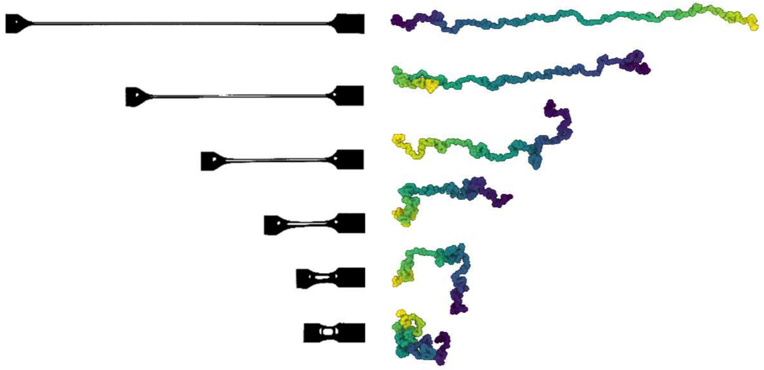
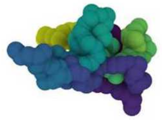
SAND2020-0013C

Ring-Linking Drives Anomalous Hardening of Ring Melts in Weak Extensional Flows





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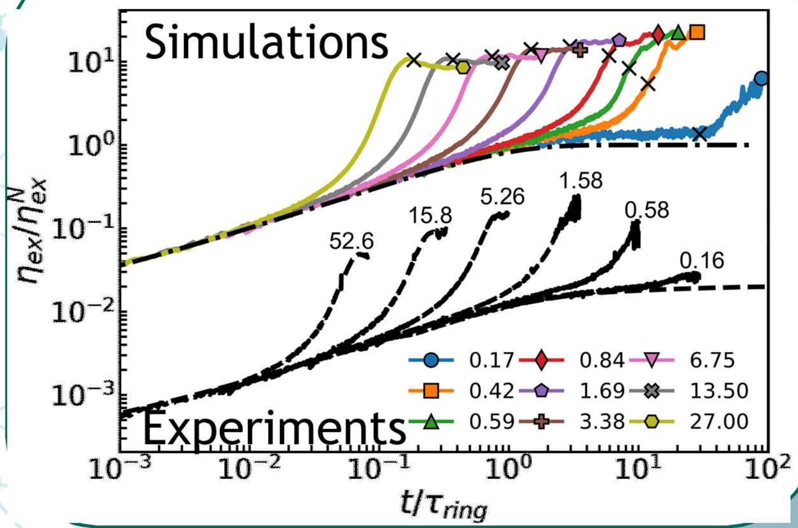

Gary S. Grest (SNL),

Ting Ge, Michael Rubinstein (DUKE)

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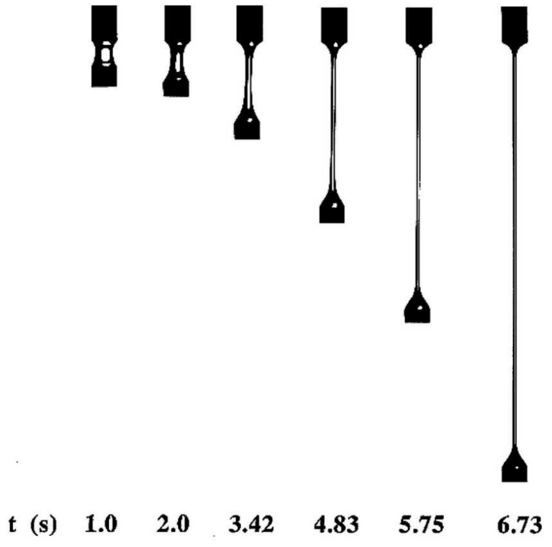
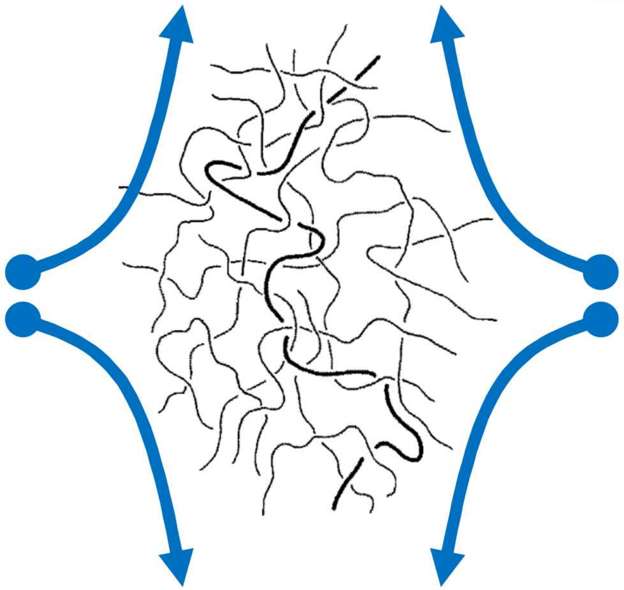
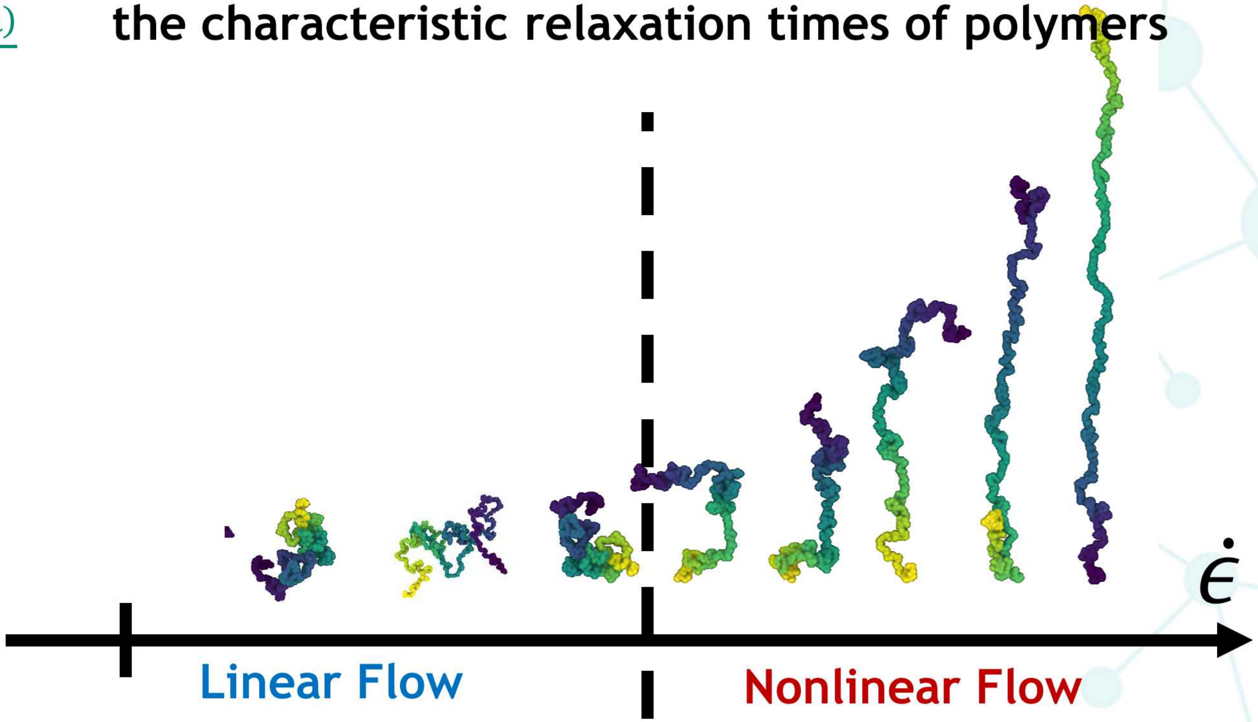
Nonlinear Extensional Flows: Competition between flow & Relaxation

Uniaxial extension flows stretch liquids exponentially in time. Rate of elongation set by the strain rate $\dot{\epsilon} \equiv \frac{\partial log(\lambda)}{\partial t}$





Nonlinear behavior occurs when $\dot{\epsilon}$ is faster than the characteristic relaxation times of polymers



