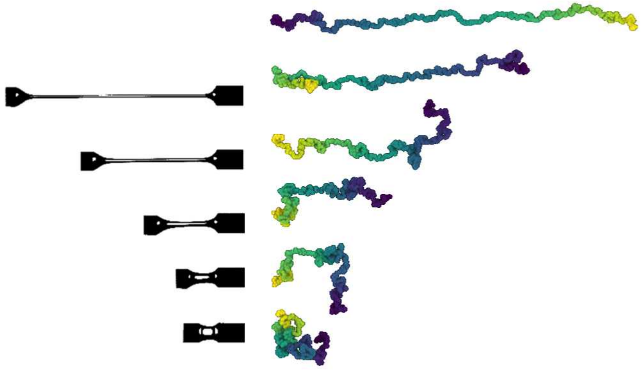
Relating Solvent Dynamics to the Extensional Viscosity of Entangled Polymer Solutions



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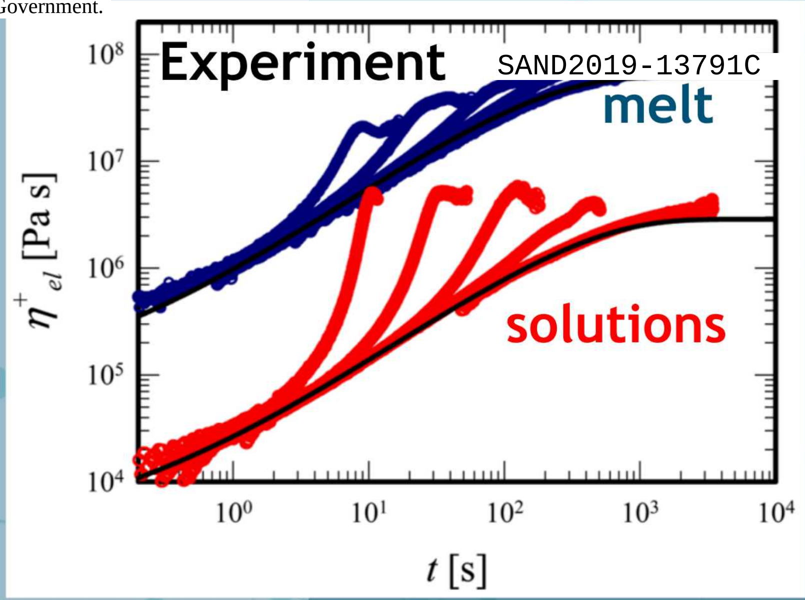

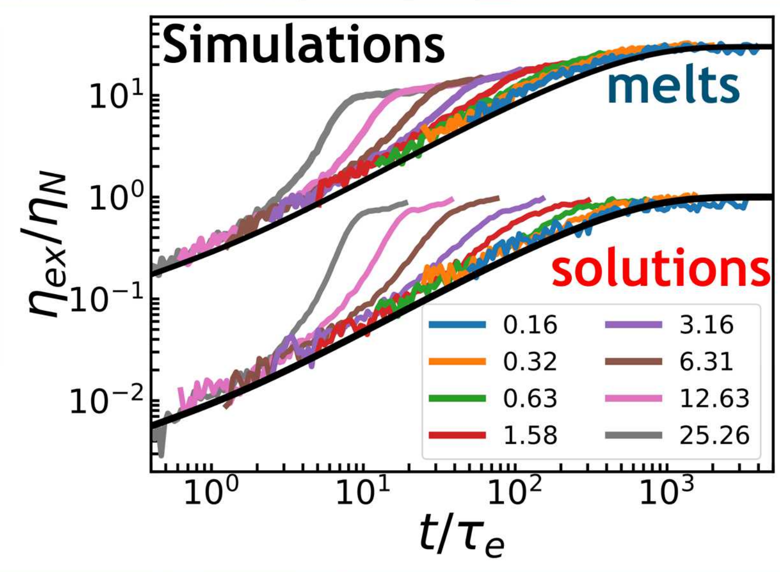

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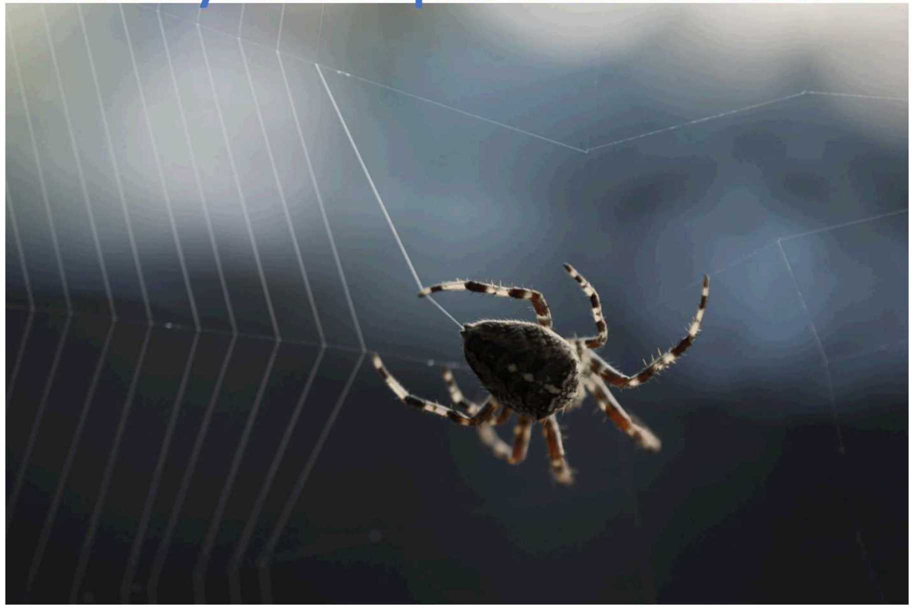
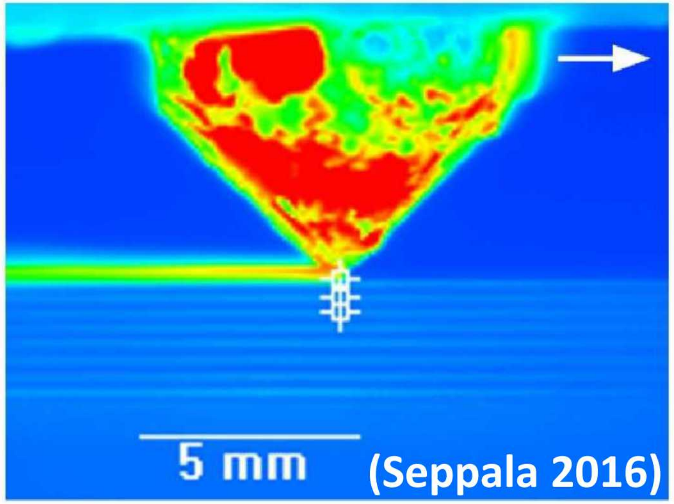
Processing Polymer Solutions

Semi-crystalline spun fibers in Nature



Polyethylene Fiber Mooring Lines

Filament Deposition AM



Spun Polymer Fibers

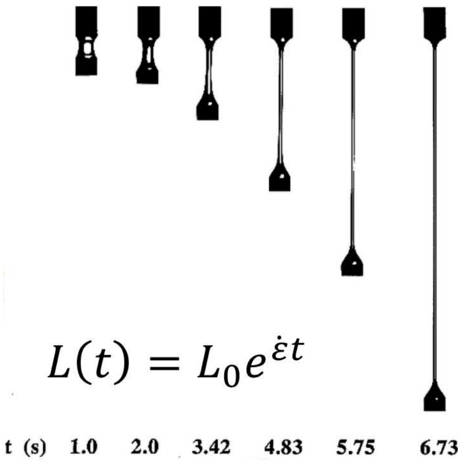
Blown Polymer Films

Diluting Polymers in solvents allows *large* deformations at modest temperatures.

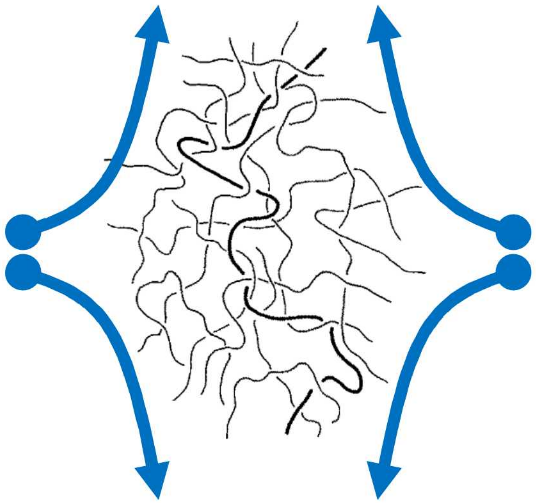
Exploited in nature where temperature control is not possible. In industry when not desirable.

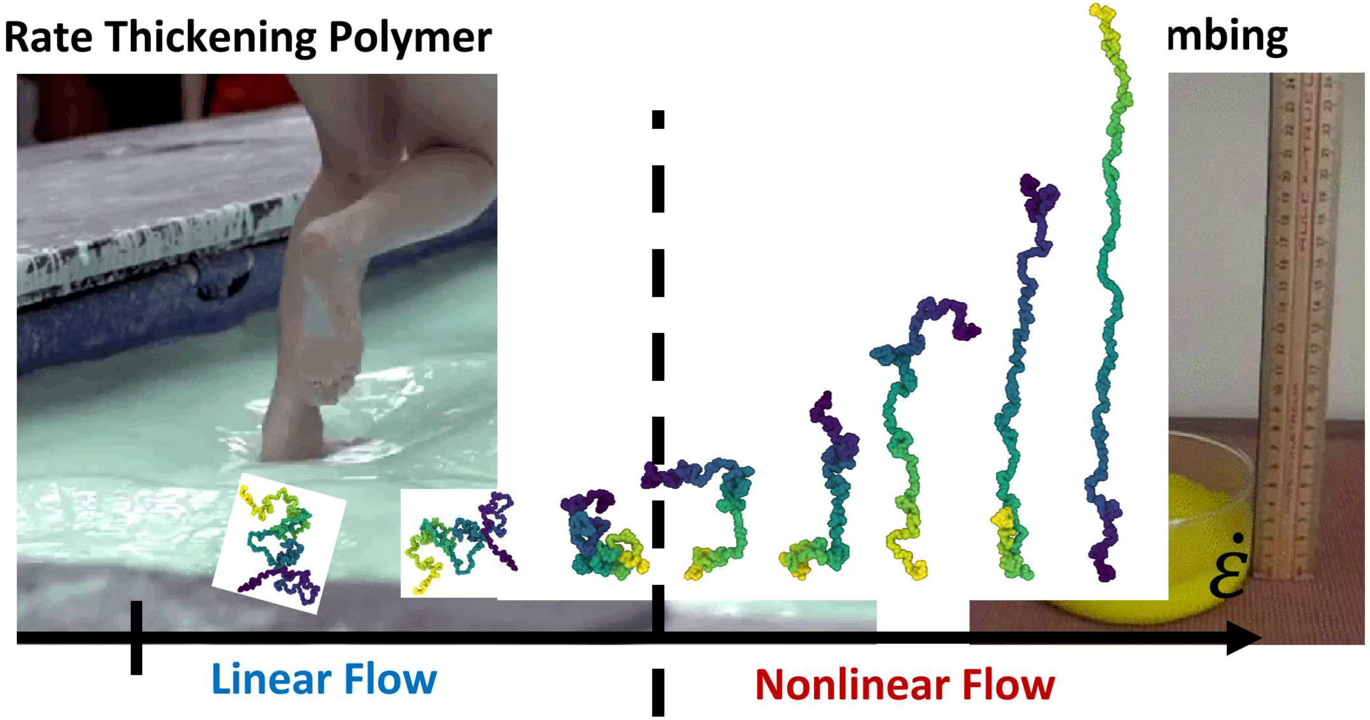
Most Industrial Processing Flows Are Highly Nonlinear

