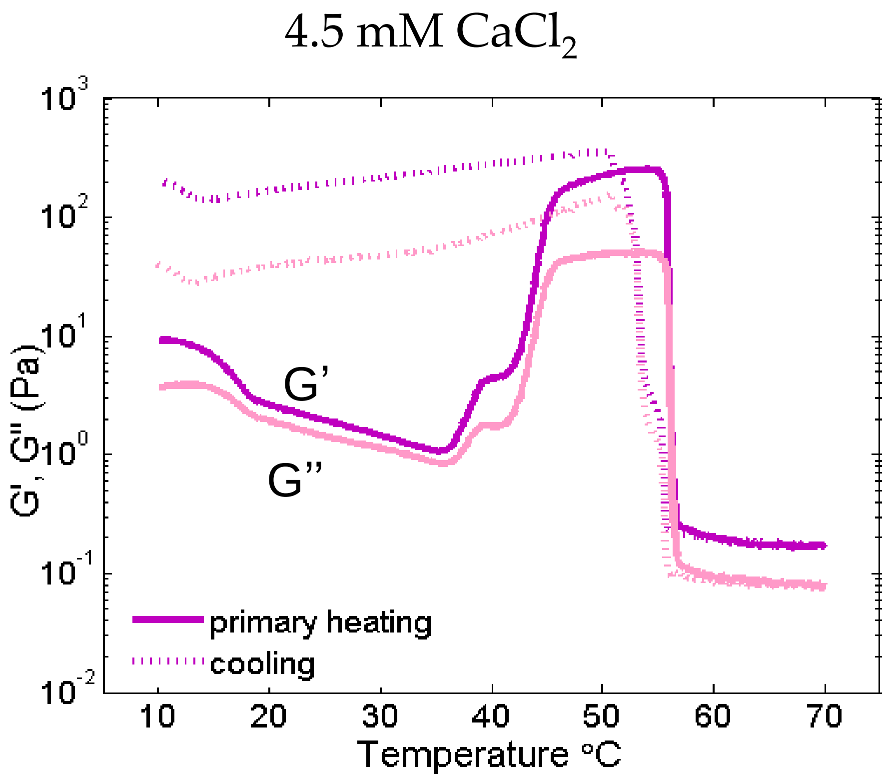


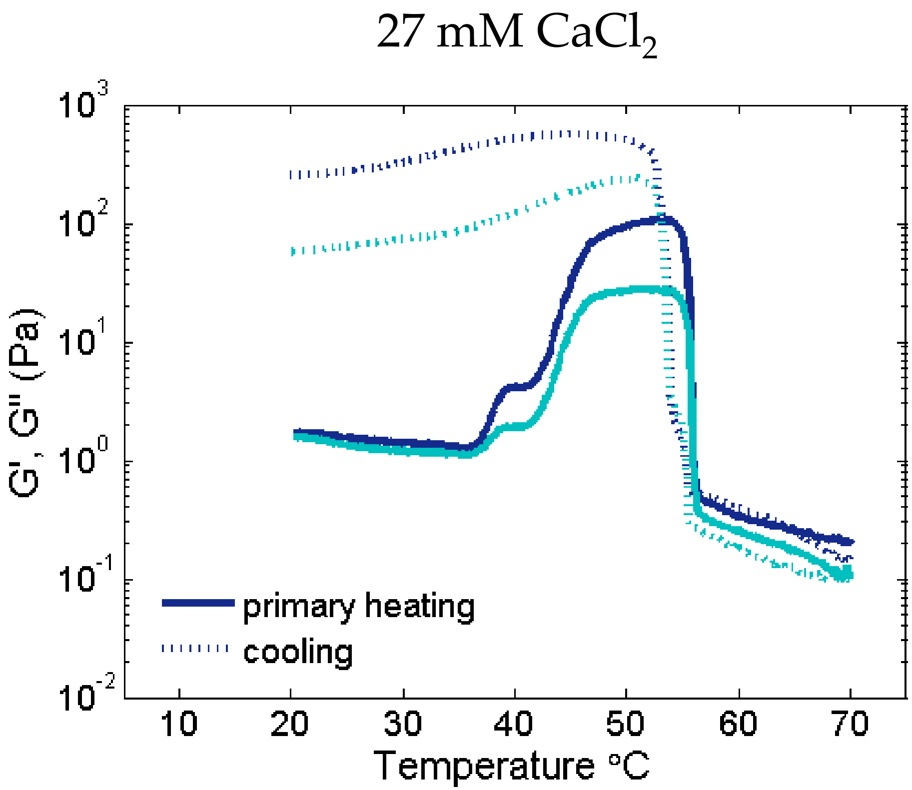
Small amplitude oscillatory shear at 2pi rad/s (1 Hz), With temp change at 1° C/min

Storage modulus

(Loss Modulus is similar but smaller)

Rheology of unextruded DEEDMAC suspensions





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

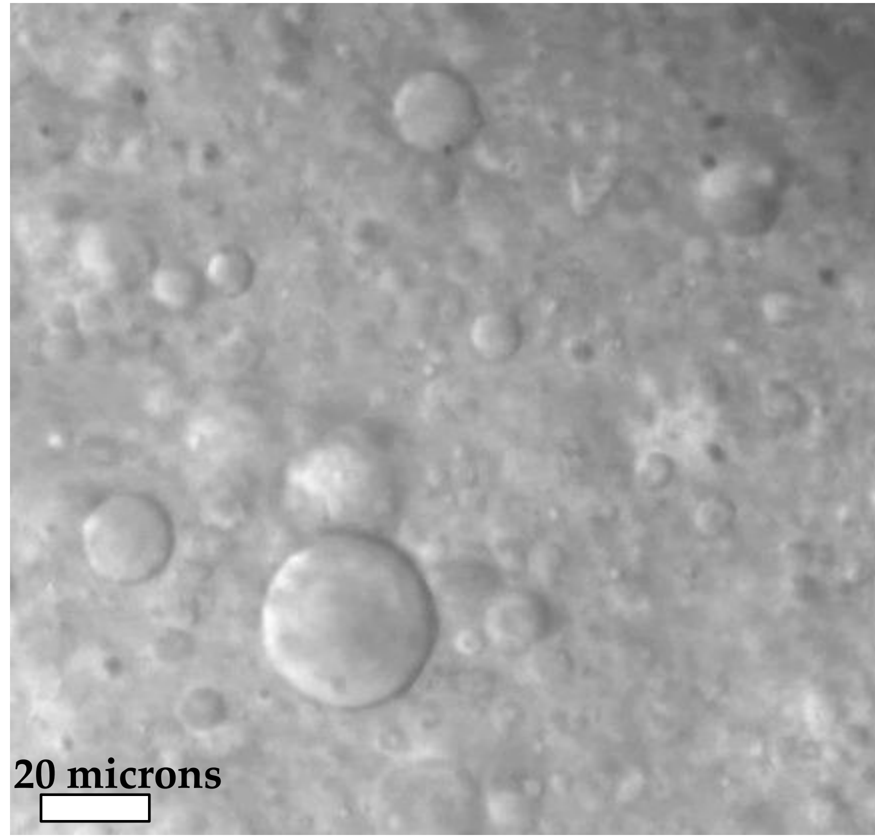
Note: Control of rheology via temperature, and salt levels for a given amount of surfactant

Un-Extruded Sample

Actual suspension

Liquid-like consistency

Phase contrast microscopy image



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

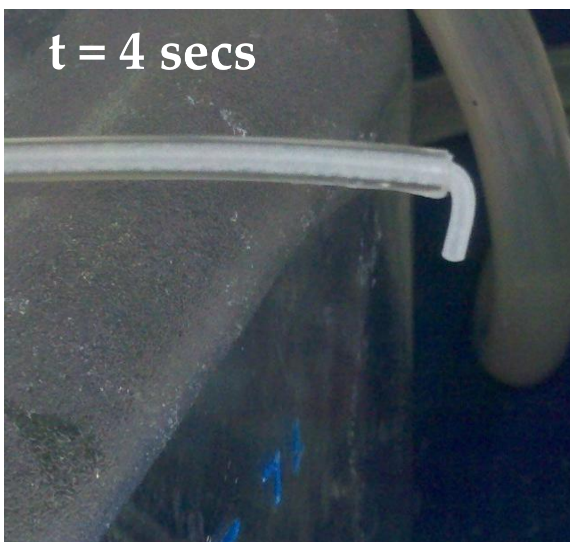
Effect of extrusion – Formation of Vesicle Gel

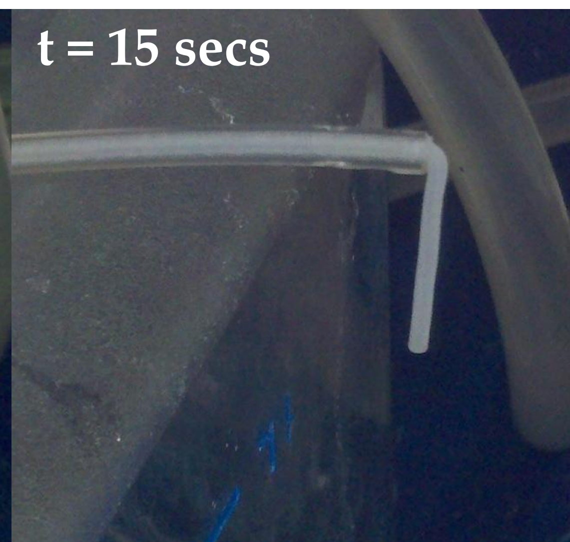
35mg/ml (50 mM) total surfactant concentration