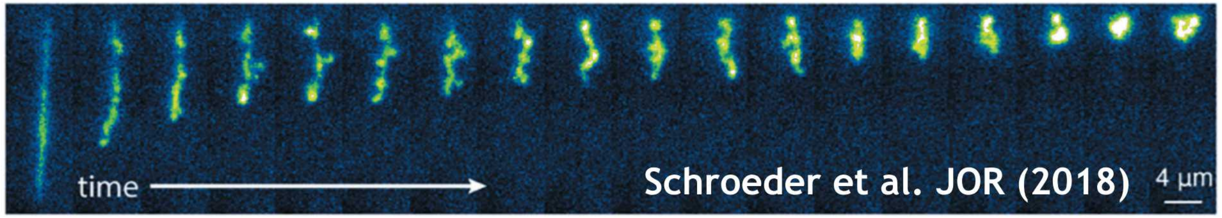
Measure flow strength with a Weissenberg number:

$$Wi_R = \dot{\epsilon}\tau_R$$

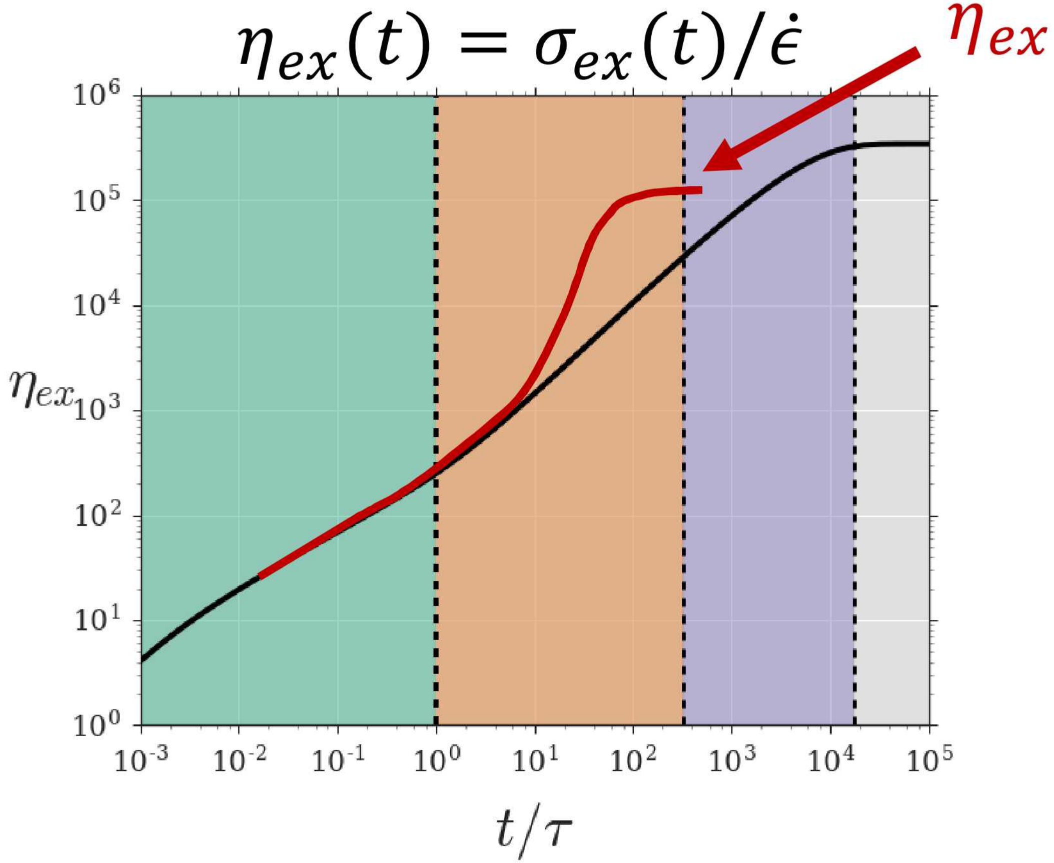
$Wi_R \to 0$ Newtonian

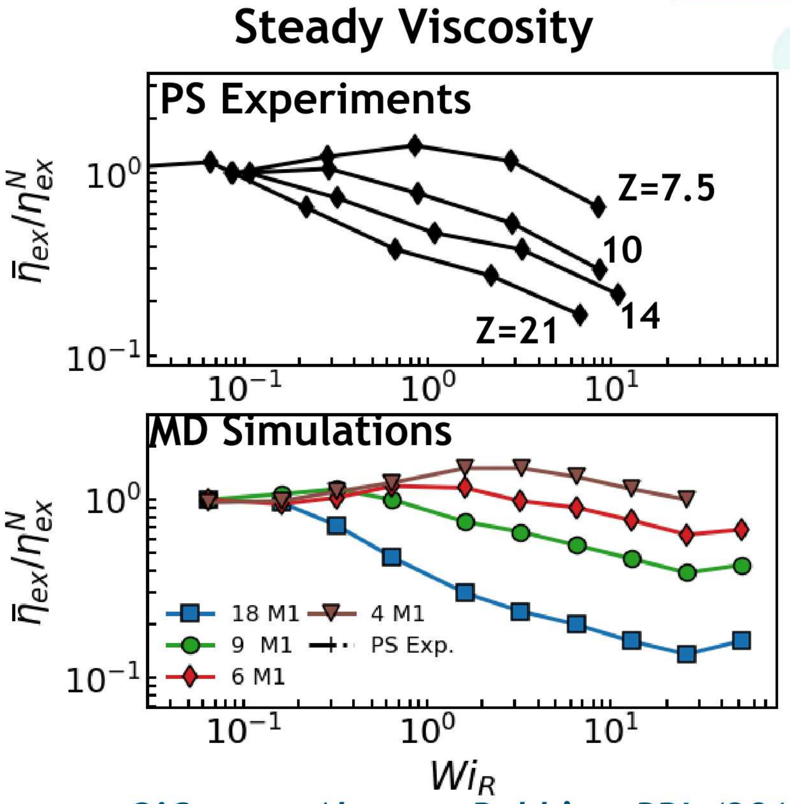
$Wi_R > 1$ Elongation

Linear chains relax stretch over the Rouse time $\tau_R \sim N^2$



Macroscopic Viscosity Encodes Chain Dynamics





O'Connor, Alvarez, Robbins, PRL (2018)

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

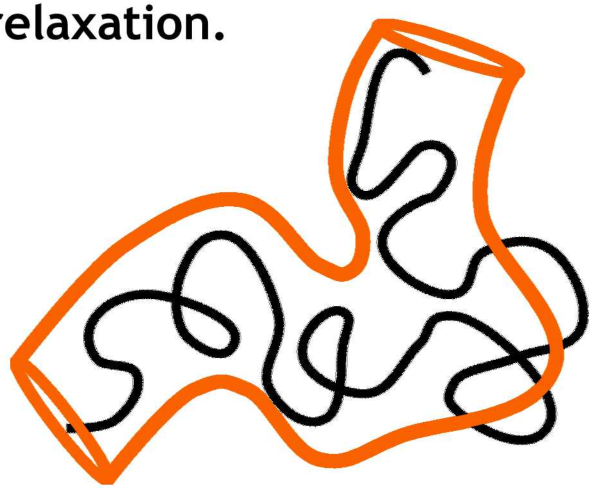
- Viscosity evolves along a limiting curve (LVE), and plateaus to Newtonian viscosity.
- Controlled by equilibrium chain dynamics - very different for linear & ring polymers.

Strong Nonlinear Flows ($Wi > 1$):

- Viscosity increases more rapidly than the LVE and plateaus to a nonlinear value $\eta_{ex}(\dot{\epsilon})$.
- MD reproduces nonlinear rate-dependence and relates to chain conformations: *O'Connor et al., PRL (2018)*

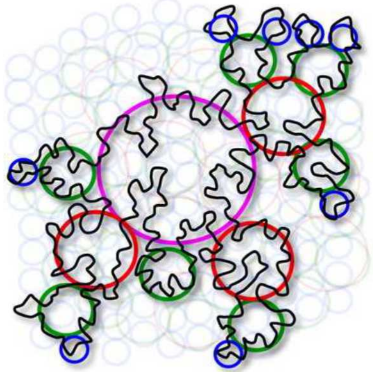
2) Dynamic Linking In Ring Polymer Melts

The entanglement tube defines a length-scale that dominates relaxation.