Rapidly deforming polymer liquids can change chain conformations and alter flow behavior.



$$L(t) = L_0 e^{\dot{\varepsilon} t}$$





Uniaxial Extension Flow:

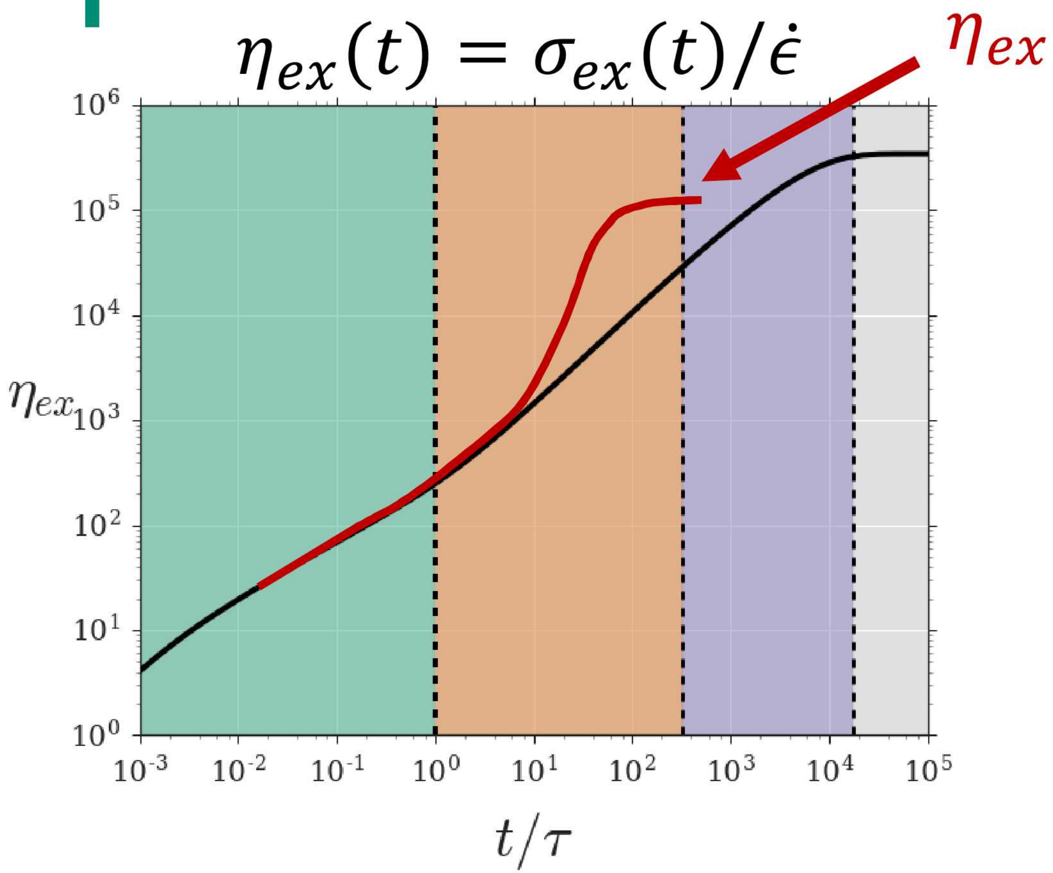
Stretches fluid along the vertical direction and shrinks laterally with a strain rate $\dot{\varepsilon} = \frac{\partial ln(\lambda)}{\partial t}$.

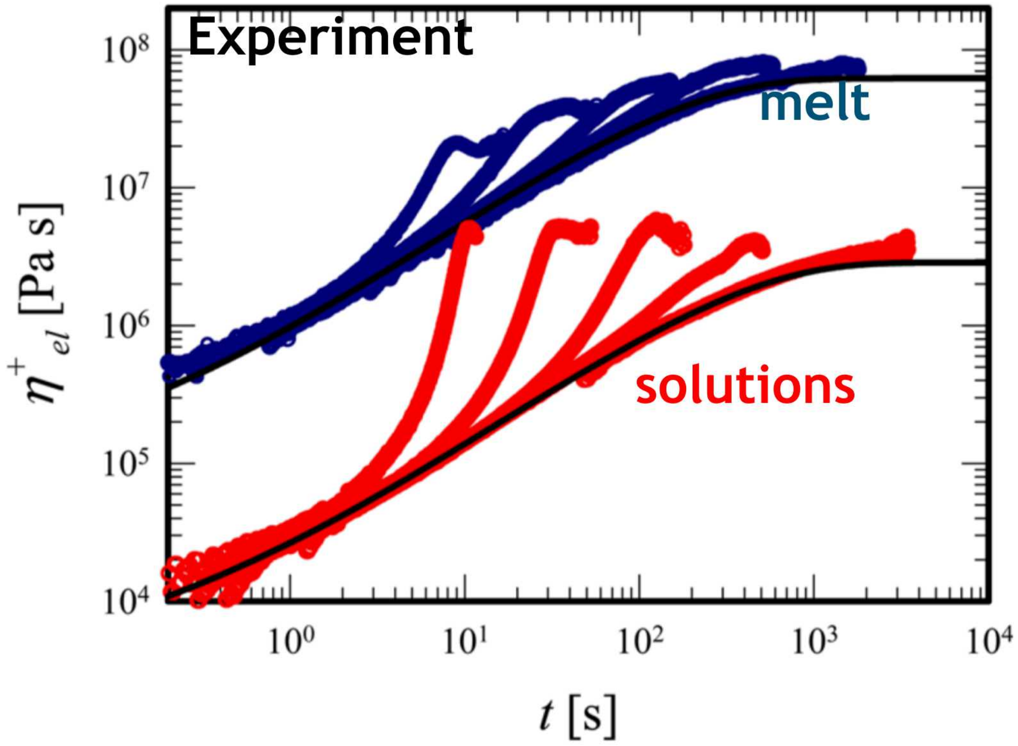
Nonlinear Flow:

- **Strain rate $\dot{\varepsilon}$ deforms chains faster than their relaxation time τ**
- **Elongated molecules dramatically alter the liquids viscosity**

Macroscopic Viscosity Encodes Chain Dynamics

$$\eta_{ex}(t) = \sigma_{ex}(t)/\dot{\epsilon}$$





Weak Linear Flows ($Wi \to 0$):

- Viscosity evolves along a limiting curve (LVE), and plateaus to Newtonian viscosity.
- Controlled by equilibrium chain dynamics – very different for linear & ring polymers.

Strong Nonlinear Flows ($Wi > 1$):

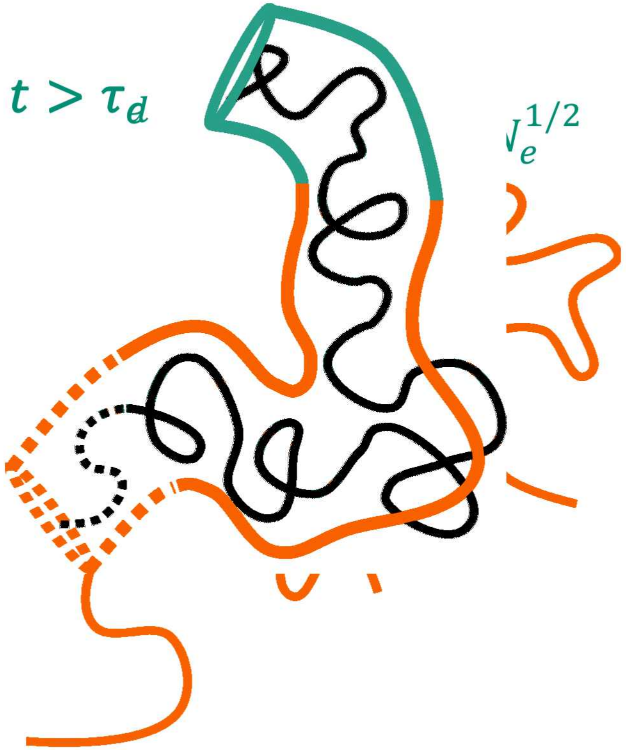
- Viscosity increases more rapidly than the LVE and plateaus to a nonlinear value $\eta_{ex}(\dot{\epsilon})$.
- Different liquids with the same LVE have qualitatively different rate-dependent steady-state viscosity.