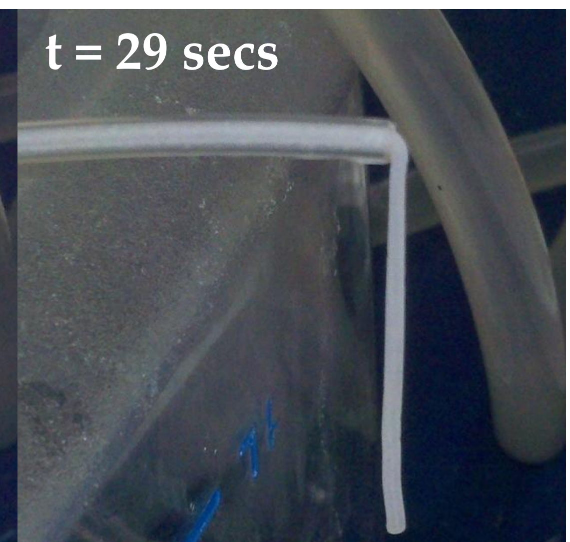
Vesicle Suspension

Extrude through
800nm pores
60° C
→
Cools to room
temperature at
extruder outlet

Instantaneous 'Gel' Formation

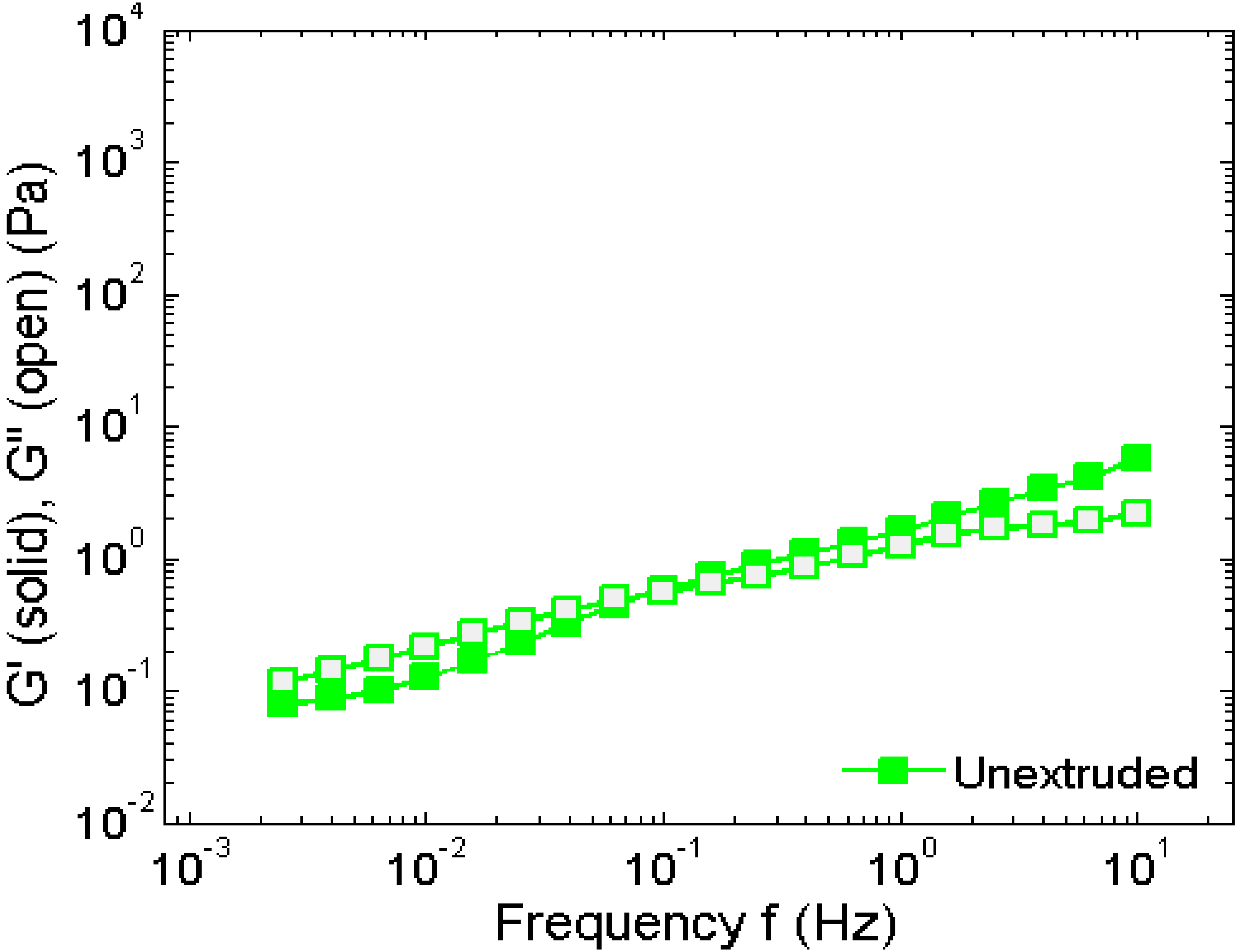






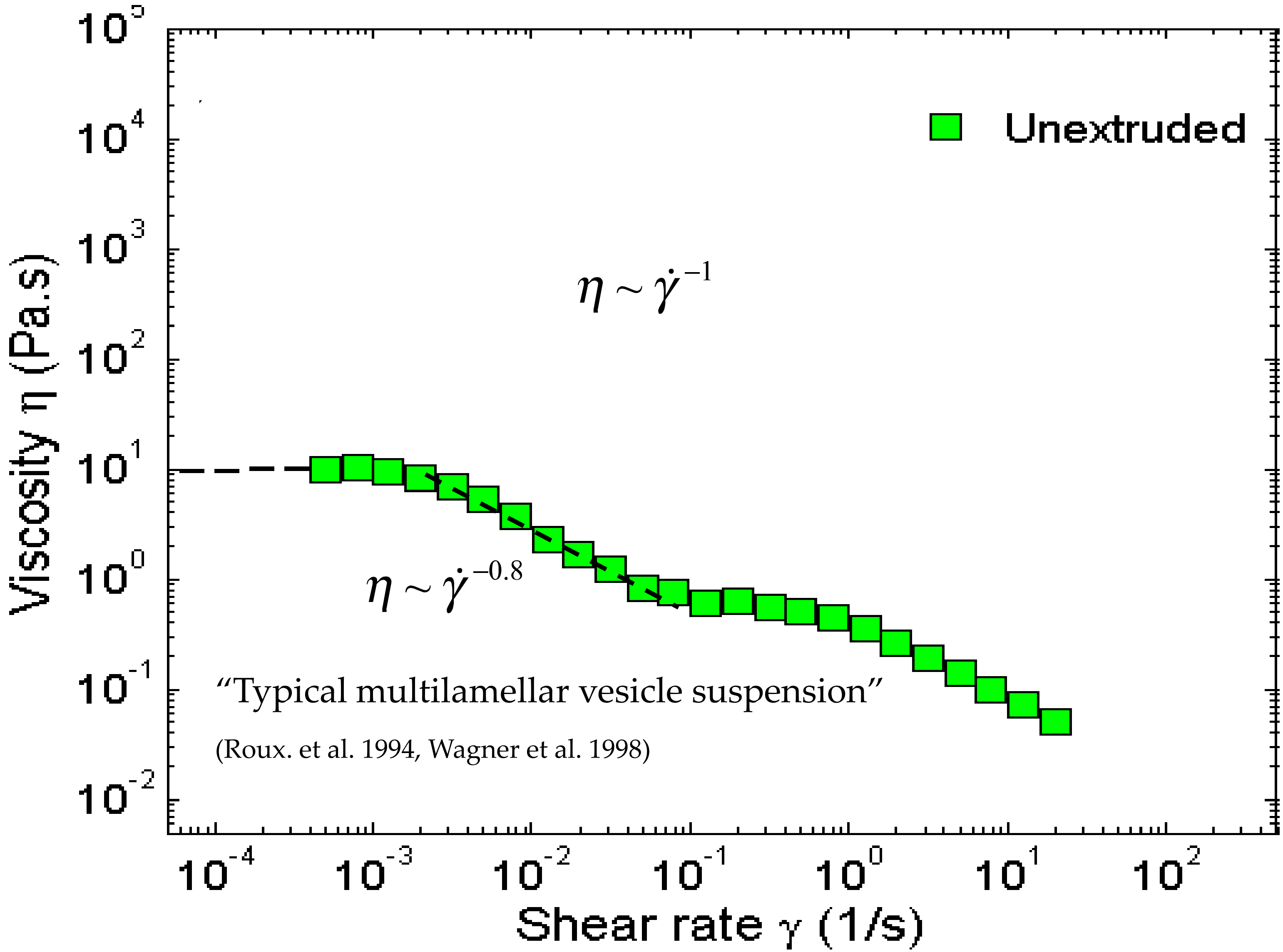
Note **: Original (pre-extruded) suspension retains (low) viscosity upon cooling to room temperature**

Effect of extrusion on oscillatory rheology(20C)



G′,G′′ increase by 3-4 orders of magnitude upon extrusion

Effect of extrusion on ‘steady’ shear rheology



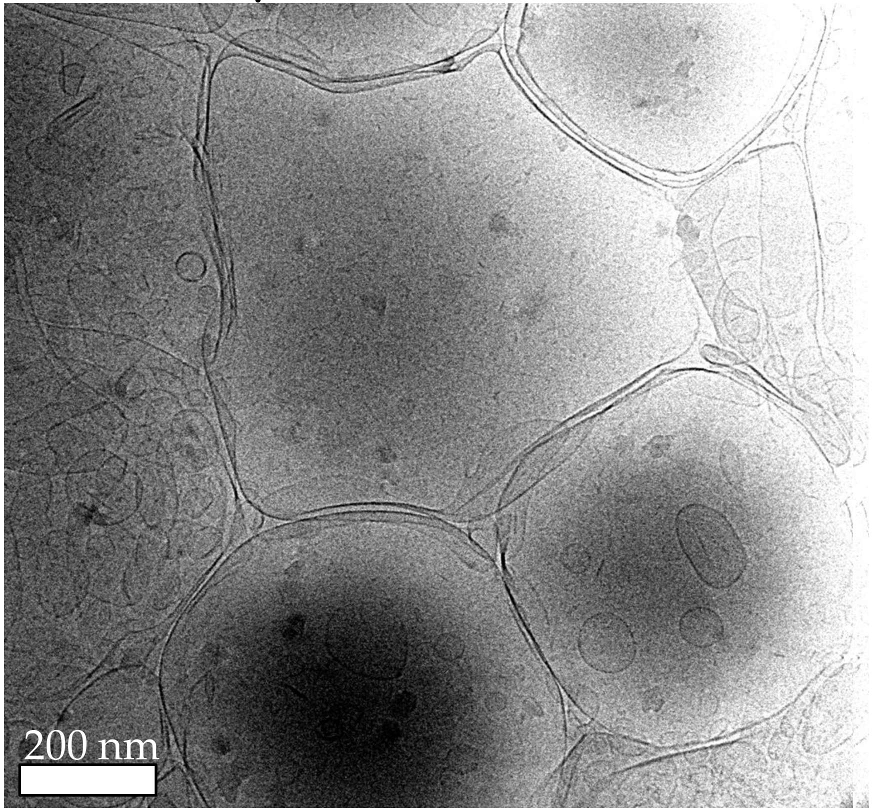
Instantaneous formation of a yield stress material

Extruded Sample - Microstructure

Actual suspension

Solid–like

Cryo-TEM



Large, 400nm – 600nm size vesicles

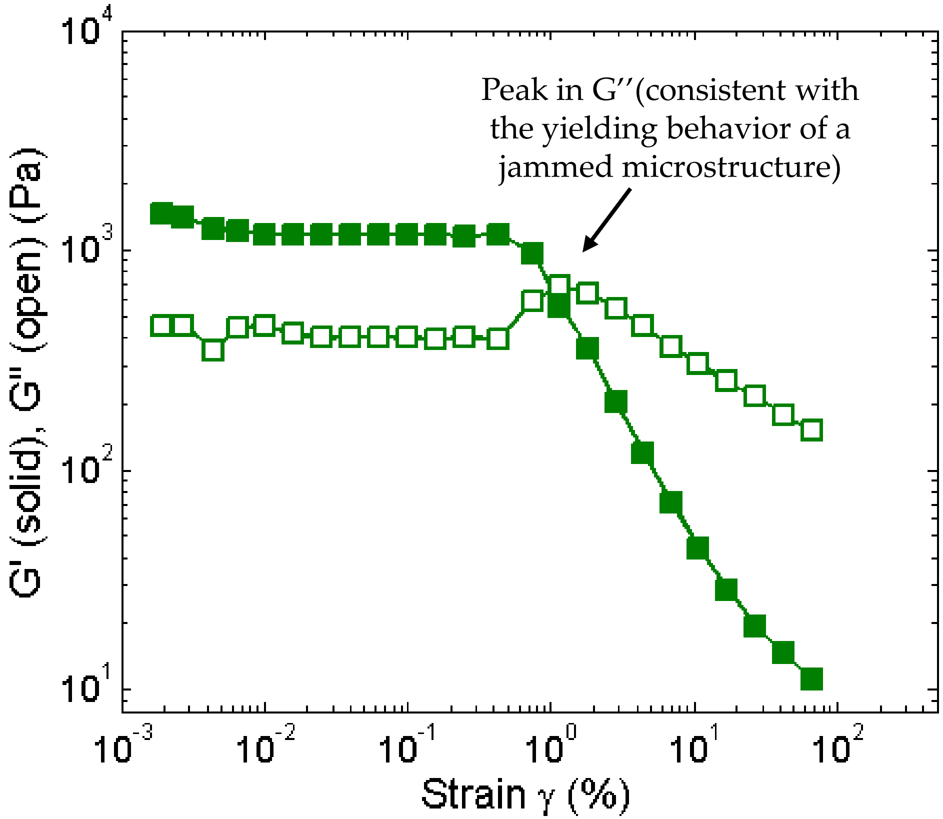
But many smaller monodisperse vesicles too