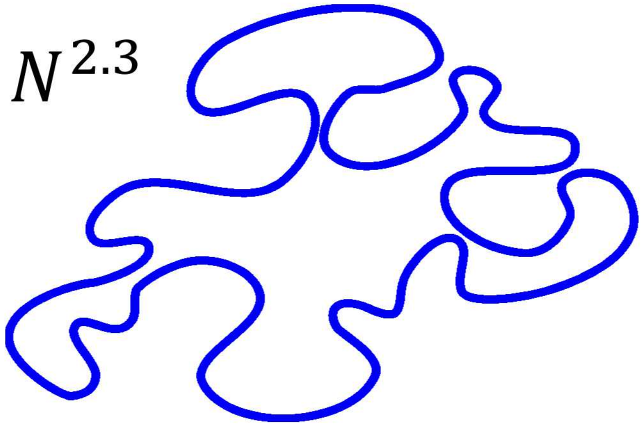


$$\eta_N \sim Z^{3.4} \sim \left(\frac{N}{N_e}\right)^{3.4}$$

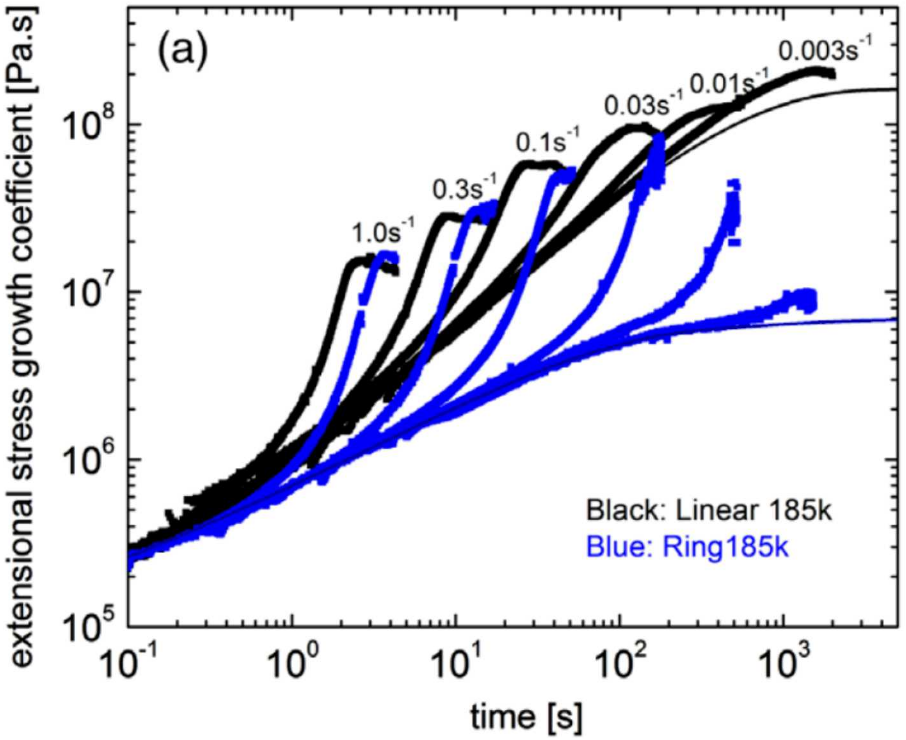
Replacing linear chains with rings destroys the entanglement network and lowers the viscosity.



$$\eta_N \sim N^{2.3}$$



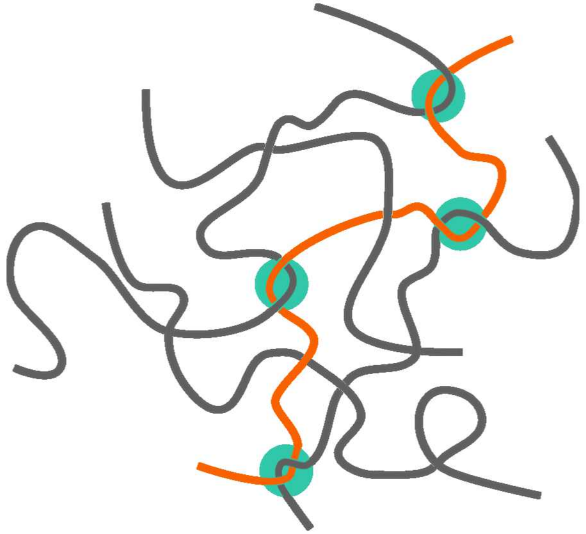
Rings are fractal & relax self-similarly at all scales

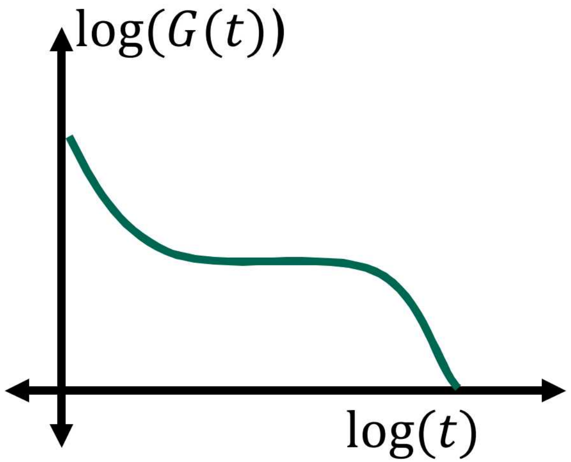


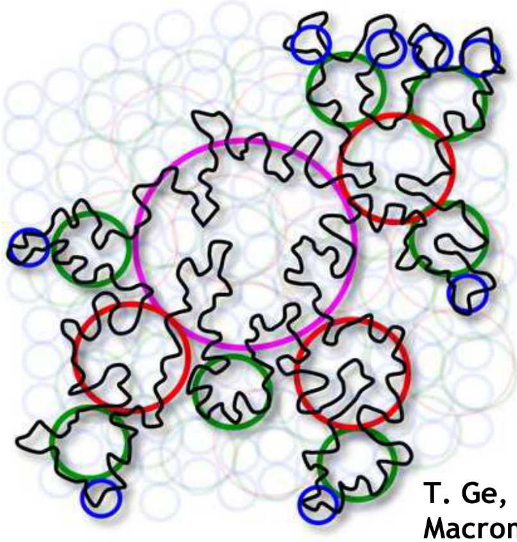
Newtonian viscosity of rings is much lower than linears with the same molecular weight.

But rings show an extraordinary sensitivity to extensional flow. Massive rise in viscosity!

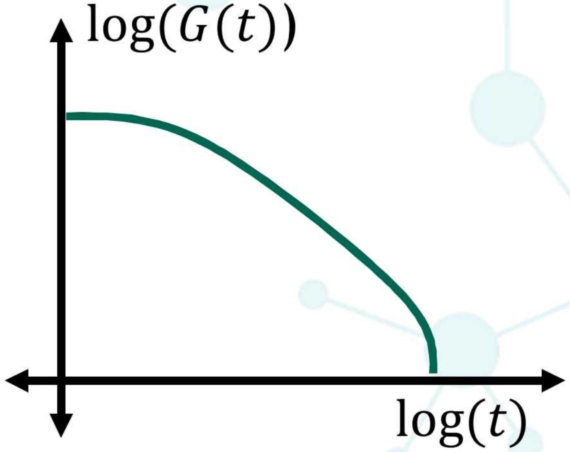
Melts & Rings Have Different Equilibrium Relaxation







T. Ge, M. Rubinstein, Macromol. (2016)

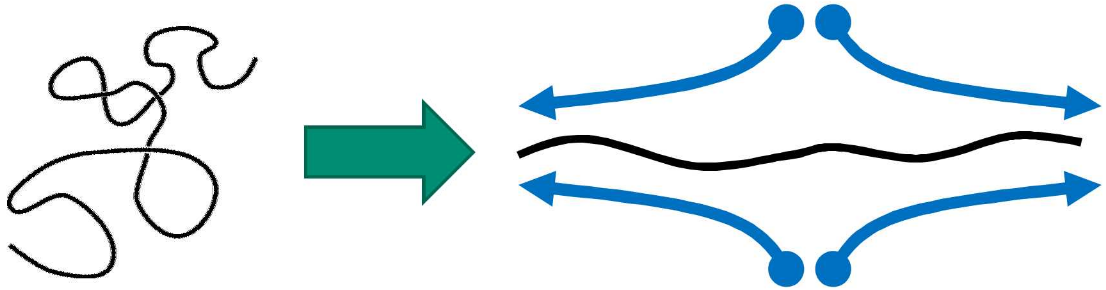


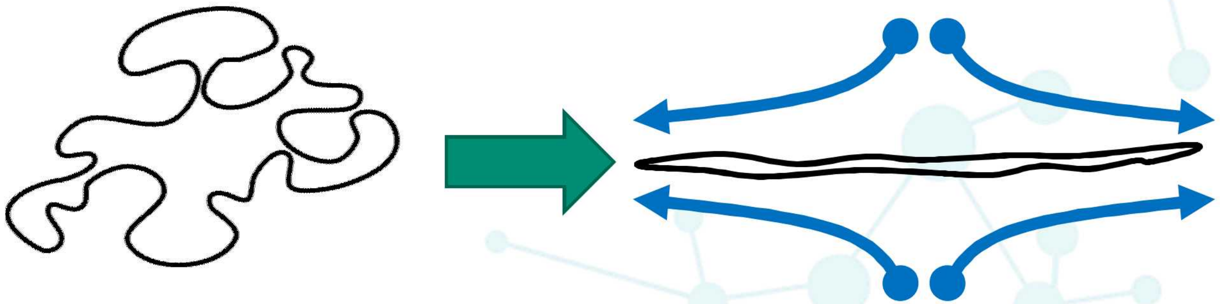
Entanglements confine chains to a primitive path, & create a hierarchy of exponential relaxation times.