Linear Viscoelastic Flow Controlled By Entangled Dynamics

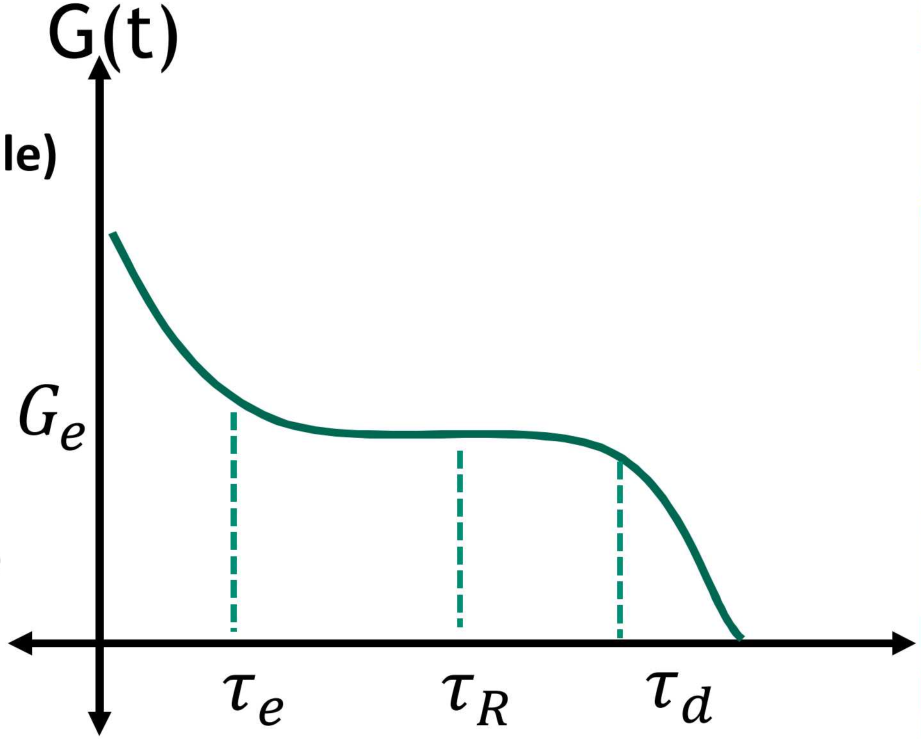
Entanglement network confines each polymer to tube-like region with a lifetime τ_d

Chains first feel the constraints of the tube at the entanglement time τ_e

Polymers can relax within the tube over the Rouse time τ_R

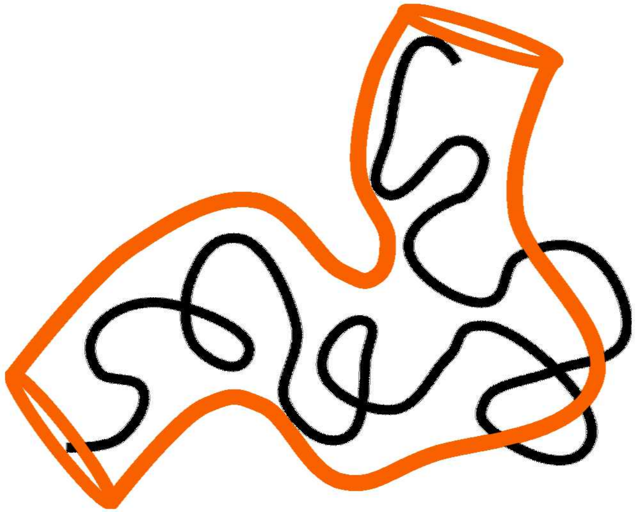


N_e	**Entanglement length (network scale)**
$Z = N/N_e$	**# of entanglements**
$\tau_e \sim N_e^2/k_bT$	**Chain trapped**
$\tau_R = \tau_e Z^2$	**Chain relaxes in tube**
$\tau_d = 3\tau_e Z^{3.4}$	**Chain escapes tube**



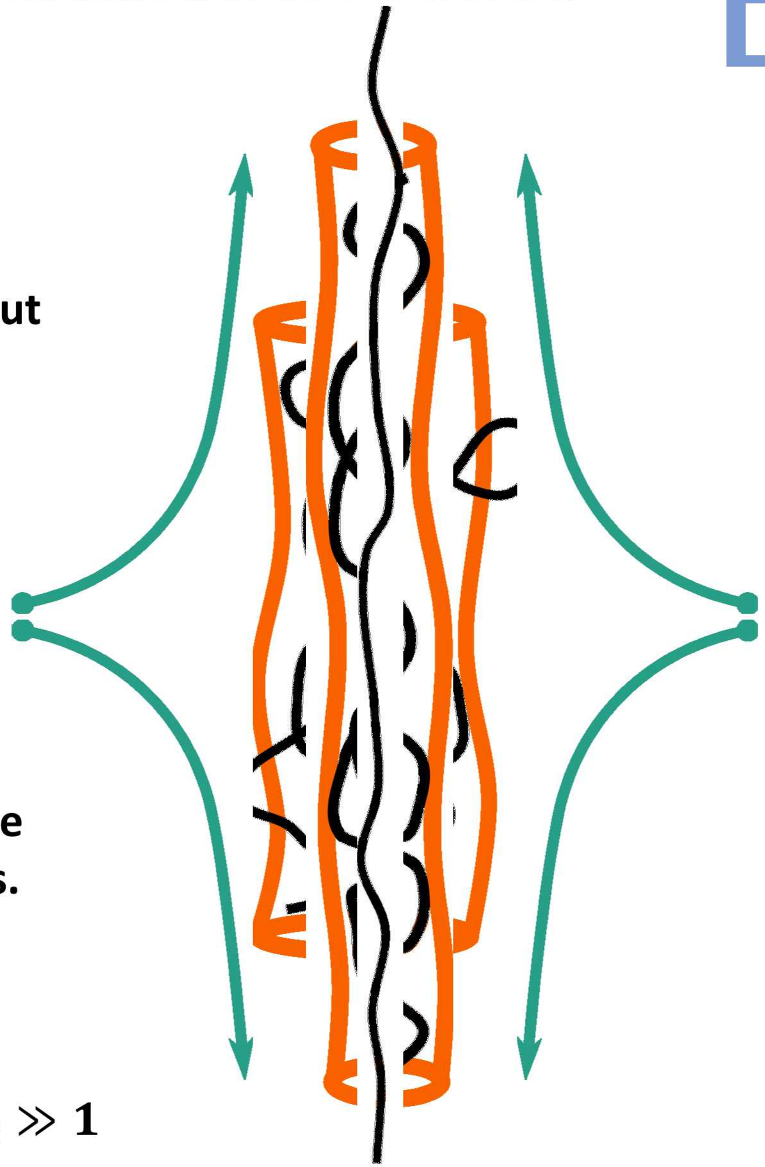
The Newtonian viscosity is dominated by the longest relaxation time: $\eta_{ex}^N \approx 3G_e\tau_d \sim Z^{3.4}$

Nonlinear Flows Compete With Equilibrium Relaxation Times



$$\dot{\varepsilon} > \frac{1}{\tau_d}$$

Flow orients confining tube but chain remains unstretched.



$$\dot{\varepsilon} > \frac{1}{\tau_R}$$

Chains stretch within the tube which elongates and narrows.

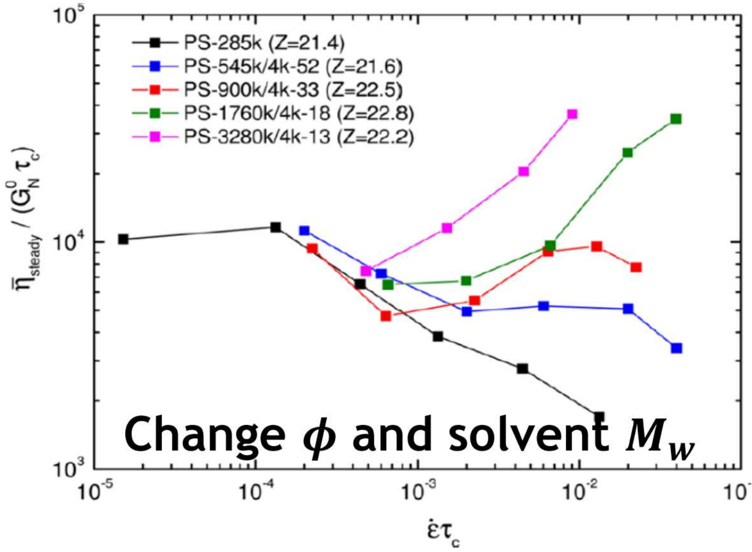
Weissenberg number is a measure of flow strength

$$Wi_R \equiv \dot{\varepsilon}\tau_R$$

Strong elongation when $Wi_R \gg 1$

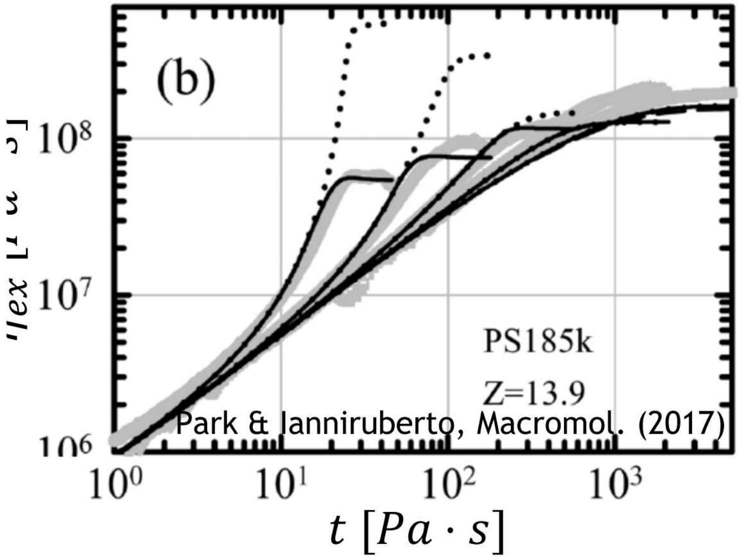
Does Solvent Change the Extension Dynamics of Chains?

