Exploring Shear Thickening of Telechelic Associating Polymers through Stochastic Simulations

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INITIAL TRAINING NETWORK

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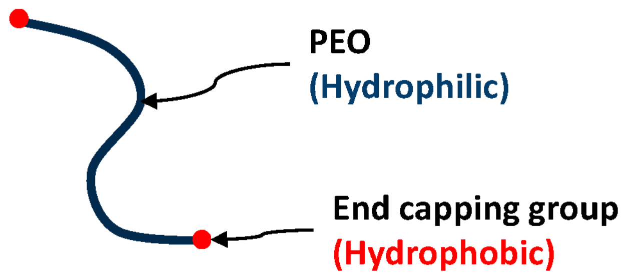
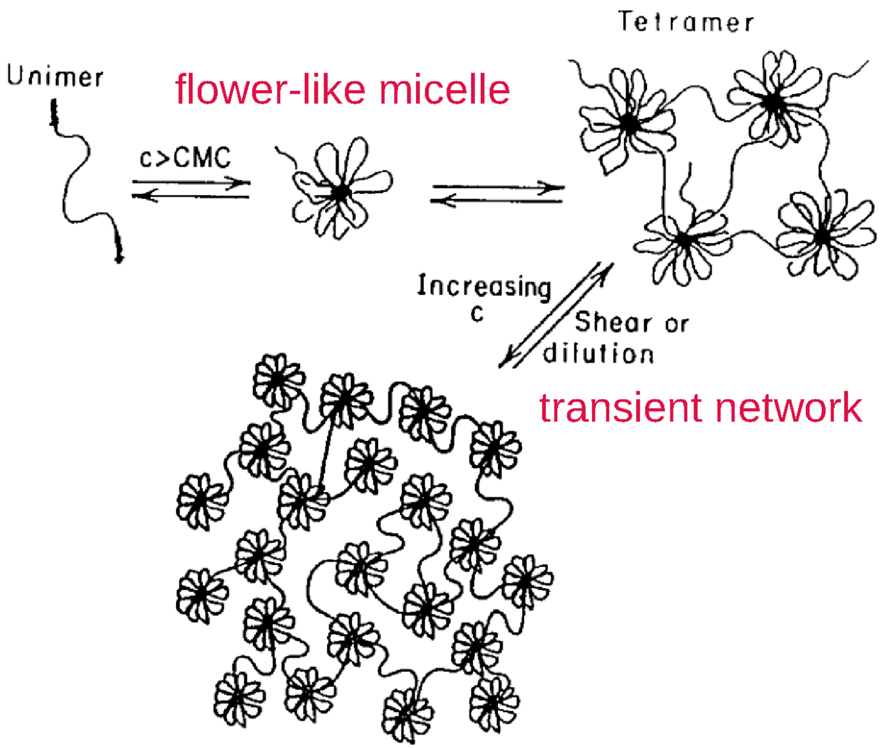
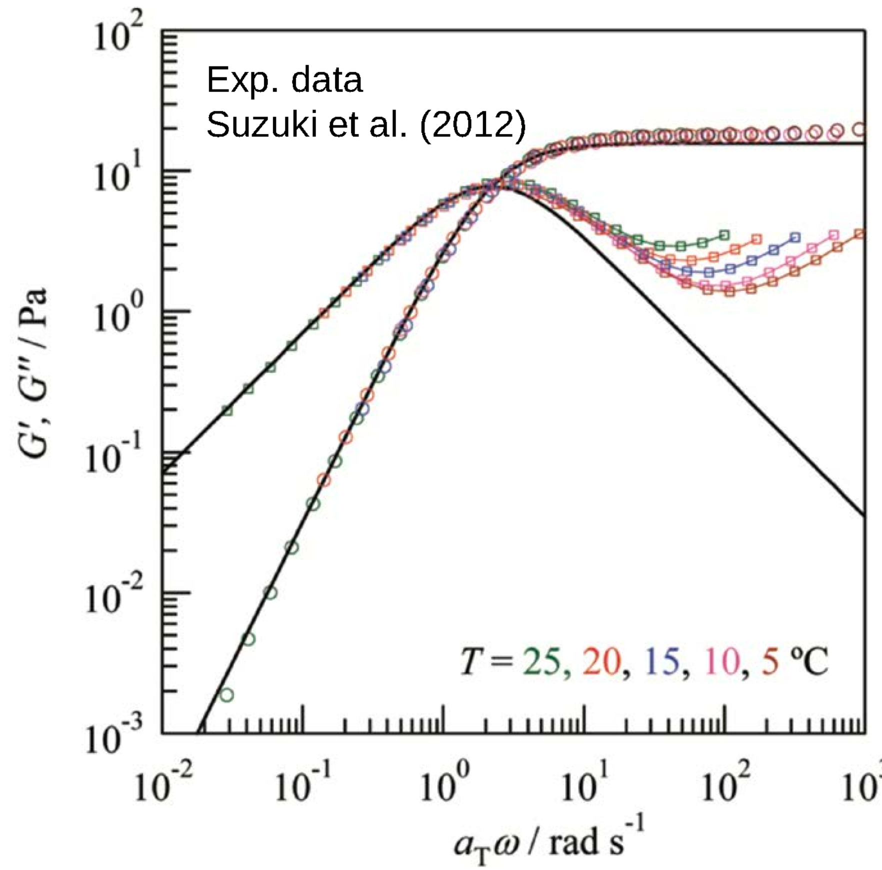
Telechelic Associating Polymers





