Introduction to Molecular Dynamics Simulations of Elongational Behavior of Polymeric Systems

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DoDyNet DTU - 2019

Introduction

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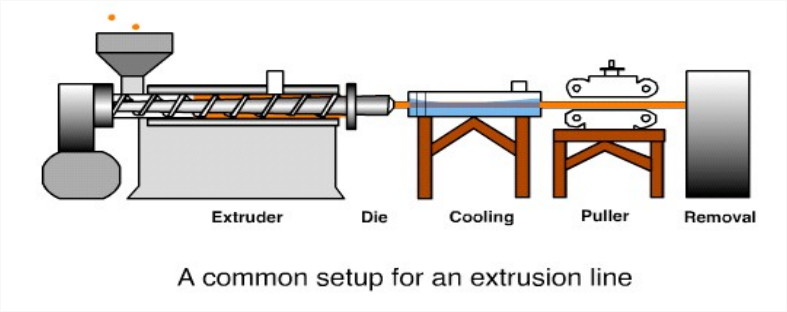
Polymer Melts



A common setup for an extrusion line

Molecular structure

ensemble of molecules

analytical rheology

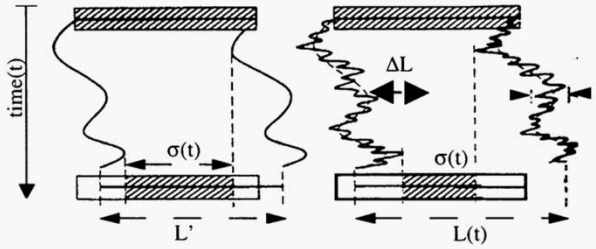
rheological modeling

rheological behavior

Processing property

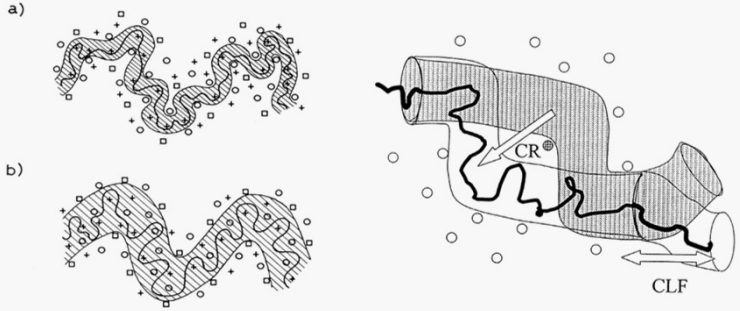
"Tube" Model: de Gennes, Doi and Edwards

1. Reptation
2. Contour length fluctuation



Doi & Edward, 1985

3. Constraint release:



Tube dilation CR Rouse motion

Marrucci, 1985 *Viovy et al., 1990*

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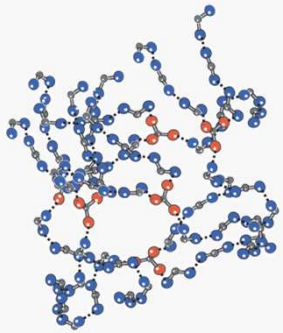
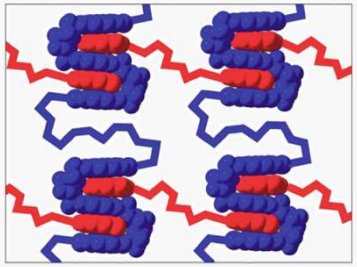
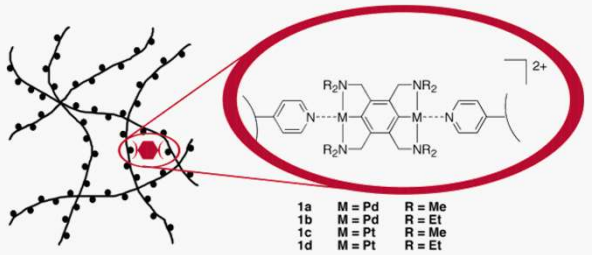
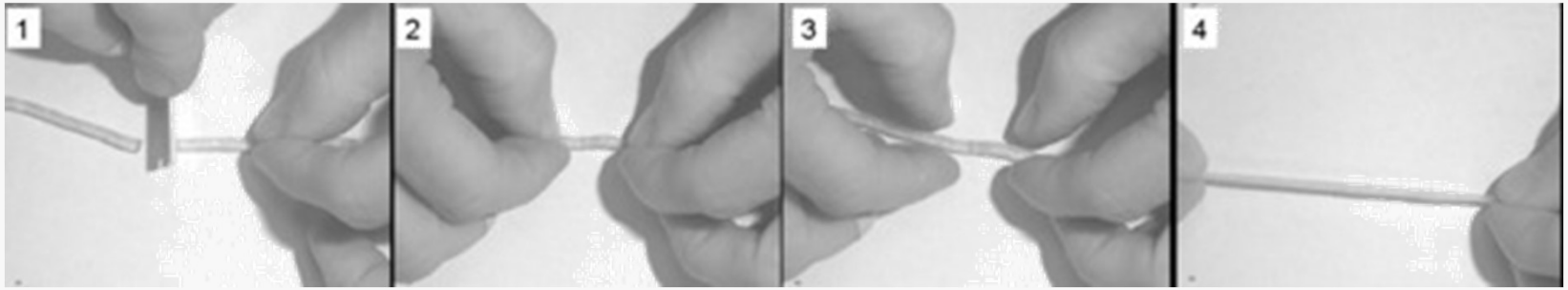
Supramolecular Polymer Networks







Cordier *et al.*, *Nature* 2008 Burattini *et al.*, *Chem. Commun.* 2009 Loveless *et al.*, *Macromol.* 2005



Unique features due to reversible crosslinking:

Self-healing; Superior processing and recycling properties, shape memory, stimuli sensitive matrices

Shear and Extensional Rheology of Entangled Polymers

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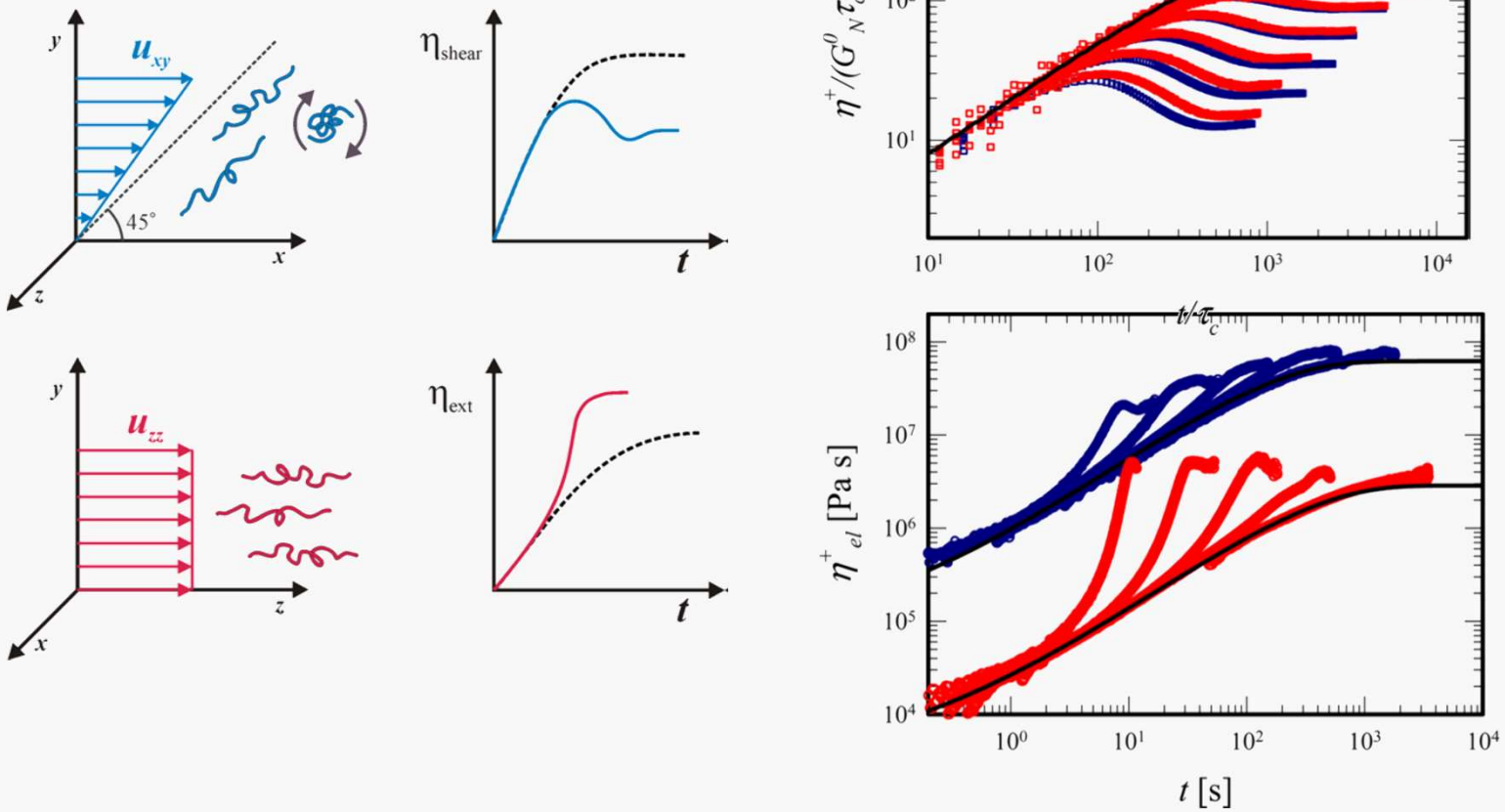
Transient viscosity and extensional stress growth coefficient



Costanzo,Huang, Iannirubertо, Marrucci, Hassager and Vlassopoulos, Macromolecules 49 (2016) 3925

Molecular Dynamics Simulation Model

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- **Kremer-Grest Bead-Spring model** (*JCP, 92 (1990)* 5057)

  ➢ ***Lennard-Jones Potential***

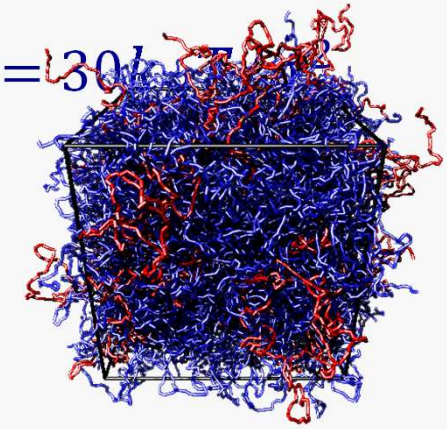
$$U_{LJ}(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} + \frac{1}{4}\right),\ r \le r_c\left(= 2^{\frac{1}{6}}\sigma\right), \varepsilon = 1k_BT$$

  ➢ ***Finite Extensible Nonlinear Elastic Potential (FENE)***

$$U_{FENE}(r) = -\frac{1}{2}kR_0^2 \ln\left(1 - \frac{r^2}{R_0^2}\right),\ R_0 = 1.5\sigma, k = 30k_BT$$

  ➢ ***Bending Potential***

$$U_{bend} = k_b(1 - \cos\theta),\ k_b = 0 \sim 3k_BT$$



- **System parameters**
  - Number density of monomers: $\rho = 0.85$
  - Chain length: $N = 5 \sim 3500$
  - Entanglement length: $N_e = 23 \sim 86 \Rightarrow Z \approx 0.1 \sim 72$

Simulated Entangled Polymer Melts

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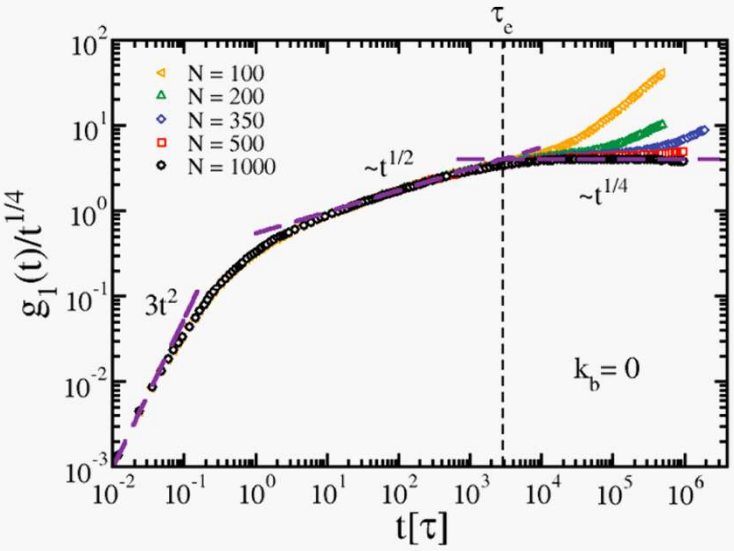
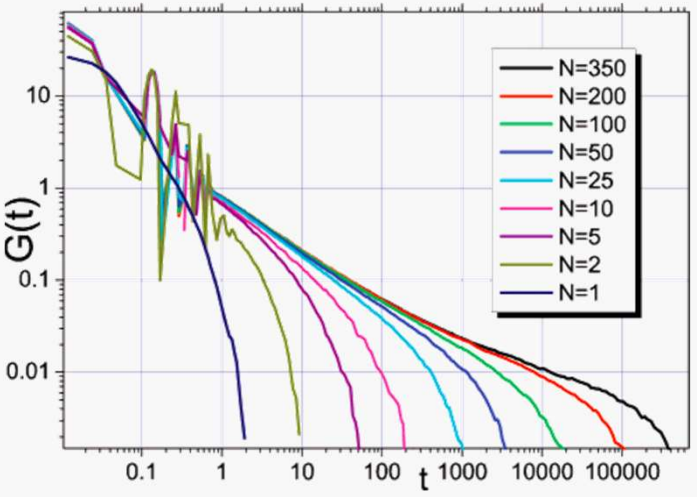
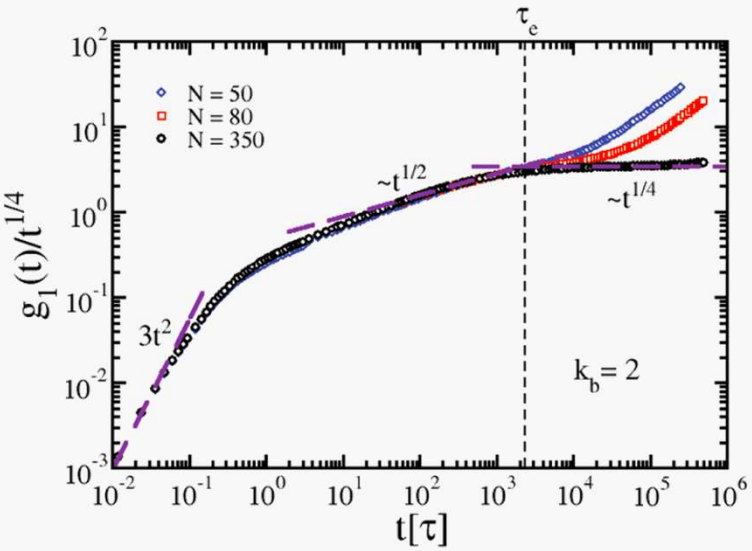
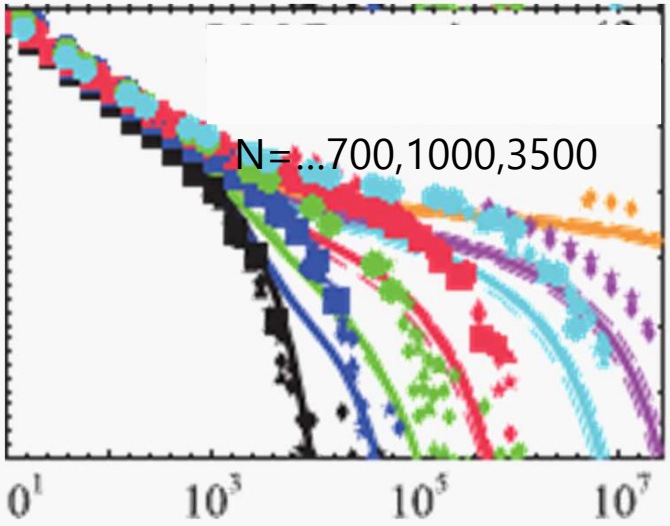