Slutions & Melts w/ Same LVE



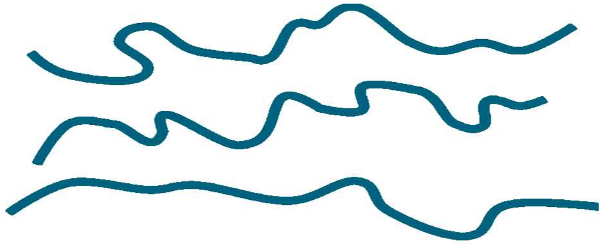
Change ϕ and solvent M_w

Recent Models

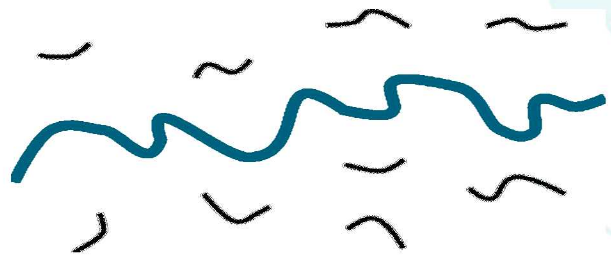


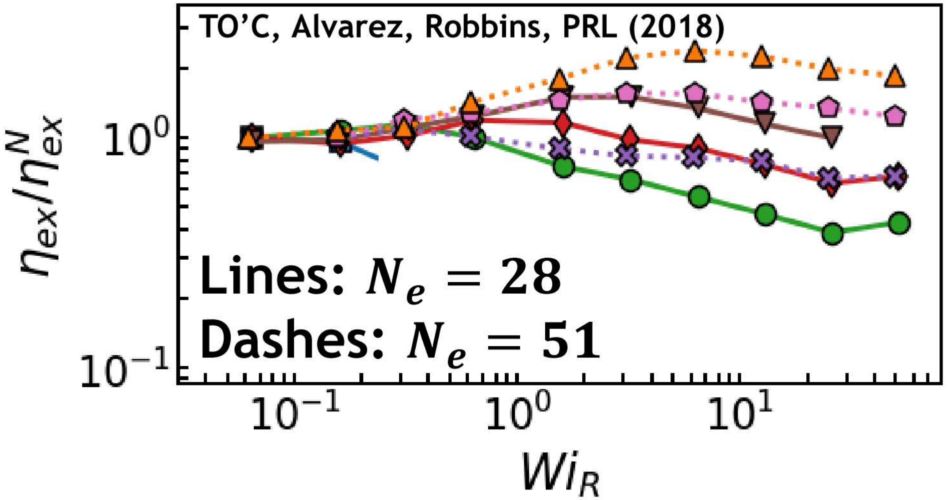
Park & Ianniruberto, Macromol. (2017)

High Orientation → Lower Friction



Low Orientation → Higher Friction





TO'C, Alvarez, Robbins, PRL (2018)

Lines: $N_e = 28$

Dashes: $N_e = 51$

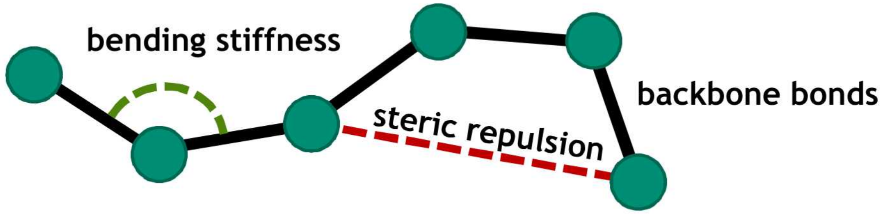
Experiments on solutions and melts with the same Z observe that melt viscosities decrease more with Wi_R.

Recent models capture this by predicting that solvent imposes a different effective friction on long chains.

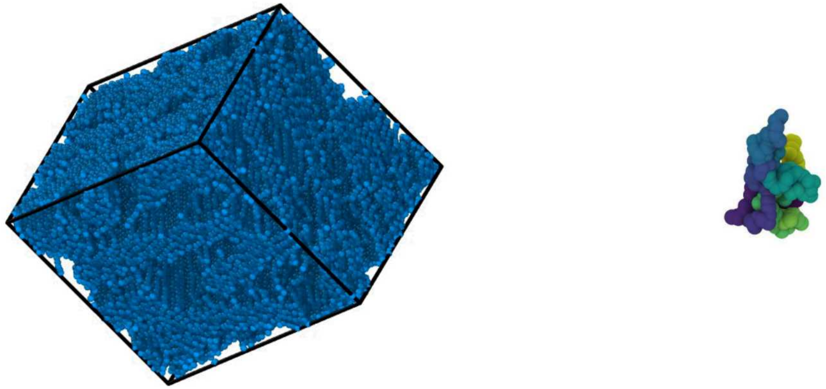
Challenge: dilution in solvent also swells the entanglement length N_e, which also changes trends in η_{ex} at constant Z

Nonlinear Elongation of Entangled Solutions

Model: Semiflexible bead-spring model



- linear properties well known ($N_e \approx 28$ beads)
- Polymers with various N=100-500; Z=4-18
- Solvent oligomers with N=4
- Tune model to separately vary ϕ, Z, N_e



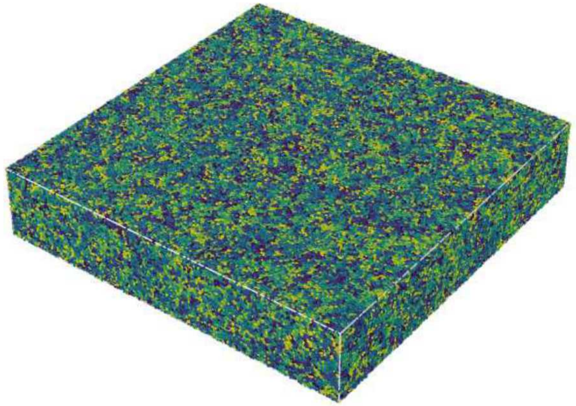
Constant-rate uniaxial extensional flows

- Elongate to strain $\epsilon > 6.0 \rightarrow$ resolve steady-state
- Vary $Wi = \dot{\epsilon}\tau = 0.16 - 0.25$
- Relate rate-dependence to chain dynamics

How does diluting polymer in solvent to a volume fraction ϕ change extensional dynamics and viscosity?

Separate the effects of solvent on friction from its effect on entanglement density?

State of the Art Simulations For Extensional Flow



Huang et al. PRL (2019)

Standard extension simulation

- **Millions of atoms → expensive to simulate**
- **Rapidly grows too skinny and eventually crashes**

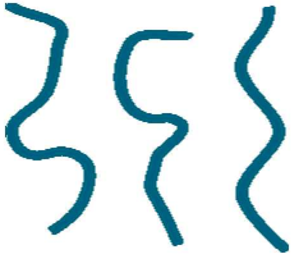
Generalized Kraynik-Reinelt BC

- **$\sim$100K beads**
- **stretch indefinitely without getting too skinny**

Nicholson & Rutledge, JCP 2016; ***T.C. O'Connor****, N.J. Alvarez, M.O. Robbins, PRL 2018*

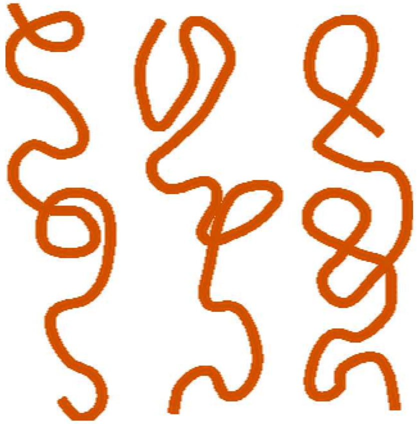
Use Simulations To Independently Vary Entanglement Properties

$N = 500$ beads



Like Exp.

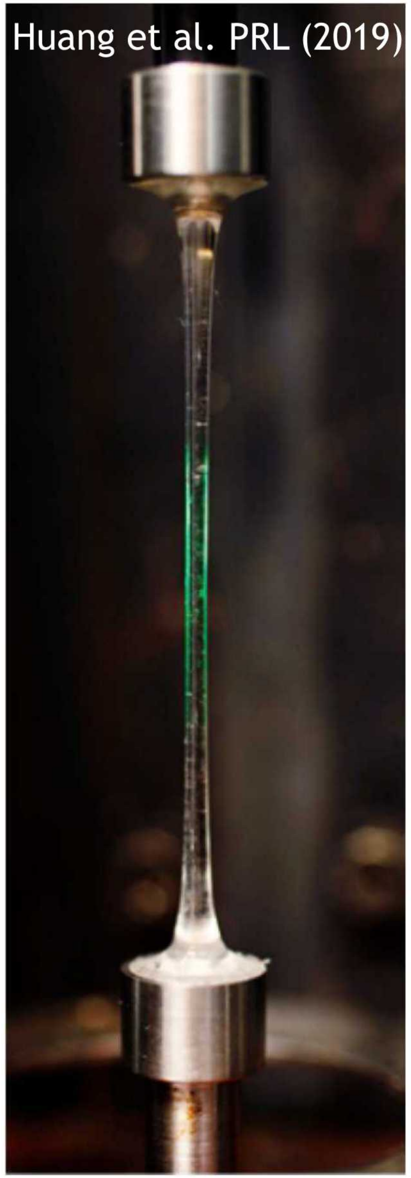
$\phi = 1$ $\phi = 1$



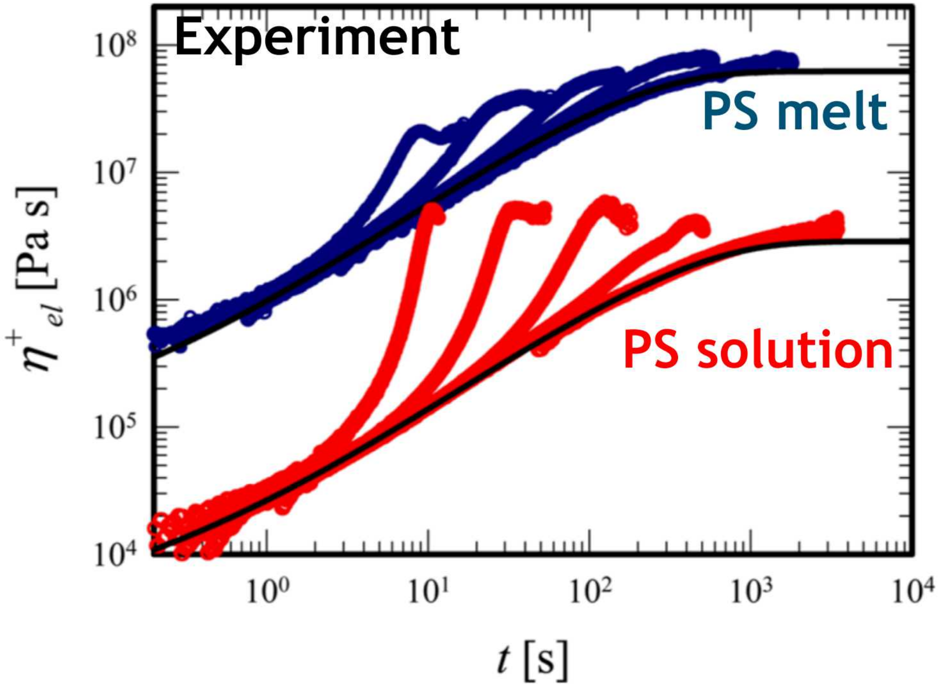
18M1: Melt 1, Z=18	**9M1:** Melt 1, Z=9	**9S1:** Solution 1, Z=9	**9M2:** Melt 2, Z=9
$N = 500$ beads	$N = 250$ beads	$N = 500$ beads	$N = 400$ beads
$n_k = 2.8$ beads	$n_k = 2.8$ beads	$n_k = 2.8$ beads	$n_k = 2.2$ beads
$N_e = 10$ Kuhn steps	$N_e = 10$ Kuhn steps	$N_e = 20$ Kuhn steps	$N_e = 22$ Kuhn steps
$Z = 18$	$Z = 9$	$Z = 9$	$Z = 9$
$\phi = 1$	$\phi = 1$	$\phi = 0.5$	$\phi = 1$