Extremely ‘jammed’ microstructure

Reminiscent of compressed emulsions/foams

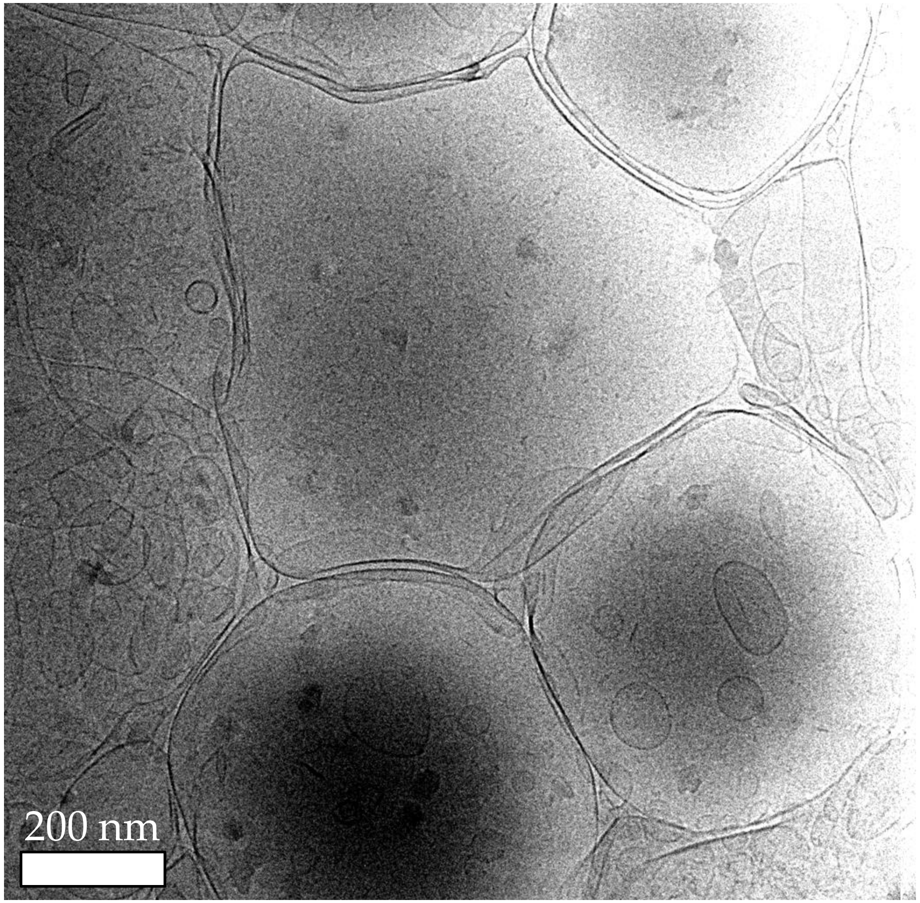
Extruded Sample - Microstructure

Rheology - strain amplitude sweep



Characteristic of soft, glassy materials

Cryo-TEM image



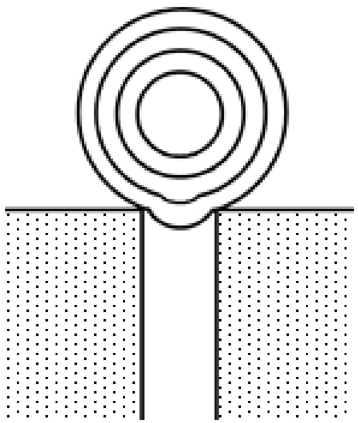
Large, 400nm – 600nm size vesicles

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



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

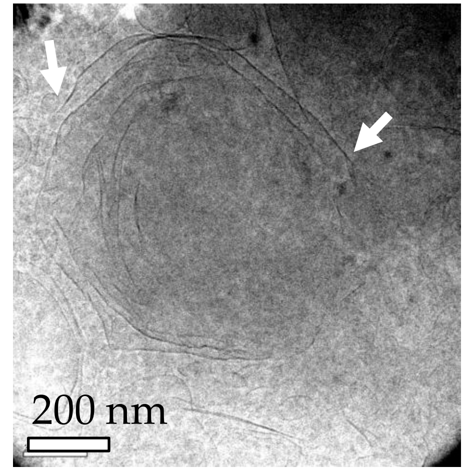
For $\Delta P = 200\,psi$

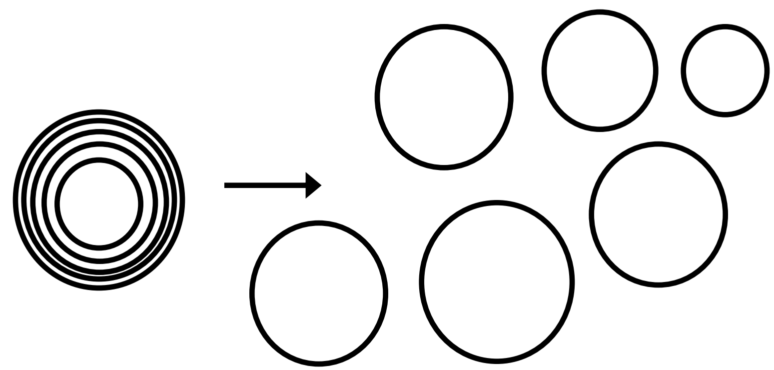
$2R_0 = 1\ \mu m$

$2R_p = 800\ nm, \qquad \tau = 1379\,mN/m$

$$\tau > \tau_{rup} \sim O(10\,mN/m)$$

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



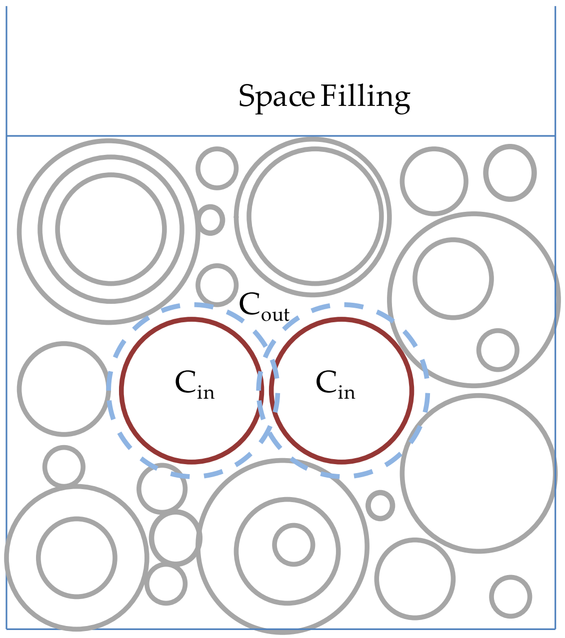


Reduces lamellarity and size but increases number density of vesicles

Extrusion leads to the formation of a ‘crowded’ suspension;
Another consequence of preserving bilayer surface area instead of vesicle volume

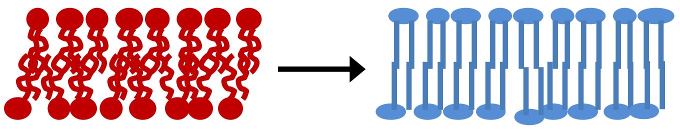
Effect of increasing bending rigidity

Post-extrusion



As temperature drops below T_m, membrane solidifies

Bending rigidity increases

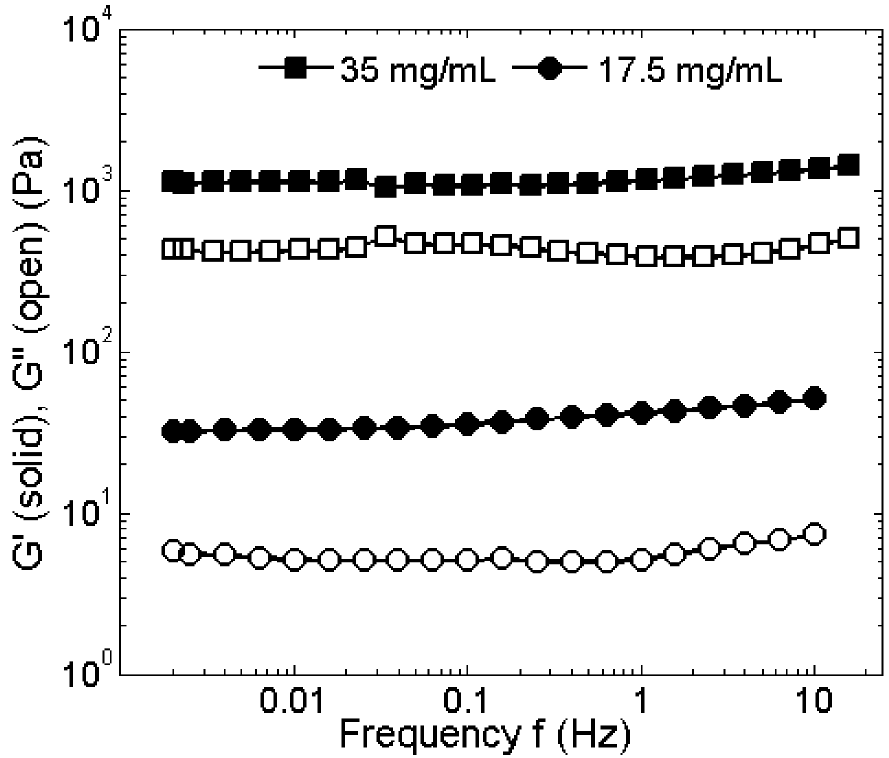


At higher bending rigidity, larger vesicles will resist deflation due to bending costs and the suspension is trapped in the crowded state (no relaxation to reduced volume fraction)

↓

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) voesicles.

