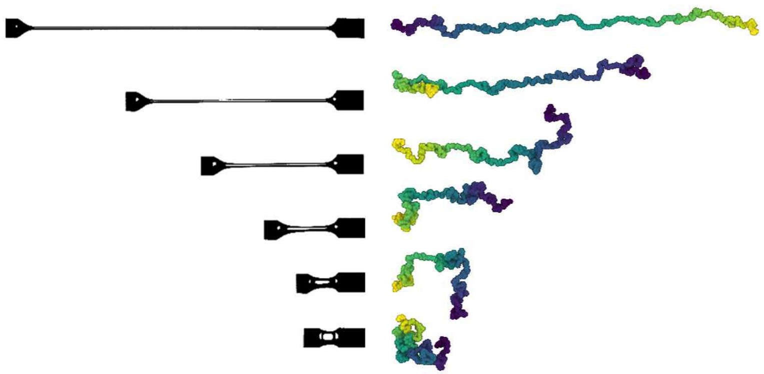
This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

SAND2019-2214C

Unexpected Extensional Rheology in Ring Polymer Melts



PRESENTED BY

Thomas C. O'Connor

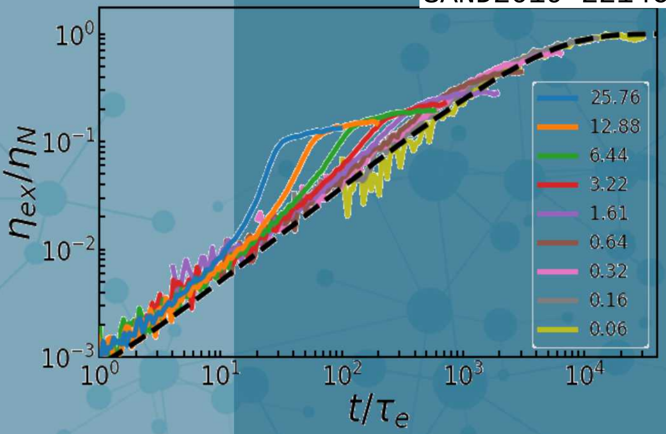
Harry S. Truman Fellow

Sandia National Laboratories

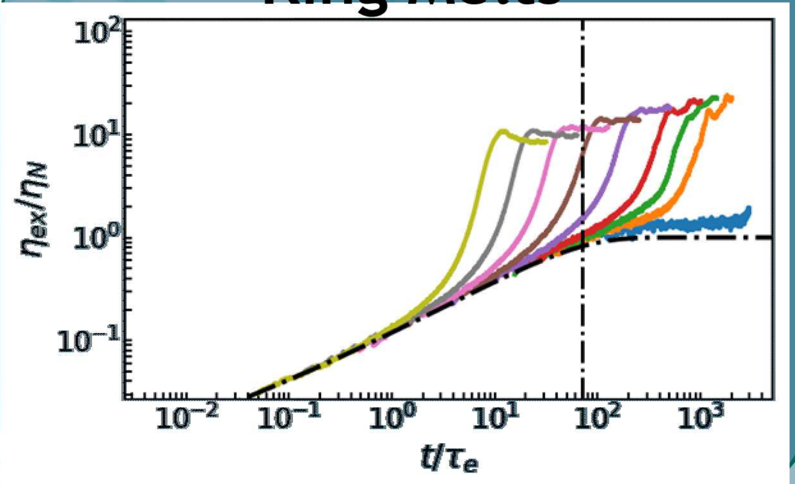
Gary S. Grest (SNL),

Ting Ge, Michael Rubinstein (DUKE)