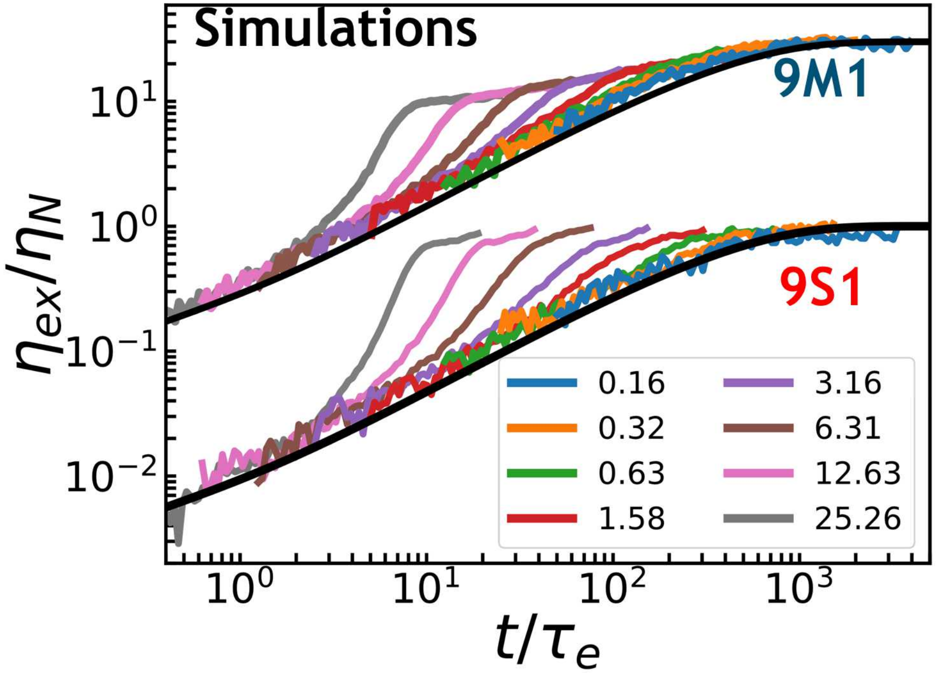
Simulations allow us to separately vary $Z, N_e, \& \ \phi$ and study how rate-dependence of η_{ex} changes.

MD Simulations Directly Reproduce & Inform Experiments



Huang et al. PRL (2019)



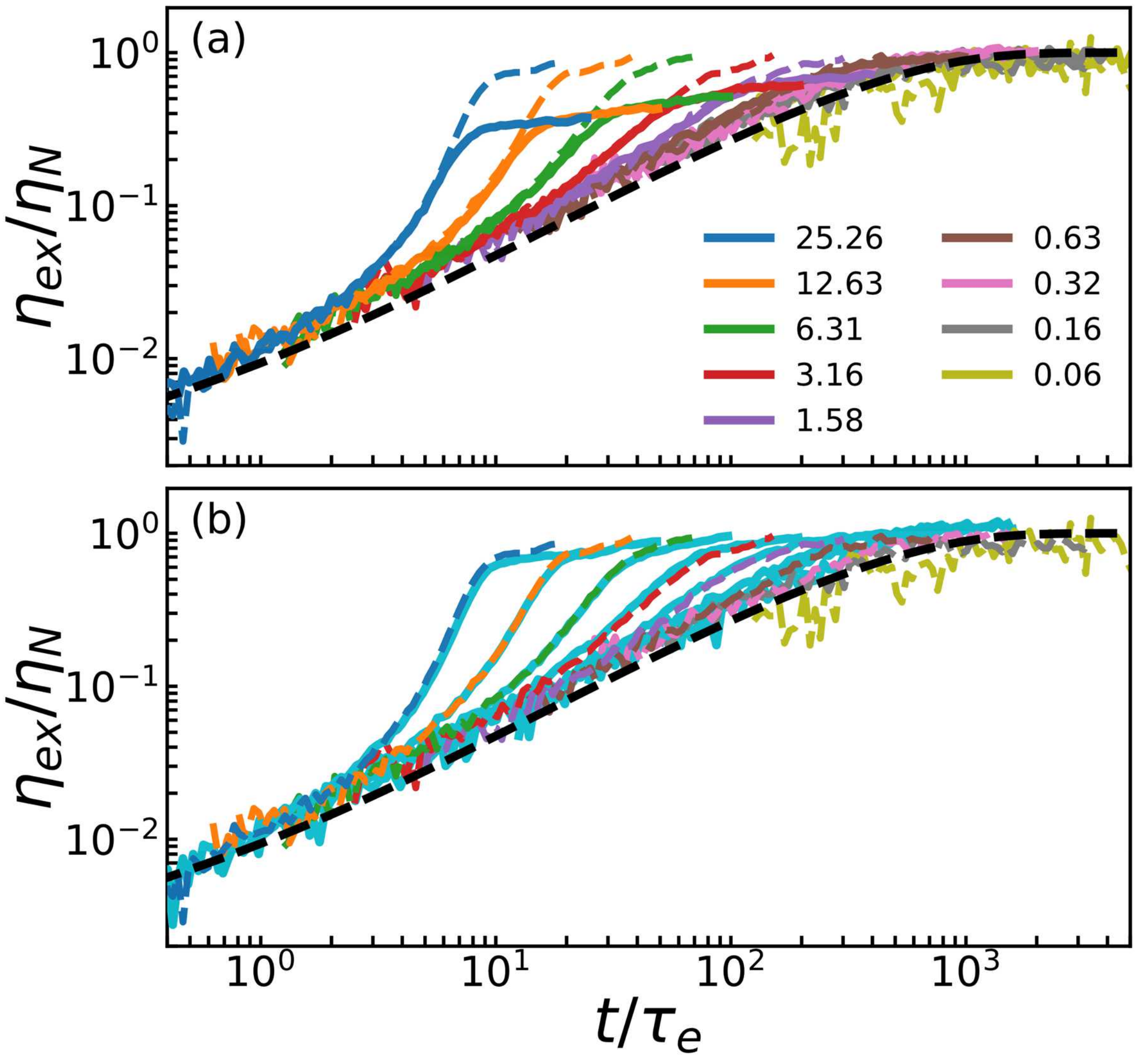


Simulations resolve full range from linear response to highest Wi_R flows.

Reproduce the different nonlinear trends in η_{ex} for melts and solutions.

Are differences due to solvent changing friction, swollen N_e or both?

Solution Start-up & Steady-State Viscosities



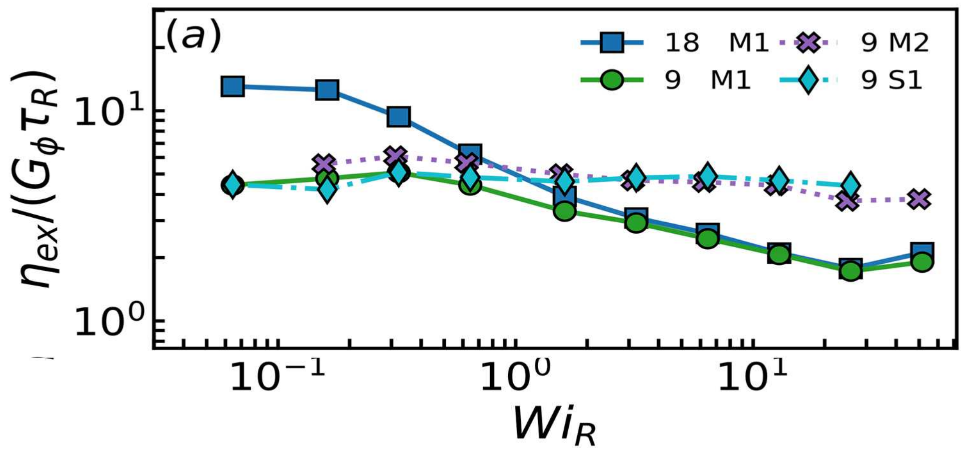
A melt and solution with same Z & different N_e

- Melt viscosity thins more than solution viscosity
- Consistent with experiments and constitutive models