Likhtman et al. Macromol. 2007



Wang et al., Macromolecules 45(2012)3557



Hou et al. PRL 105 (2010) 068301

Equations of Motion

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- **Equilibrium Systems**

  Langevin equation

$$m\ddot{\boldsymbol{r}}_i = \boldsymbol{F}_i - \Gamma\dot{\boldsymbol{r}}_i + \boldsymbol{W}_i(t)$$

$$\boldsymbol{F}_i = -\boldsymbol{\nabla}U(\boldsymbol{r}_i)$$

- **Nonequilibrium Systems**

  SLLOD equations

$$\dot{\boldsymbol{r}}_i = \frac{\boldsymbol{p}_i}{m} + \boldsymbol{r}_i \cdot \nabla\boldsymbol{u}$$

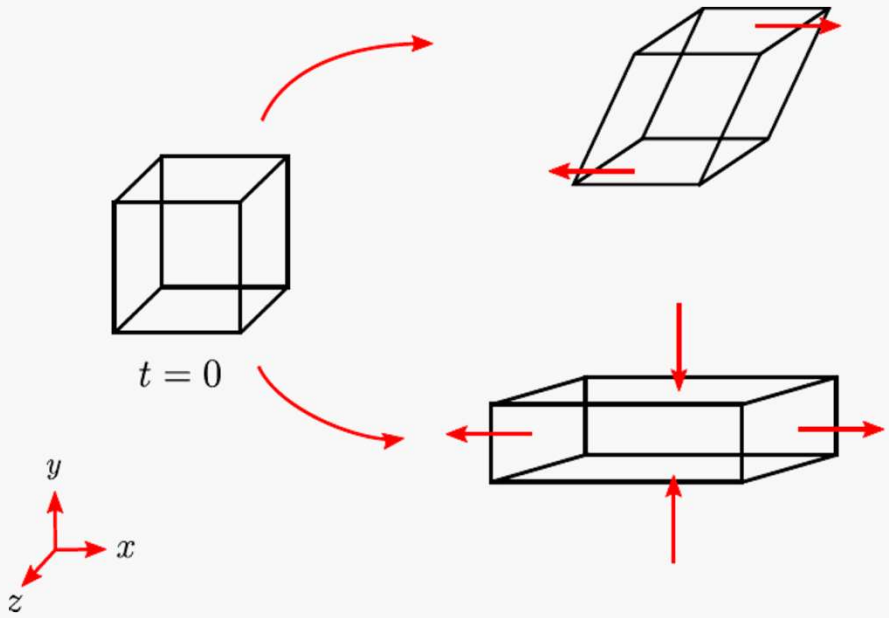
$$\dot{\boldsymbol{p}}_i = \boldsymbol{F}_i - \boldsymbol{p}_i \cdot \nabla\boldsymbol{u} - \zeta_{new}\,\boldsymbol{p}_i$$

  with modified Gaussian multiplier

$$\zeta_{new} = \zeta_\alpha + \zeta_0 \left[\frac{\sum_i \frac{\boldsymbol{p}_i^2}{m} - 3Nk_BT}{3Nk_BT}\right] where\ \zeta_\alpha = \frac{\sum_i \boldsymbol{p}_i \cdot (\boldsymbol{F}_i - \boldsymbol{p}_i \cdot \nabla\boldsymbol{u})}{\sum_i \boldsymbol{p}_i}$$

Evans & Morris, 1990; Todd & Daivis, JCP 2000; Mol. Simul. 2007

Strain Rate Tensors



Shear

$$\nabla \boldsymbol{u} = \begin{pmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Uniaxial Elongation

$$\nabla \boldsymbol{u} = \begin{pmatrix} \dot{\epsilon} & 0 & 0 \\ 0 & -\frac{\dot{\epsilon}}{2} & 0 \\ 0 & 0 & -\frac{\dot{\epsilon}}{2} \end{pmatrix}$$

Planar Extension

$$\nabla \boldsymbol{u} = \begin{pmatrix} \dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon} & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Periodic Boundary Conditions

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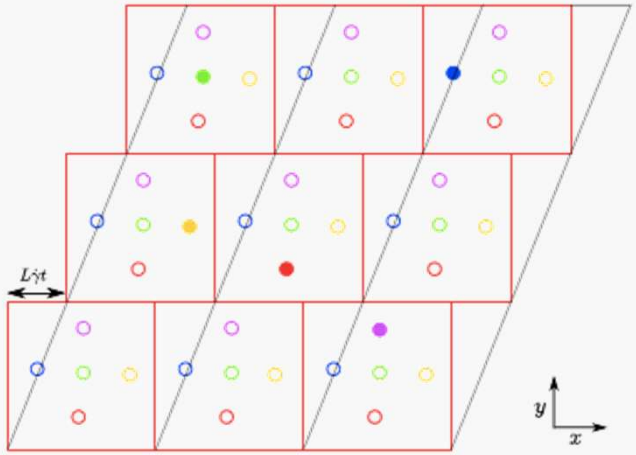
- **Shear flow**

  Lees-Edwards sliding brick PBC [*J. Phys. C, 5 (1972) 1921*]



- **Uniaxial elongation**

  Box elongation

- **Planar elongation**

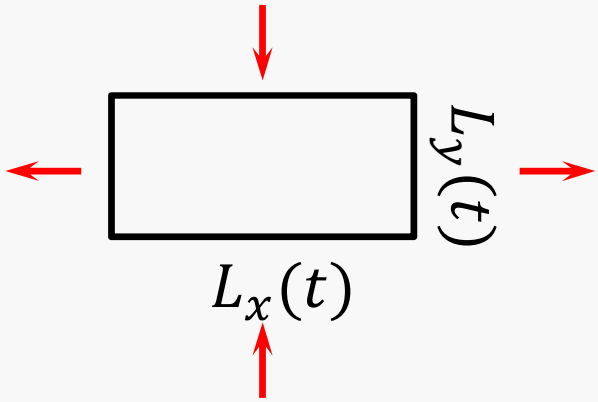
  1. Box elongation
  2. Kraynik-Reinelt PBC

1. Box Elongation

Equation of Isochoric box deformation

$$\dot{\boldsymbol{L}}_j(t) = \boldsymbol{L}_j(x) \cdot \nabla \boldsymbol{u}$$

e. g., for Uniaxial elongation



$$\begin{cases} L_x(t) = L_x(0)\exp(\dot{\epsilon}t) \\ L_y(t) = L_y(0)\exp\left(-\frac{1}{2}\dot{\epsilon}t\right) \\ L_z(t) = L_z(0)\exp\left(-\frac{1}{2}\dot{\epsilon}t\right) \end{cases}$$

Volume: $V = L_x(t)\ L_y(t)\ L_z(t) = Const$

Example of Box Elongation Simulation

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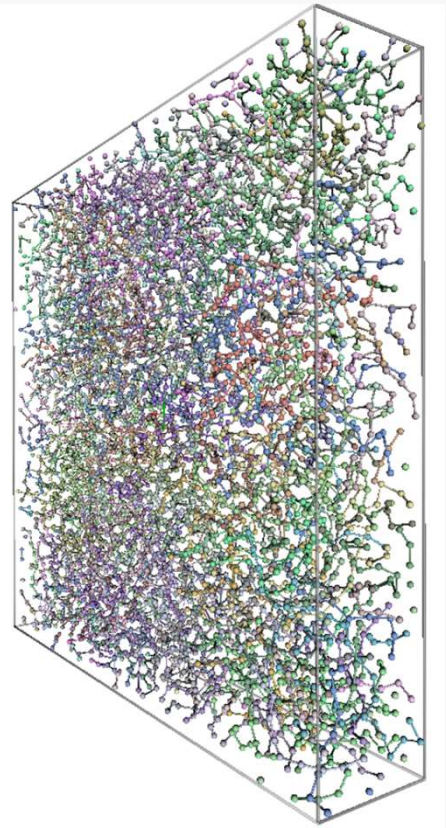
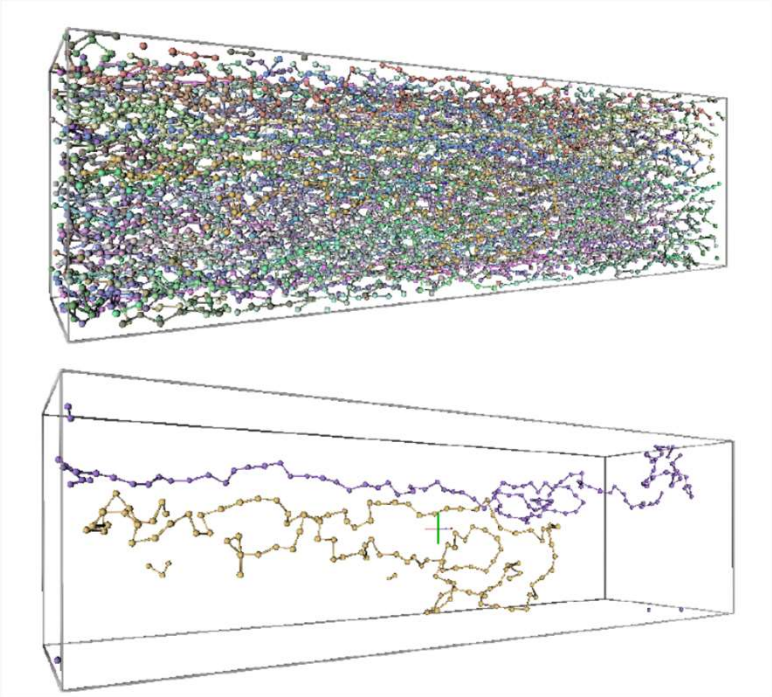
Naomi Withey



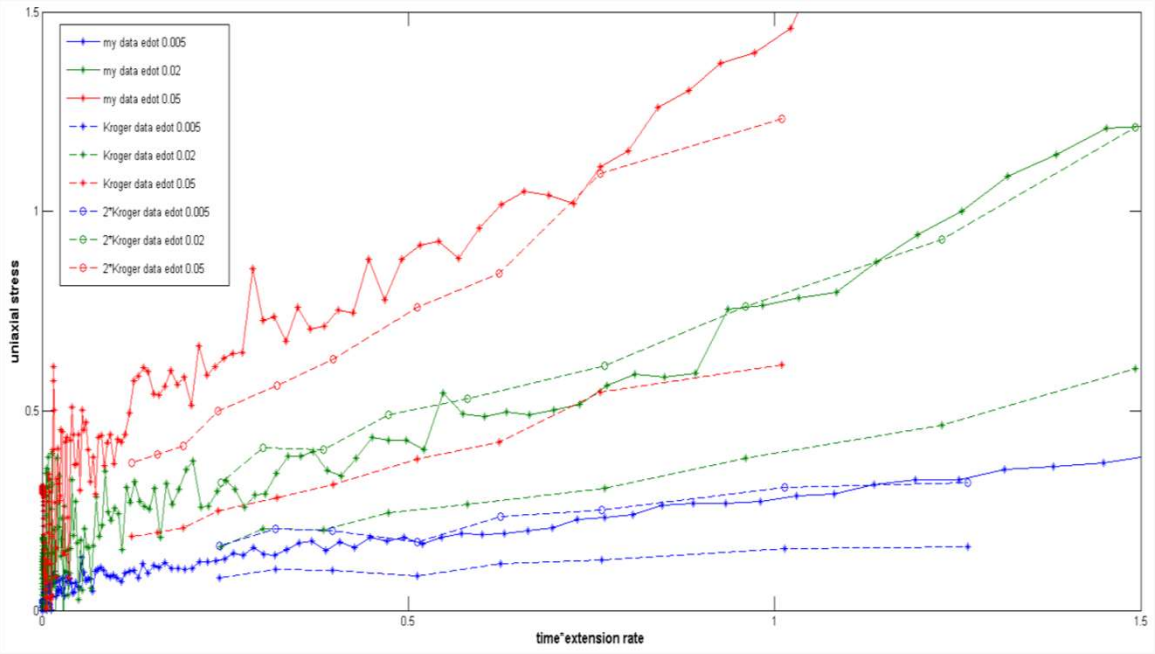
t=0



Simulation ends when width of the box in the contracting direction(s) reaches twice the cut-off distance for LJ interaction

Uniaxial Elongation Behavior

Tensile stress



N = 30, N_c = 280

Uniaxial extensional viscosity:

$$\eta_{uni} = \frac{\sigma_{xx} - \frac{1}{2}(\sigma_{yy} + \sigma_{zz})}{3\dot{\varepsilon}}$$

- Consistent with previous simulation data (*Kroger, Macromol. 30 (1997) 526*)

Planar Elongation Behavior

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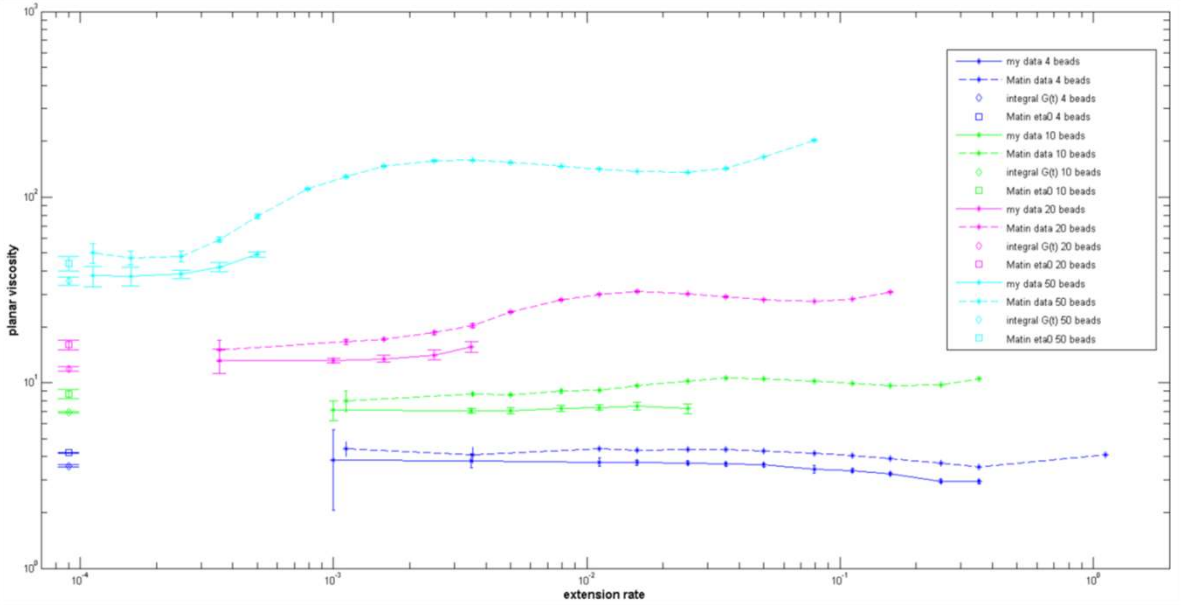
"Steady-state" extensional viscosity