Linear Melts



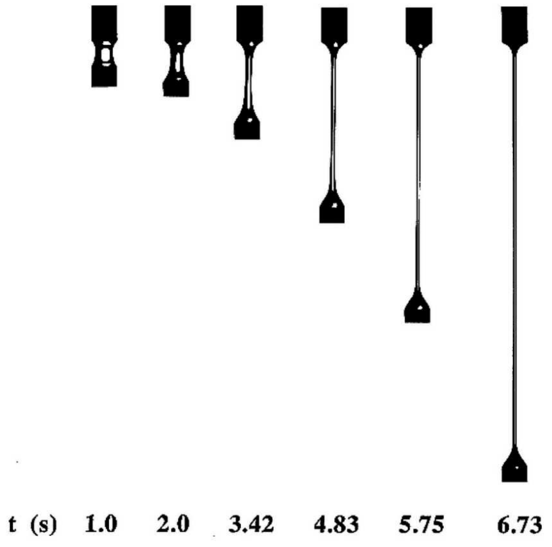
Ring Melts

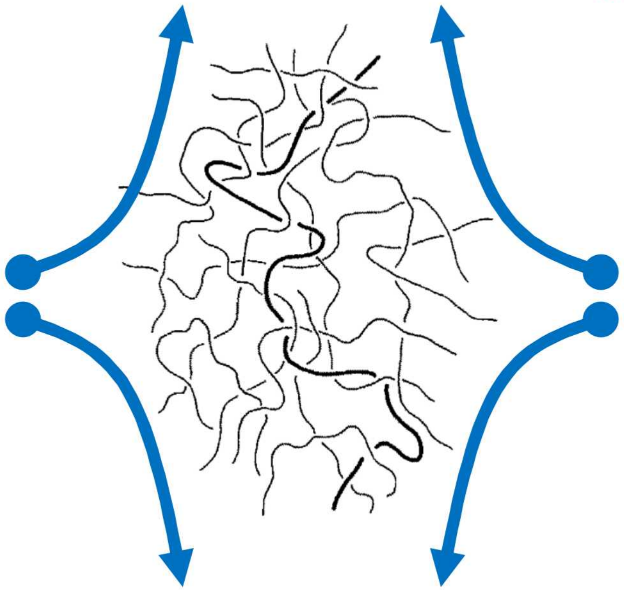


Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

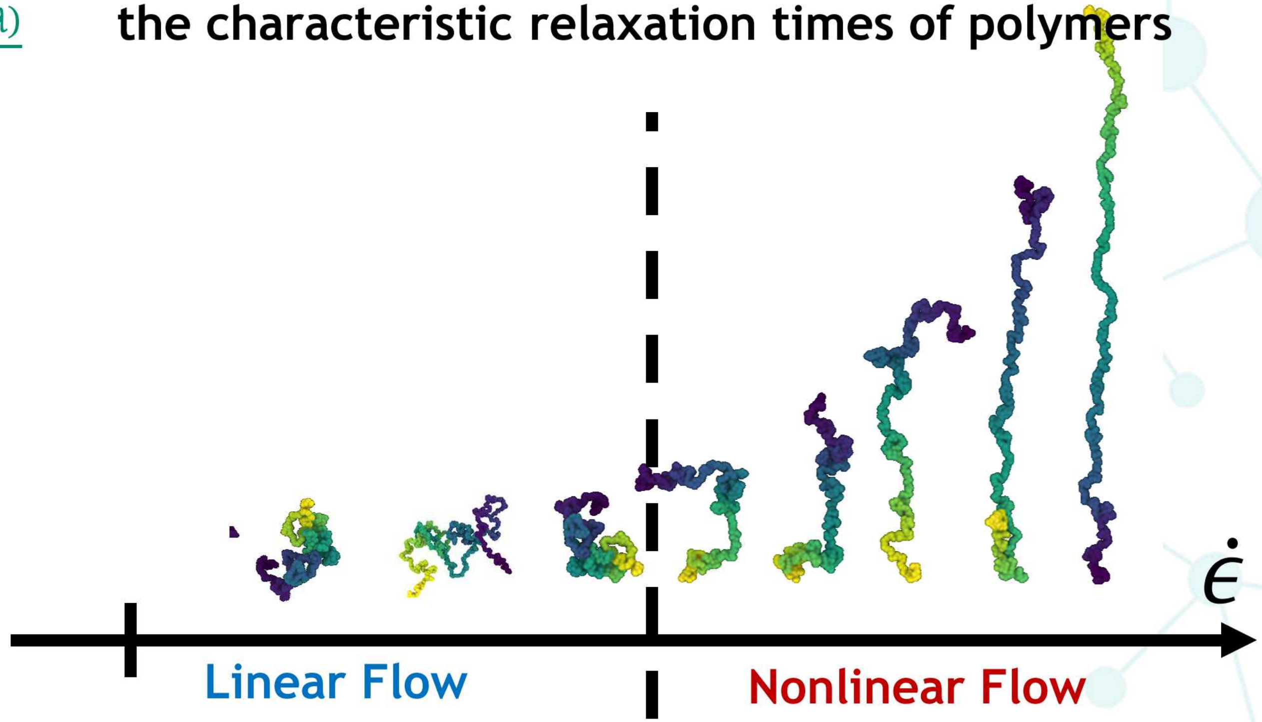
Nonlinear Extensional Flows Alter Chain Conformation

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



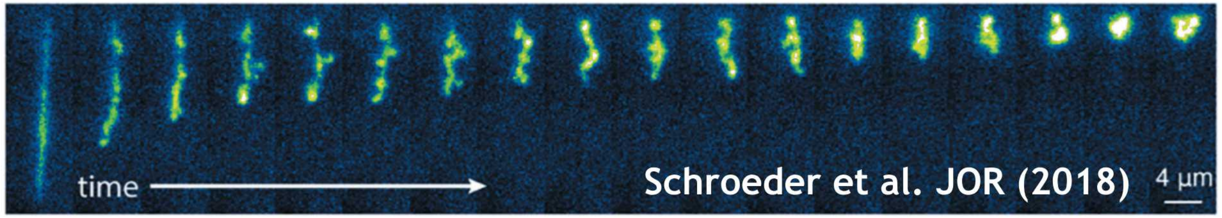
Measure flow strength with a Weissenberg number:

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

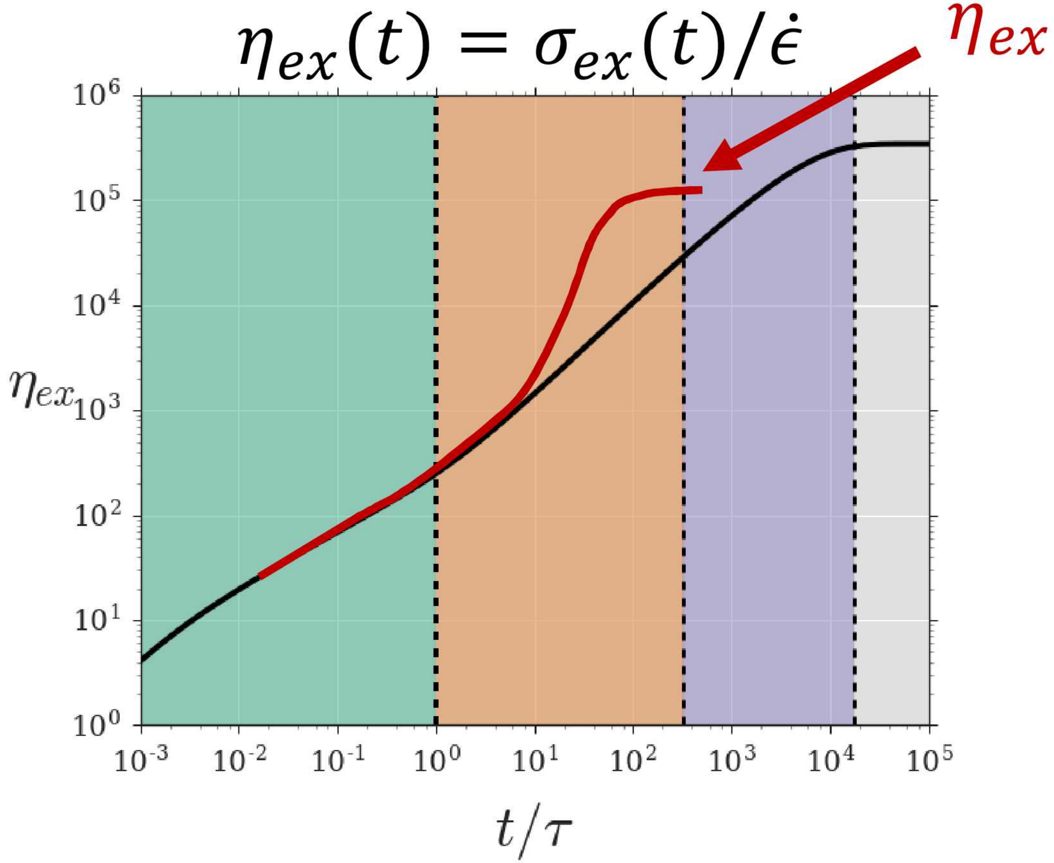
$Wi_R \rightarrow 0$ Newtonian

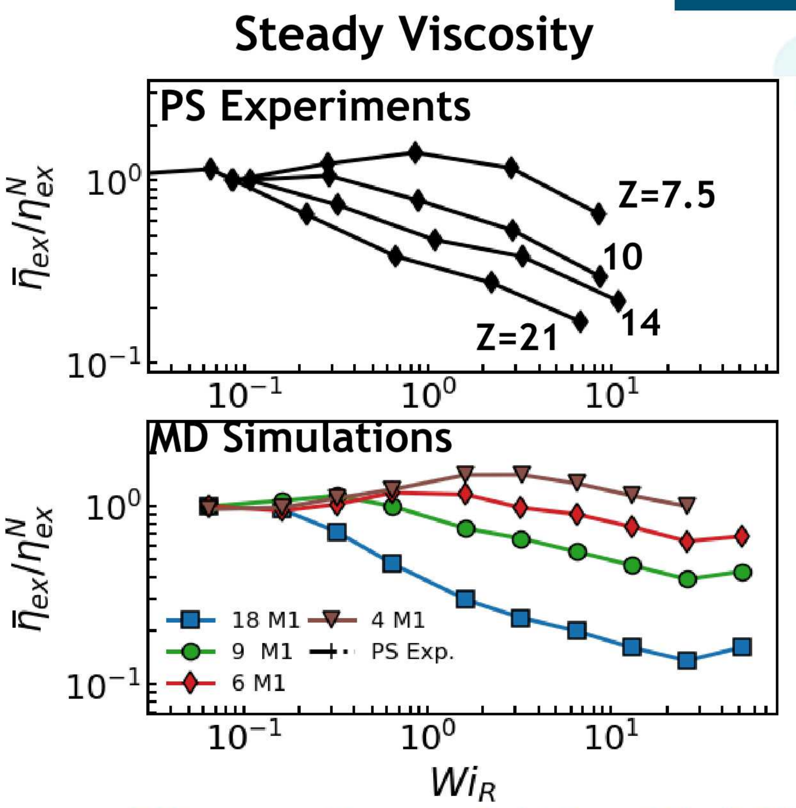
$Wi_R > 1$ Elongation

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



MD Captures Nonlinear Dynamics and Rheology





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

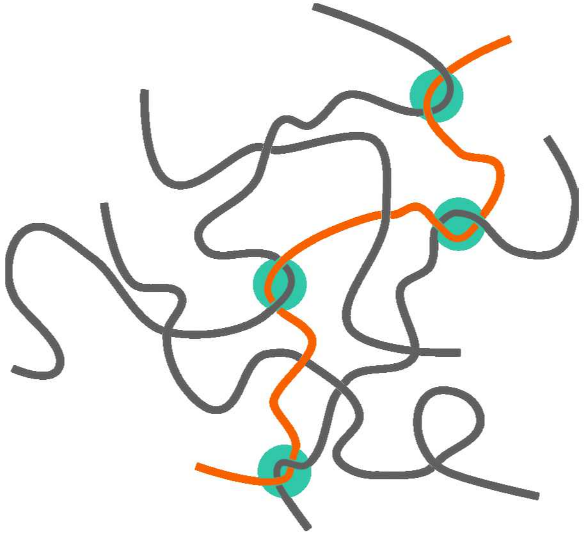
Weak Linear Flows ($Wi \to 0$):

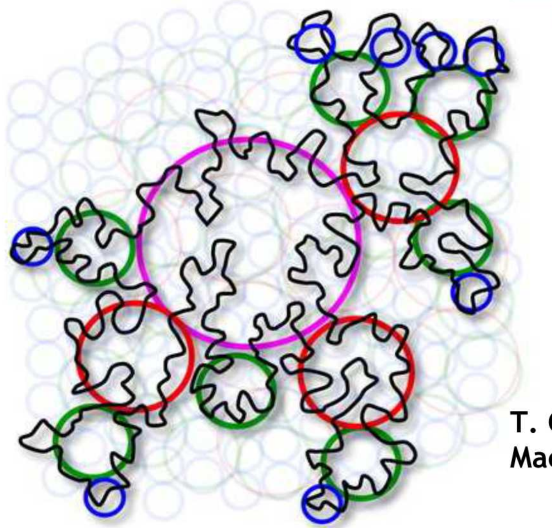
- Viscosity evolves along a limiting curve (LVE), and plateaus to Newtonian viscosity.
- Controlled by equilibrium chain dynamics - very different for linear & ring polymers.