Xu et al. (1996)



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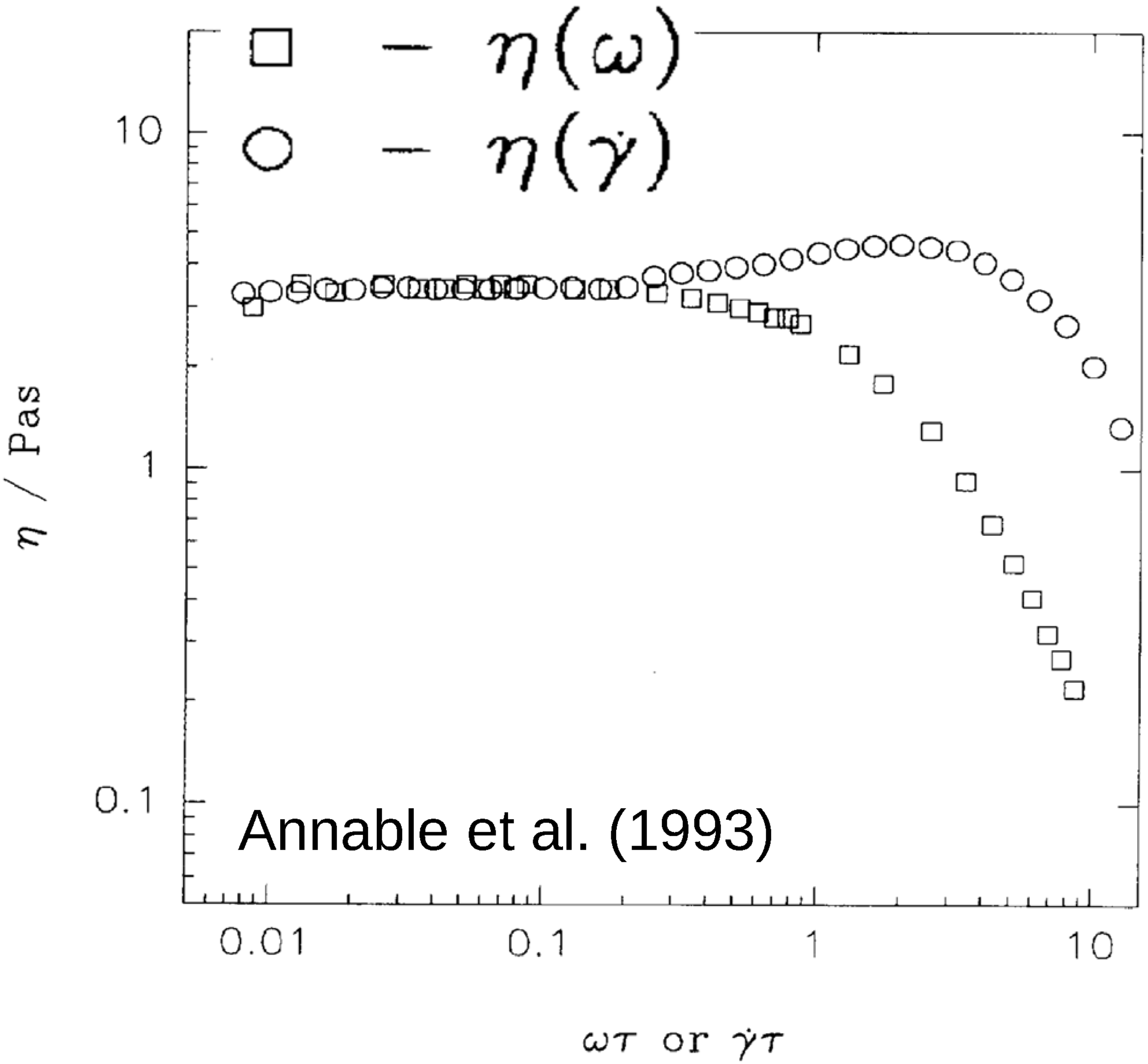
Steady Shear and Dynamic Viscosities