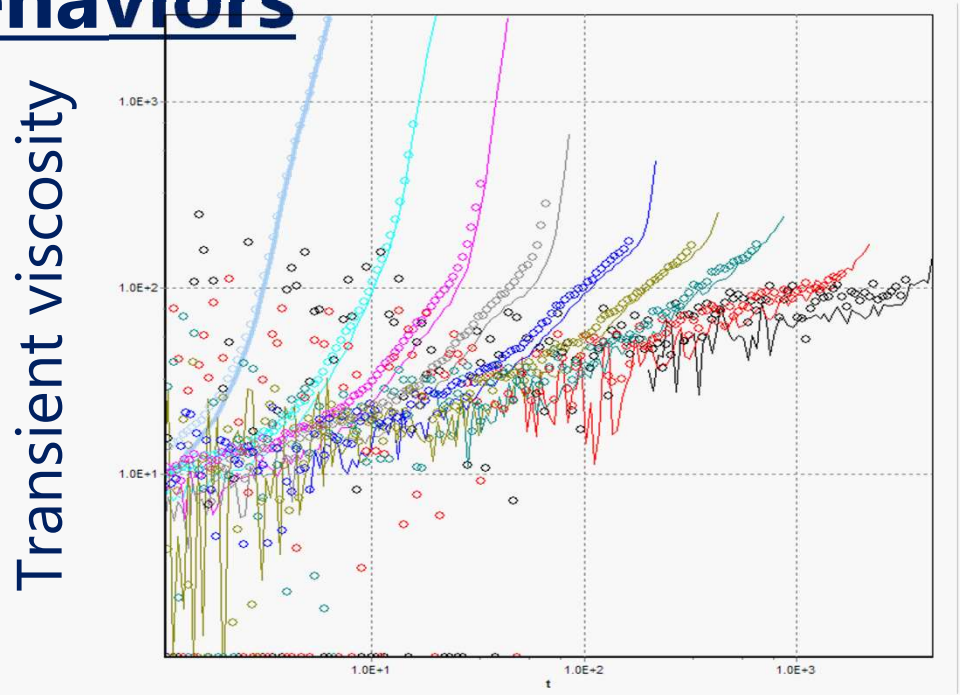
N=4-50, N_c = 500

Planar extensional viscosity:

$$\eta_{planar} = \frac{\sigma_{xx} - \sigma_{yy}}{4\dot{\varepsilon}}$$

- Qualitative agreement with previous simulation data obtained using Kraynik-Reinelt PBC, but can only access limited time period
- Quantitative difference may arise from using atomistic vs molecular approach for applying the deformation (*Martin, PhD thesis, 2001*)

Comparison between Uniaxial and Planar Elongation Behaviors



- Uniaxial and planar elongations can provide consistent results
- Box elongation method has limitations for studying steady-state rheological behavior, but is useful for step-strain relaxation.

Elongation Effect on Entanglement Structure and Force Distribution

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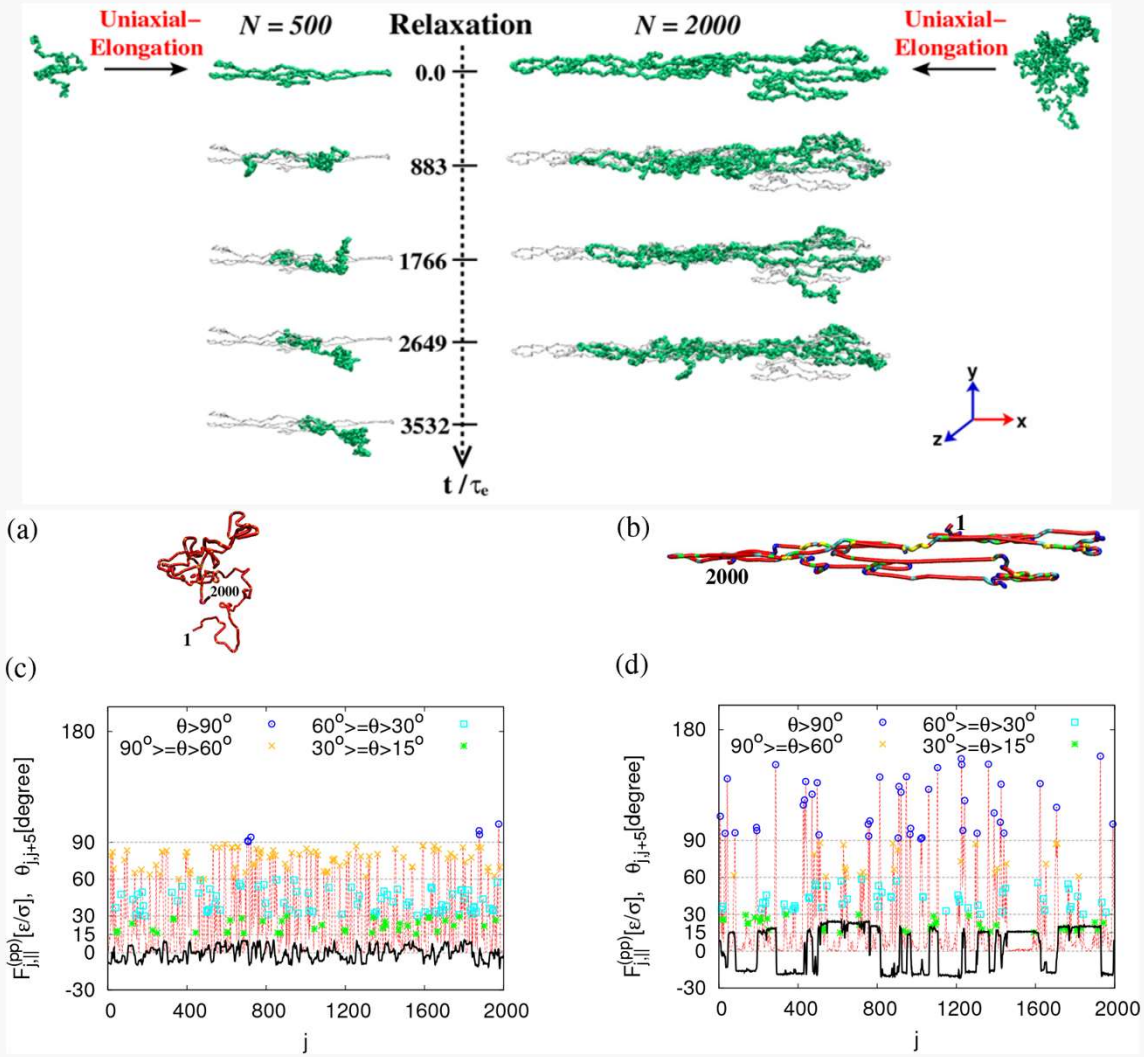
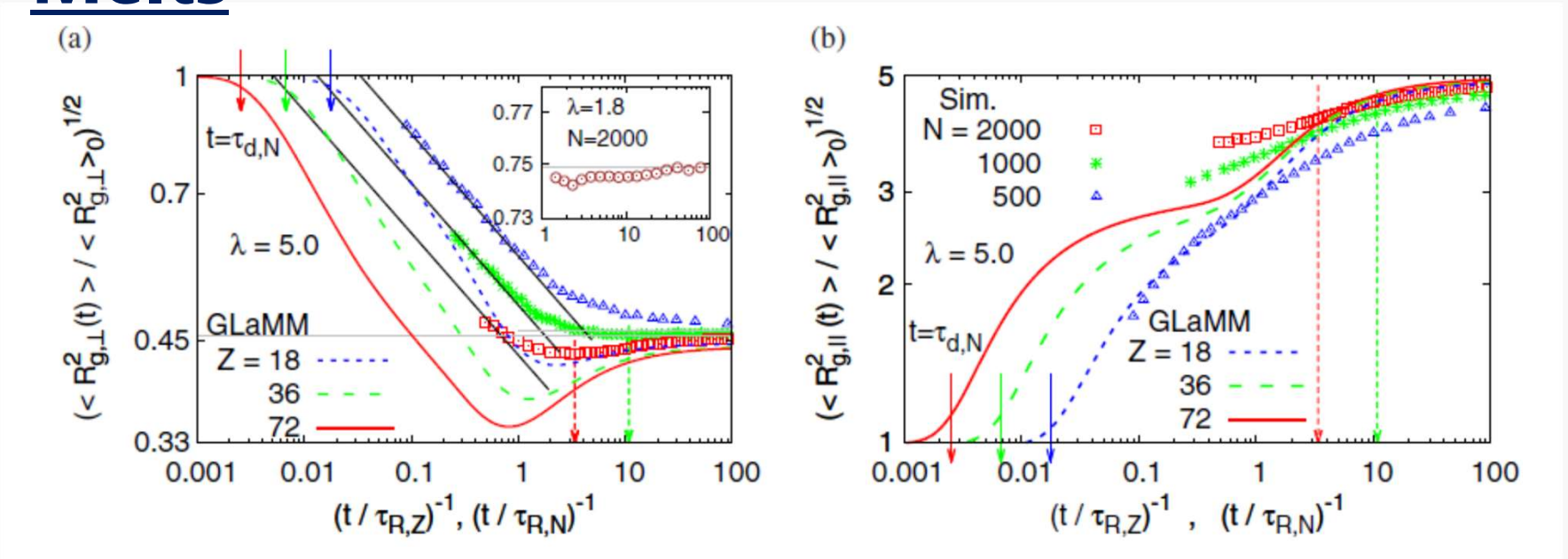


Large, less entangled regions of the chains stabilize regions of high density of kinks

Hsu & Kremer, ACS Macro Lett. 7 (2018) 107

Chain Retraction in Highly Entangled Stretched Polymer Melts



Chain retract in all directions during initial relaxation before reaching the Rouse time, which is more pronounced with increasing Z as predicted by the GLaMM model, but the effect is significantly weaker than the theoretical prediction.

Hsu & Kremer, Phys. Rev. Lett. 121 (2018) 167801

2. Kraynik-Reinelt PBC

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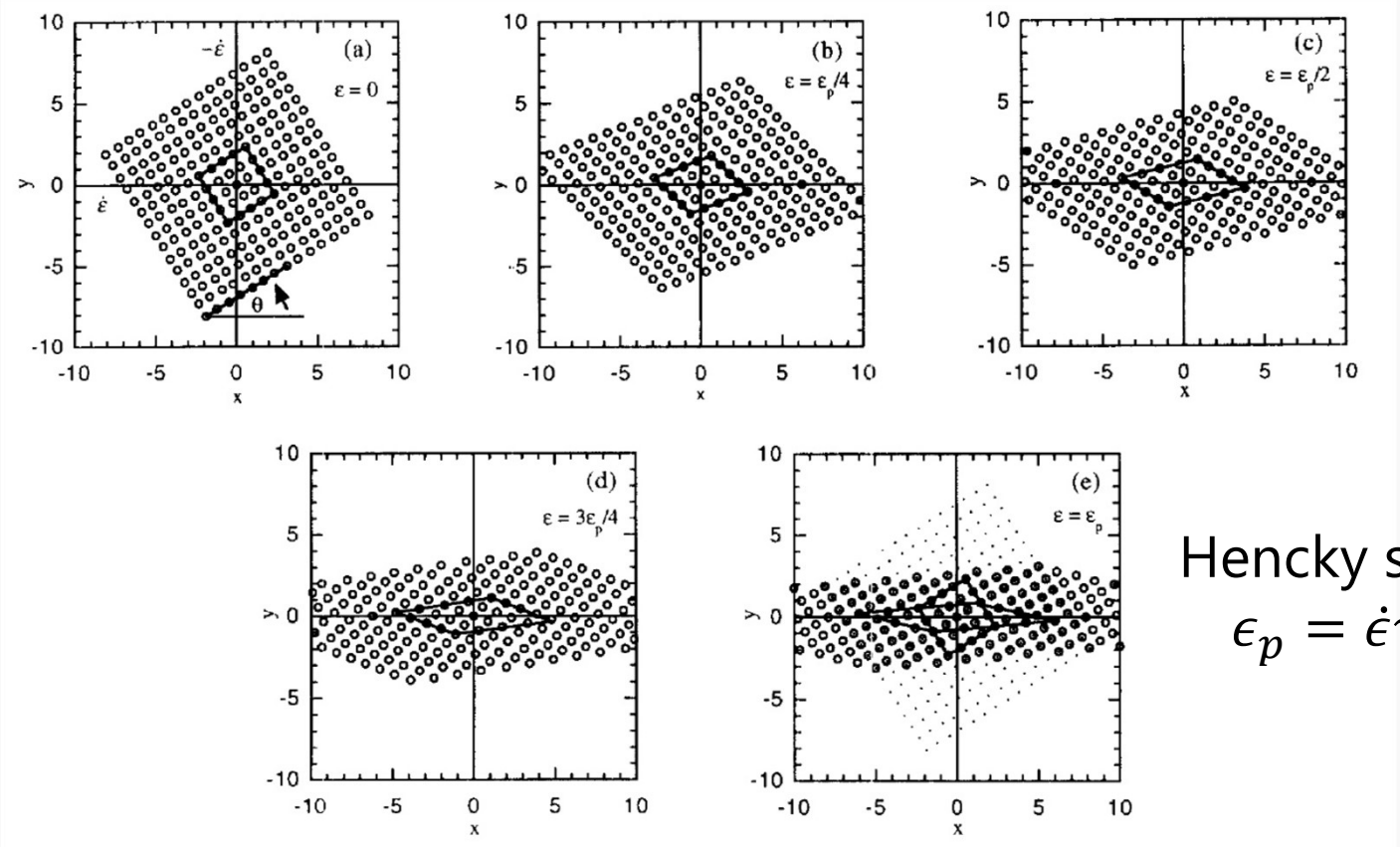
Spatially and temporally periodic BC *(K-R, Int. J. Multiphase Flow 18 (1992) 10*



Hencky strain

$$\epsilon_p = \dot{\epsilon}\tau_p$$

Fig. 1. Evolution of a square Kraynik–Reinelt (KR) lattice under planar elongational flow as a function of time. The orientation angle is $\theta(t = 0) = 31.7°$, and $\varepsilon_p = 0.9624$. At $\varepsilon = \varepsilon_p/2$, the lattice is the same as the original lattice, but with a different orientation. At $\varepsilon = \varepsilon_p$ the lattice reproduces itself. The fully extended (o) lattice is superimposed upon the original (.) lattice for comparison purposes.