Strong Nonlinear Flows ($Wi > 1$):

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

Comparing Linear Melts and Ring Melts In Extensional Flow





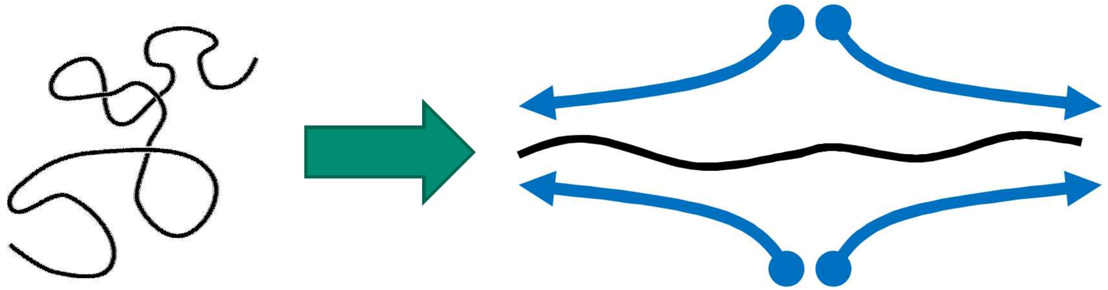
T. Ge, M. Rubinstein, Macromol. (2016)

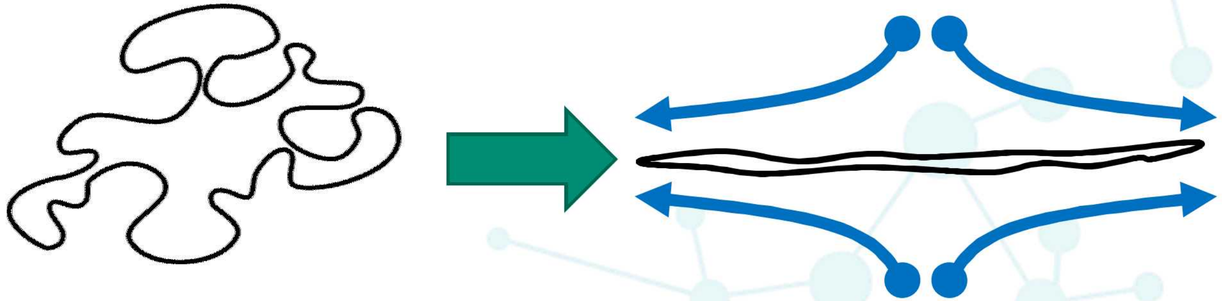
Entanglements confine chains to a primitive path, & create a hierarchy of exponential relaxation times.

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

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

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

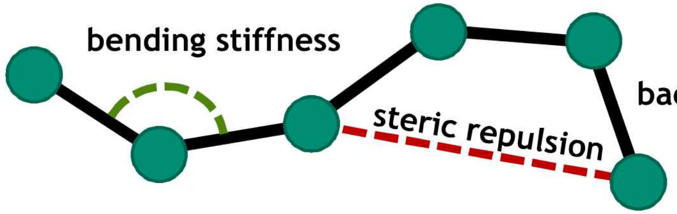


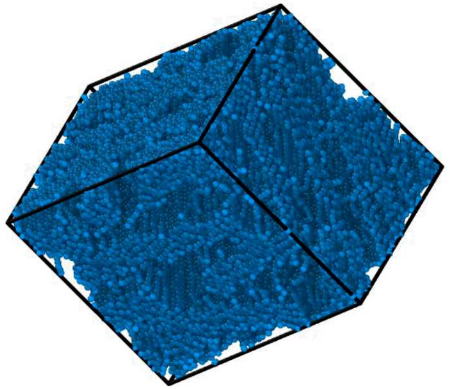


Equilibrium dynamics are very different, but elongated states are similar. Ring to linear crossover?

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

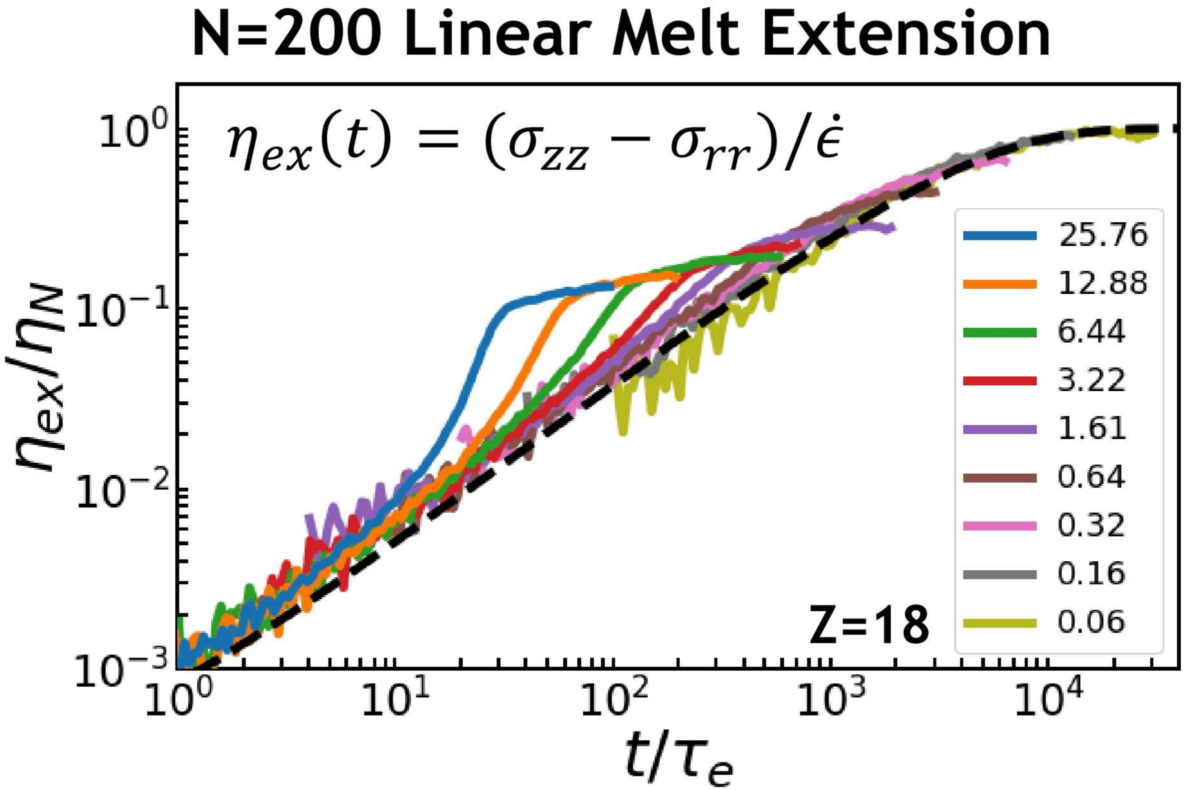
Constant-rate uniaxial extensional flows