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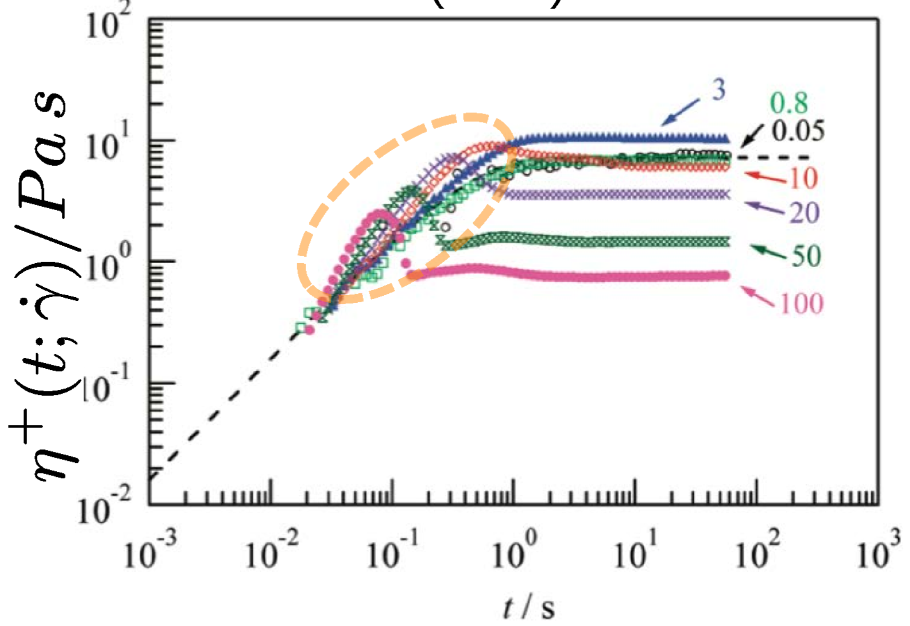
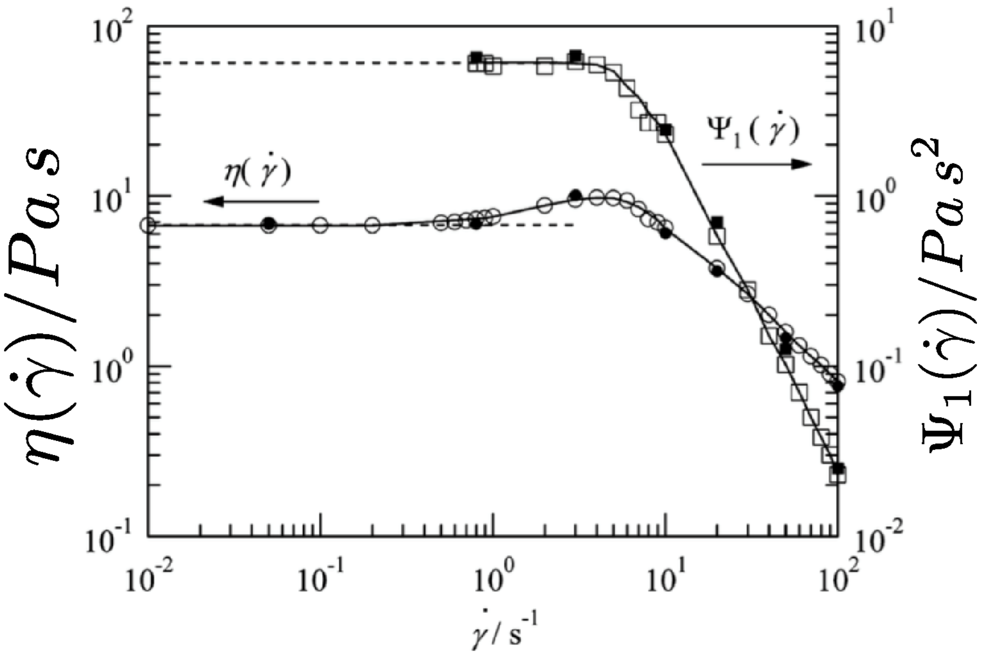
Non-Linear Rheological Data

Suzuki et al. (2012)





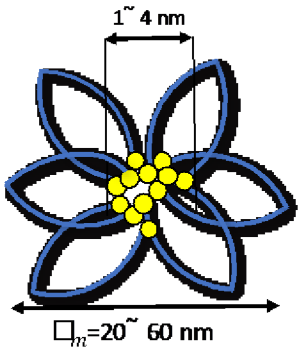
Strain-hardening in shear startup

Shear thickening in $\eta(\dot\gamma)$
No thickening for $\Psi_1(\dot\gamma)$

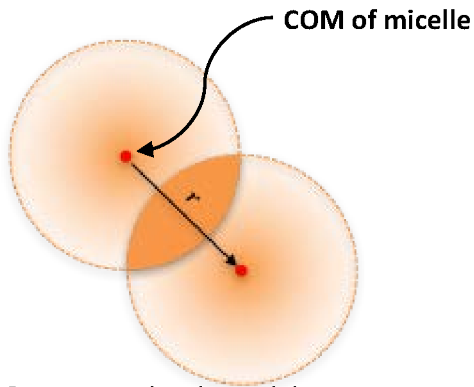
Research Objectives

1. single Maxwell relaxation
2. breakdown of Cox-Merz Rule
3. strain-hardening in shear startup
4. shear thickening

Diffusion of Micelles with fixed network connectivity



Simplified micelles with frictionless segments of chains



Coarse-grained repulsive interactions between micelles

Brownian force

$$\langle \boldsymbol{F}_i^{(Br)}(t)\boldsymbol{F}_i^{(Br)}(t')\rangle = 2k_BT\zeta_i\delta(t-t')\boldsymbol{I}$$