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 56C 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

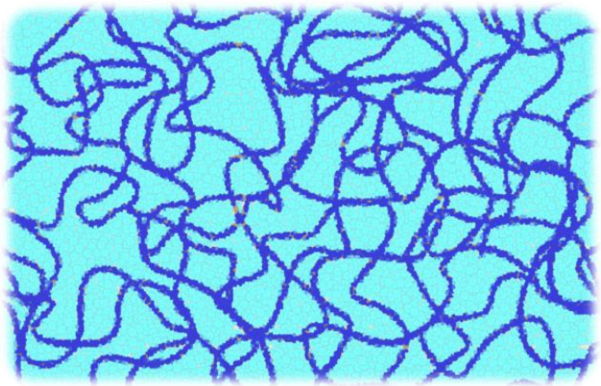
Part 2: Flow-induced demixing in polydisperse blends

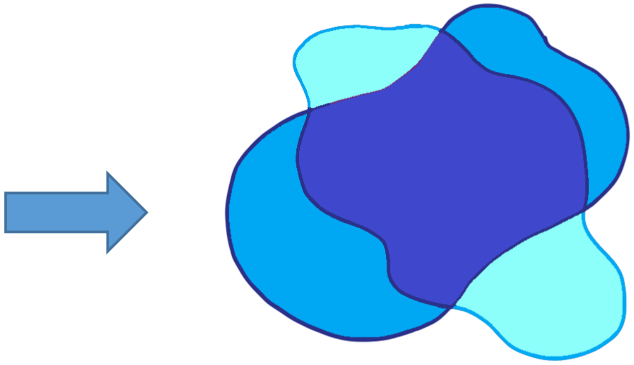
Joseph D. Peterson, Glenn H. Fredrickson, L. Gary Leal

03/21/18

Semi-dilute entangled polymer solutions

The Two-Fluid Model





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

Polymers: originally for Stress Enhanced Concentration Fluctuations
(Helfand and Fredrickson (1989), Doi and Onuki (1992). Milner (1991))

Similar equations exist for dry grains and dense suspensions

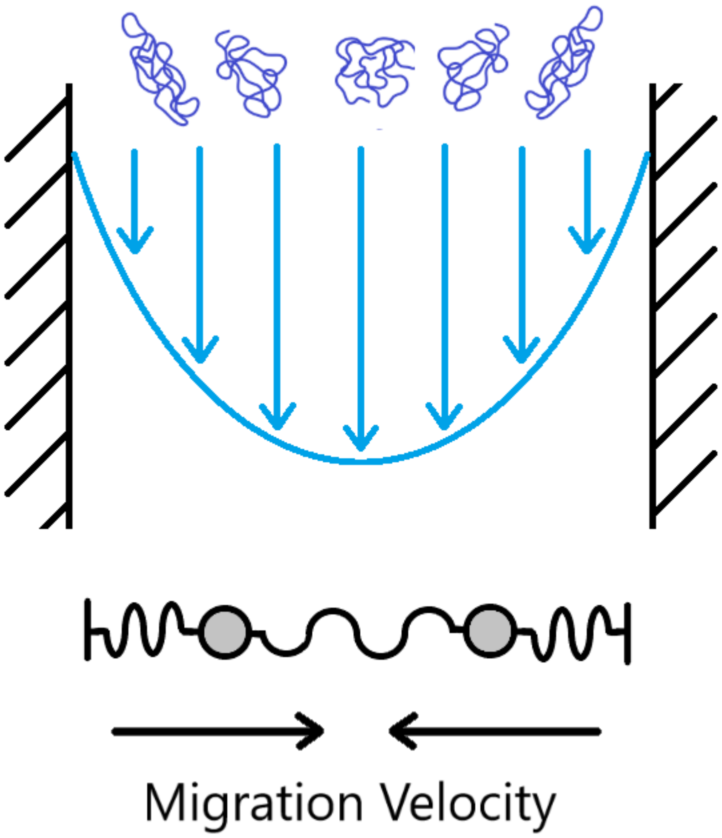
Flow-induced migration in a two-fluid model

Centerline: polymers are isotropic

Walls: polymers are compressed in the flow gradient direction

Migration up stress gradients:

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



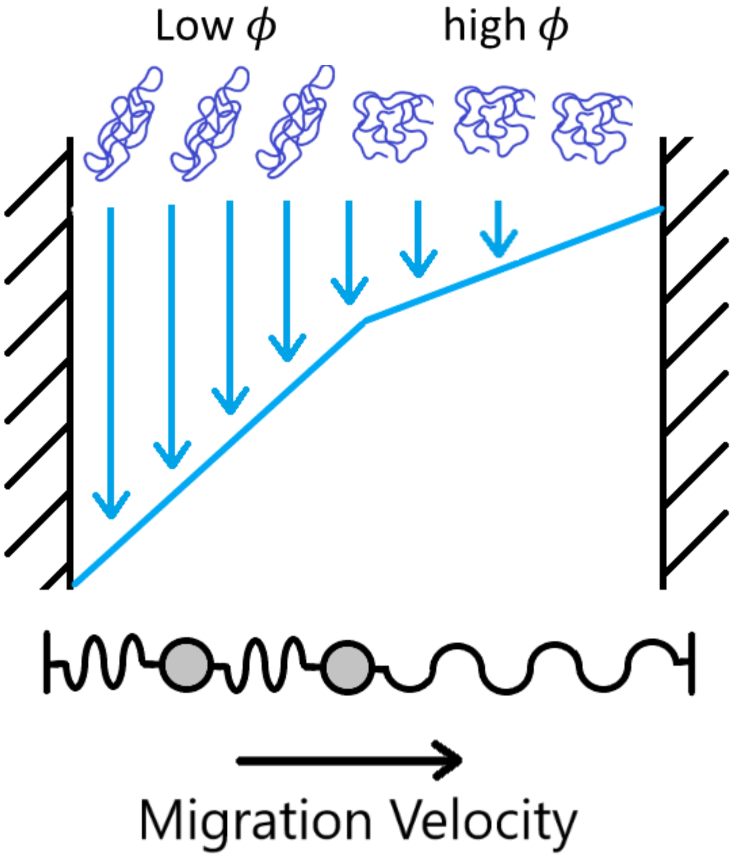
Flow-induced demixing in a two-fluid model

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

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



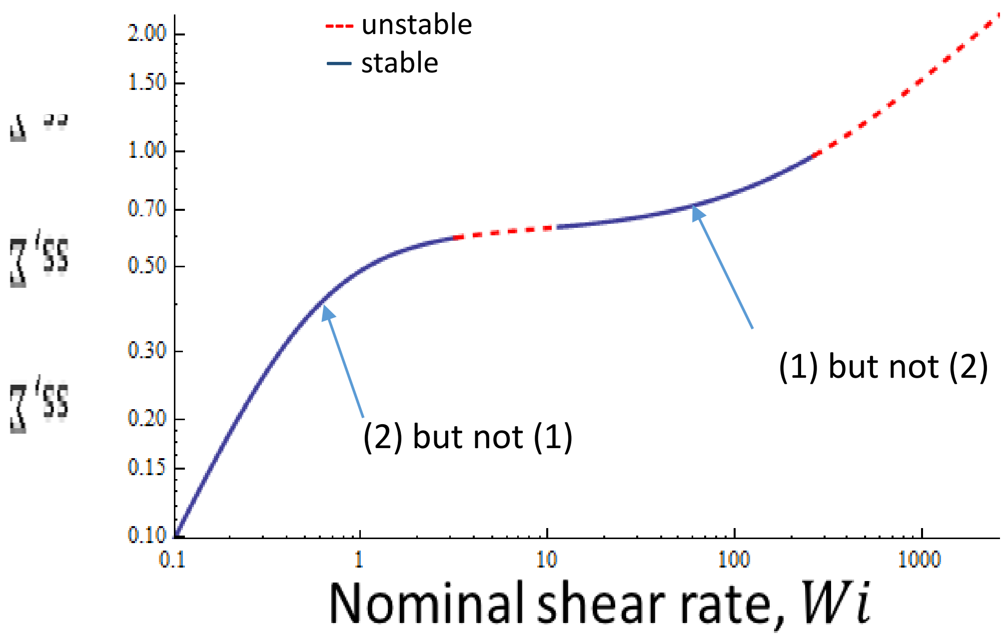
Flow-Induced Demixing in Polymer Solutions

<u>Condition for Shear Induced Demixing</u>

(1) Elastic stresses are large enough to compete with osmotic stresses

(2) Changes in shear rate effect normal stresses more than shear stresses

Stress plateau: most unstable at Wi ~5

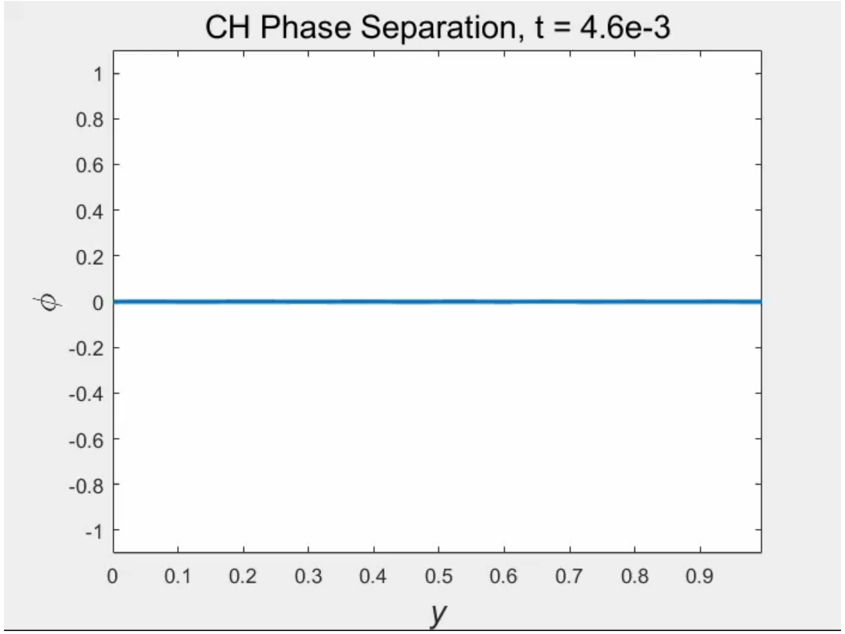


E = elastic/osmotic modulus

Dimensionless Group	Interpretation
$E = 0.15$	moderate mixing forces
$\theta = 120$	strongly entangled
$\eta_S = 10^{-5}$	weak solvent contribution
$\xi = 0.3$	large coupling friction
$\bar{H} = 10$	moderate gap size

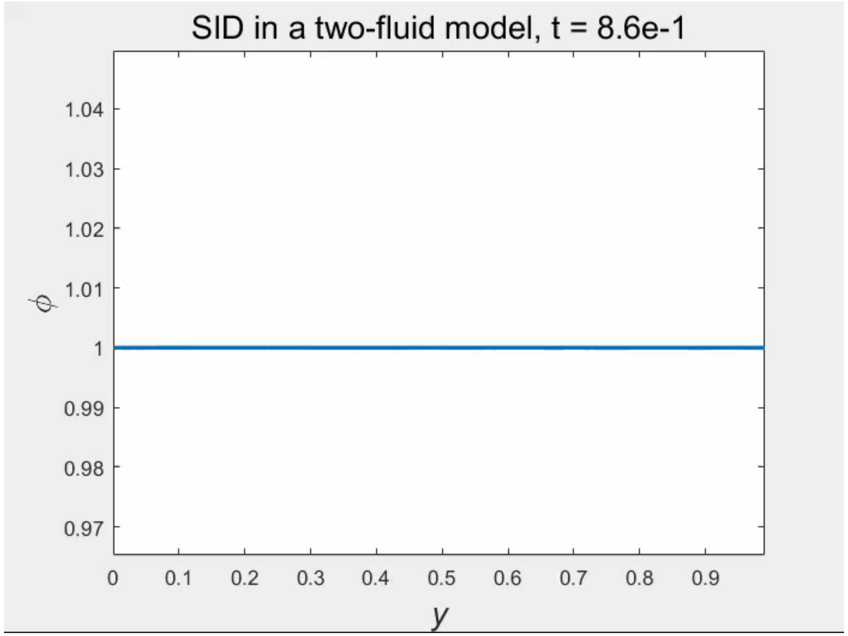
Shear Induced Demixing (SID) vs Cahn Hilliard

Cahn-Hilliard Demixing



SID in two-fluid model

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



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

$$v_P - v_S = -\frac{1}{\zeta}\frac{\partial}{\partial y}\pi^{eff}(\phi, \Sigma)$$

$$\pi^{eff}(\phi, \Sigma) = \pi(\phi) - \sigma_{yy}^{eff}(\phi, \Sigma)$$

Concentration equation looks like Cahn Hilliard

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

What is the effective free energy?