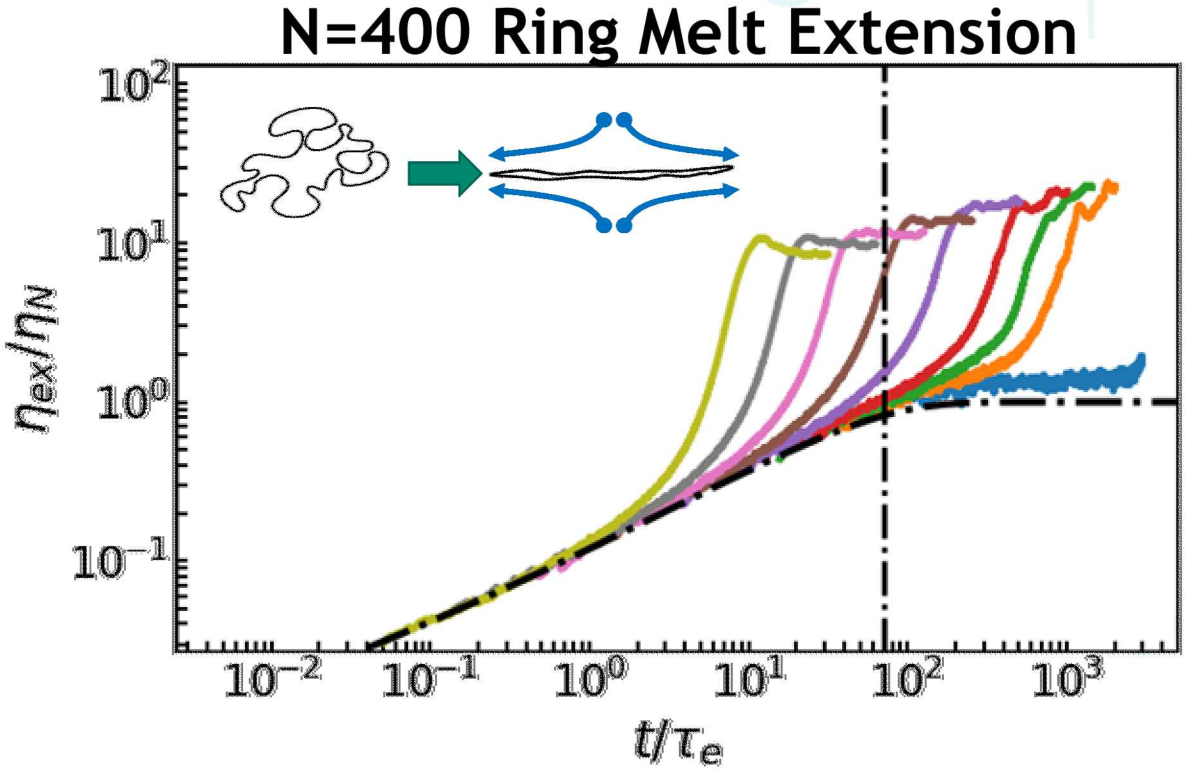
- Elongate to strain $\epsilon > 6.0$ → resolve steady-state
- Vary $Wi = \dot{\epsilon}\tau = 0.16 - 0.25$
- Linear: $Wi = \dot{\epsilon}\tau_R$ Ring: $Wi = \dot{\epsilon}\tau$
- Relate rate-dependence to chain dynamics