Repulsive interaction

$$\mathbf{F}^{(rep)}(\mathbf{r}) = -C_{rep}k_BT\frac{D_m^2 - r^2}{D_m^3}\hat{\mathbf{r}}$$

$$C_{rep} = C_0p^k \Rightarrow C_{rep} = \langle C_0p^k \rangle$$

(adjustable parameter)

Configurational Langevin equation:

$$\frac{1}{\zeta_k}\left(\frac{\partial \mathbf{r}_k}{\partial t} - \boldsymbol{\kappa}\cdot\mathbf{r}_k\right) = \sum_i \mathbf{F}_{ik}^{(rep)} + \sum_{i\in\mathscr{C}_k} \mathbf{F}_{ik}^{(el)} + \mathbf{F}_k^{(Br)}$$

Fixed Connectivity

Lees Edwards boundary condition

$$\tau_m = \frac{D_m^2}{k_BT/\zeta}$$ micelle diffusion time

ζ_k: micelle friction coefficient of k-th micelle
$\boldsymbol{r}_k$: COM position vector of k-th micelle
$\boldsymbol{r}_{ik}$: relative vector between i-th and k-th micelles
$\boldsymbol{F}_{ik} = \boldsymbol{F}(\mathbf{r}_{ik}) = F(r_{ik})\hat{\boldsymbol{r}}_{ik}$
$\boldsymbol{\kappa}$: velocity gradient tensor

Key parameters of micelle dynamics:

- repulsion coefficient (C_{rep})
- chain end-to-end distance/micelle diameter (R_c/D_m)
- maximally extendable chain length (FENE) (R_{max}/R_c)

Topological Rearrangement of Network (instant time)

Dissociation

$$P_{ij}^{dissoc} = \min\{1, \beta_{ij}\delta t\}$$

dissociation probability

$$\beta_{ij} = \beta_0 \exp\left(\frac{F^{(el)}(\mathbf{r}_{ij})l}{k_B T}\right)$$

Classical detachment frequency

Association

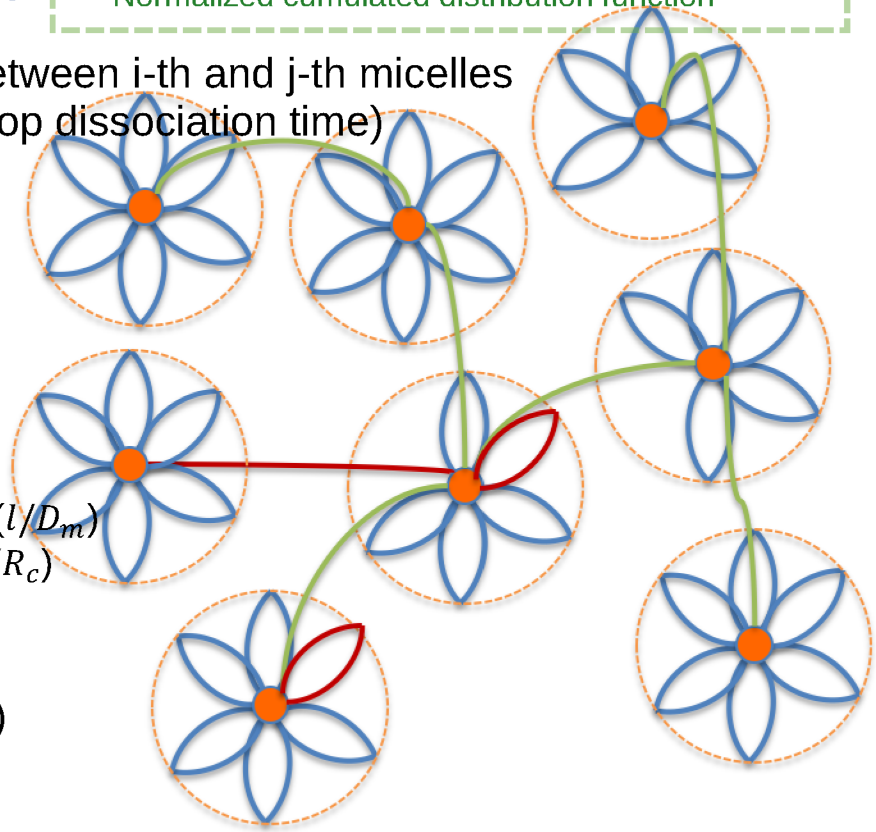
$$P_{ij}^{assoc} = \exp\left(-\frac{U(\mathbf{r}_{ij})}{k_B T}\right)$$

Boltzmann distribution

$$F_j(n) = \frac{1}{Z_j}\sum_{i=1}^{n} P_{ij}^{assoc}$$

Normalized cumulated distribution function

F^{el} : force exerted on network strands between i-th and j-th micelles
β_0 : thermal detachment frequency (= loop dissociation time)
$\tau_0 = \beta_0^{-1}$: Loop dissociation time