What is the flow-induced shift?

Define an 'effective' free energy, $\mathcal{L}$, as the free energy of mixing, F^{mix}, plus a correction with free energy density Δf:

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

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

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

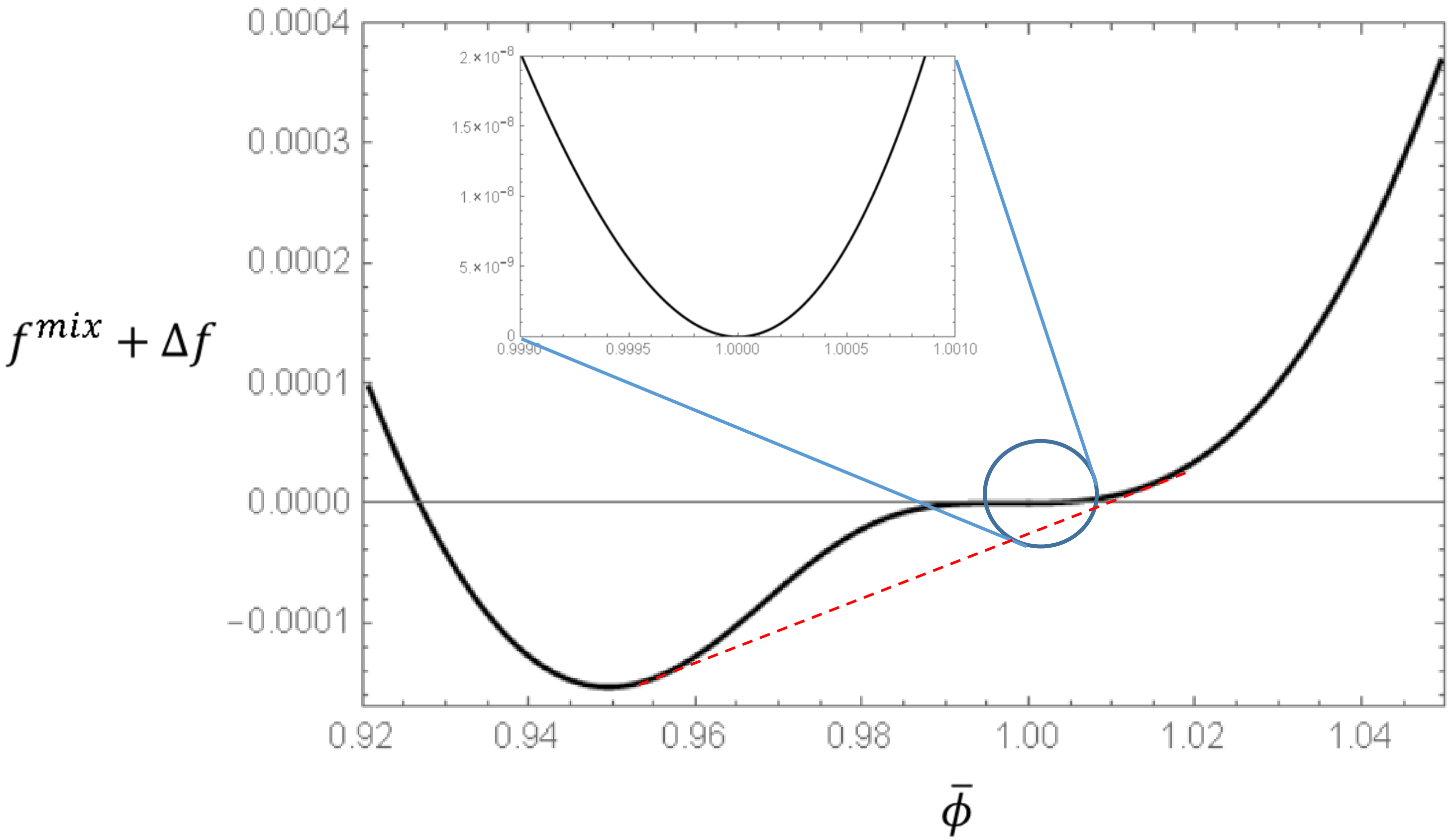
Solve to obtain Δf:

$$\Delta f(\phi, \Sigma) = -\phi \int_{\phi_{ref}}^{\phi} d\phi' \left(\frac{\sigma_{yy}(\phi', \Sigma) - \sigma_{yy}(\phi_{ref}, \Sigma)}{\phi'^2} \right)$$

Global Stability Analysis Example

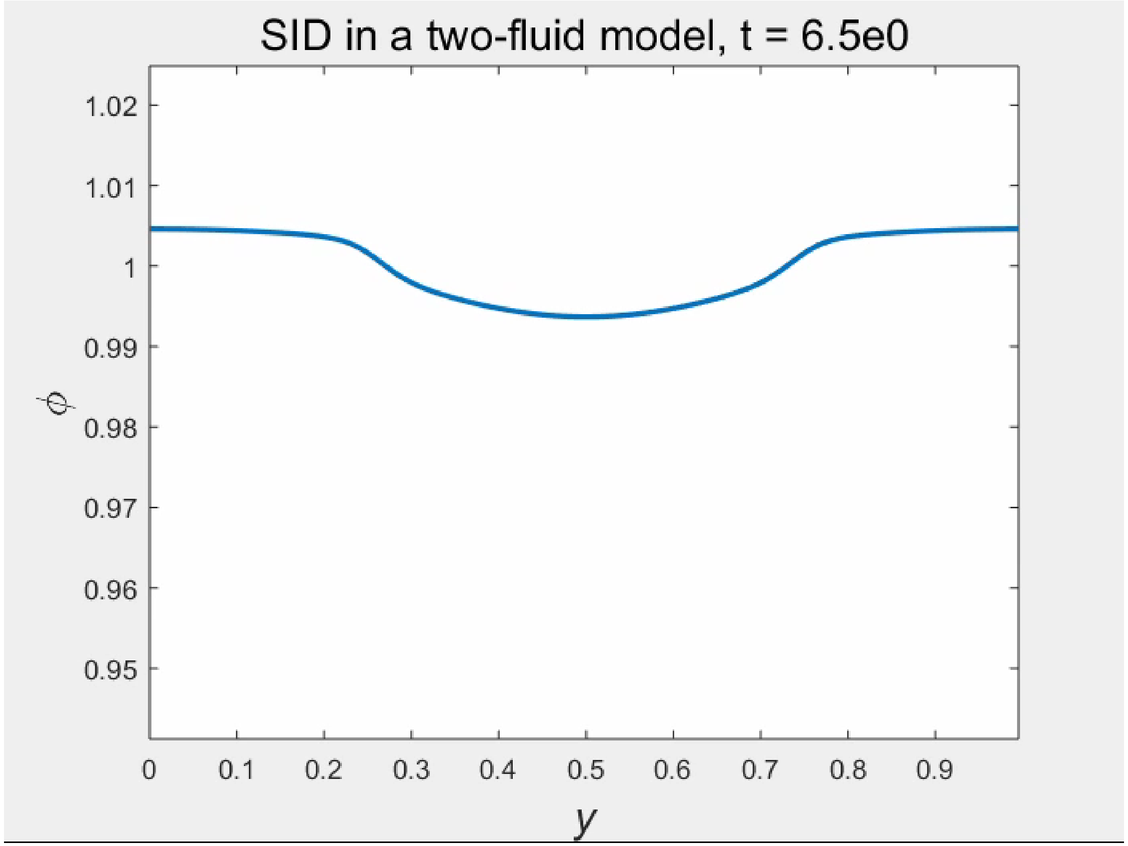
Example 1: Identifying metastable states

$$\theta = 120, E = 0.15, \eta_S = 10^{-4}, \Sigma = 0.59 \quad \bar{\xi}/\bar{H} \ll 1$$



Nucleating a Shear Band

$$\theta = 120, E = 0.15, \eta_S = 10^{-4}, \bar{\xi} = 10^{-2}, \bar{H}/\bar{\xi} = 100, \Sigma = 0.59$$



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 ϕ

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

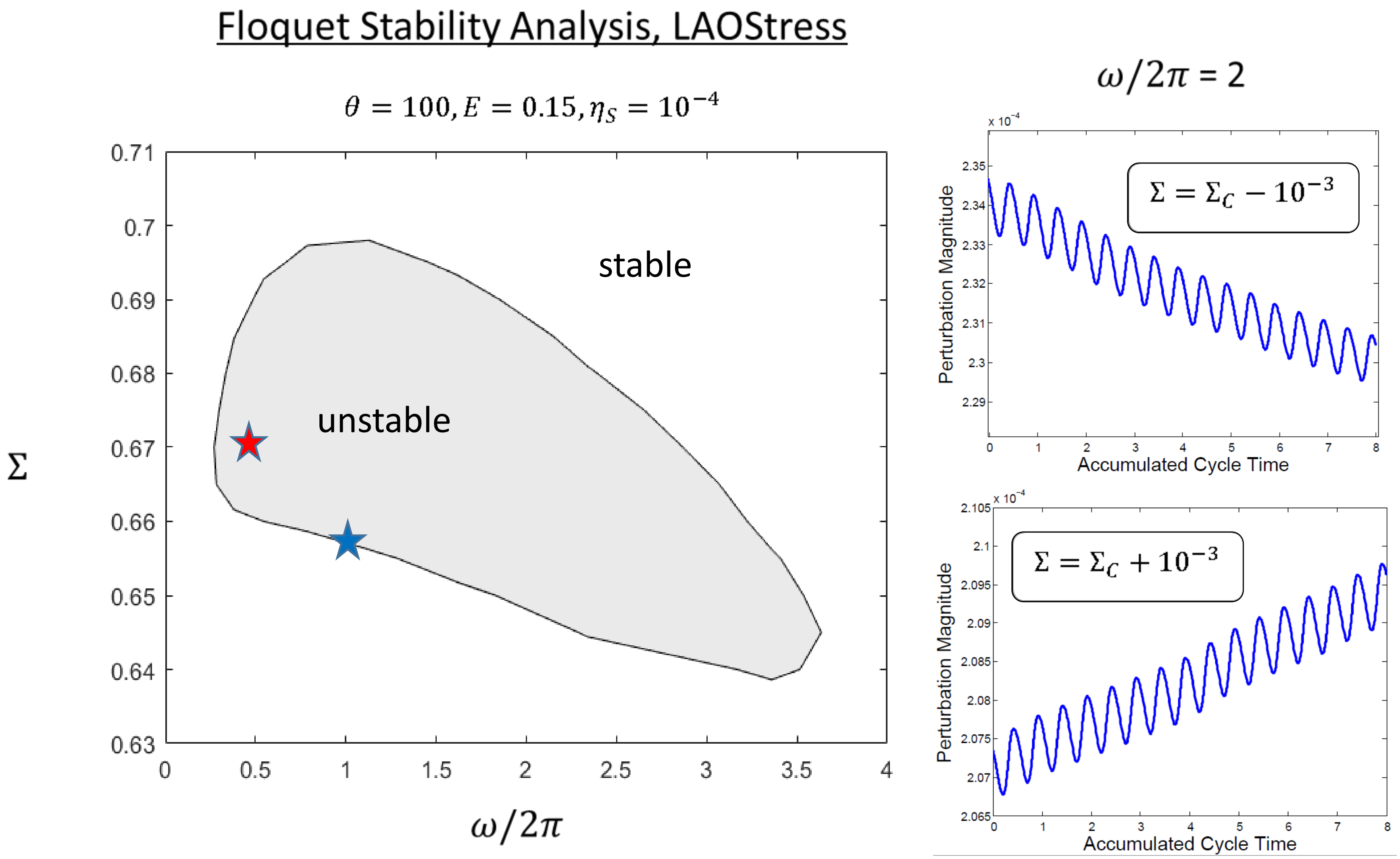
$$\langle \pi^{eff} \rangle(t) = 2\pi\omega \int_0^{[2\pi\omega]^{-1}} \pi_{LC}^{eff}\left(t, \phi(\tau)\right)$$