Longest relaxation time $\tau_d \sim N^{3.4}$

Fractal hierarchy of interpenetrating loops that gives a power-law viscoelastic relaxation

Longest relaxation time $\tau \sim N^{2.33}$

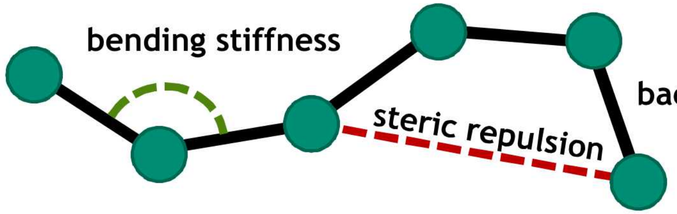




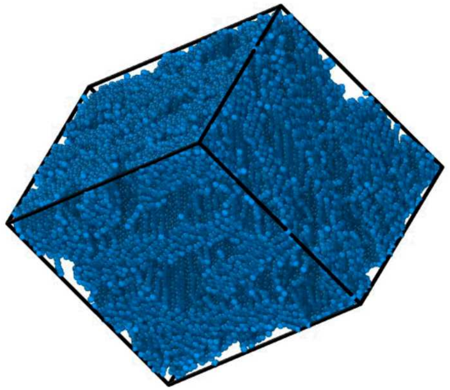
Equilibrium dynamics are very different, but elongated states are similar. Ring to linear crossover?

Nonlinear Elongation of Ring Polymer Melts

Model: Semiflexible bead-spring model



- linear properties well known ($N_e \approx 28$ beads)
- Rings with N=200, 400, & 800 beads
- Compare to linears with N=100, 200, & 400 beads
- Same contour length at full extension



Constant-rate uniaxial extensional flows

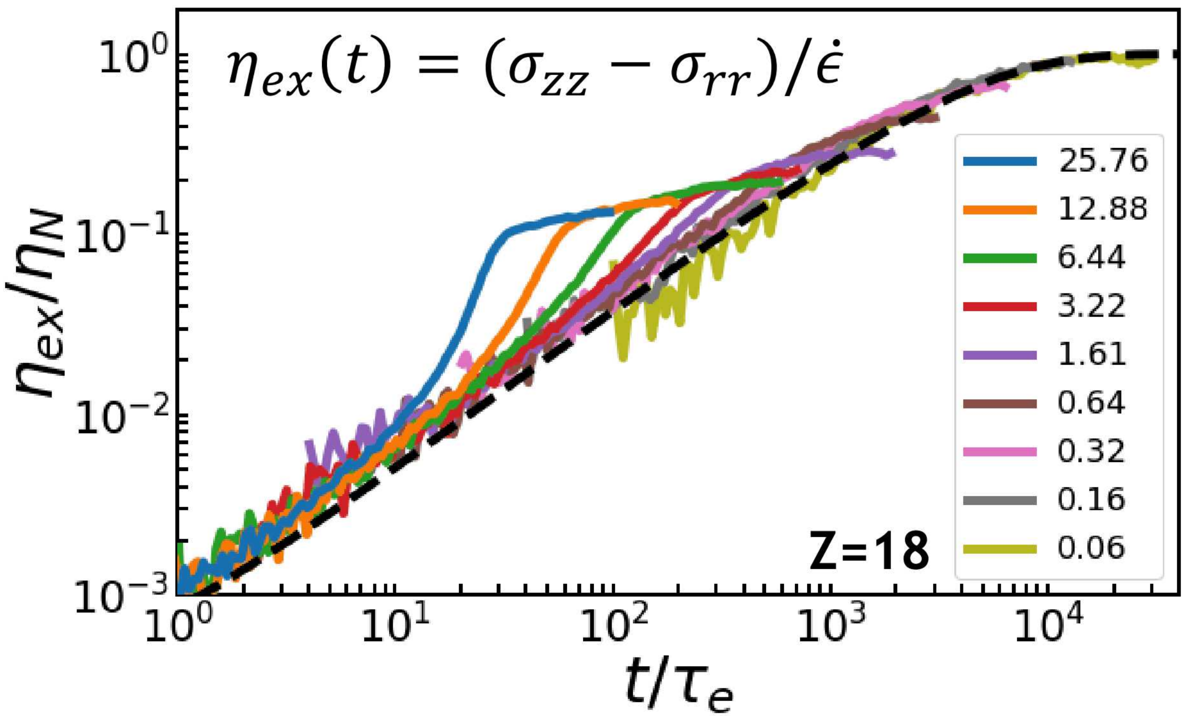
- Elongate to strain $\epsilon > 6.0$ → resolve steady-state
- Vary $Wi = \dot{\epsilon}\tau = 0.16 - 0.25$
- Linear: $Wi = \dot{\epsilon}\tau_R$ Ring: $Wi = \dot{\epsilon}\tau$
- Relate rate-dependence to chain dynamics

Rate dependence – do highly extended rings behave like linear chains?

Dynamics - how do rings elongate in the absence of entanglements?

Massive and Delayed Viscosity Rise During Ring Extension

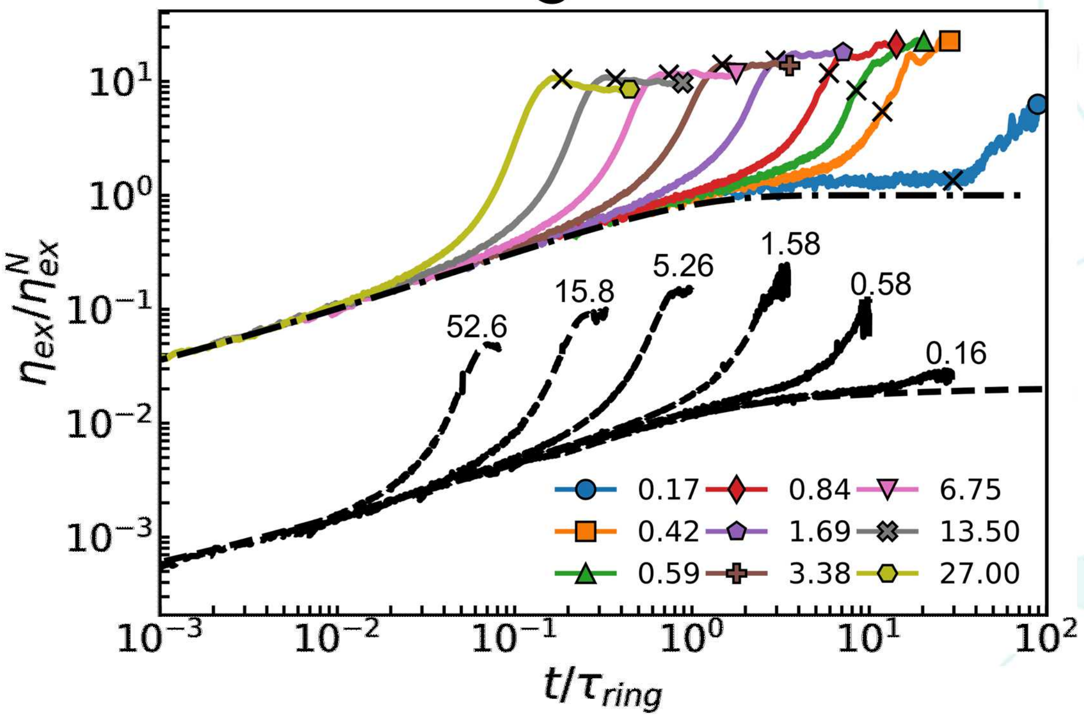
N=200 Linear Melt Extension



η_{ex} collapses onto LVE (dashed) as Wi→0

Steady viscosity decreases with increasing Wi, typical of well-entangled melts.