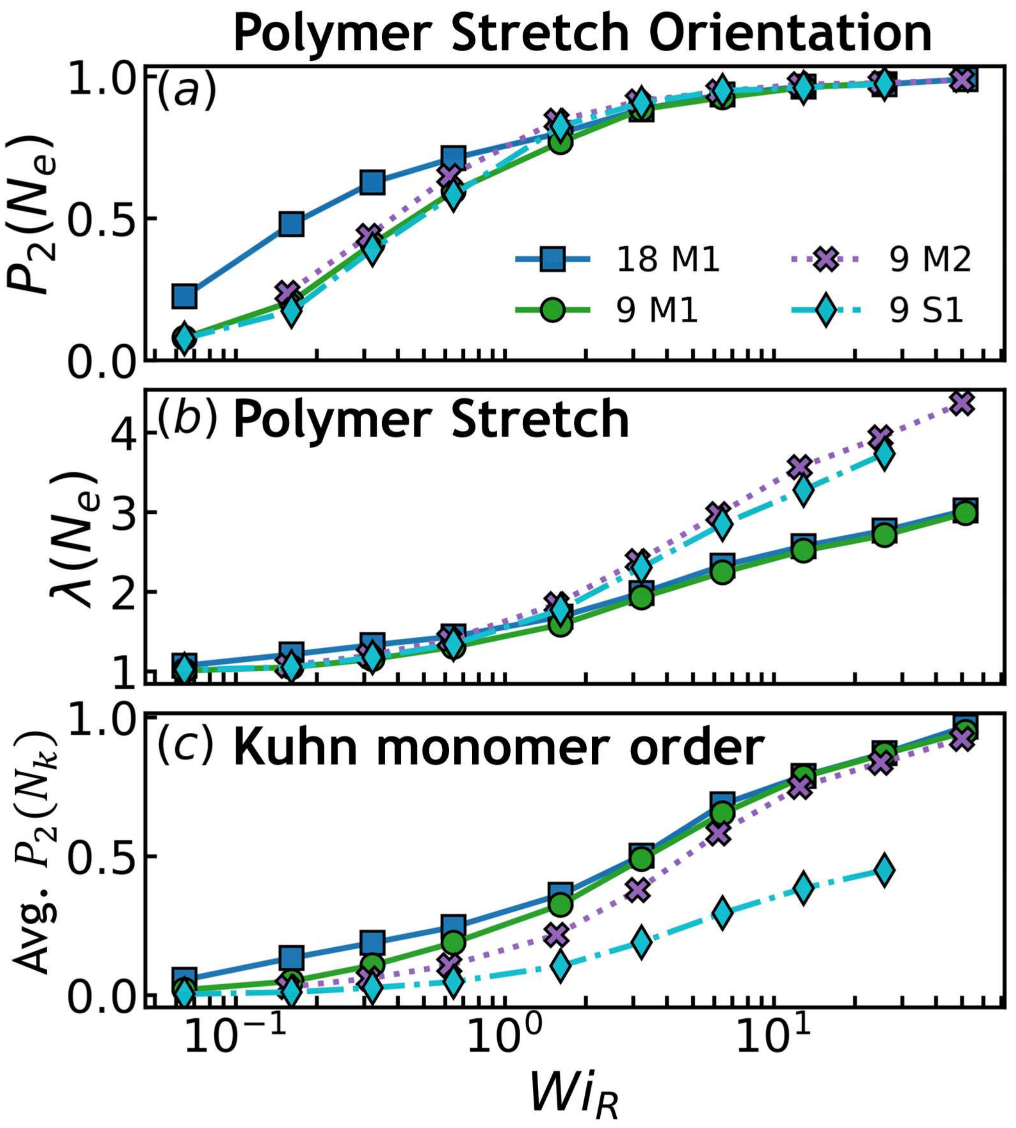
A solution and melt with the same Z & same N_e

- Solution and melt have similar viscosity at all Wi_R
- Solution is 50% unoriented oligomers, but no reduction in viscosity from the higher order in the melt

Steady-State Viscosity



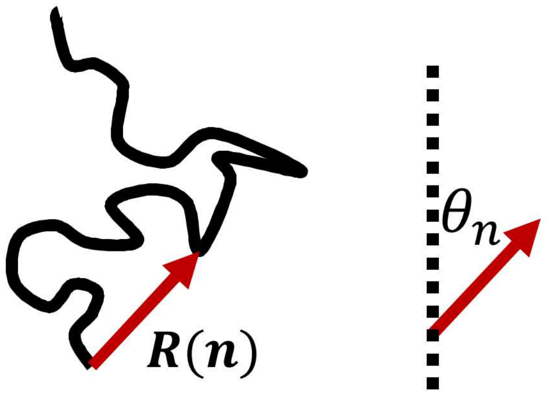
Steady-State Stretch and Orientation of Polymers During Flow



Orientation of the tube only affected by Z

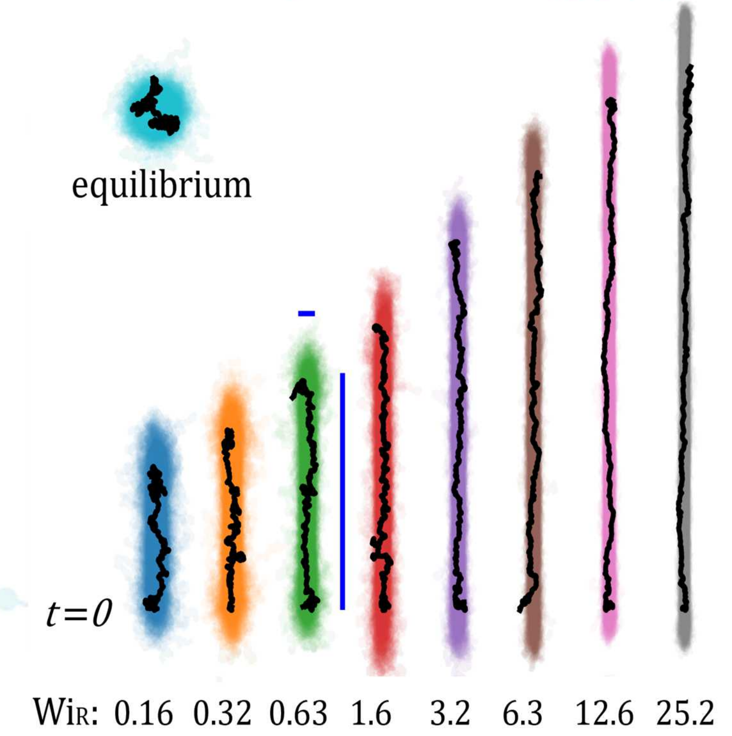
$Wi_R > 1$: chains elongate within tube. Stretching behavior similar same for melts & solutions w/ same N_e

Stretch in solution not enhanced by lower orientational order of the solvent oligomers, (but large diff. in $\eta_{ex}(\dot{\varepsilon})$)



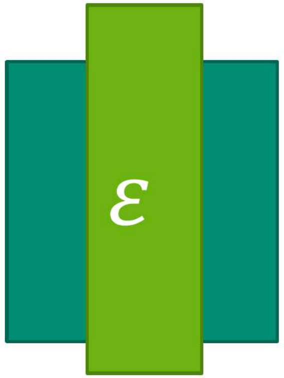
$$P_2(n) = \frac{1}{2}\left(3\langle\cos^2\theta_n\rangle - 1\right)$$

$$\lambda(n) = R(n)/R_{eq}(n)$$



Deriving the High-Rate Limiting Viscosity For Elongated Chains

The steady-state viscosity gives the macroscopic dissipation rate.



$$\dot{\varepsilon} = \frac{d\varepsilon}{dt}$$

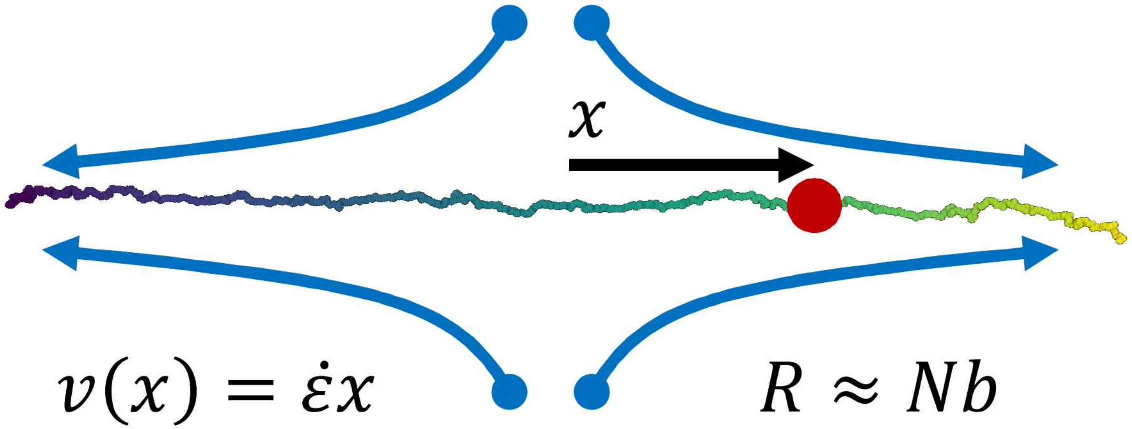
Dissipation rate: $\eta_{ex}\dot{\varepsilon}^2$

Macro **Micro**

$$\eta_{ex}\dot{\varepsilon}^2 = \frac{1}{12}\rho\zeta\, N^2b^2\dot{\varepsilon}^2$$

$$\eta_{ex} = \frac{1}{12}\rho\zeta\, N^2b^2$$

Straight chains → simple scaling of dissipative drag



$v(x) = \dot{\varepsilon}x$ $R \approx Nb$

Monomers move with same average velocity, but surrounding fluid has relative $v(x) = \dot{\varepsilon}x$

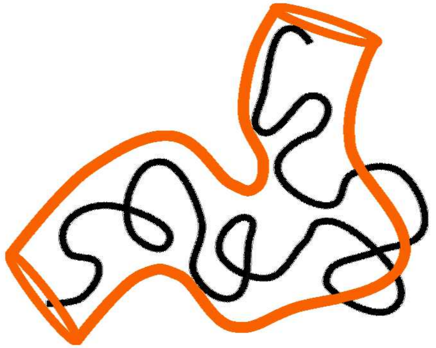
The drag force on a monomer at x is $\zeta v(x)$ and the energy dissipated is: $\zeta v(x)^2 = \zeta\dot{\varepsilon}^2x^2$

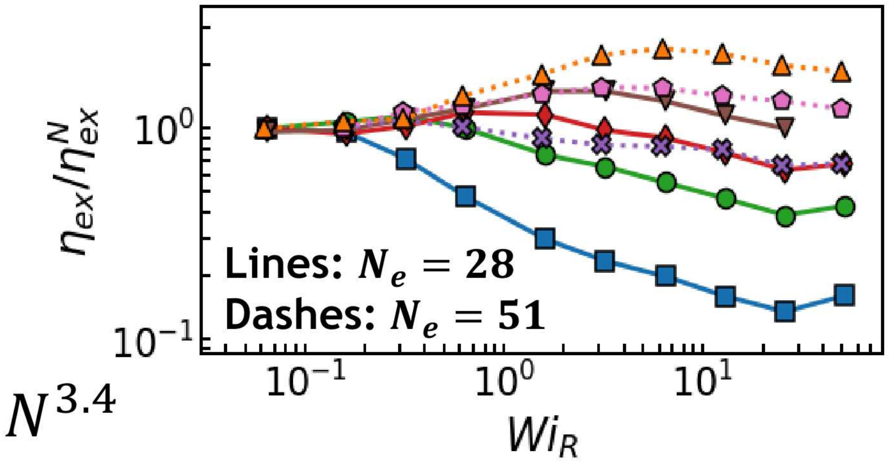
Average monomer dissipation:

$$\langle\zeta v^2\rangle = \frac{1}{N}\int_{-\frac{N}{2}}^{\frac{N}{2}} \zeta\, v^2(n)dn = \frac{1}{12}\zeta\, N^2b^2\dot{\varepsilon}^2$$