Concentration equation looks like Cahn Hilliard

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

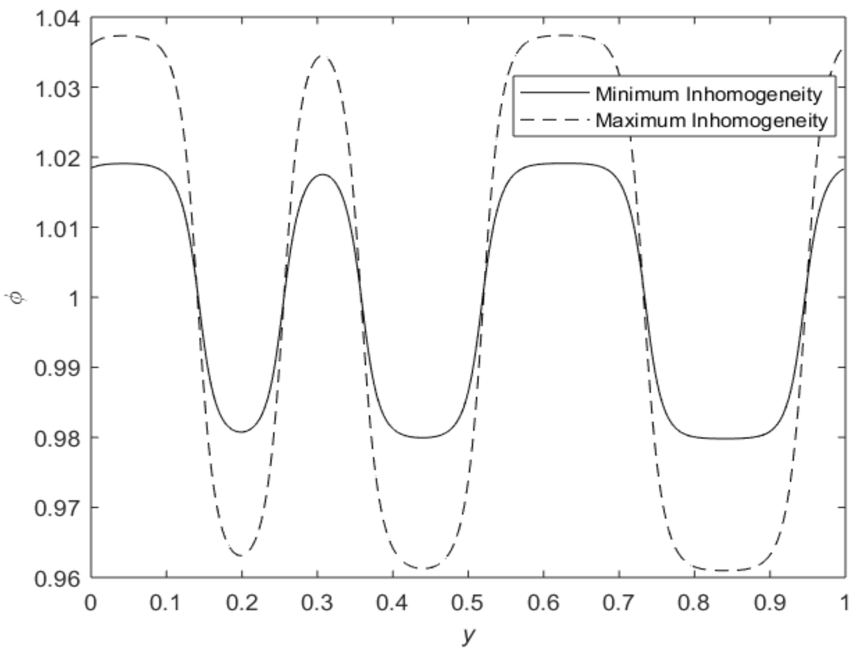
Only works for linear stability analysis! Nonlinear dynamics can be very different!

Sidebar: linear stability boundaries

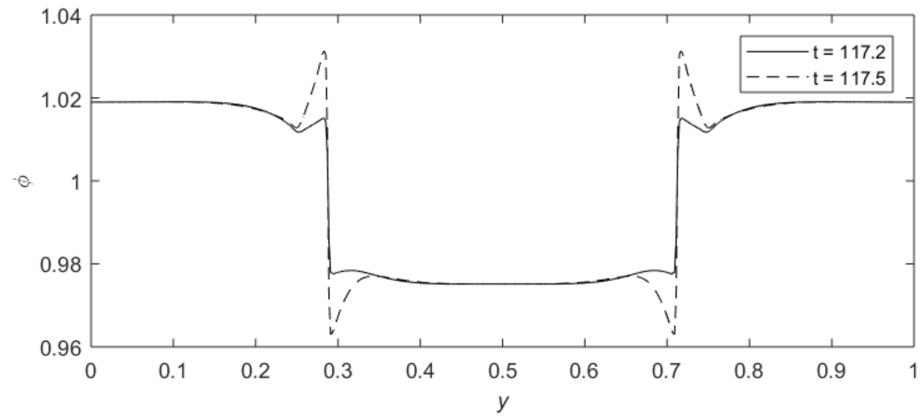


Examples: Unusual nonlinear dynamics

Lack of coarsening after demixing
(seeded from random noise)



Interface is non-monotone in ϕ
(seeded with macroscopic inhomogeneity)



$$\theta = 120, E = 0.15, \eta_S = 10^{-4}, \bar{\xi} = 10^{-2}$$
$$2\pi\omega = 0.5, \Sigma = 0.67$$

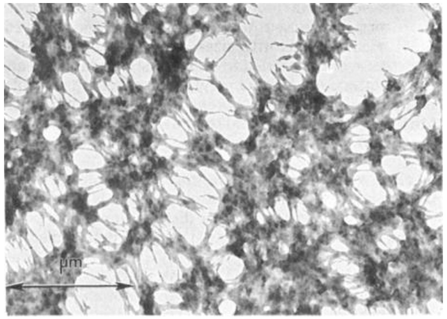
$$\bar{H} = 1 \text{ (left)} \quad \bar{H} = 16 \text{ (above)}$$

The culprits:

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

Shear Induced Demixing in Polymer Blends

<u>Experimental Observations</u>: 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)

<u>**Theoretical Studies** (based on two-fluid approx. for **bidisperse** systems)</u>

- 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

<u>**What do we hope to contribute?**</u>

- 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**

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

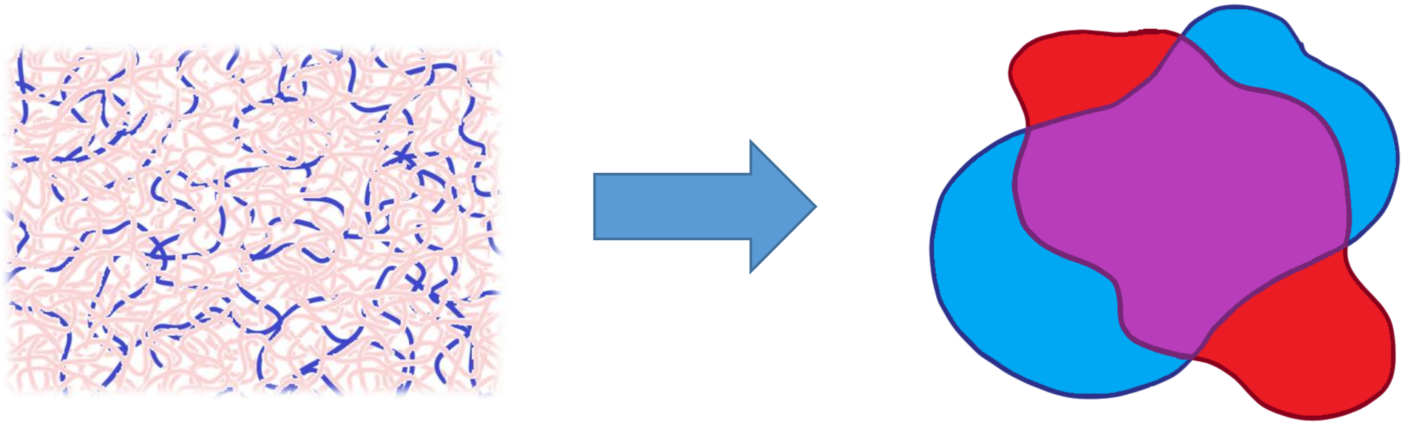
- $Z_S \to Z_L$, vanishing contrast between chains: **Polydispersity is destabilizing**

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

$$I_P - 1 \sim \frac{1}{\bar{\bar{Z}}}$$

What happens to polydisperse blends in flow?

Two Fluid Modelling of Bi-Disperse Polymer Blends



<u>Two-Fluid Approximation</u>

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)

<u>Constitutive Theory</u>: 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