N=400 Ring Melt Extension



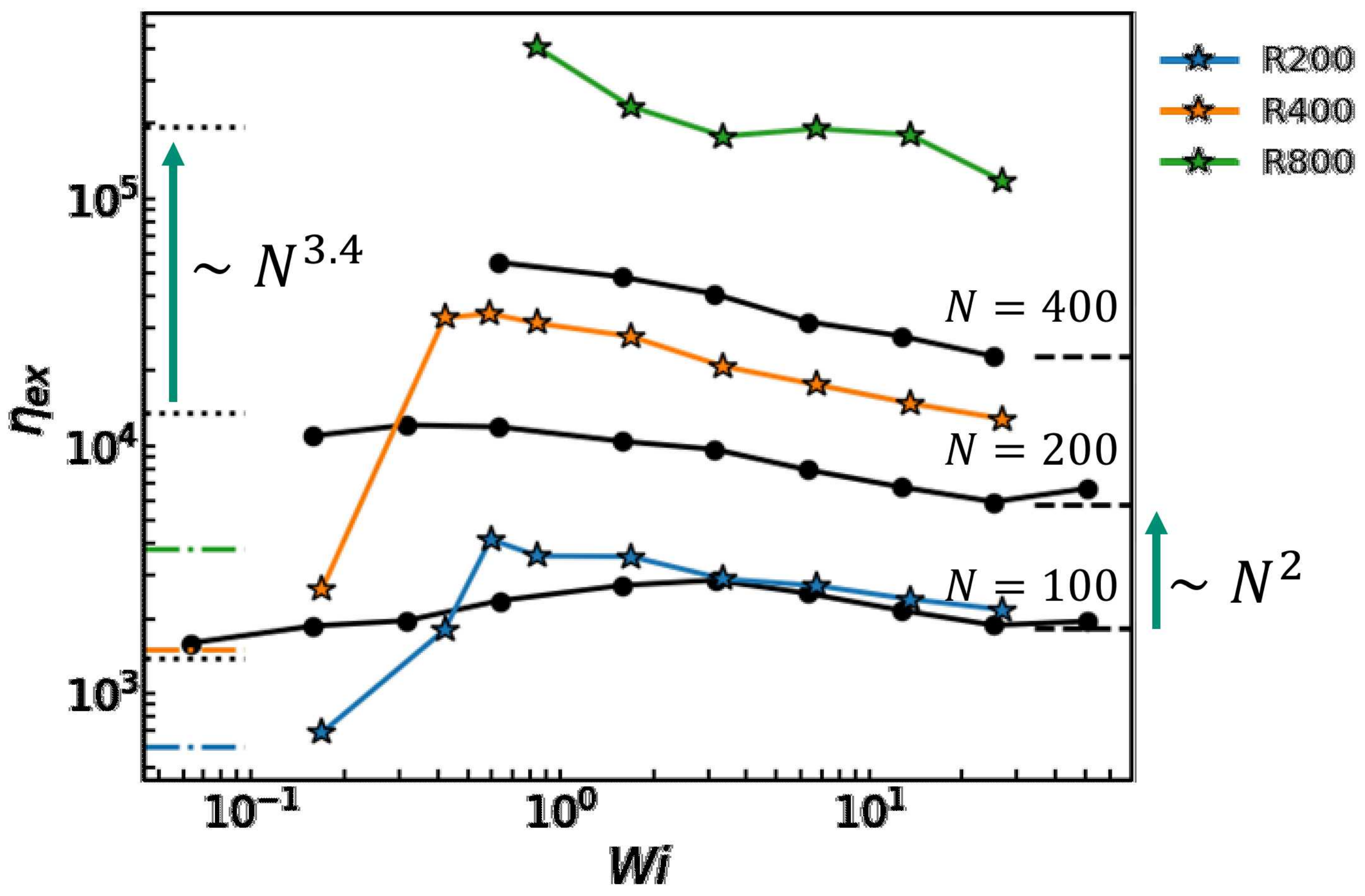
10x rise in viscosity at *ALL* Wi even Wi<<1

Rise at low Wi *delayed* for many ring relaxation times (vertical dashed line)

MD simulations reproduce experimental rheology, but what is the driving mechanism?

Steady Viscosities For Different Molecular Weights

Steady-State Extensional Viscosity



Linear melts with N=100,200,400

Newtonian viscosity $\sim N^{3.4}$ tube theory

High Wi viscosity set by drag on highly extended chains $\eta_{ex} \sim \zeta N^2$.

O'Connor, Alvarez, Robbins, PRL (2018)

Ring melts with N=200,400,800

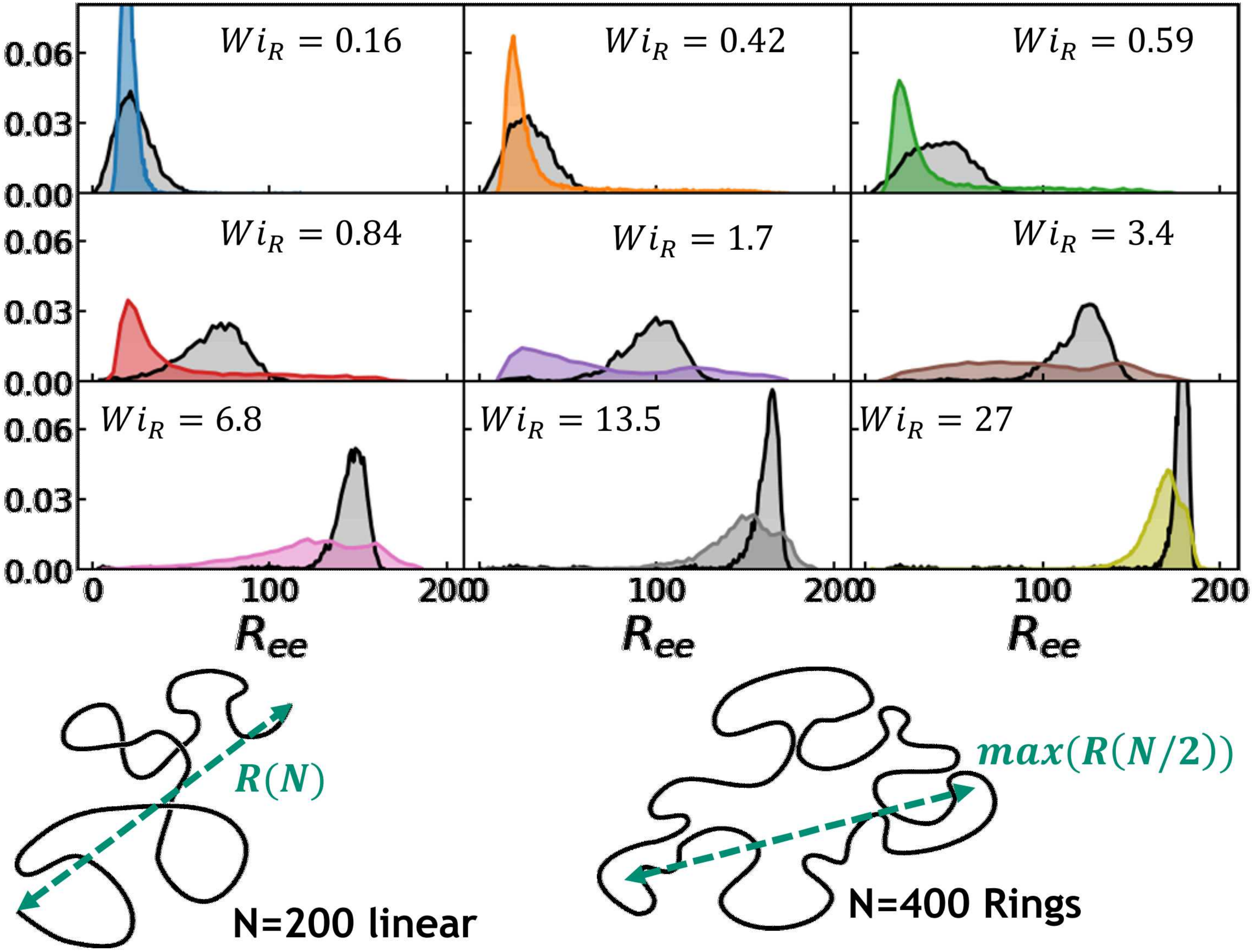
N=200 ring viscosity appears to follow N=100 linear melt for Wi > 1.

Agreement breaks down as *N* increases.

Ring viscosity grows faster with *N* than it does for linear chains.