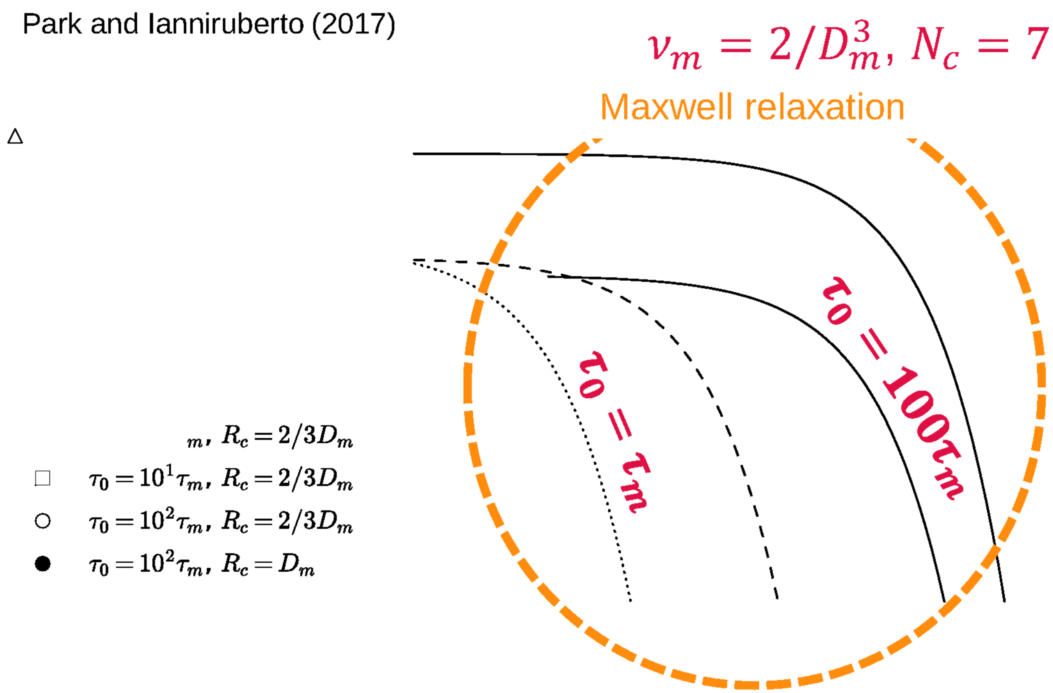
Key parameters for association/dissociation kinetics:

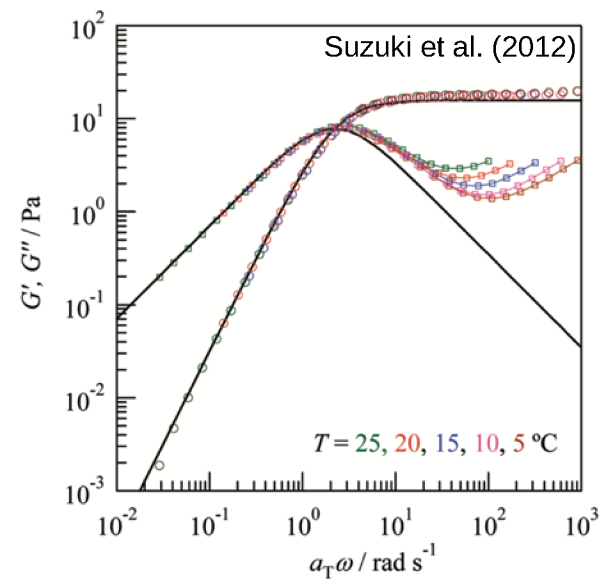
- Number of chains per micelles (N_c)
- length related to energy landscape of association (l/D_m)
- maximally extendable chain length (FENE) (R_{max}/R_c)
- Loop dissociation time / Brownian time (τ_0/τ_m)

For details:

Park and Ianniruberto, J. Rheol. **61**, 1293 (2017)