Todd & Daivis, Comp. Phys. Comm. 117 (1999) 191

Implementation of KR PBC

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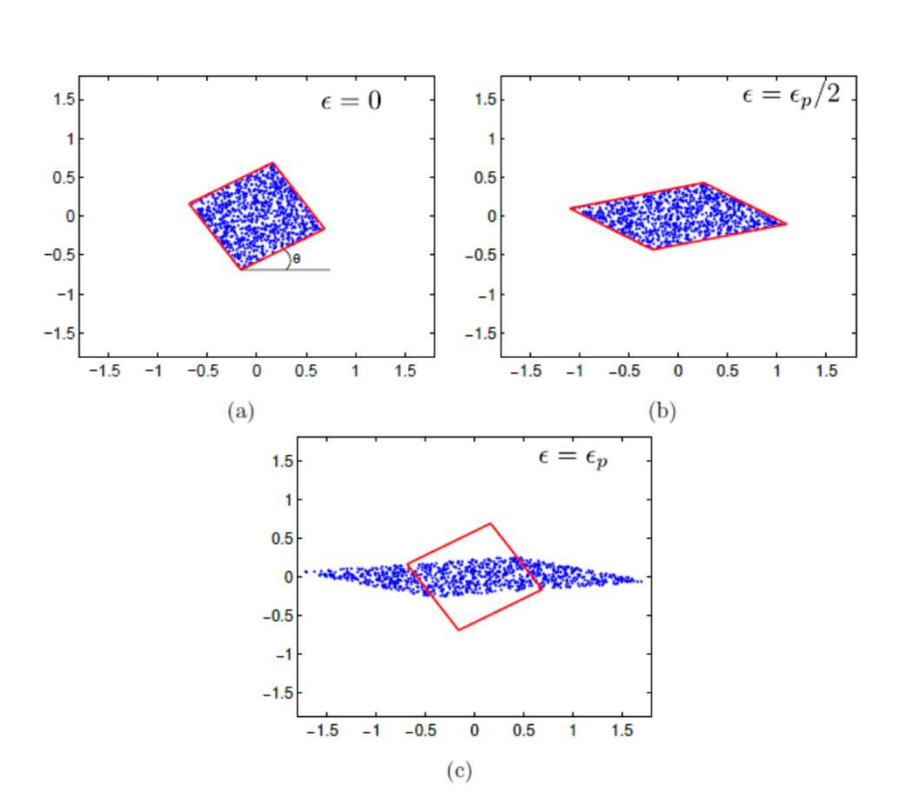
Dipesh Amin



- Lattice vectors of simulation cell rotate as

$$\boldsymbol{L}_i(t) = \boldsymbol{L}_i^0 \cdot e^{\nabla \boldsymbol{u} t}$$

- Follow the recipe in

Todd & Daivis
Comp. Phys. Comm.
117 (1999) 191

- GPU implementation

Dipesh Amin, PhD Thesis, 2016

Snapshot of Elongated Polymer Melt

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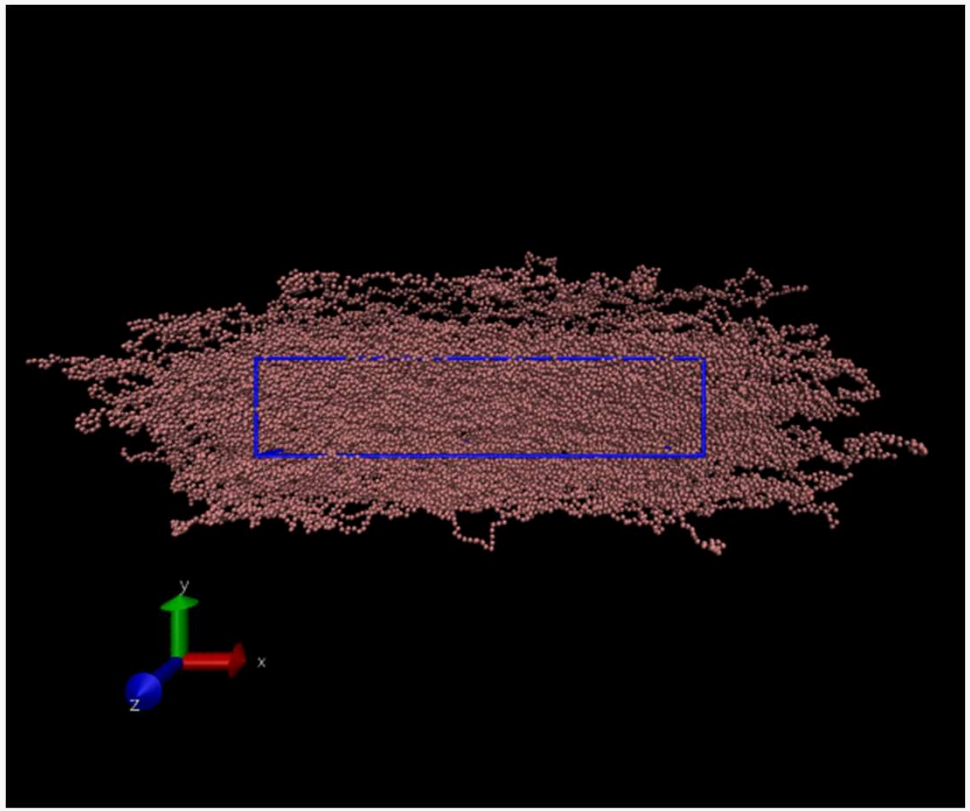

N=235 under planar extentson with $\dot{\epsilon} = 5 \times 10^{-5} \tau_{LJ}^{-1}$ at t = $1.55 \times 10^{5} \tau_{LJ}$

Simulation Model for SPNs

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- Hybrid MD/MC algorithm
  - *MD for chain dynamics*
  - *MC for controlling formation/breaking of sticky bond*
  - *Kinetics controlled by frequency of MC attempts*
- **Telechelic chains** represented by Kremer-Grest bead-spring model
- End stickers interact via "sticky bond" potential

$$U_{sb}(r,\varepsilon) = U_{FENE}(r) - U_{FENE}(r_0) - \varepsilon$$

- Sticker functionality: *minimally* f = 3 *required for network formation*

Cordier et al., Nature 2008; Burattini et al. , ChemComm, 2009; Liu et al., Macromol. 2012

- System parameters:

ρ = 0.85, N=25~128, ε = 0 ~12 k_BT, τ_{MC}= 0.01-1τ_{LJ}

Hoy & Fredrickson, JCP 2009; Amin, Likhtman & Wang, Macromolecules 2016

Association of Stickers

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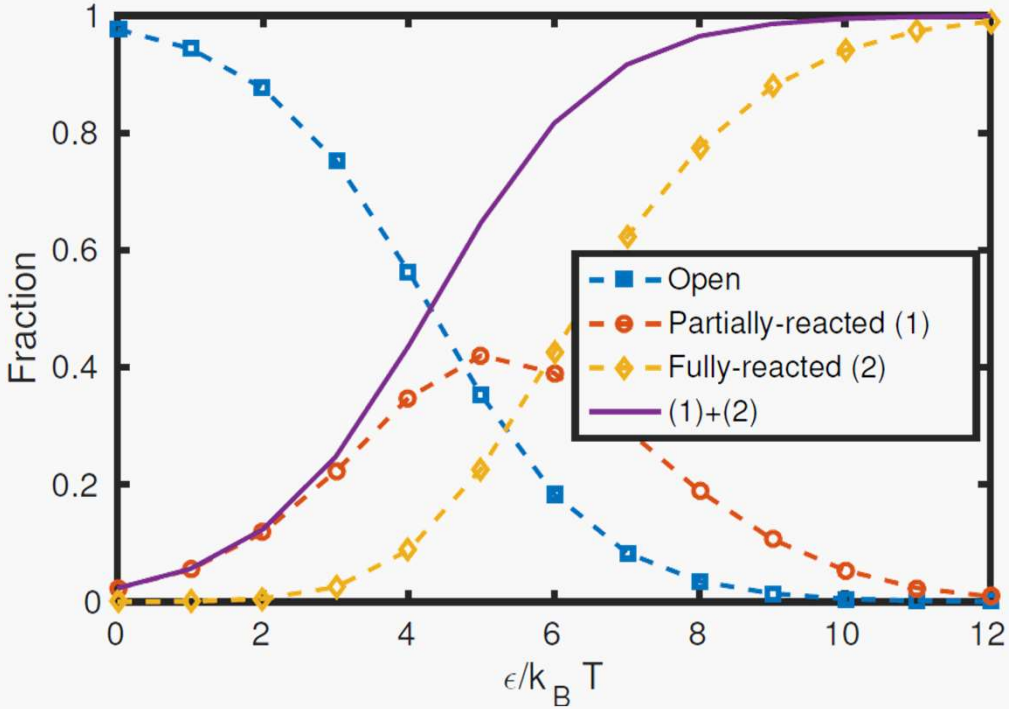
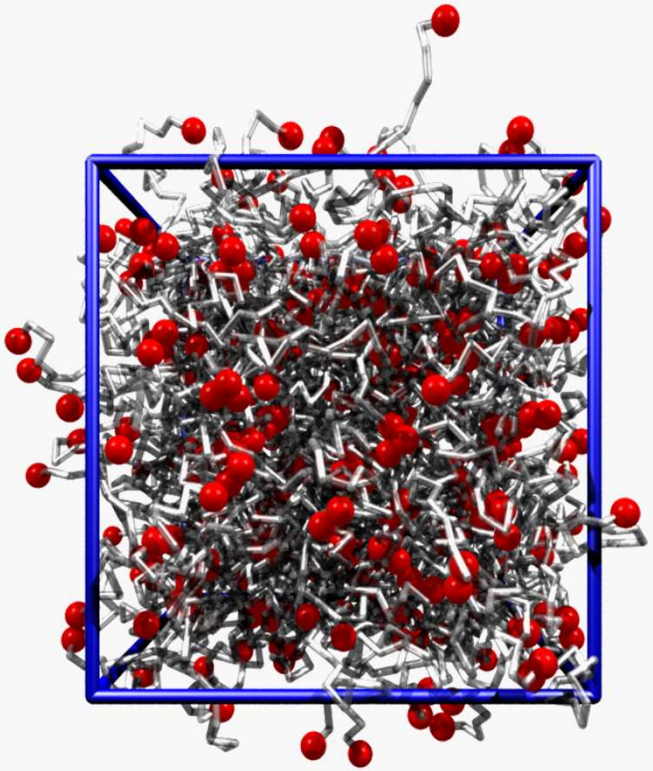
Probability for a sticker to find partners



N=25



$\varepsilon/k_B T=10$

- Probability for each sticker to form saturated number (2) of sticky bonds increases with increase of association energy ε

Amin, Likhtman & Wang, Macromolecules 49 (2016) 7510

Characteristic Times of Sticker Diffusion

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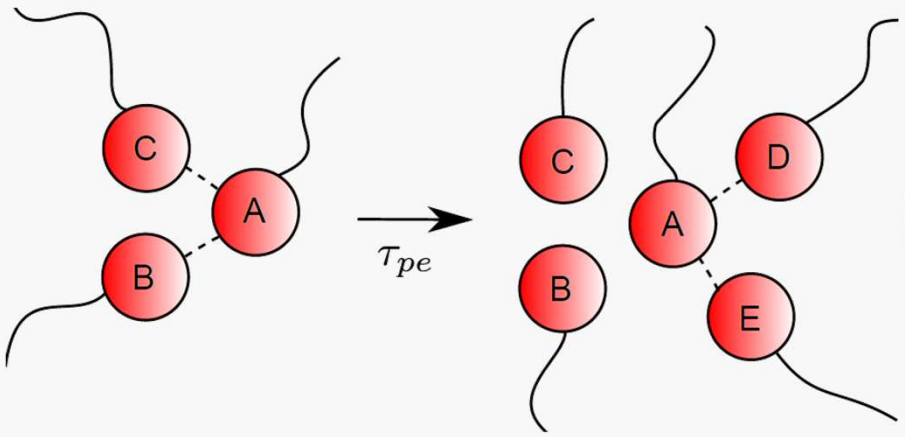
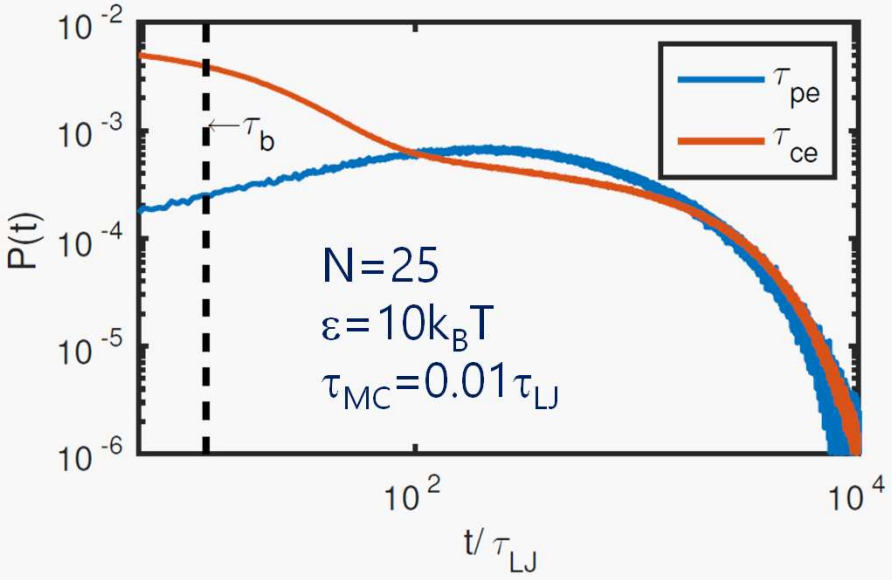
- Renormalization of bond lifetime previously considered for binary bonding cases (Rubinstein, 2001; Hoy, 2009)
- Two definitions of characteristic times in clustering case
  - **Partner Exchange time (τ_{PE})**: *average time taken a sticker from being first bonded with two partners until associated two new ones*
  - **Cluster Exchange time (τ_{CE})**: *average time taken a sticker from being initially associated with one cluster until joining a new one with all new n*



Partner Exchange



- Two definitions are consistent at time scales beyond τ_b

Rheological Behavior

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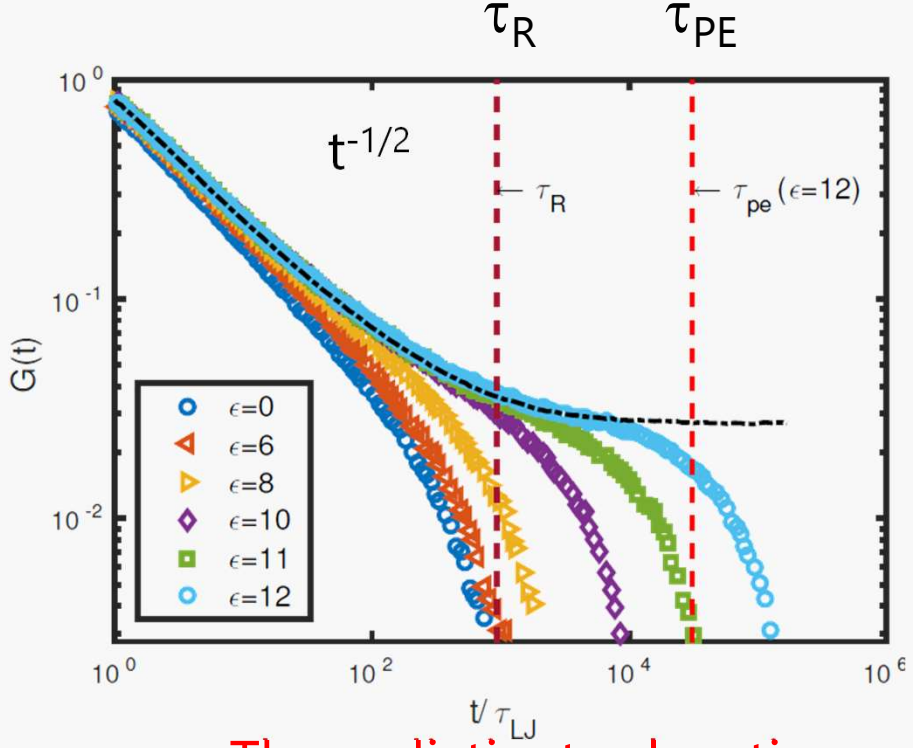
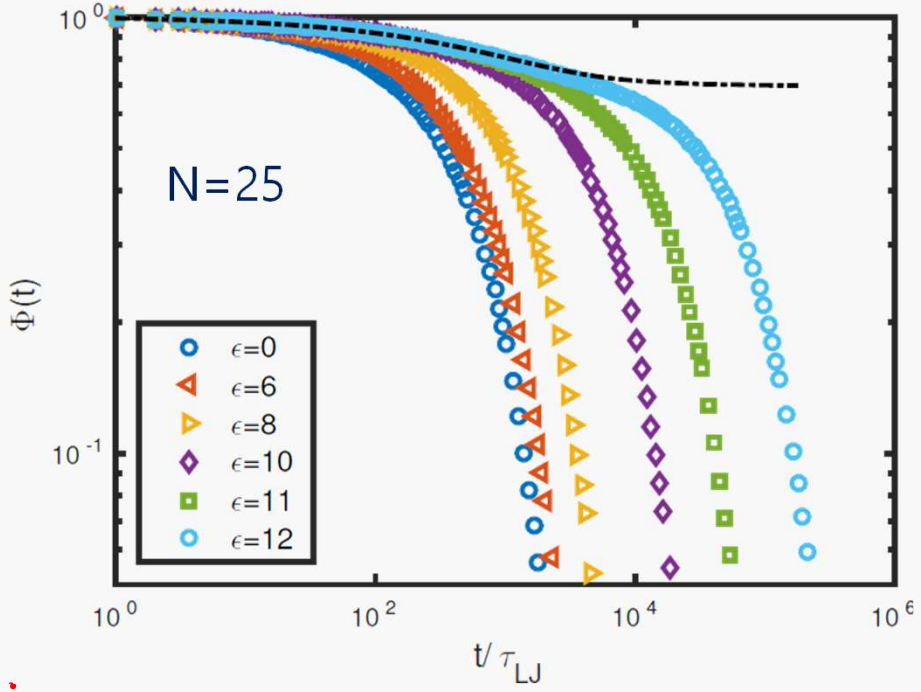
Stress relaxation