Chain Extension

Steady-State End-End Distributions



Network Stretches Linear Chains ~Affinely

Chains stretch uniformly with single peak captured by average stretch λ in models

Rings Dominated By Large Fluctuations

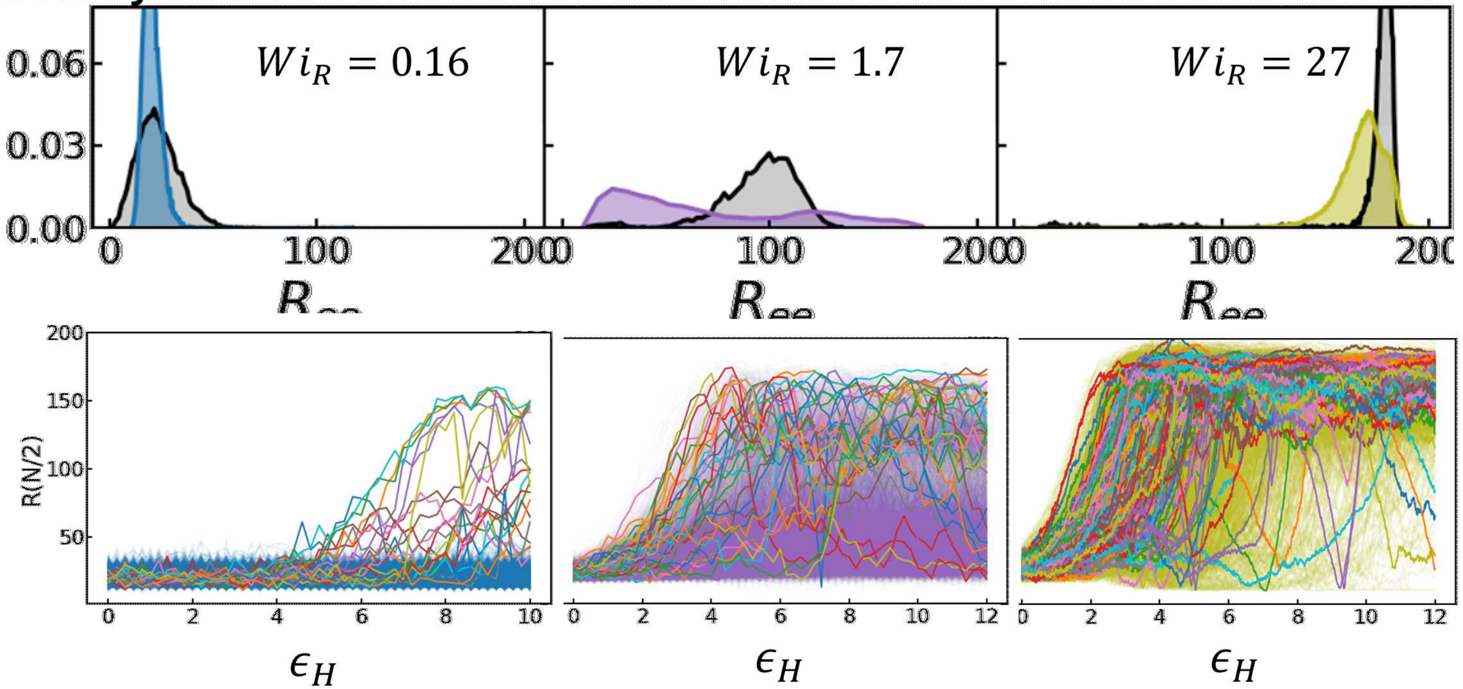
Develop long tale at low Wi of few highly stretched and retracting rings

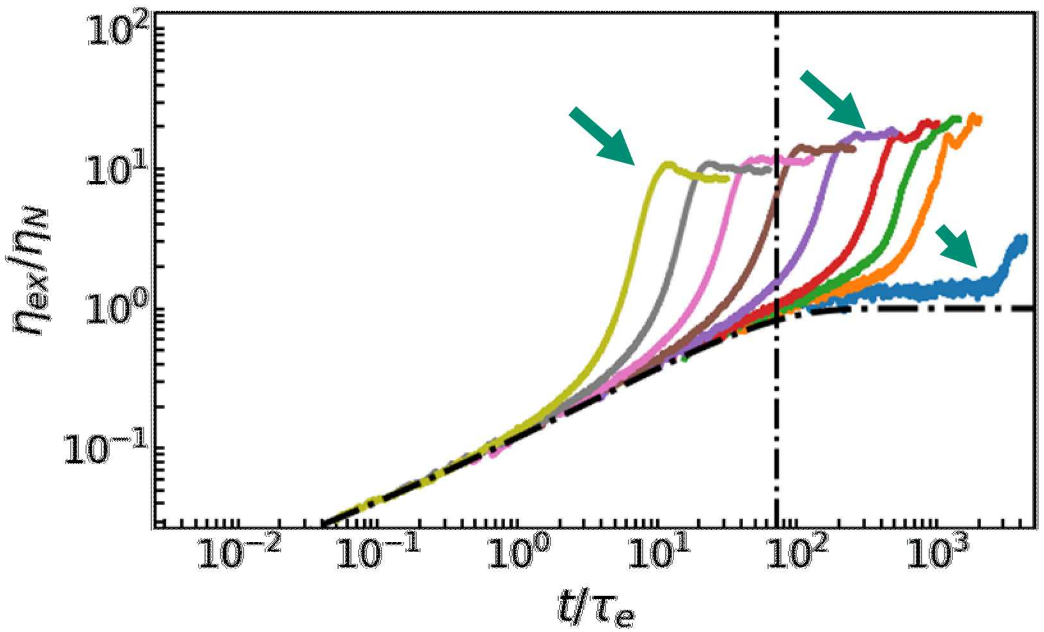
Grows into a broad distribution of highly fluctuating rings at Wi~1

Large fluctuations cannot be described by averages

Individual Chains Fluctuate Between Extended & Retracted

Steady-State End-End Distributions





Individual chains fluctuate between fully extended & retracted at all Wi

Even at highest Wi=27, some chains still fully retract & then reextend.

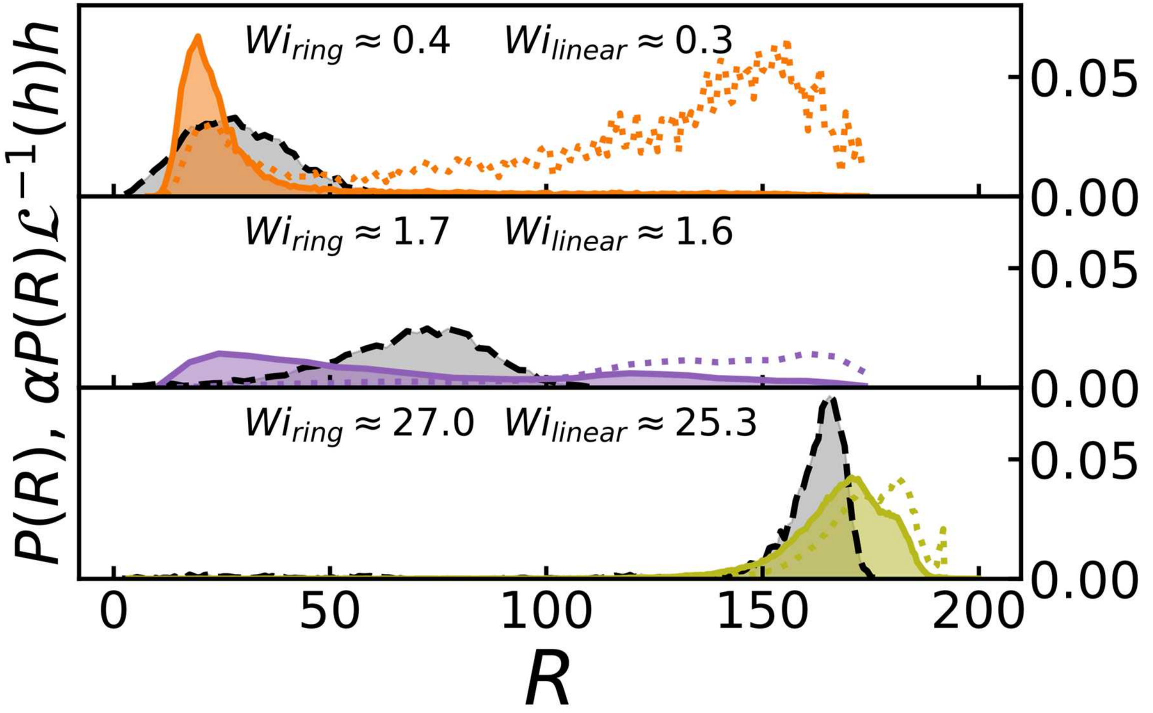
Do not observe this behavior in linear melts. Globular rings aren't very easy to elongate.