Elongation Changes How Chains Dissipate Energy

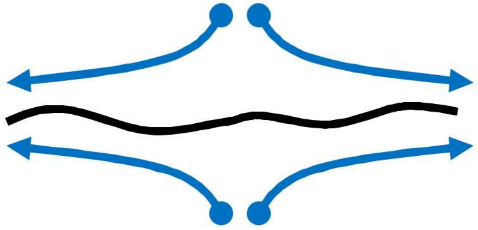
Low Wi_R Viscosity: due to relaxation by reptation



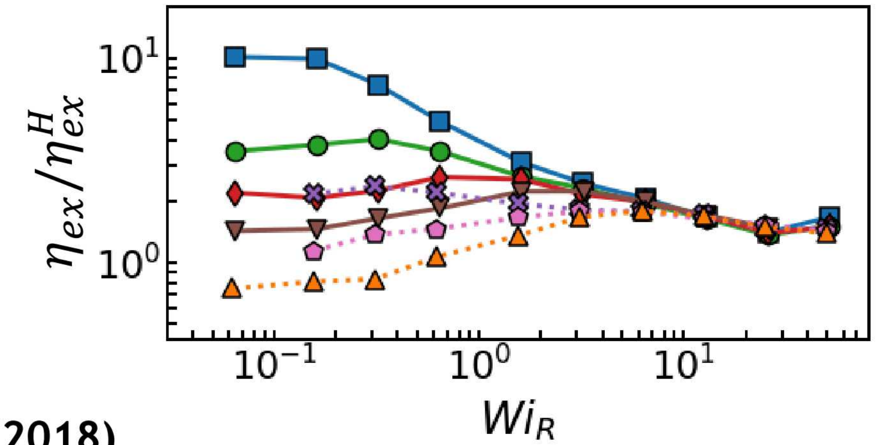


$$\eta_{ex}^N \approx G_e \tau_e Z^{3.4} \sim N^{3.4}$$

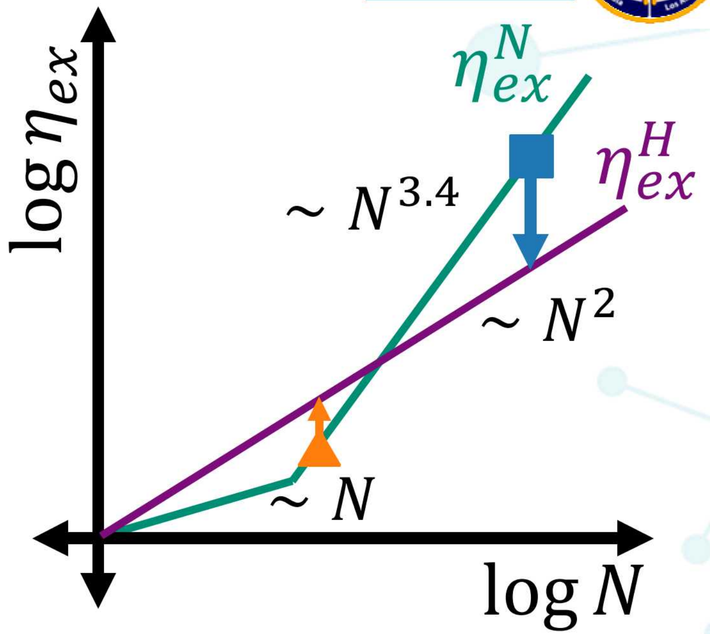
High Wi_R Viscosity: due to drag on elongated molecules



$$\eta_{ex}^H = \frac{1}{12} \rho \zeta b^2 N^2$$



TO'C, Alvarez, Robbins, PRL (2018)



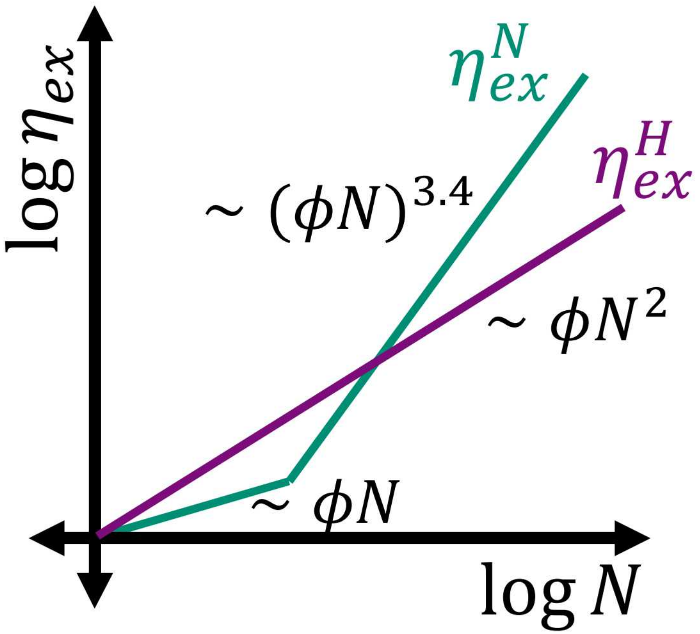
Trend depends on ratio of low/high rate limits

$$\frac{\eta_{ex}^N}{\eta_{ex}^H} \sim \frac{Z^{1.4}}{N_e} \frac{\zeta_0}{\zeta} \quad \begin{matrix} \gg 1 & \text{thinning} \\ \ll 1 & \text{thickening} \end{matrix}$$

monomer friction

Dilution Swells Entanglements, Reduces Thinning

Cross-Over For Solutions



Trend depends on ratio of low/high rate limits

$$\frac{\eta_{ex}^N}{\eta_{ex}^H} \sim \frac{Z^{1.4}}{N_e}\frac{\zeta_0}{\zeta} \begin{array}{ll} > 1 & \text{thinning} \\ < 1 & \text{thickening} \end{array}$$

Dilution to Polymer Fraction $\phi < 1$

$N_e \to N_e \phi^{-1}$ entanglement network swells

$Z \to Z\phi$ Fewer entanglements per chain

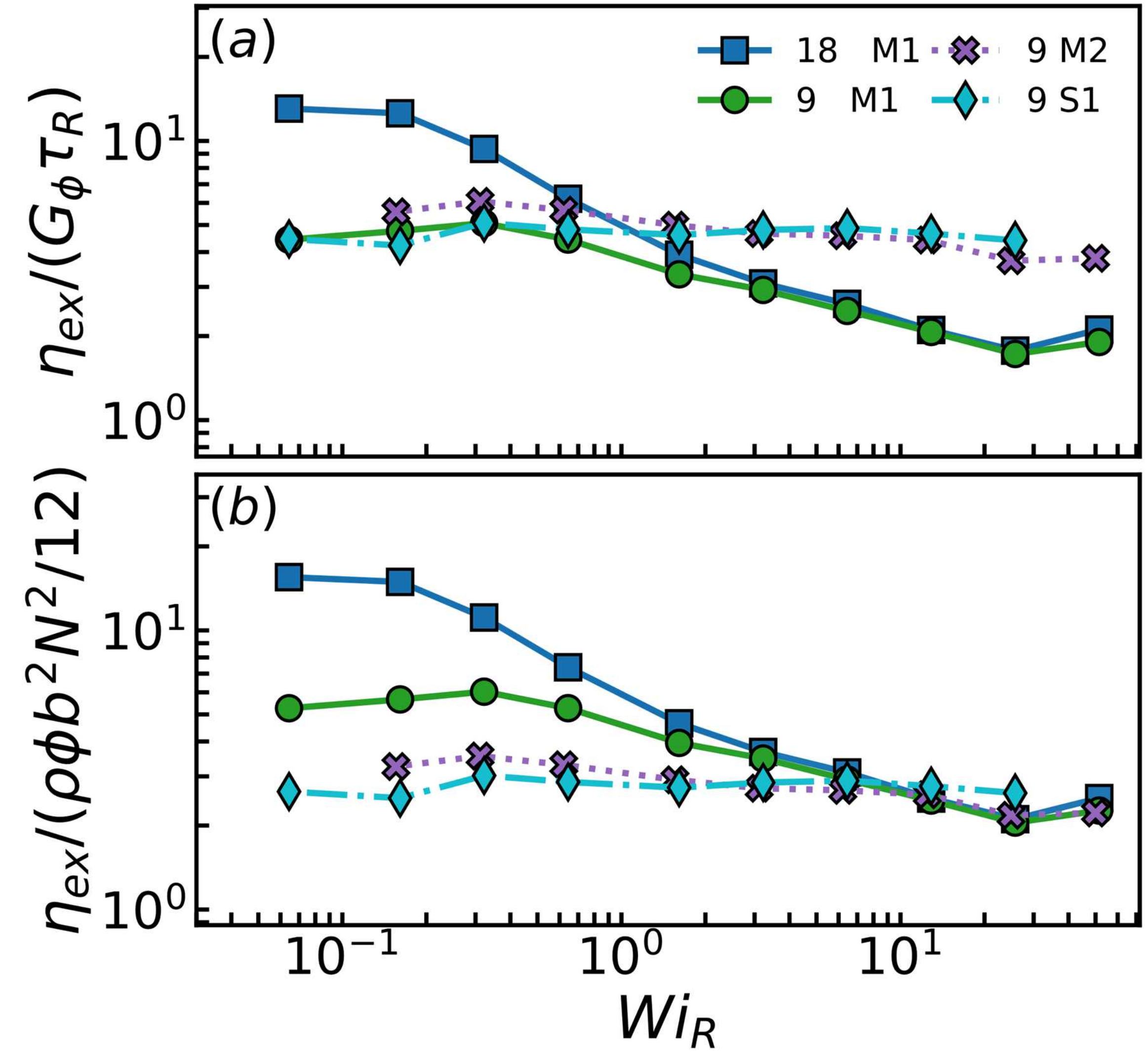
$\zeta \to \zeta(\phi)$ Friction can change due to solvent

$$\frac{\eta_{ex}^N}{\eta_{ex}^H} \sim \phi^{2.4} \frac{Z^{1.4}}{N_e}\frac{\zeta_0}{\zeta(\phi)} \sim \phi \frac{Z^{1.4}}{N_e}\frac{\zeta_0}{\zeta(\phi)}$$

(fixed N) **(fixed Z)**

Dilution of entanglements significantly reduces thinning, in addition to affects of changing friction.

Use The High-Rate Limit to Measure High-Rate Friction



Low-rate limit: reptation in swollen network

$$\eta_{ex}^N \approx 3 G_e \tau_e \phi^{3.4} Z^{3.4}$$

High-Rate Limit: ϕ fewer elongated chains

$$\eta_{ex}^H = \frac{1}{12} \rho \phi \zeta N^2 b^2$$

Rescale viscosity to get high-rate monomer friction

$$\zeta = \eta_{ex}^H / (\rho \phi b^2 N^2 / 12)$$

Simulations find slightly larger ζ ($\sim 10\%$) for solutions then for the melts.