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





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

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

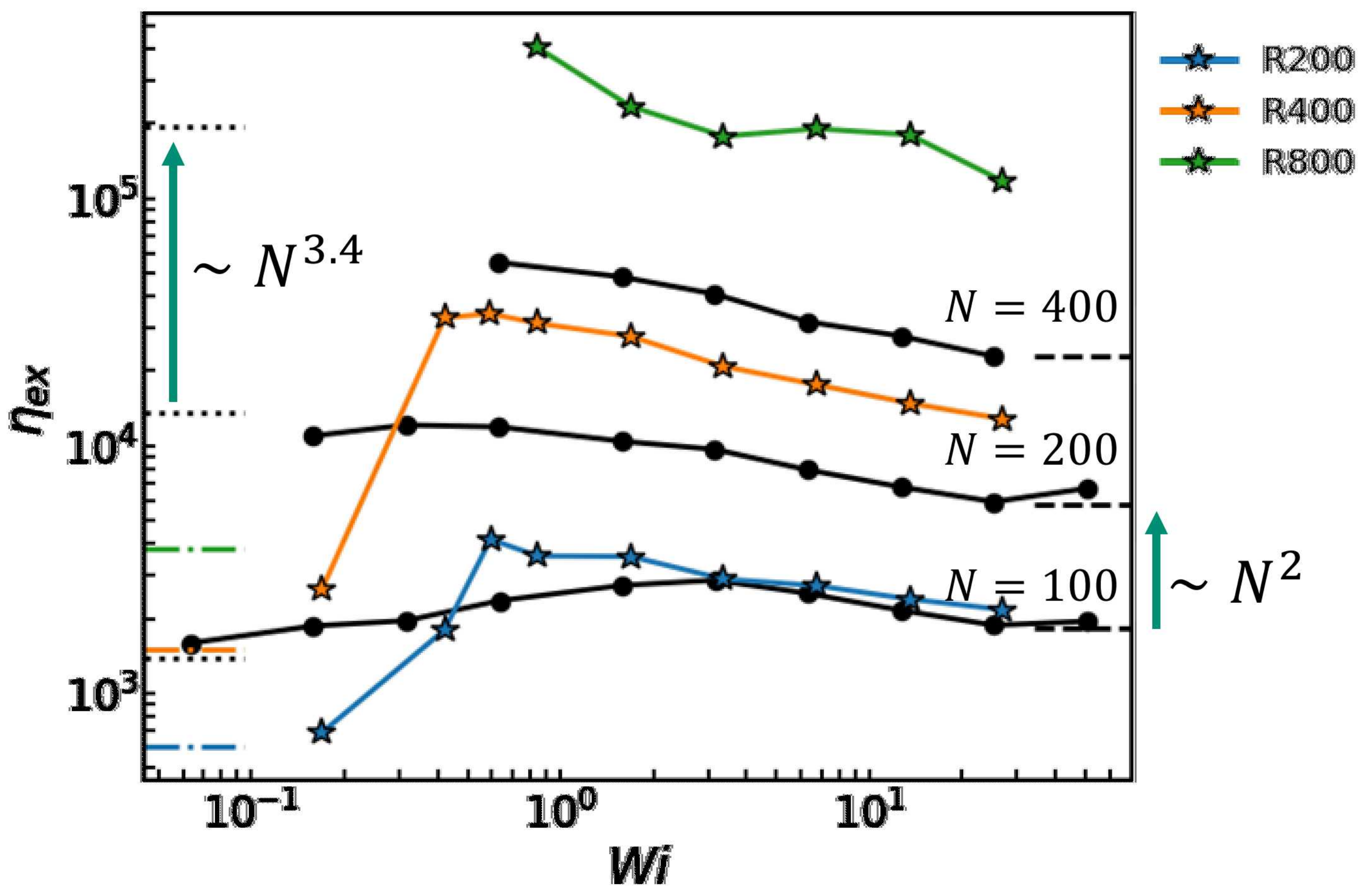
10x rise in viscosity at *ALL* Wi even Wi<<1

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

Is dramatic viscosity rise due to elongated rings behaving like slower linear chains?

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

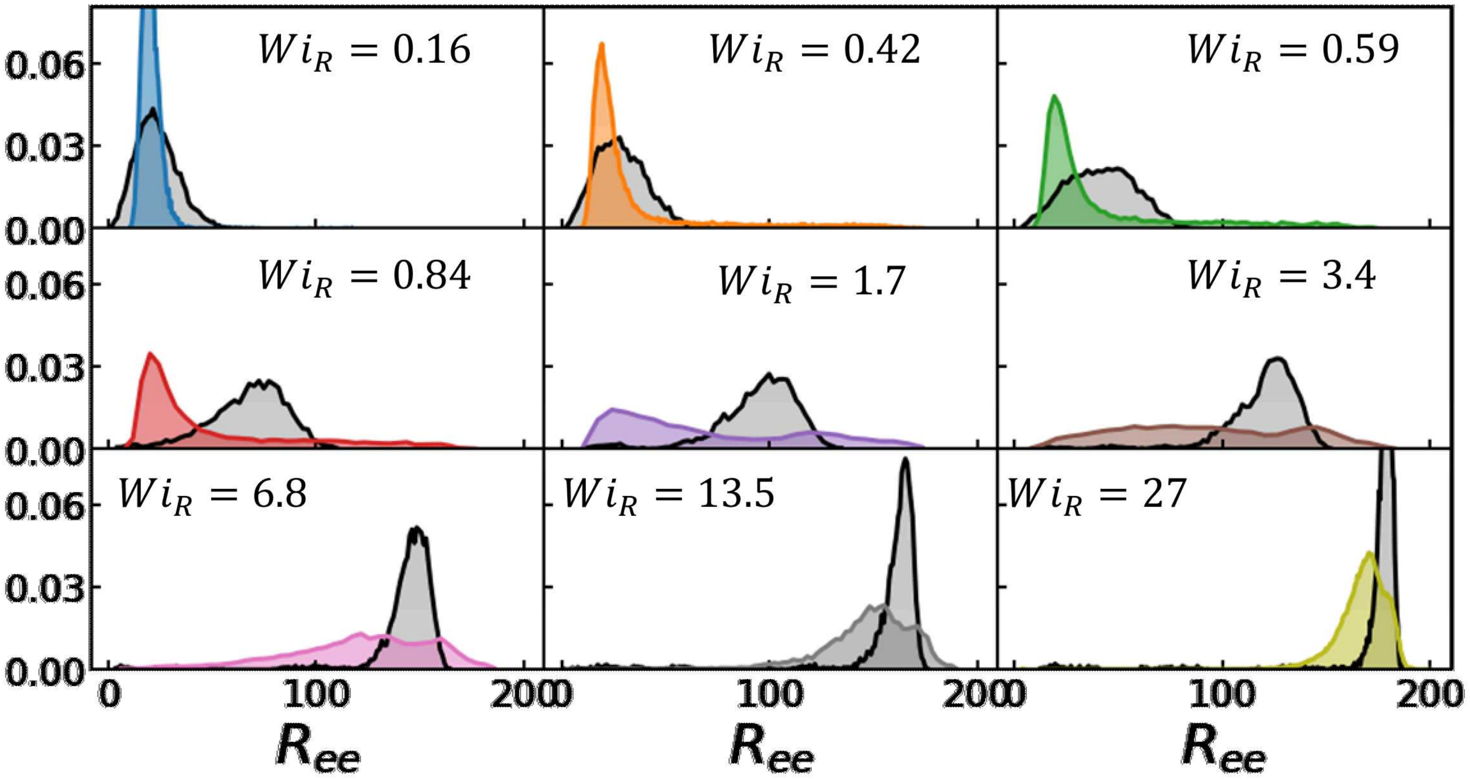
N=200 ring viscosity appears to follow N=100 linear melt for Wi > 1.