End-to-end vector correlation function



- Three distinct relaxation regimes:
  - a) $t < \tau_R$ Rouse behavior;
  - b) $\tau_R < t < \tau_{PE}$, plateau regime due to network formation;
  - c) $t > \tau_{PE}$, terminal relaxation

Yan *et al. Macromol. 2017*

- Terminal relaxation times, $\tau_d^{ee} \approx 2\tau_d^{stress}$, Rouse-like behavior

Startup Shear of Unentangled Systems

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Transient shear viscosity

$$\eta(t) = \frac{\sigma_{xy(t)}}{\dot{\gamma}}$$

First normal stress coefficient

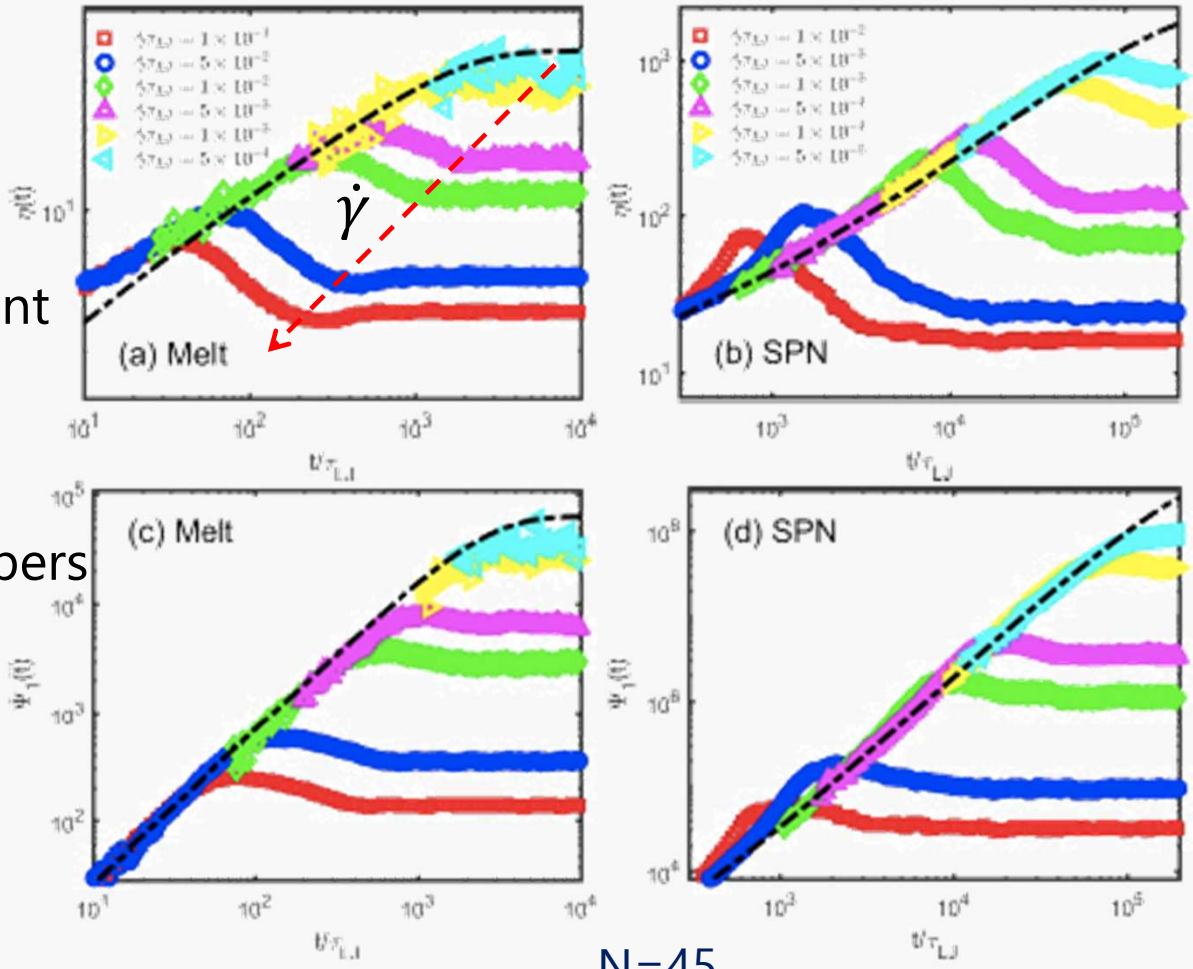
$$\psi_1(t) = \frac{\sigma_{xx(t)} - \sigma_{yy(t)}}{\dot{\gamma}^2}$$

Range of Wissenberg numbers

$$W_i = \dot{\gamma}\tau_d$$

$$W_{i,M} \in (0.61, 1.21 \times 10^3)$$

$$W_{i,S} \in (12.3, 2.46 \times 10^3)$$



- Melt: overshoot followed by undershoot; $\psi_1(t)$ overshoot starts at higher $\dot{\gamma}$
- SPN: strain hardening, higher peak values at lower W_i than in melt

Smaller W_i for $\psi_{1,max}$ under

Startup Shear of Weakly Entangled Systems

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Wissenberg numbers

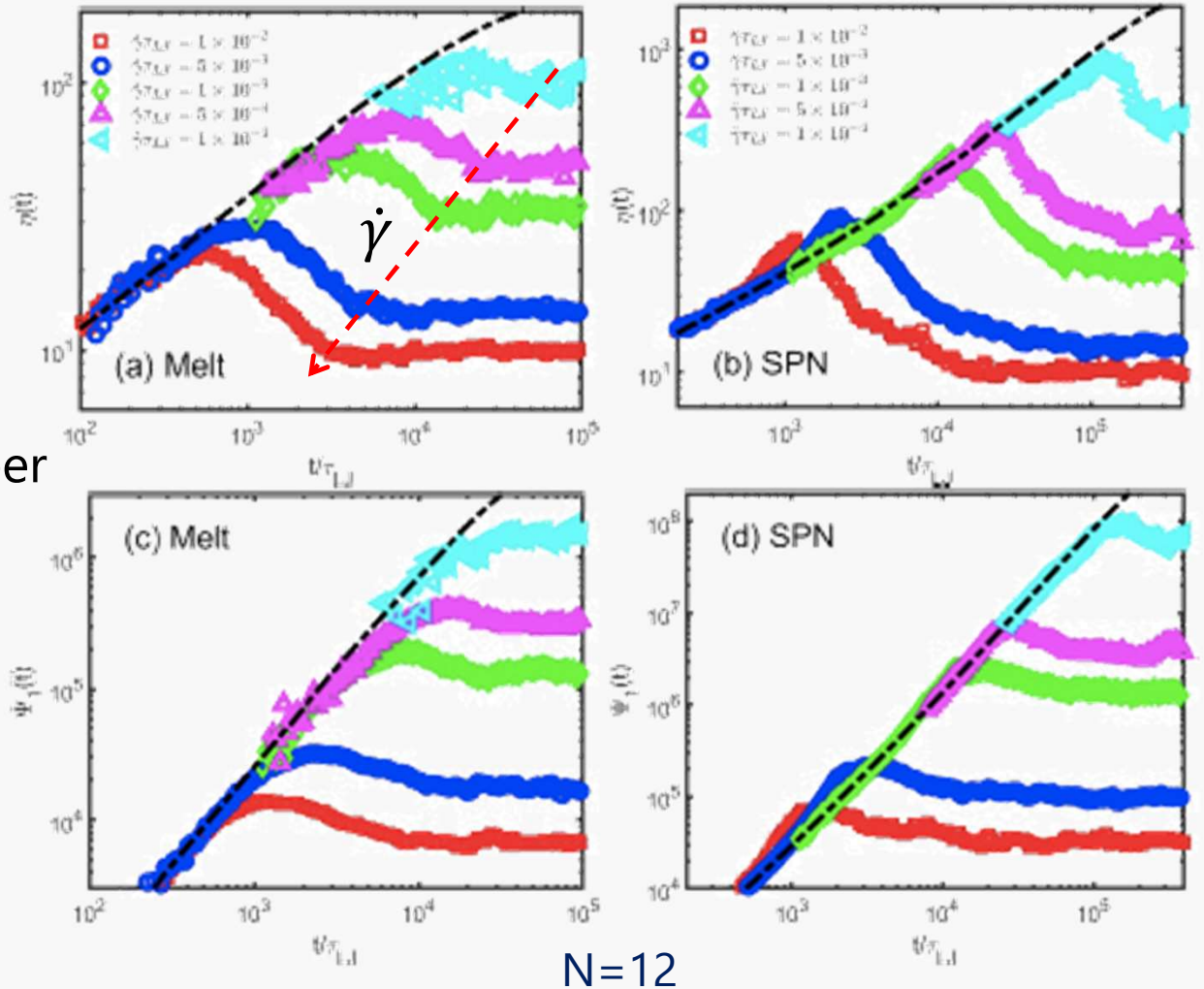
$$W_i = \dot{\gamma}\tau_d$$

$$W_{i,M} \in (2.44, 2.44 \times 10^2)$$

$$W_{i,S} \in (26.3, 2.63 \times 10^3)$$

Rouse Wissenberg number

$$W_{i,R} = \dot{\gamma}\tau_R \in (1.5, 150)$$



N=128

- Qualitatively similar behavior to unentangled

Startup Extension of Unentangled Systems

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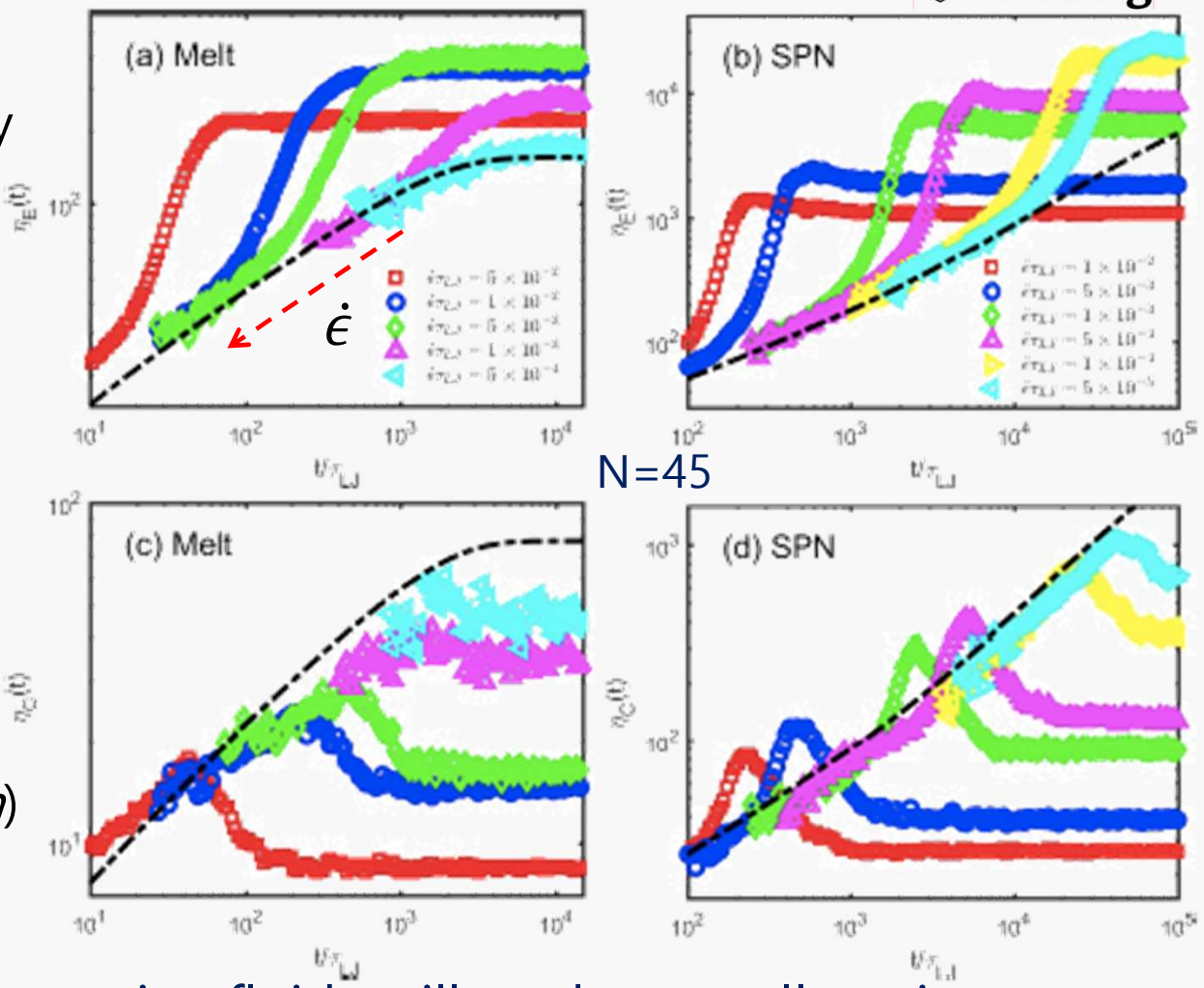
Planar extension viscosity

$$\eta_E(t) = \frac{\sigma_{xx(t)} - \sigma_{yy(t)}}{4\dot{\epsilon}}$$

Cross viscosity

$$\eta_C(t) = \frac{\sigma_{zz(t)} - \sigma_{yy(t)}}{4\dot{\epsilon}}$$

Linear viscosity
$\eta^*(t)$ × *Trouton ratios (4 and 2 for Newtonian fluids in planar extension*)



- Trouton ratios for Newtonian fluids still work at small strains
- Melt: strain hardening in η_E, but no overshoot; η_C other way around
- SPN: strain hardening and overshoot in both η_E and η_C