Low & high Wi have qualitatively different distributions but similar nonlinear η_{ex}

Wi=0.16: small fraction of highly stretched chains produce larger η_{ex} than fully stretched Wi=27

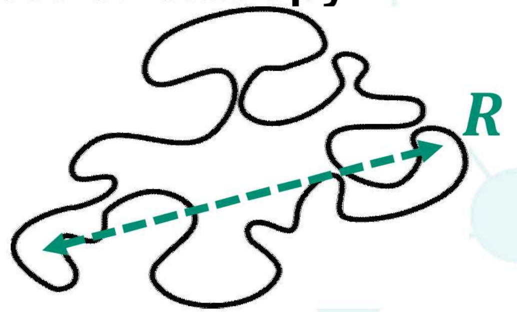
Individual Chains Fluctuate Between Extended & Retracted

Steady-State End-End Distributions



Stress from each ring due to loss of entropy

$$F_{ent} \propto \frac{2R}{Nb} L^{-1}\left(\frac{2R}{Nb}\right)$$



Relative of contribution of rings at each R to σ_{ex}

$$\propto P(R)F_{ent}$$

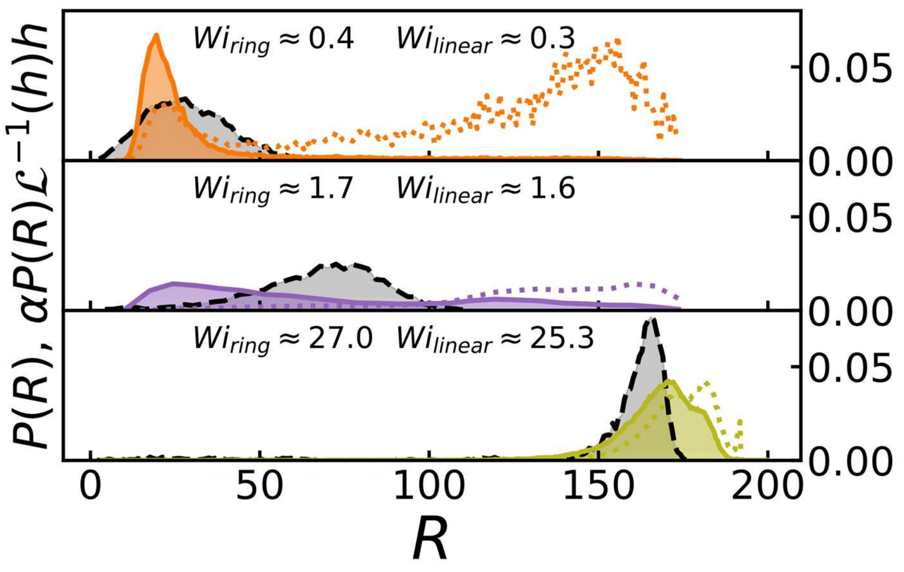
Nonlinear stresses in rings are driven by a small number of chains at low Wi_R

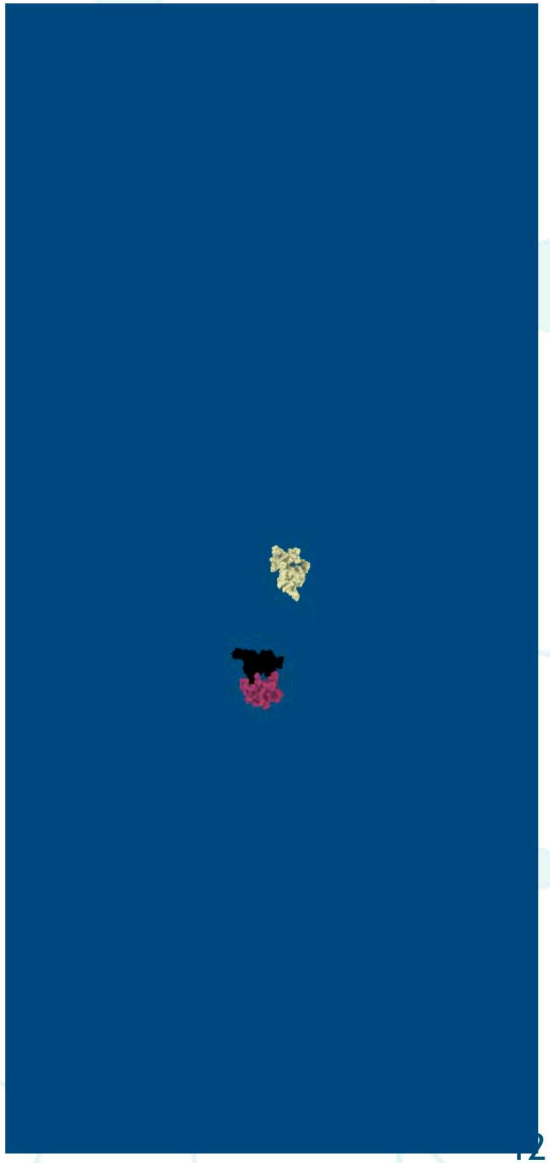
Can compute the relative contribution of each ring to the stress.

Most stress is contributed by the most elongated rings.

Less then 1% elongated rings at $Wi = 0.4$ give similar η_{ex} as 90% elongated at $Wi \approx 27$?

Extreme Elongation Is Driven By Topological Linking of Rings

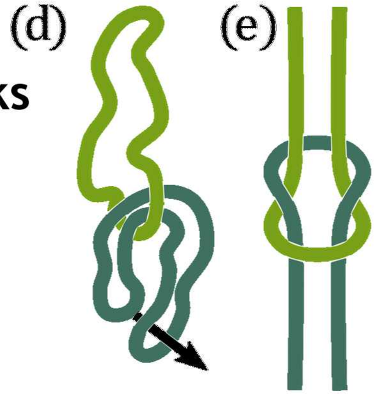




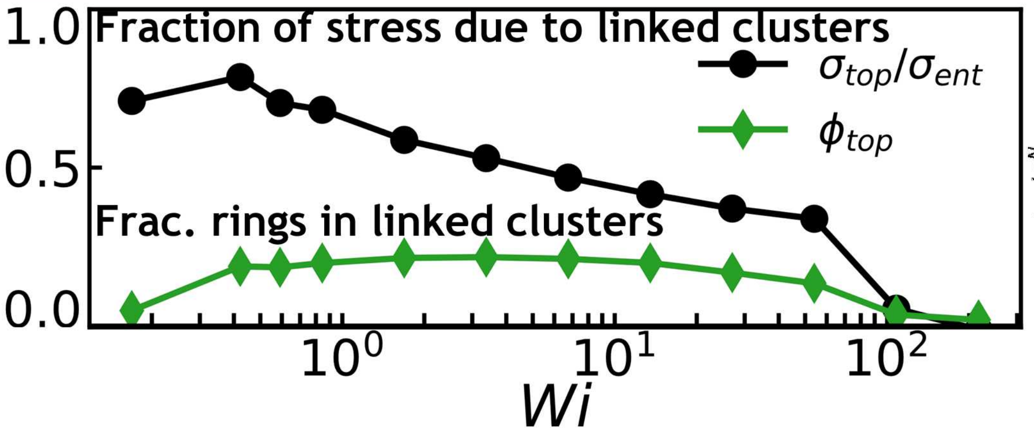
Rings can interpenetrate and link by forming "cow hitches"

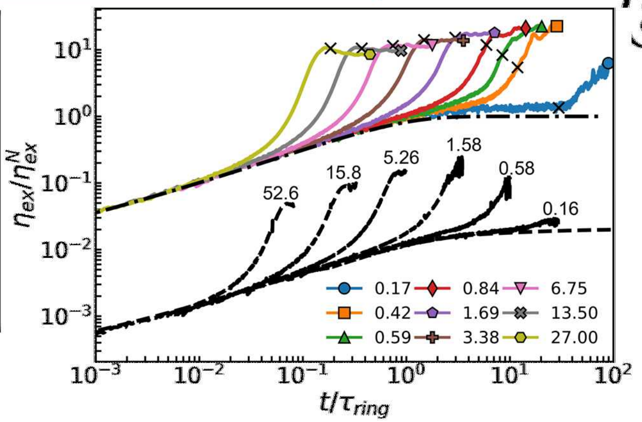
Elongation flow stabilizes these links & derives supramolecular chains to strongly elongate even at low Wi.