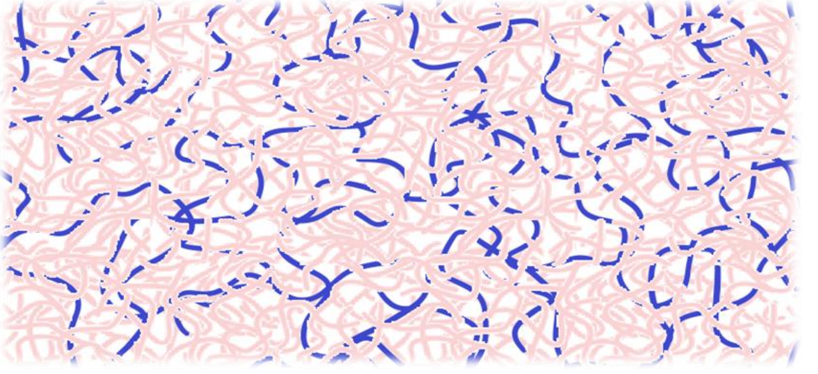
Polymer Blend

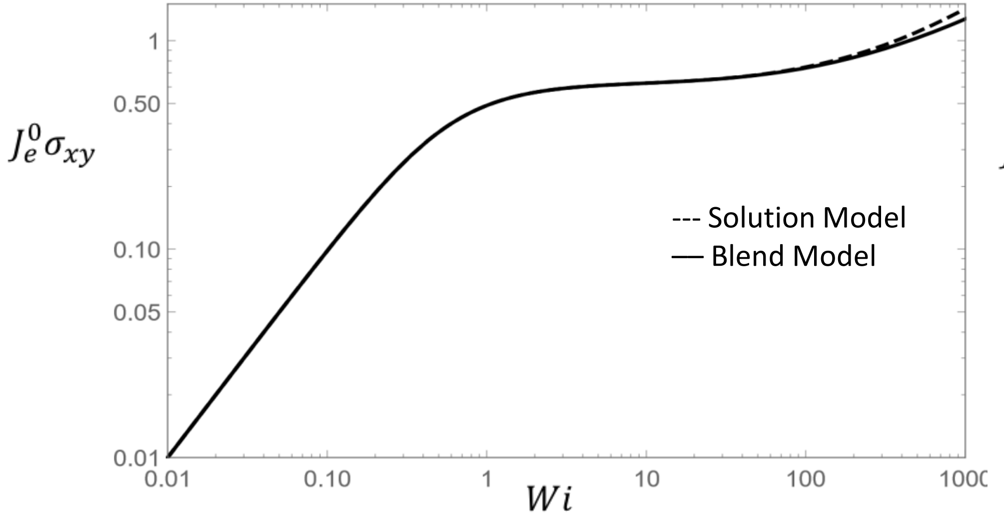
$Z_L = 625, Z_S = 5$

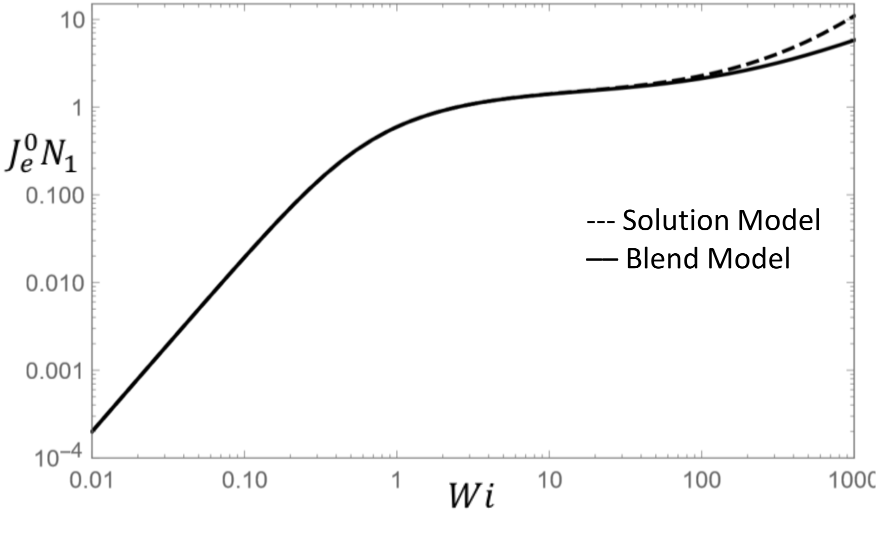
$\phi_L = 0.10$

Polymer Solution

$Z = 62.5, \quad \varpi = 7 \cdot 10^{-5}$







$$J_e^0 = \lambda_0 / \eta_0 = \underset{\omega \to 0}{\ell im} \left[\frac{G'}{G''^2} \right]$$

(creep compliance to normalize for differences in modulus)

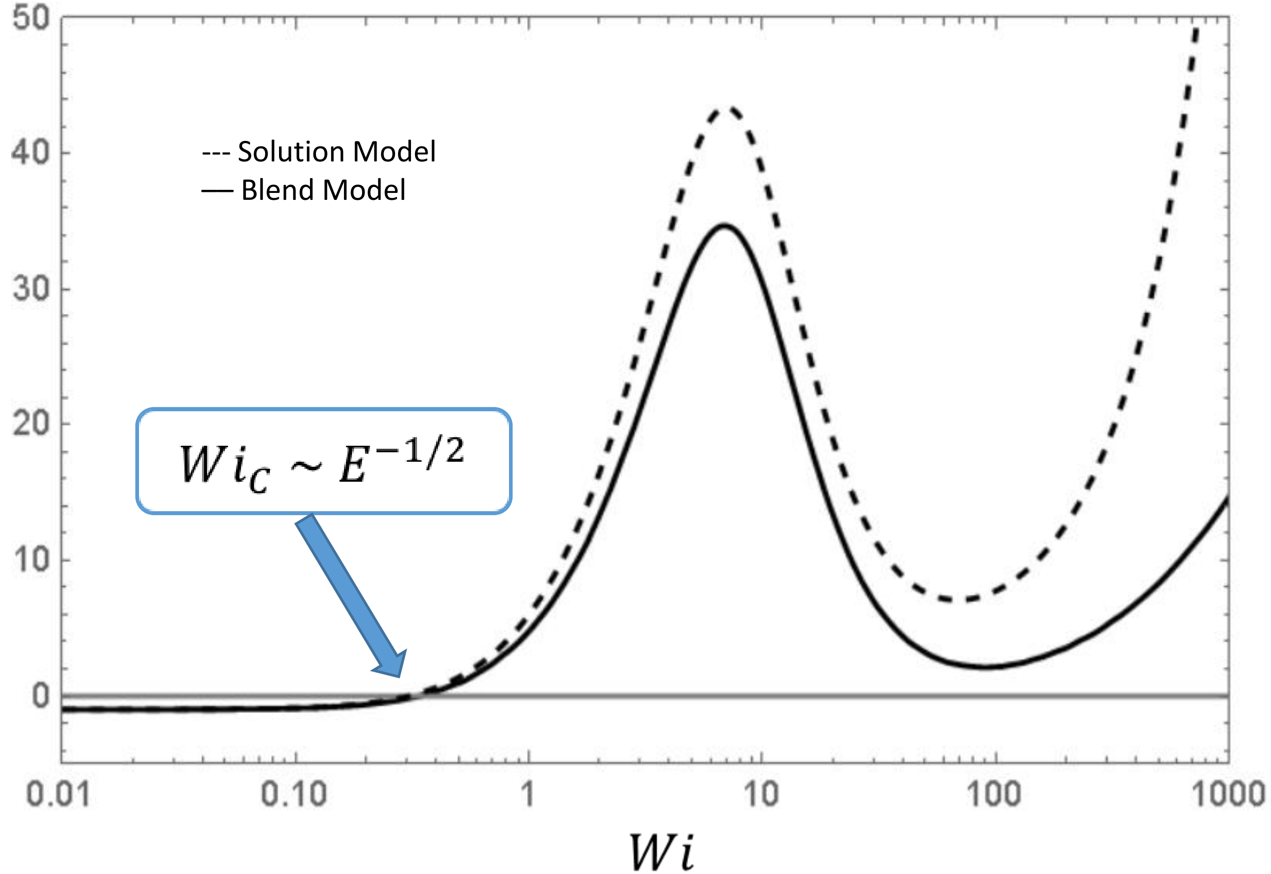
Consistency Check:
Transition to Solvent-like Short Chains (demixing)

Polymer Blend

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

Modeled as a "Polymer Solution"