Calculated Relaxation Modulus



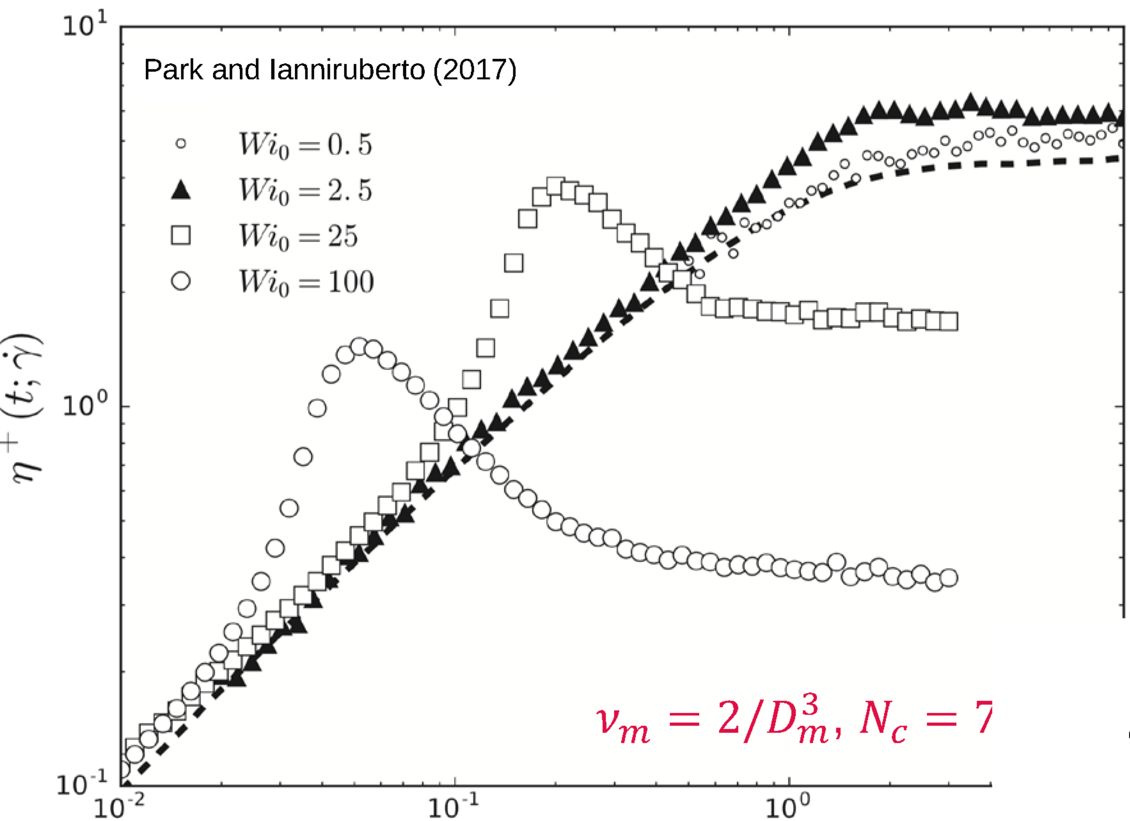


Symbols: calculated relaxation modulus (open: $R_c = 2/3D_m$, closed: $R_c = D_m$)

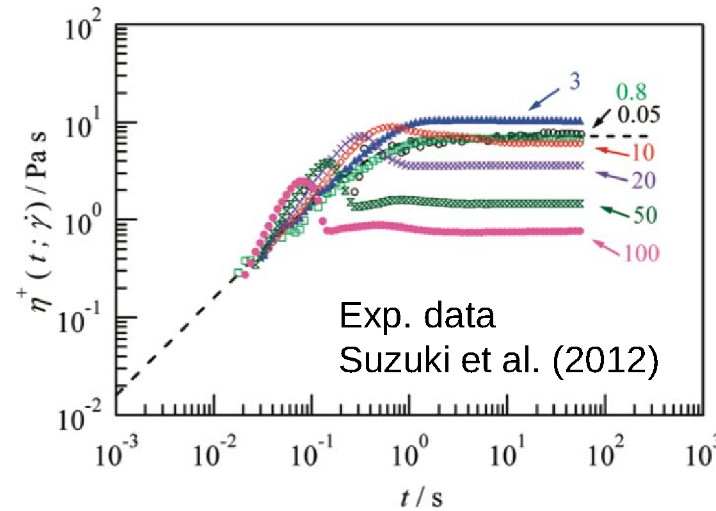
Lines: single Maxwell fit (characteristic times 0.75τ_m, 5.9τ_m, 62τ_m, and 105τ_m from left to right)

1. System exhibit two steps of relaxation, the first relaxation due to repulsive Brownian motion while the latter one is network rearrangement.
2. The second relaxation can be described by single Maxwell model where the characteristic parameter is consistent with given loop dissociation times τ_0