Acknowledgements & Conclusions

Collaborators:

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Mark Robbins (JHU)

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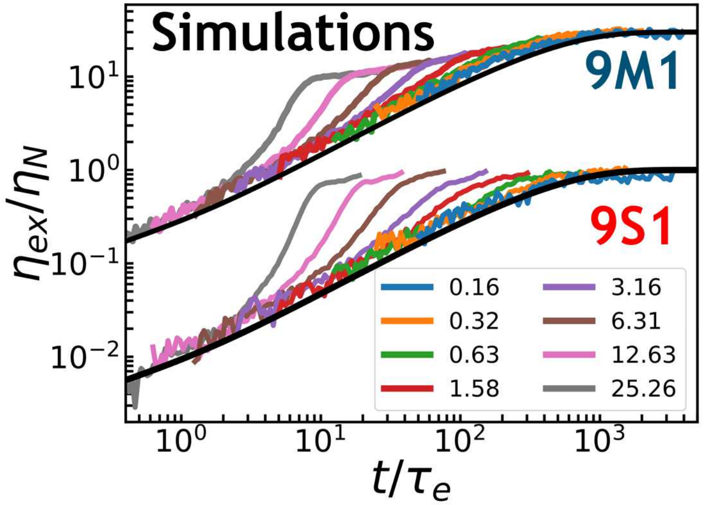
Peter Olmsted (Georgetown)
Mark Stevens (Sandia)
Giovanni Ianniruberto (Naples)
Vivek Sharma (Univ. Illinois)
Daniel Read (Leeds)

1. **Bead-spring simulations reproduce PS experiments for solutions & melts**
2. **Melts & solutions with same N_e and Z have similar nonlinear trends in ch**
3. **Trends for both captured by a cross-over in η_{ex} scaling from a reptation controlled Newtonian plateau to dissipative drag on elongated chains**
4. **Dilution can substantially reduce rate-thinning of η_{ex}, due to swelling N_e**
5. **Isolating for high-rate friction ζ, find rise of $\sim 10\%$ in oligomer solutions (shift in η_{ex}^N relative to η_{ex}^H dominates changes in rate-dependence)**



$$\frac{\eta_{ex}^N}{\eta_{ex}^H} \sim \phi^{2.4}\frac{Z^{1.4}}{N_e}\frac{\zeta_0}{\zeta(\phi)} \sim \phi\frac{Z^{1.4}}{N_e}\frac{\zeta_0}{\zeta(\phi)}$$

(fixed N) **(fixed Z)**

More details:

T.C. O'Connor, N. Alvarez, M.O. Robbins, PRL (2018)
T.C. O'Connor, A. Hopkins, M.O. Robbins, Macromol. (2019)

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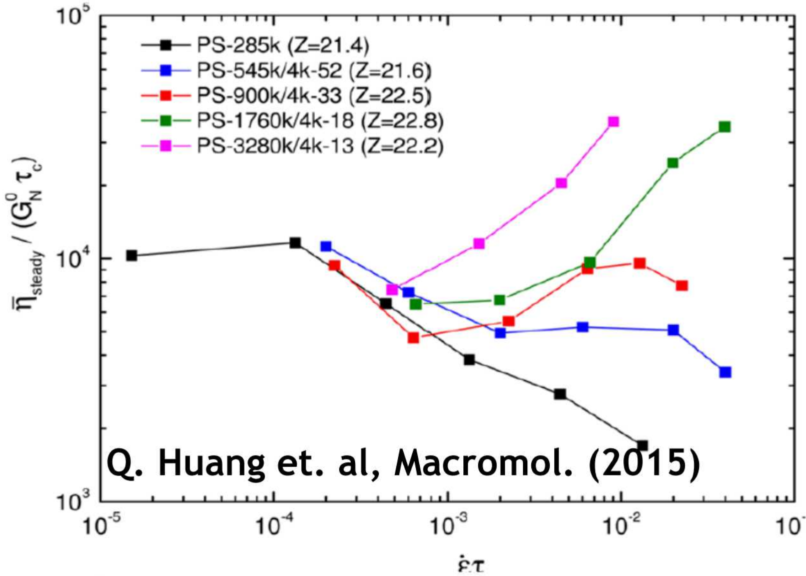
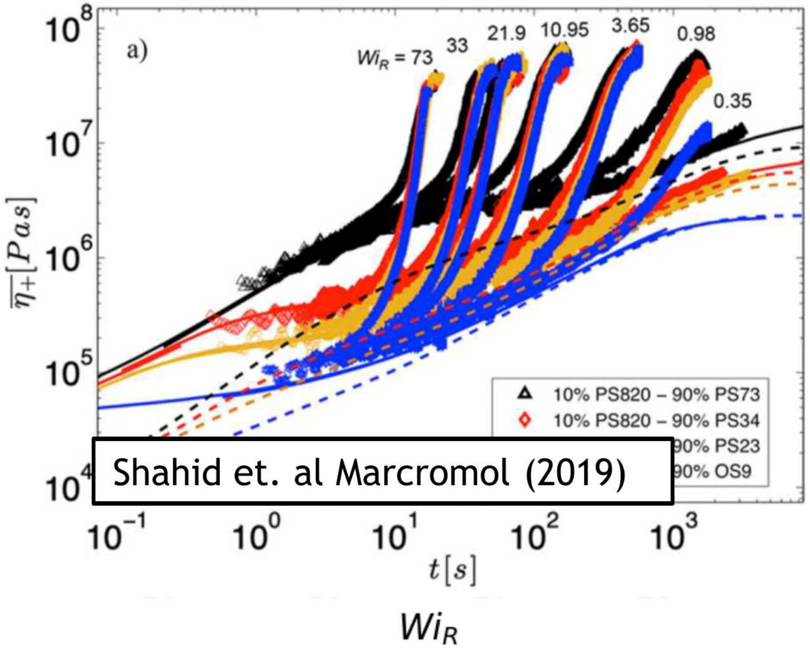
More Questions and More Mechanisms

Changing the length of solvent oligomers can also produce dramatic changes in measured viscosities.

Several studies suggest microphase separation of polymer & oligomer may be another important mechanism in extension.

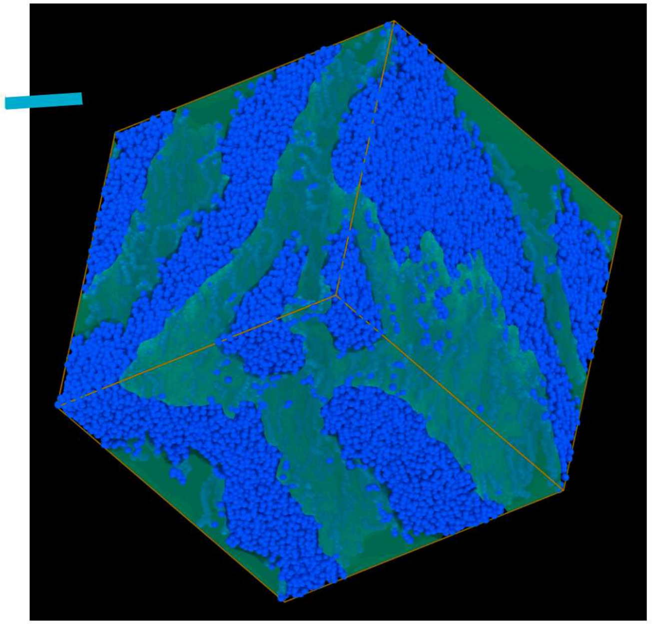


Q. Huang et. al, Macromol. (2015)

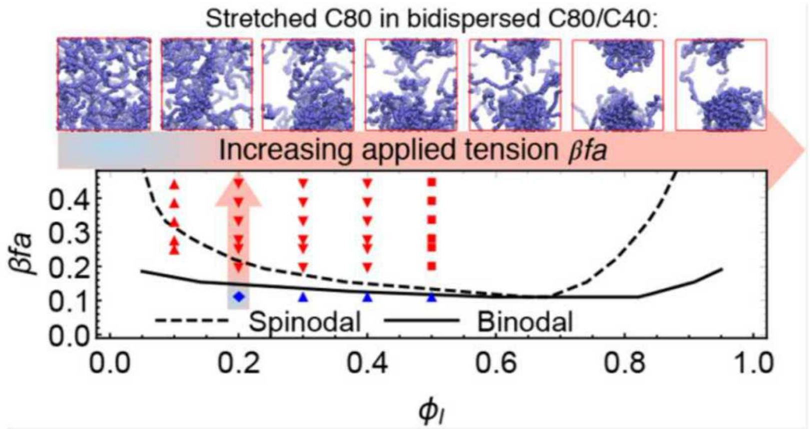


Shahid et. al Marcromol (2019)

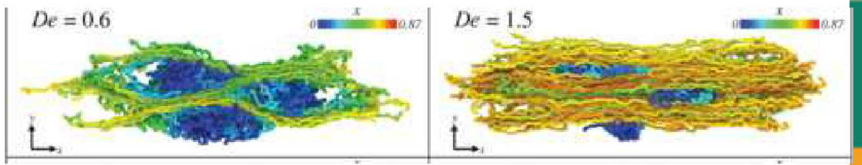
Bead-spring solution $Wi_R = 52$



W. Zhang & Larson, ACS Central Science (2018)



M. Nafar, ..., B. Khomami, PRL (2017)



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Stress Relaxation in Highly Oriented Melts of Entangled Polymers

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Supporting Information

ABSTRACT: Molecular dynamics simulations are used to study relaxation of entangled polymer melts deformed far from equilibrium by uniaxial extensional flow. Melts are elongated to a Hencky strain of 6 at Rouse−Weissenberg numbers from 0.16 to 25, producing states with a wide range of chain alignment. Then flow is ceased and the systems are allowed to relax until twice the equilibrium disentanglement time. The relaxation of the stress is correlated with changes in the conformation of chains and the geometry of the tube confining them. Independent of initial alignment, chains relax to conformations consistent with the equilibrium tube length and diameter on the equilibrium Rouse time. Subsequent relaxation is the same for all systems and controlled by the equilibrium distentanglement time. These results are counter to recent work that suggests orientation causes a large, stretch-dependent reduction in the entanglement density that can only be recovered slowly by reptation on the equilibrium disentanglement time, raising fundamental questions about the nature of entanglement in aligned polymer melts.