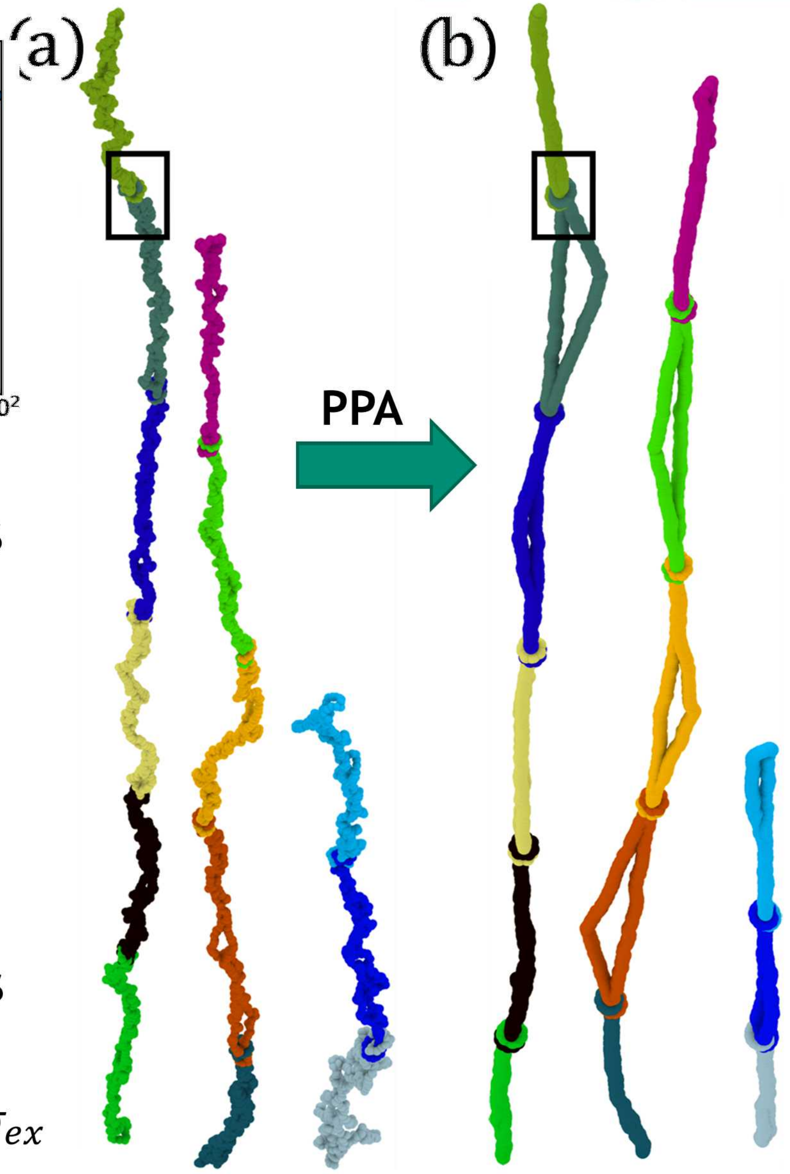
Links can form spontaneously, long after flow has begun.



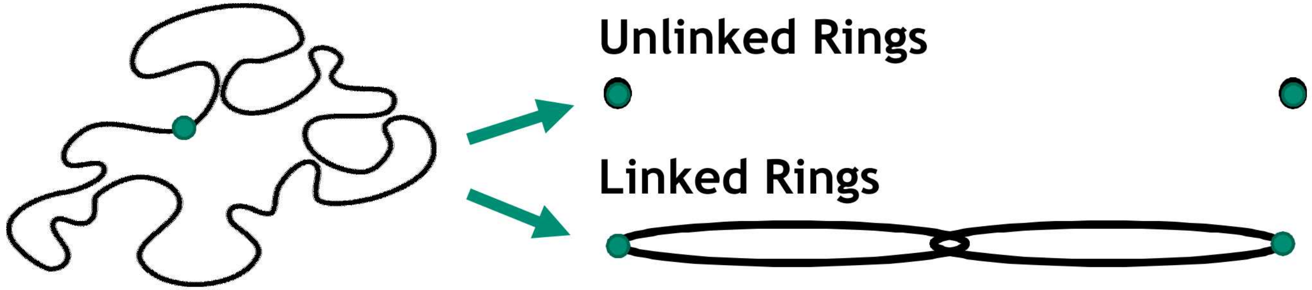
Measuring Contribution to the Stress From Linked Rings







Primitive Path Analysis can distinguish fraction ϕ_{top} of linked rings



Most of the nonlinear rise in stress at low Wi is due to linked rings

$$\sigma_{top} = \sigma_{ex}\left[\text{from } \phi_{top}\right]$$

Wi=0.1: 1% of linked chains give ~ 75% σ_{ex}

Acknowledgements & Conclusions

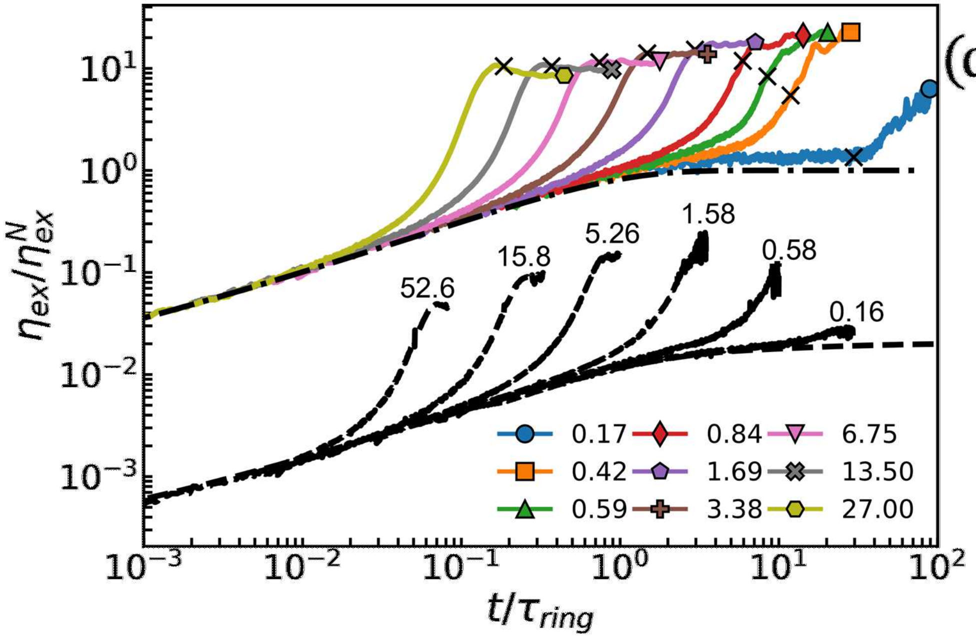
Collaborators:

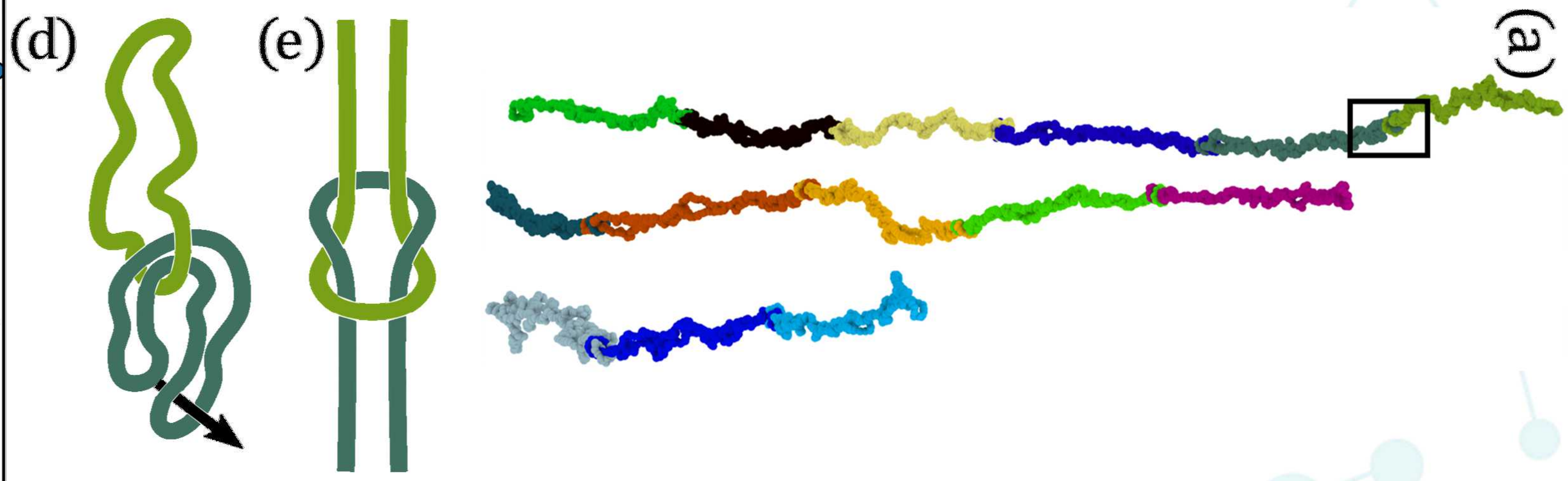
Ting Ge (Duke)
Michael Rubinstein (Duke)
Gary S. Grest (SNL)
Qian Huang (DTU)

Funding:

Harry S. Truman Fellowship (SNL)

1. Simulations reproduce anomalous extensional rheology of exps.
2. Rings exhibit a massive and delayed rise in η_{ex}, even for Wi<<1
3. Wi<<1: large η_{ex} from small # of stretched chains
4. Rings self-assemble by linking into supramolecular clusters
5. Clusters elongate strongly in flow, driving anomalous hardening
6. Fraction of supramolecules changes nonmontonically with Wi_R





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