$$Z = 62.5, \boldsymbol{E = 4.1}, \varpi = 7 \cdot 10^{-5}$$

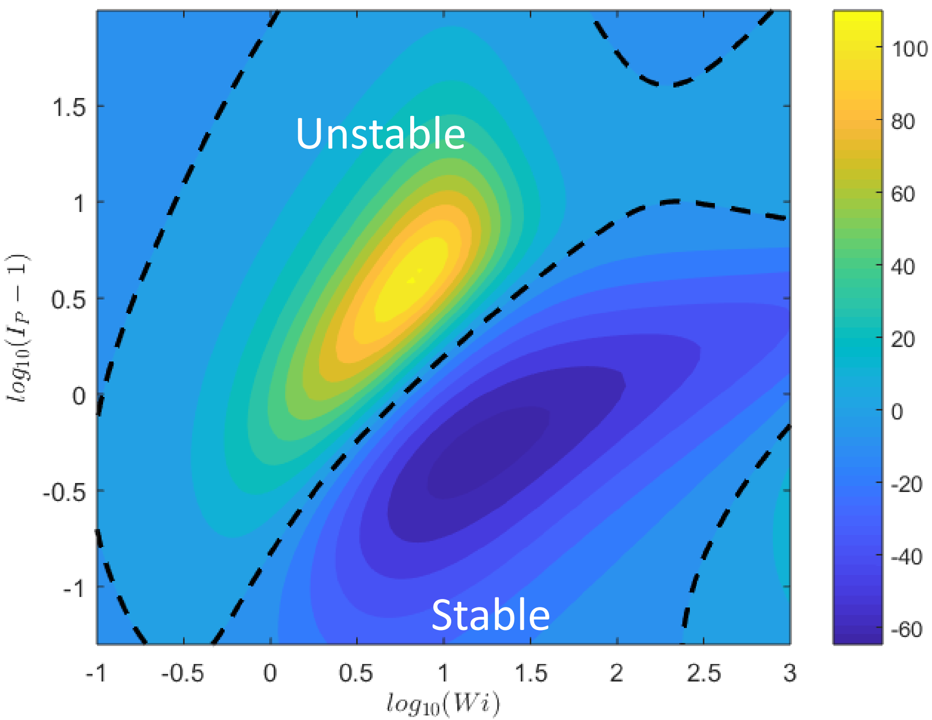


A Broader Range of Blends

$Z_L = 200, \quad \phi_L = 0.5, \quad Z_S = 2 - 320$

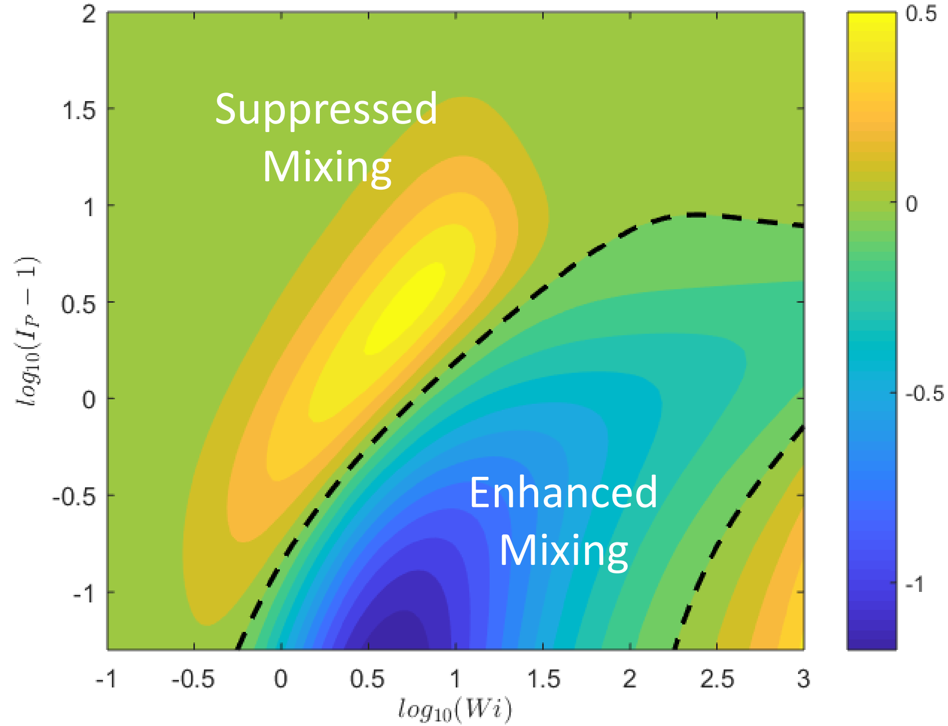
Dimensionless Growth Rate

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



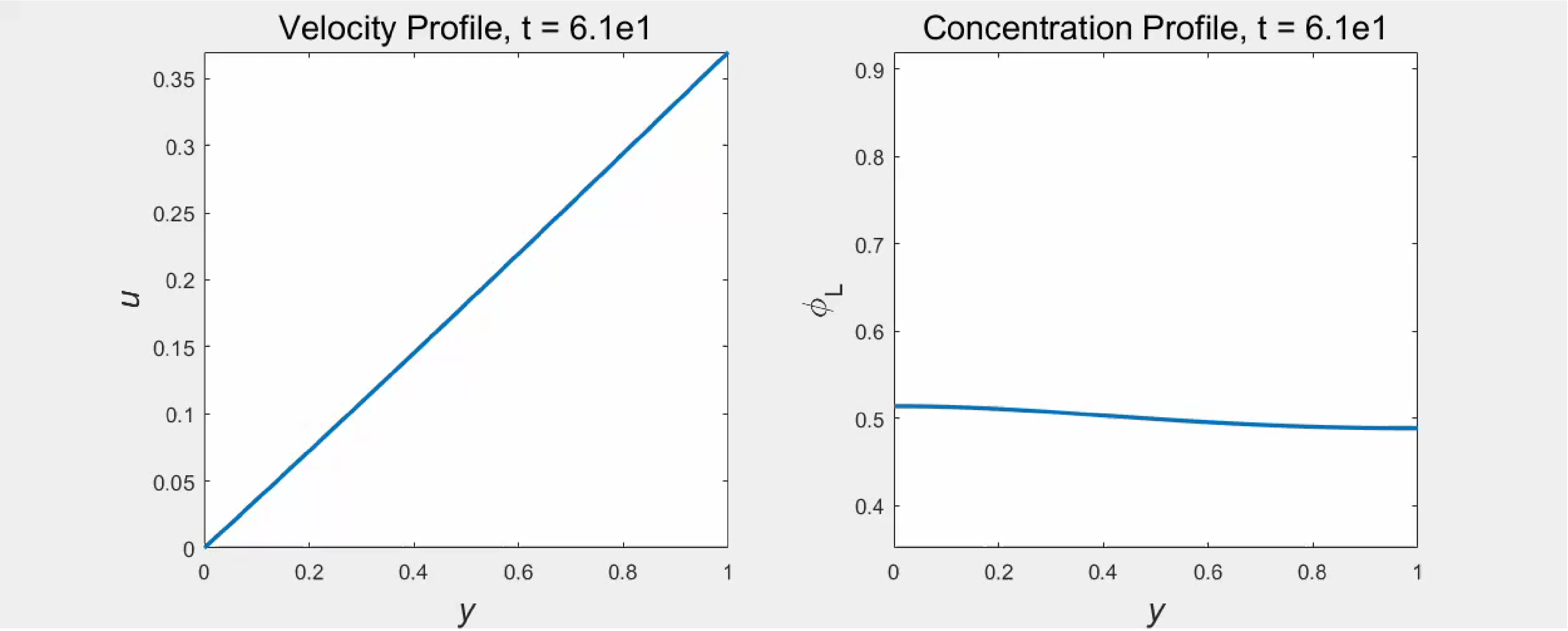
Polydispersity-induced Contrast, $\chi_{\mathcal{D}}$

$$\chi_{\mathcal{D}} = \frac{(\hat{\sigma} + 1)}{\bar{Z} m_2} \qquad m_2 = \phi_L \phi_S \left[\frac{Z_L - Z_S}{\bar{Z}}\right]^2$$



Non-linear evolution of Demixing

$$Z_L = 250, Z_S = 150, \phi_L = 0.50, R_g = 0.11, \mathrm{Wi} = 0.36$$



What about continuum polydispersity?

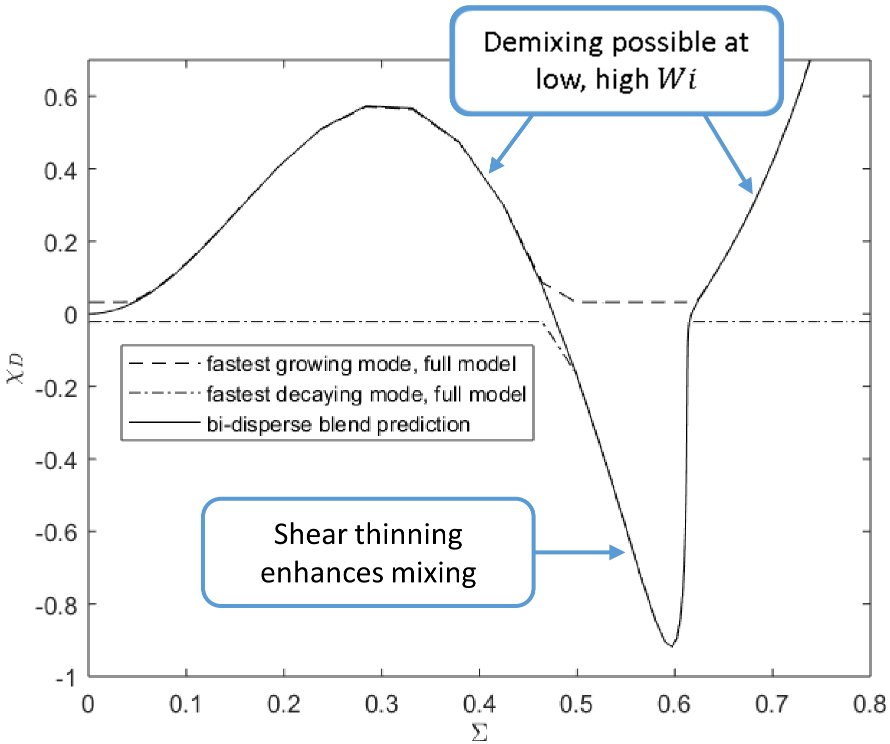
Examples: lognormal MW distribution

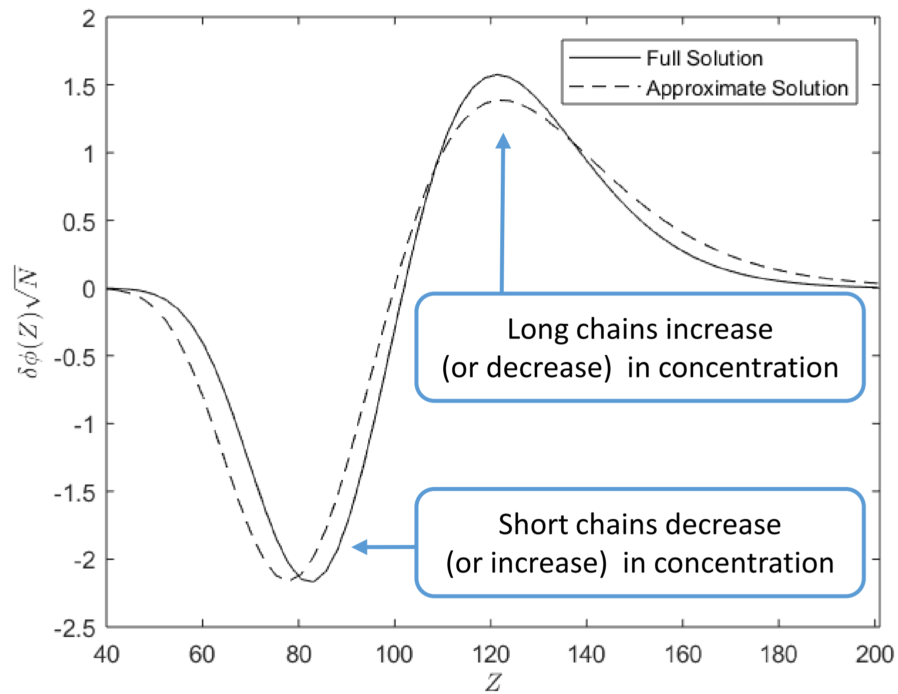
Estimating $\chi_{\mathcal{D}}$

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

Predicting $\delta\phi(Z)$

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





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

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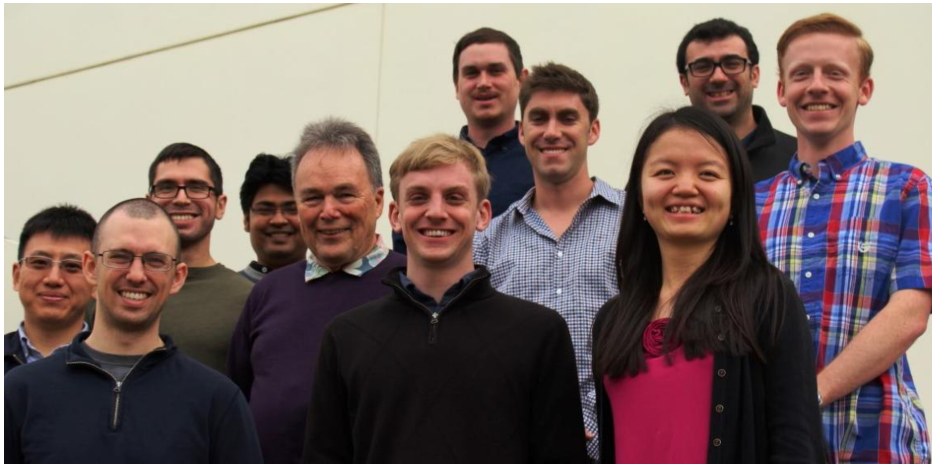
- Dr. Doug Tree
- Dr. Nino Ruocco
- Peng Cheng
- Patrick Corona
- Mike Burroughs

<u>Others</u>

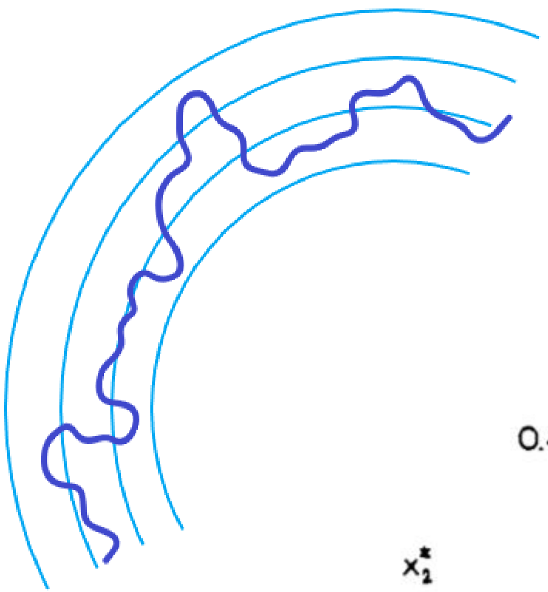
- My wife (Emily) and kids, for keeping me sane
- God, for making a world worth studying



Polymer Migration in Flow: Earliest Ideas

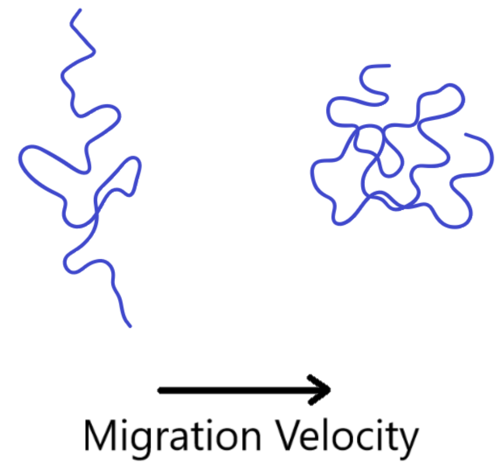
Streamline Curvature

Schafer, Laiken, and Zimm (1974)



Thermodynamics

?(1974)



Hydrodynamics

? (1974)