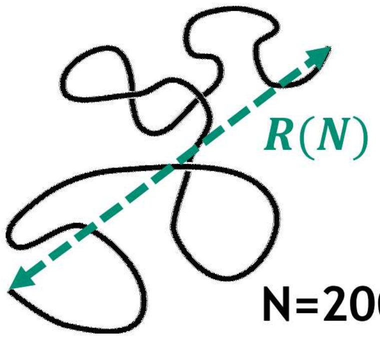
Agreement breaks down as *N* increases.

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

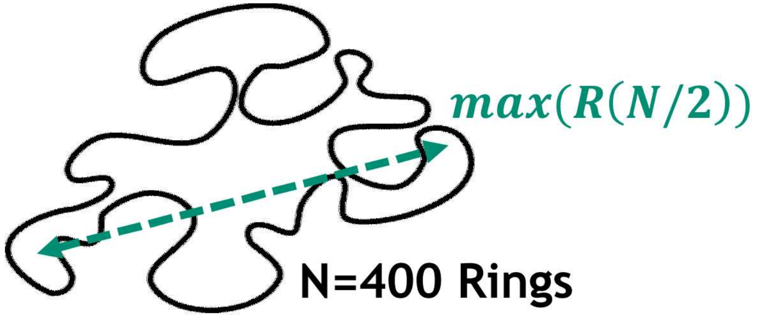
Chain Extension

Steady-State End-End Distributions





N=200 linear



N=400 Rings

Network Stretches Linear Chains ~Affinely

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

Rings Dominated By Large Fluctuations

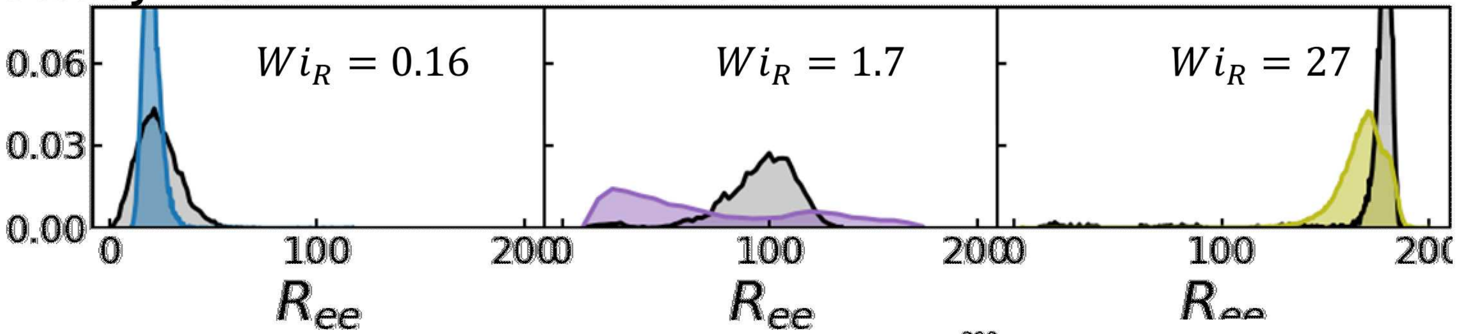
Develop long tale at low Wi of few highly stretched and retracting rings

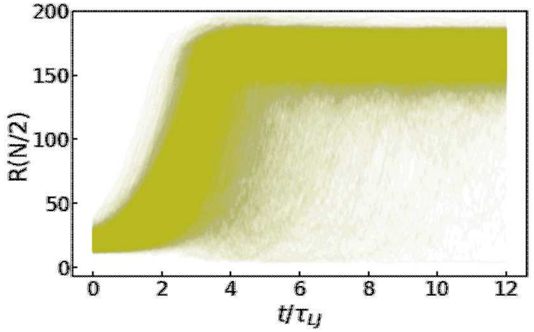
Grows into a broad distribution of highly fluctuating rings at Wi~1

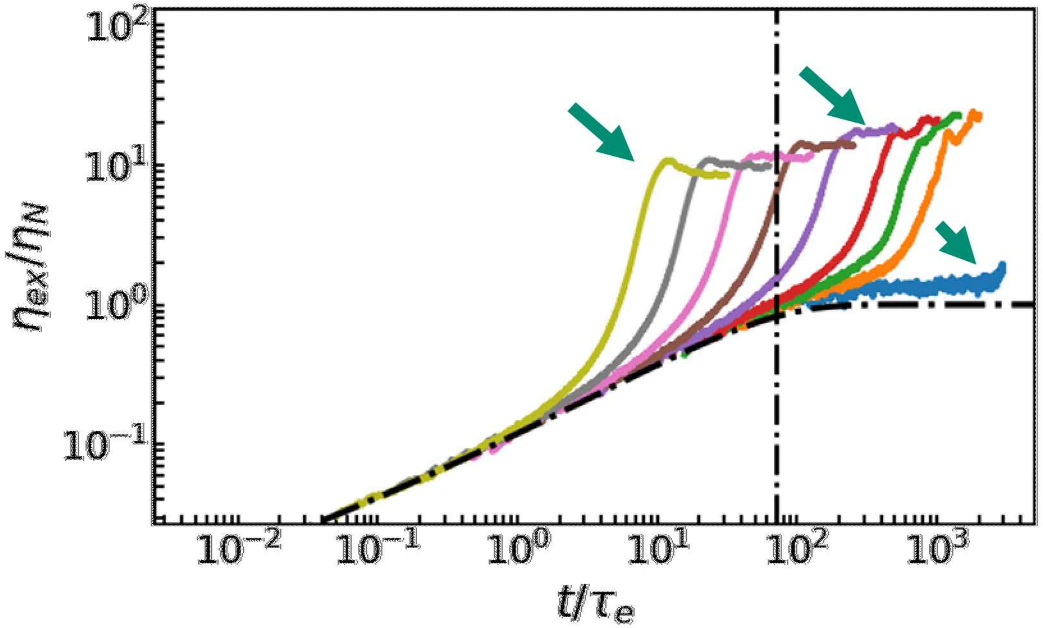
Large fluctuations cannot be described by averages