Startup Extension of Weakly Entangled Systems

Wissenberg numbers

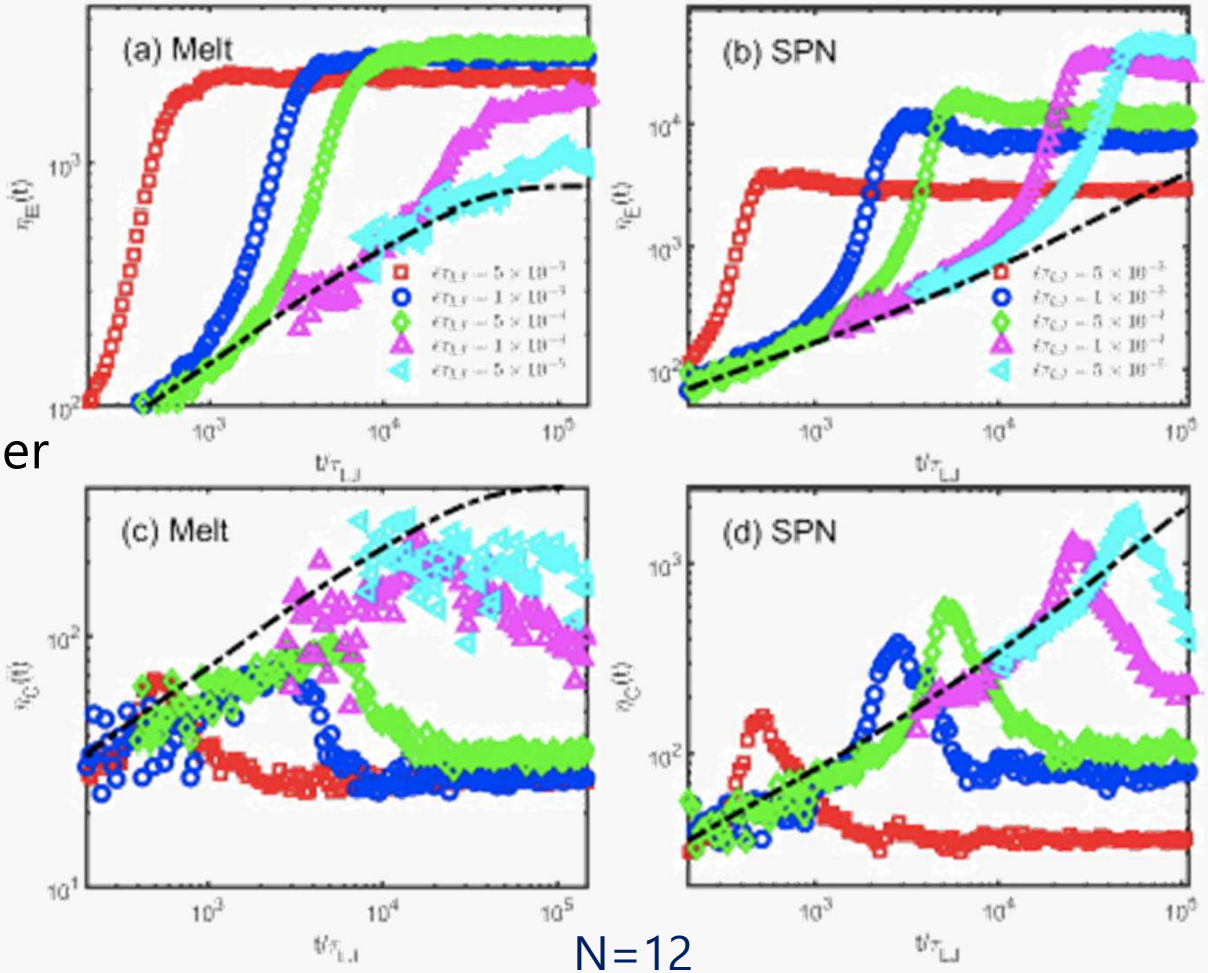
$$W_i = \dot{\gamma}\tau_d$$

$$W_{i,M} \in (1.22, 1.22 \times 10^2)$$

$$W_{i,S} \in (13.2, 1.32 \times 10^3)$$

Rouse Wissenberg number

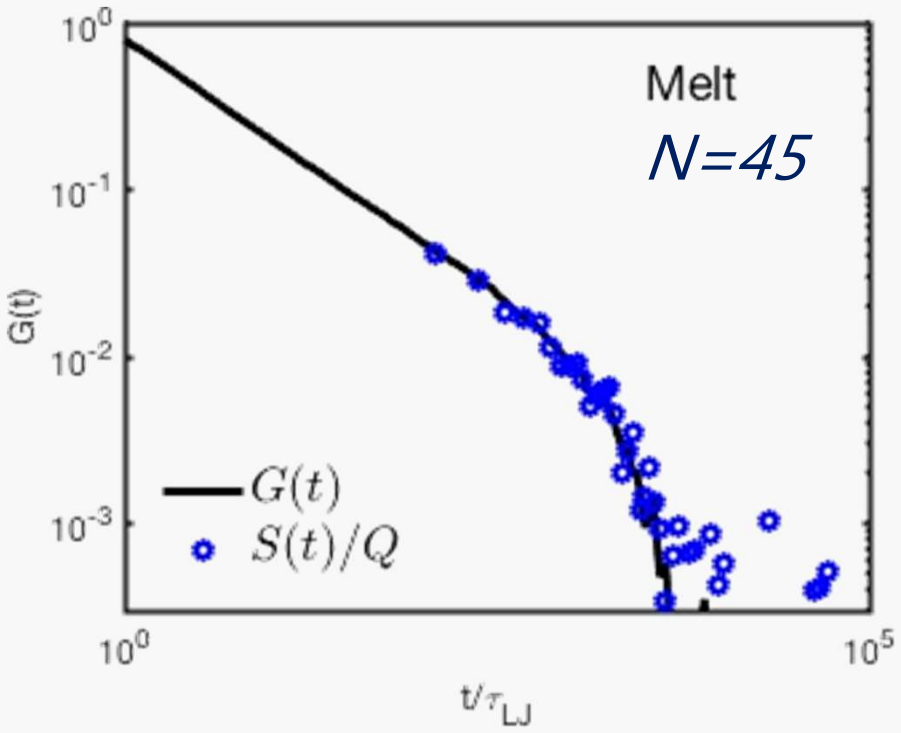
$$W_{i,R} = \dot{\gamma}\tau_R \in (0.75, 75)$$

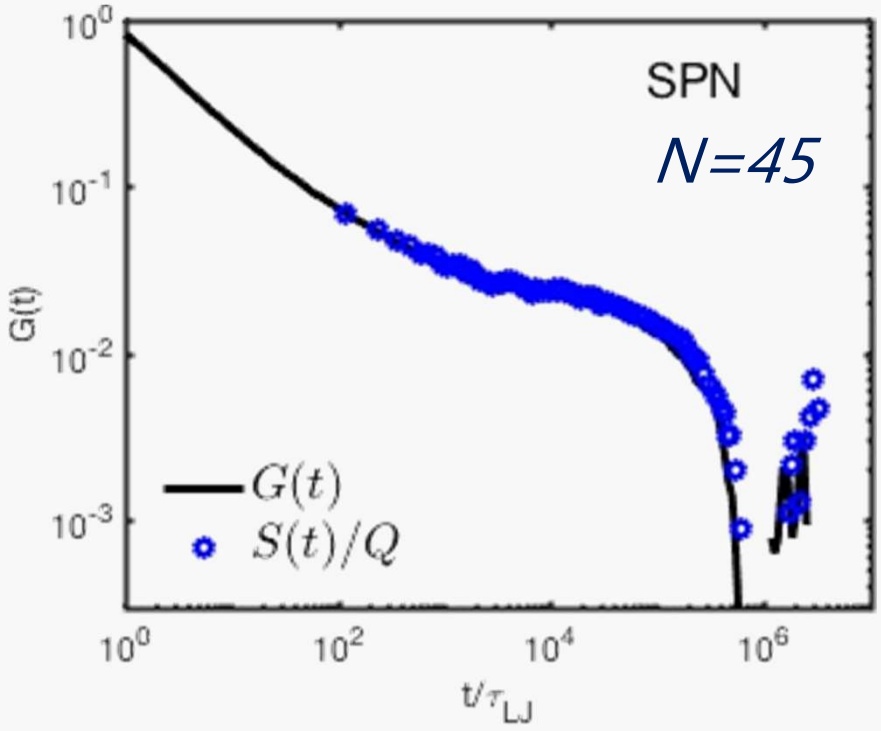


N=128

- Qualitatively similar behavior to unentangled systems

Stress-Optical Law in Equilibrium Systems





$$G(t) = \frac{V}{k_B T}\left\langle \sigma^{\alpha\beta}(t)\sigma^{\alpha\beta}(0)\right\rangle$$

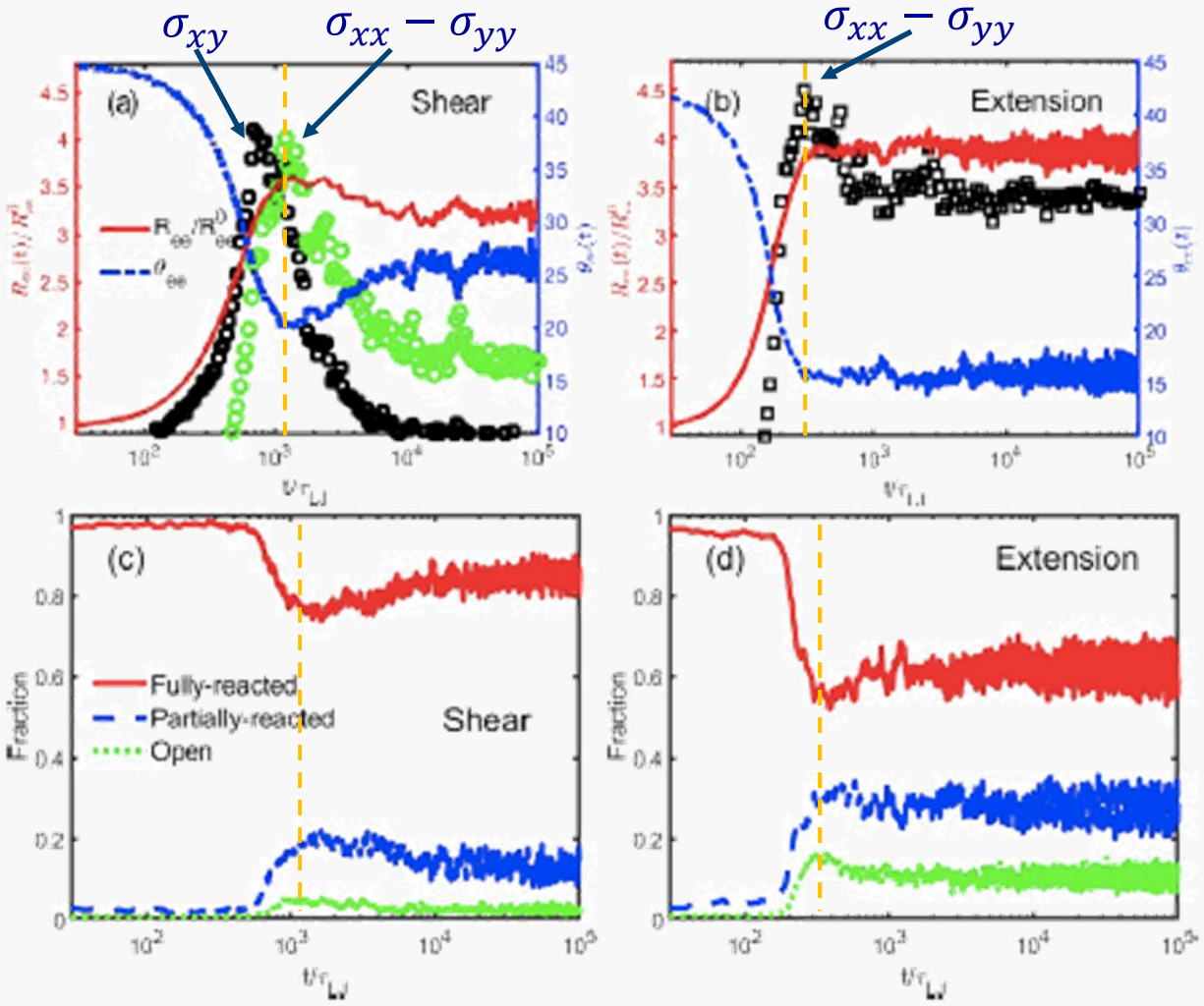
$$S(t) = \frac{N_b}{k_B T}\left\langle \frac{1}{N_b^2}\sum_{j=1}^{N_c} O_j^{\alpha\beta}(t)\sum_{j=1}^{N_c} O_j^{\alpha\beta}(0)\right\rangle$$

$$G(t) = S(t)/Q$$

$$Q \approx 0.0886$$

Cao & Likhtman, ACS Macro Lett. 2015

Contributing Factors to Nonlinear Behavior



SPN, N=45, $\dot{\gamma} = \dot{\epsilon} = 10^{-2}/\tau_{LJ}$

Stress increases with

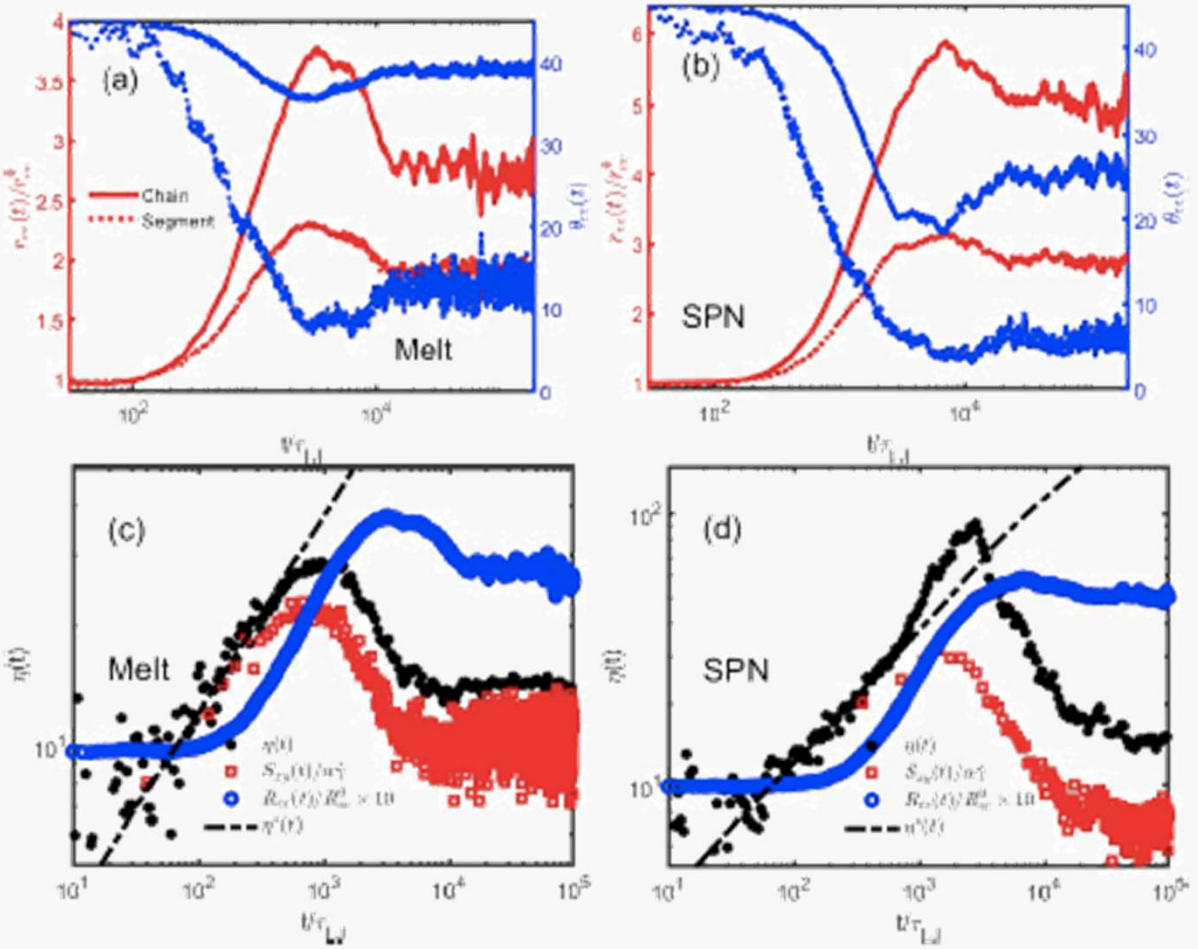
- *Chain stretching*
- *Segment reorientation*