Results of Shear Start-Up



$\nu_m = 2/D_m^3,\ N_c = 7$



$_0 = 100$

$Wi_0 = 250$

Gaussian

FENE

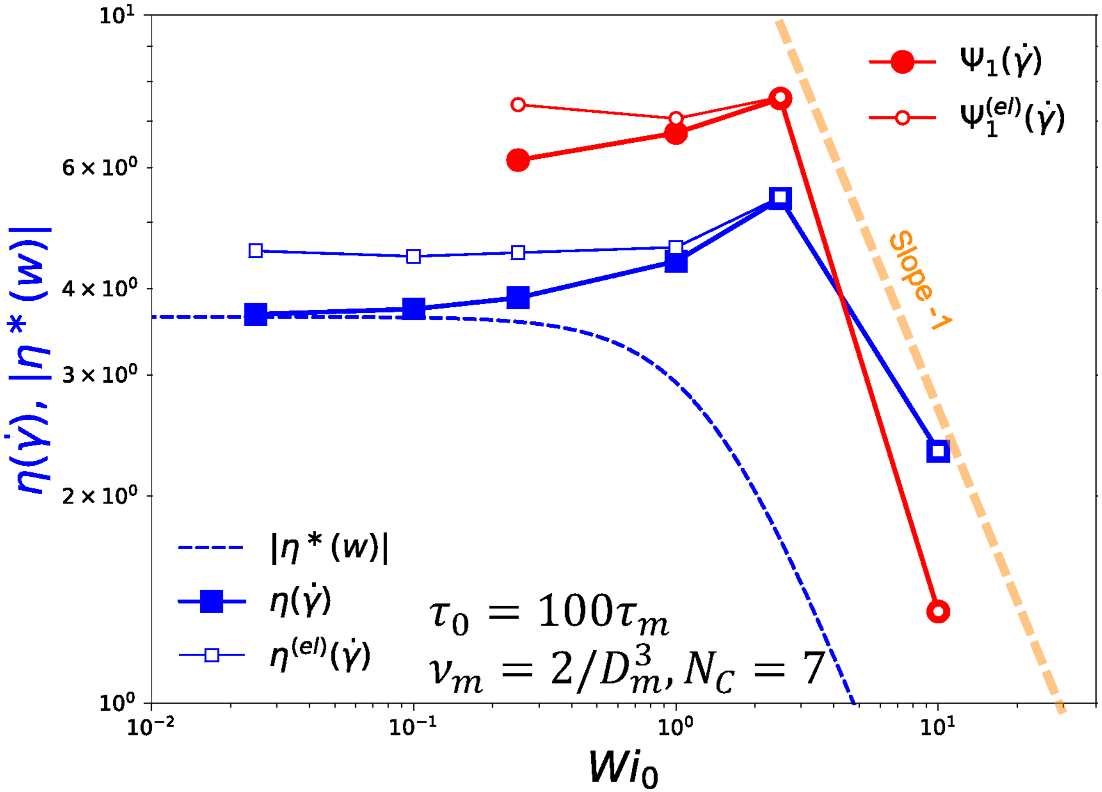
1. Strain hardening is observed, and the stress growth function dominantly controlled by its elastic contribution.

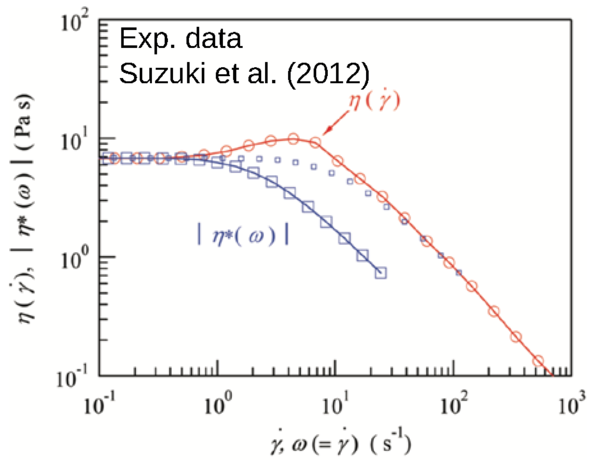
2. No strain hardening is observed for Gaussian chain.

$\nu_m = 0.1/D_m^3,\ N_c = 5$

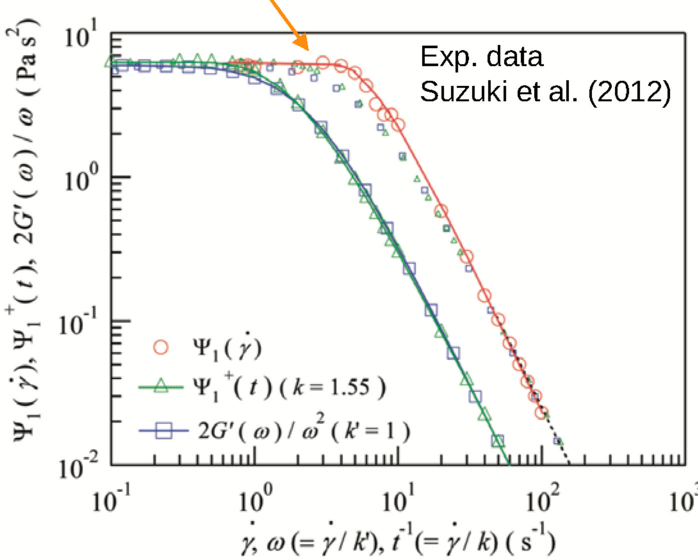
Park and Ianniruberto (2017)

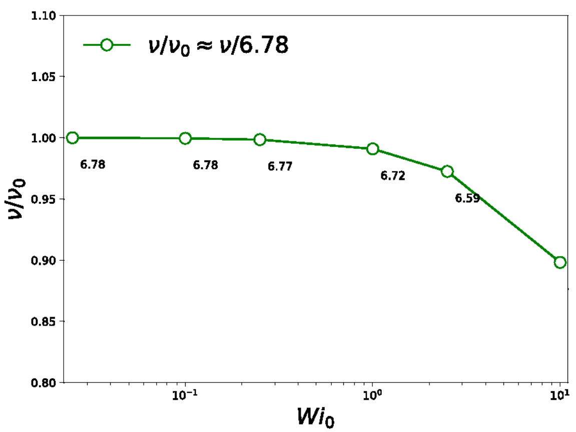
Results of Viscometric Functions





$\Psi_1(\dot\gamma)$





Directional Contributions of Network Elasticity

$$\mathbf{T} = \frac{1}{V_B}\sum_{i=1}^{N_m}\mathbf{R}_i\left(\sum_{j\in\mathbb{C}_i}\mathbf{F}_{ji}^{(el)} + \sum_j \mathbf{F}_{ji}^{(rep)}\right)$$

virial stress tensor

(el): network elasticity

(rep): micelle repulsions

$$\mathbf{T} = \mathbf{T}^{(el)} + \mathbf{T}^{(rep)}$$

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

$$\Psi_1(\dot\gamma) = \frac{T_{xx}(\dot\gamma) - T_{yy}(\dot\gamma)}{\dot\gamma^2}$$