Individual Chains Fluctuate Between Extended & Retracted

Steady-State End-End Distributions







Individual chains only remain stretched at the highest Wi~27

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

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

Acknowledgements & Conclusions

Collaborators:

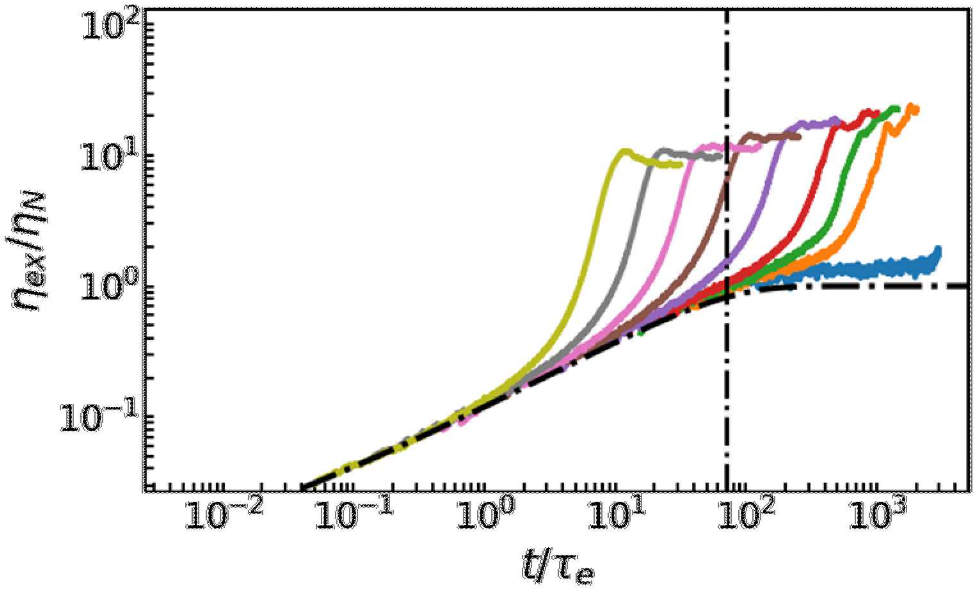
Ting Ge, Michael Rubinstein (Duke)

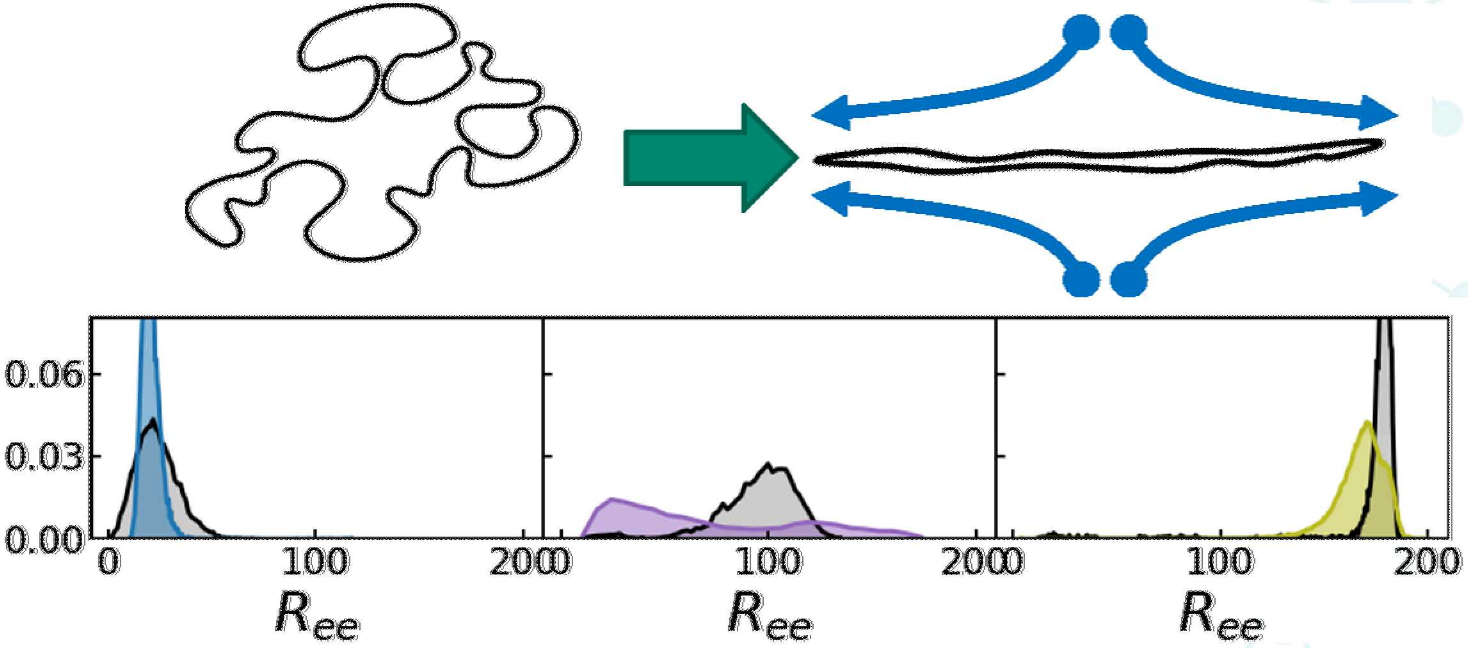
Gary S. Grest (SNL)

Funding:

Harry S. Truman Fellowship (SNL)

1. Simulations reveal unique extensional rheology for rings
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. Wi~1: broad distributions, chains stretch and retract regularly
5. Large fluctuations cannot be captured by mean-field models





Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.