decreases with

- *Decrease in fractions of associated stickers*

$\sigma_{\alpha\beta} \propto f_\alpha r_\beta$

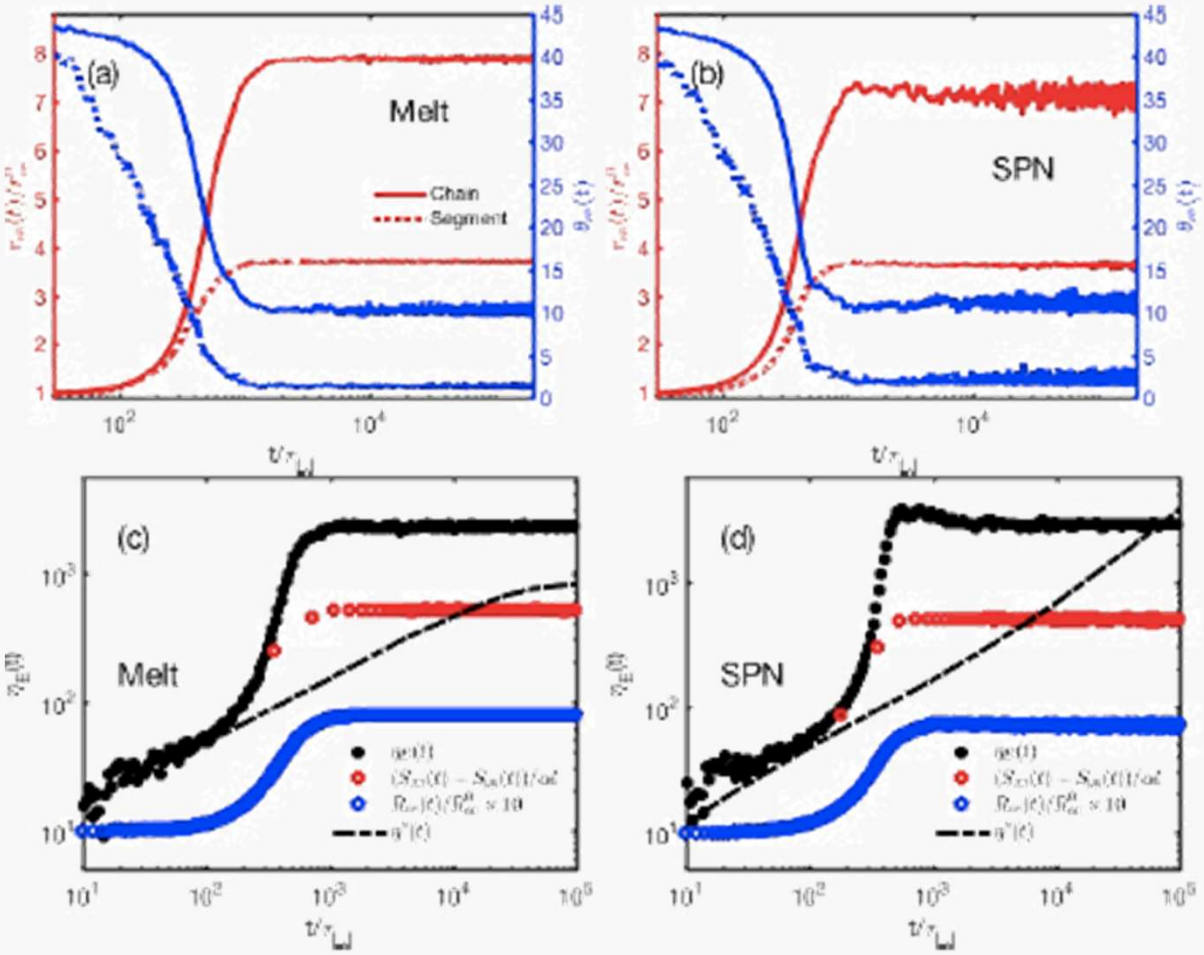
Examine Stress-Optical Law Under Shear



$N=128, \dot{\gamma} = 5 \times 10^{-3} / \tau_{LJ}$

- Stress-optical law is valid in linear regime
- Strain Harding results from nonlinear chain stretching

Weakly Entangled Systems Under Extension



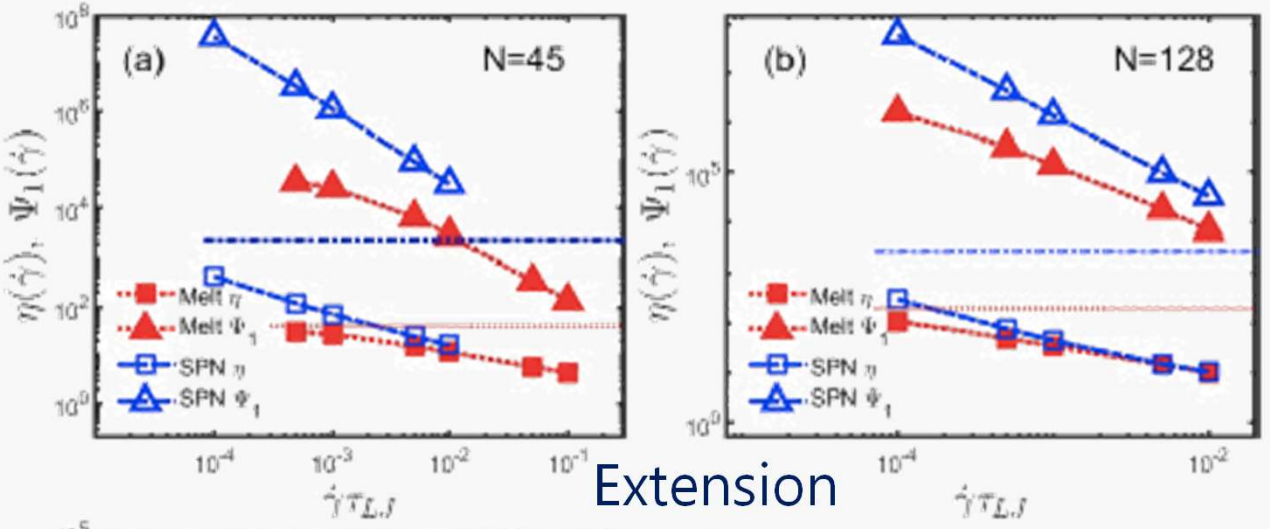
$N=128,\ \dot{\epsilon} = 5 \times 10^{-3}/\tau_{LJ}$

- Stress-optical law is valid in linear regime
- Strain hardening results from chain stretching + segment reorientation

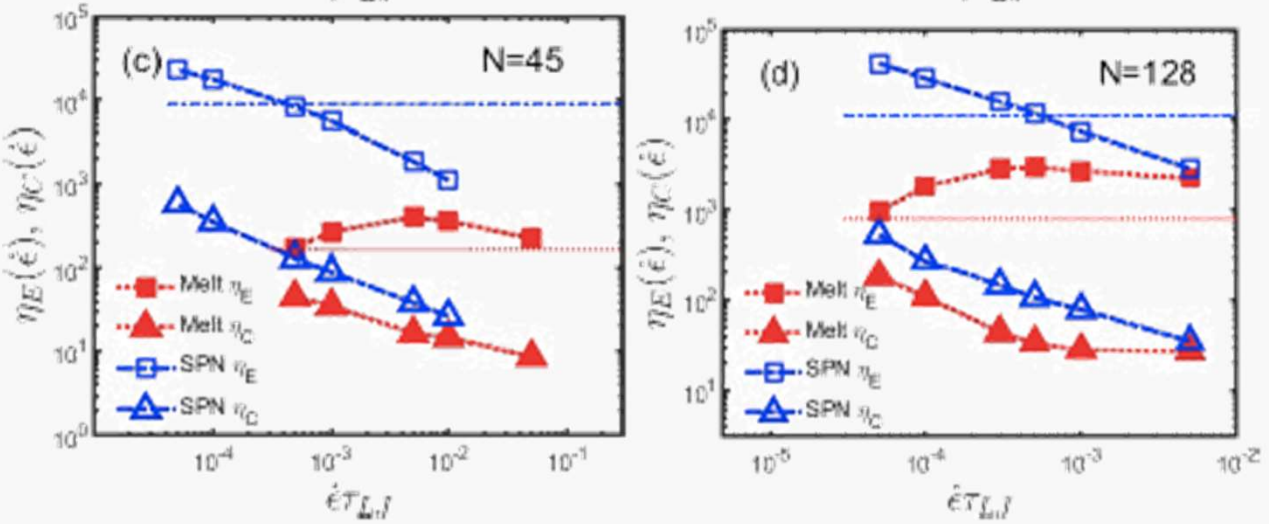
Steady-State Viscosities of Melts and SPN

University of Reading

Shear

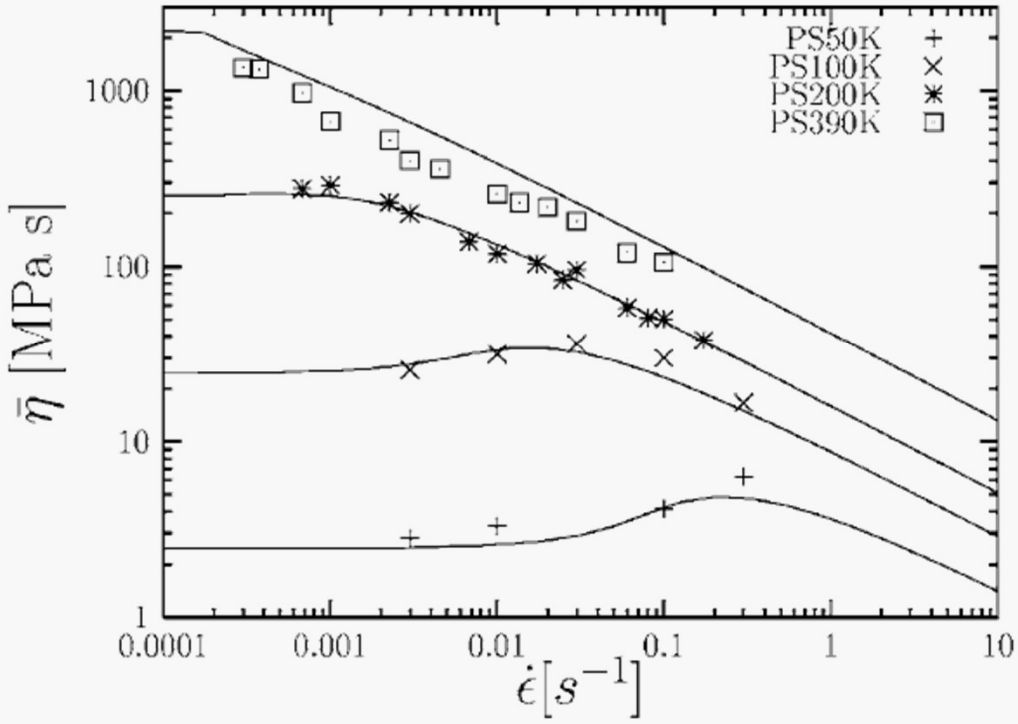


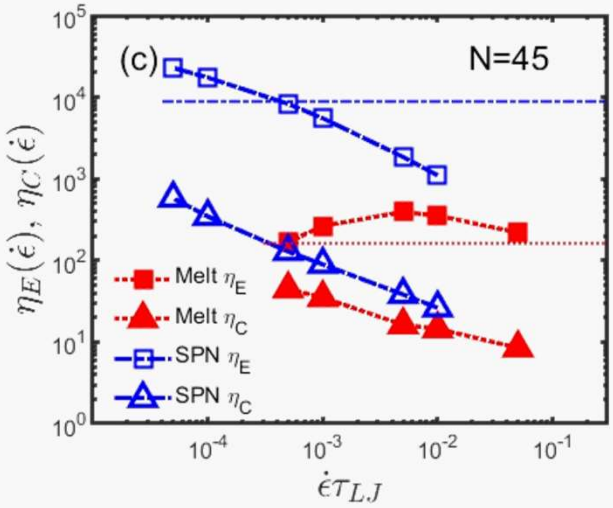
Extension

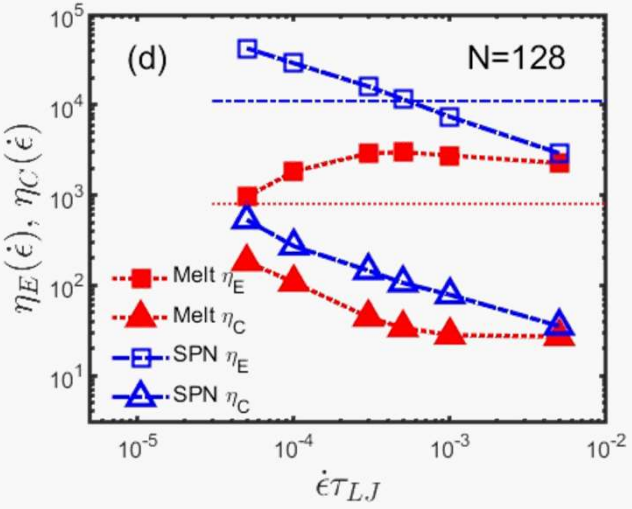


- No shear thickening in both melts and SPNs
- Extension thickening in both melts and SPNs

Steady-State Extension Viscosity Strain-rate Hardening of Unentangled Polymer Melts



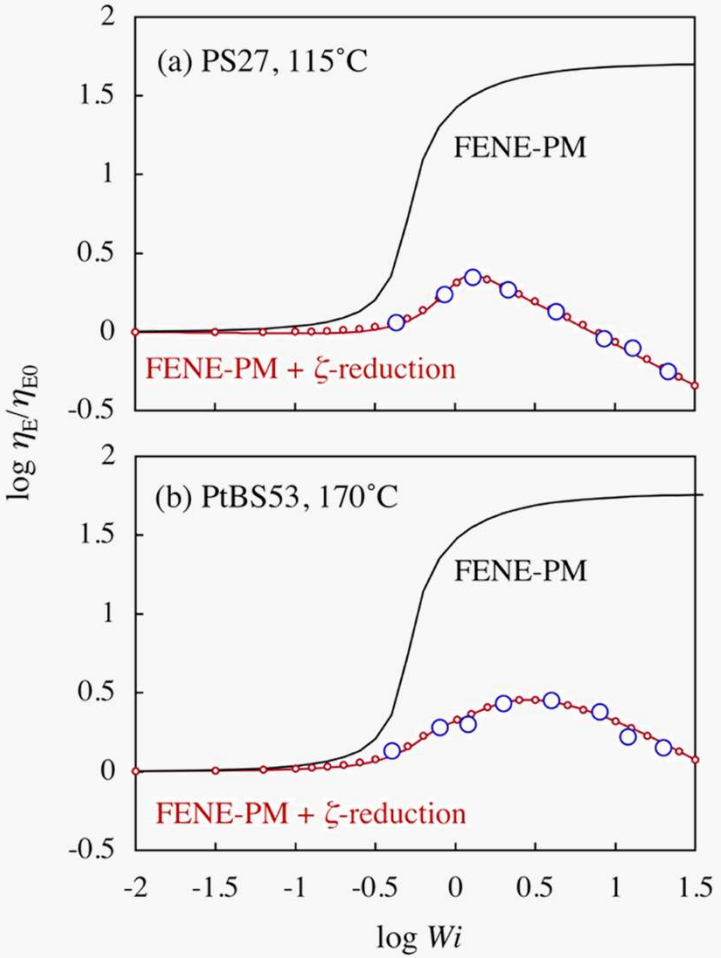


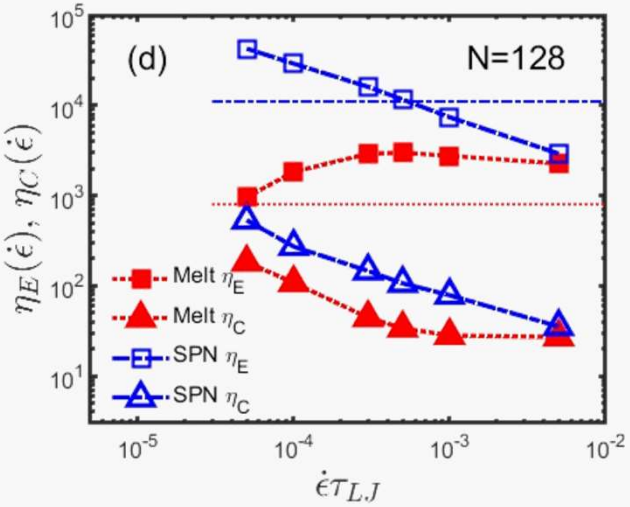


Wiest Model: (Nielsen *et al. JoR, 2006*)

- Anisotropic hydrodynamic drag
- Finite extensibility of chains

Comparison with Experiments on Melts





$W_i = \dot{\epsilon}\tau_d = 1.22\sim122$

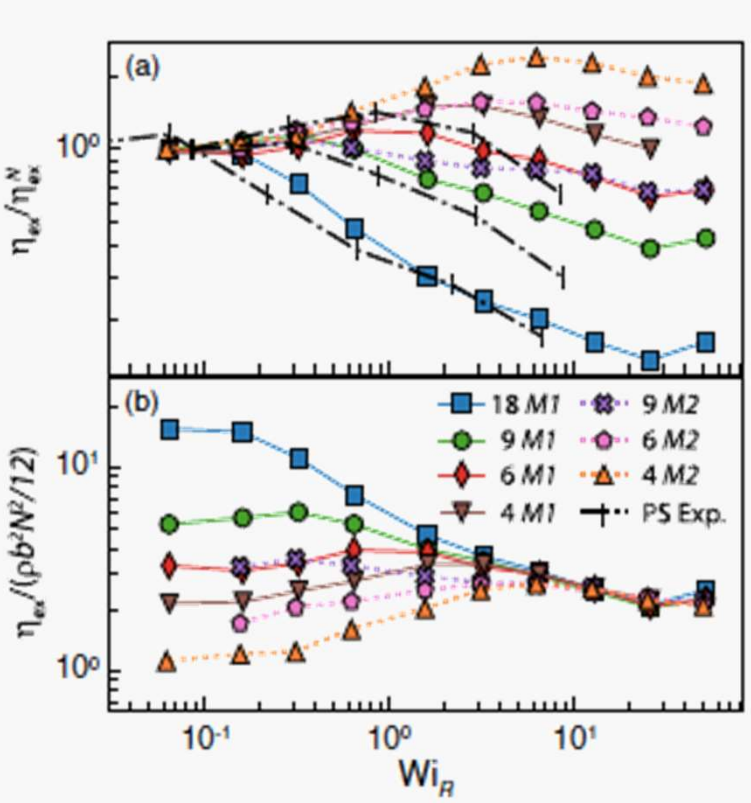
$W_{iR} = \dot{\epsilon}\tau_R = 0.75\sim75$

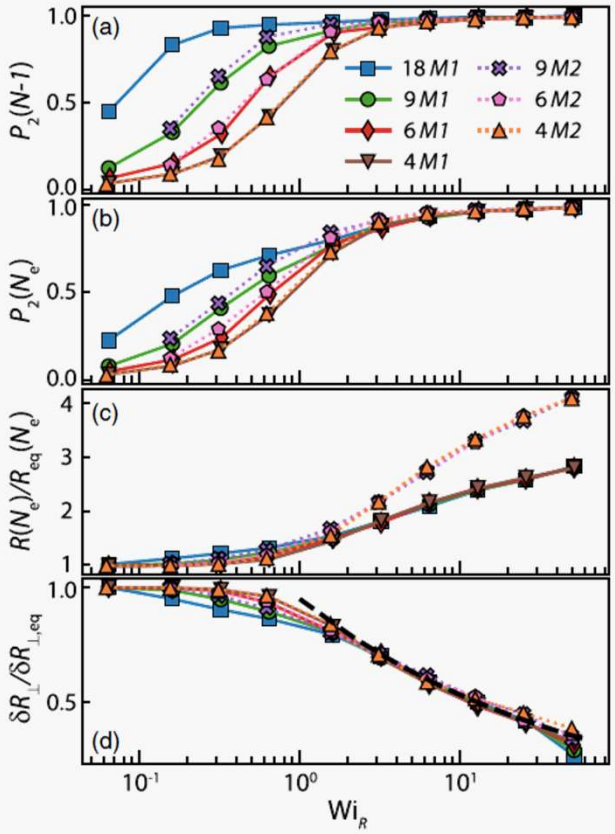
- Qualitatively consistent
- Quantitative difference, e.g. range of W_i for hardening
- Testing suggested mechanism

Suggested mechanism: FENE effect + chemistry-dependent ζ-reduction induced by orientation & stretching

Matsumiya et al., Macromol. 51 (2018) 9710

Simulation Results from Other Group

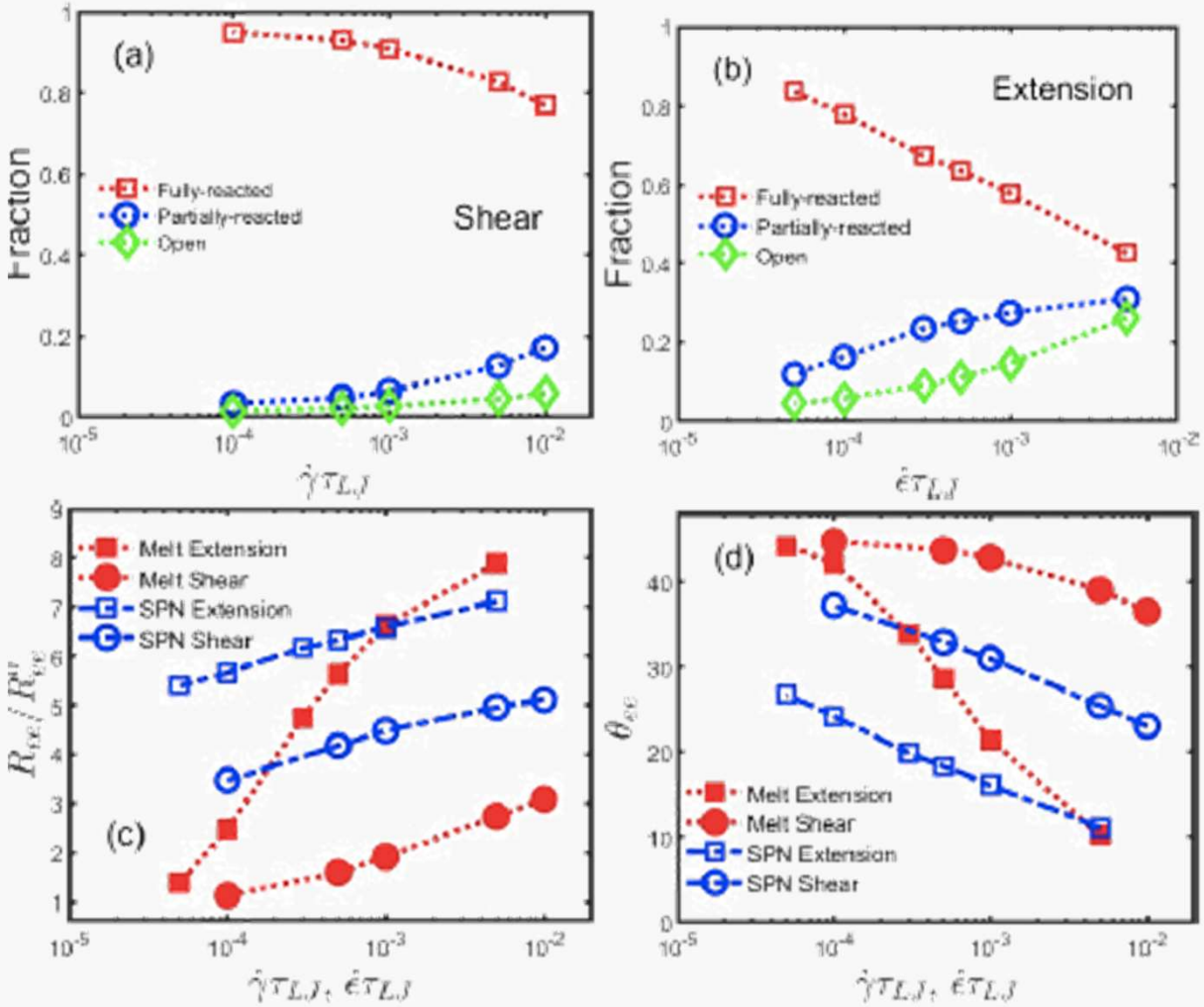




- Similar results for weakly entangled chains

O'Connor et al., PRL, 121 (2018) 047801

Steady-State Structural Properties of SPNs

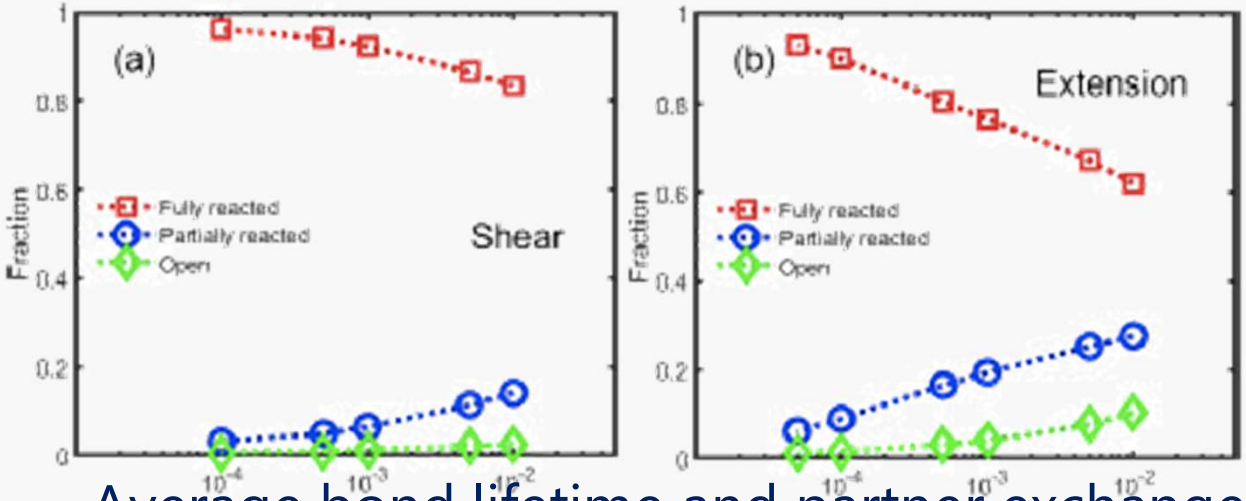


- Shear thinning due to contributions of non-Gaussian Chain stretching counter-balanced by reduction in fractions of associated stickers and so number of elastically active strands

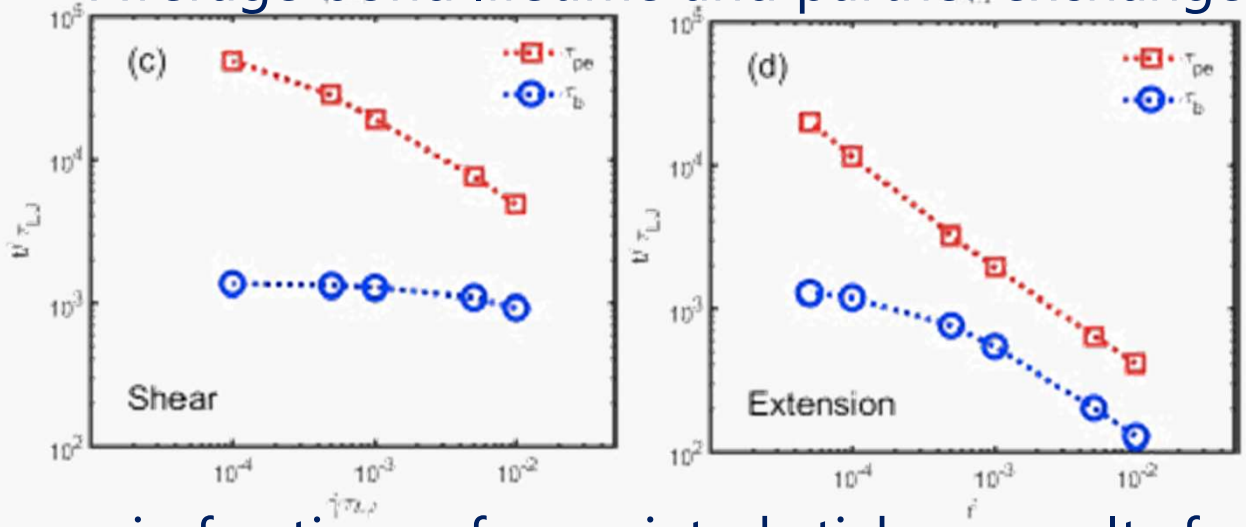
Steady-State Sticker Association Behavior

University of Reading

Fractions of associated stickers



Average bond lifetime and partner exchange time

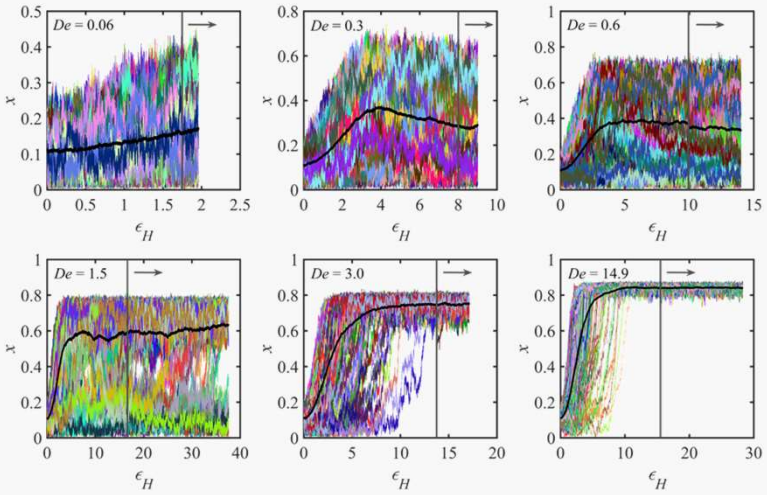


- Decrease in fractions of associated stickers results from flow-induced reduction of probabilities for stickers to re-associate with

Other Elongational Flow Simulations of Entangled Polymers

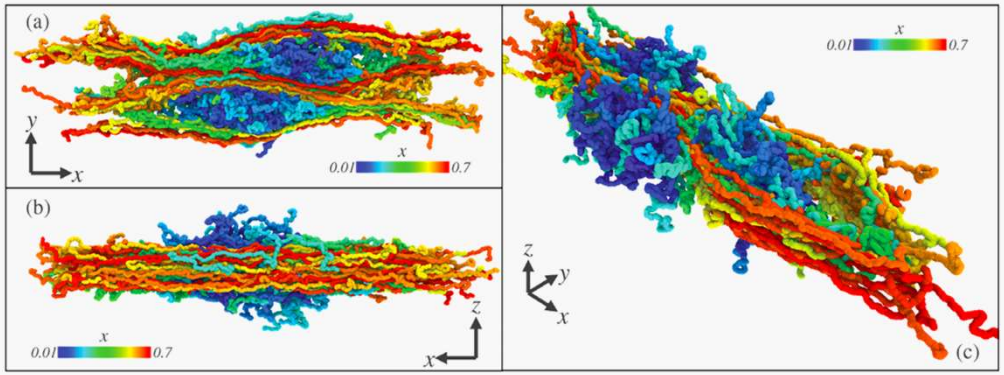
University of Reading

Coil-Stretch Transition



Sefiddashti et al., JCP 148 (2018) 141103

Configurational microphase separation



Sefiddashti et al., PRL 121 (2018) 247802;

Summary

- Computer simulations based on bead-spring model can provide microscopic insights into the flow behavior of polymeric systems
- Different extension simulation techniques are available for tackling various theoretical and experimental problems
- Quantitative discrepancies indicate that further investigation of the relaxation mechanisms and improvement of the theoretical/simulation models are still needed

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