Need to understand directional contributions of network elasticity

$$\mathbf{T}^{(el)} = \nu\langle\mathbf{QF}\rangle = \nu\int f(\mathbf{Q})\mathbf{QF}^{(el)}(\mathbf{Q})d\mathbf{Q}$$

where $\mathbf{F}^{(el)}(\mathbf{Q}) = \frac{\alpha_G}{1-(Q/Q_{max})^2}\mathbf{Q}$

$f(\boldsymbol{Q})$: PDF of elastically active bridges with bridge vector **Q**

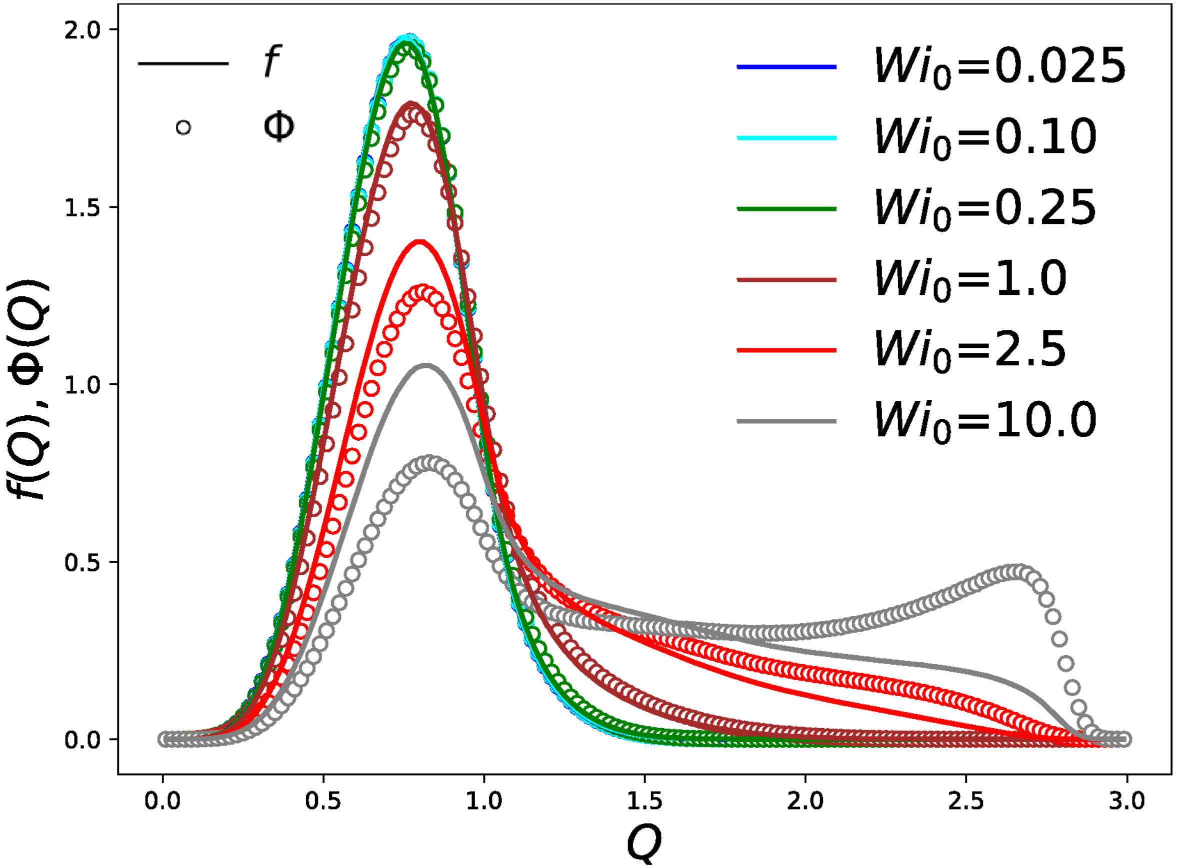
$\Phi(\boldsymbol{Q})$: PDF of stress contribution of elastically active bridges

$$Z_\Phi\Phi(\mathbf{Q}) = \frac{f(\mathbf{Q})}{1-(Q/Q_{max})^2} \quad \Rightarrow \quad \mathbf{T}^{(el)} = \alpha_G Z_\Phi \nu\int\Phi(\mathbf{Q})\mathbf{QQ}d\mathbf{Q}$$

Isotropic pre-factors

Z_Φ: normalization factor

Bridge Length Distribution



Linear

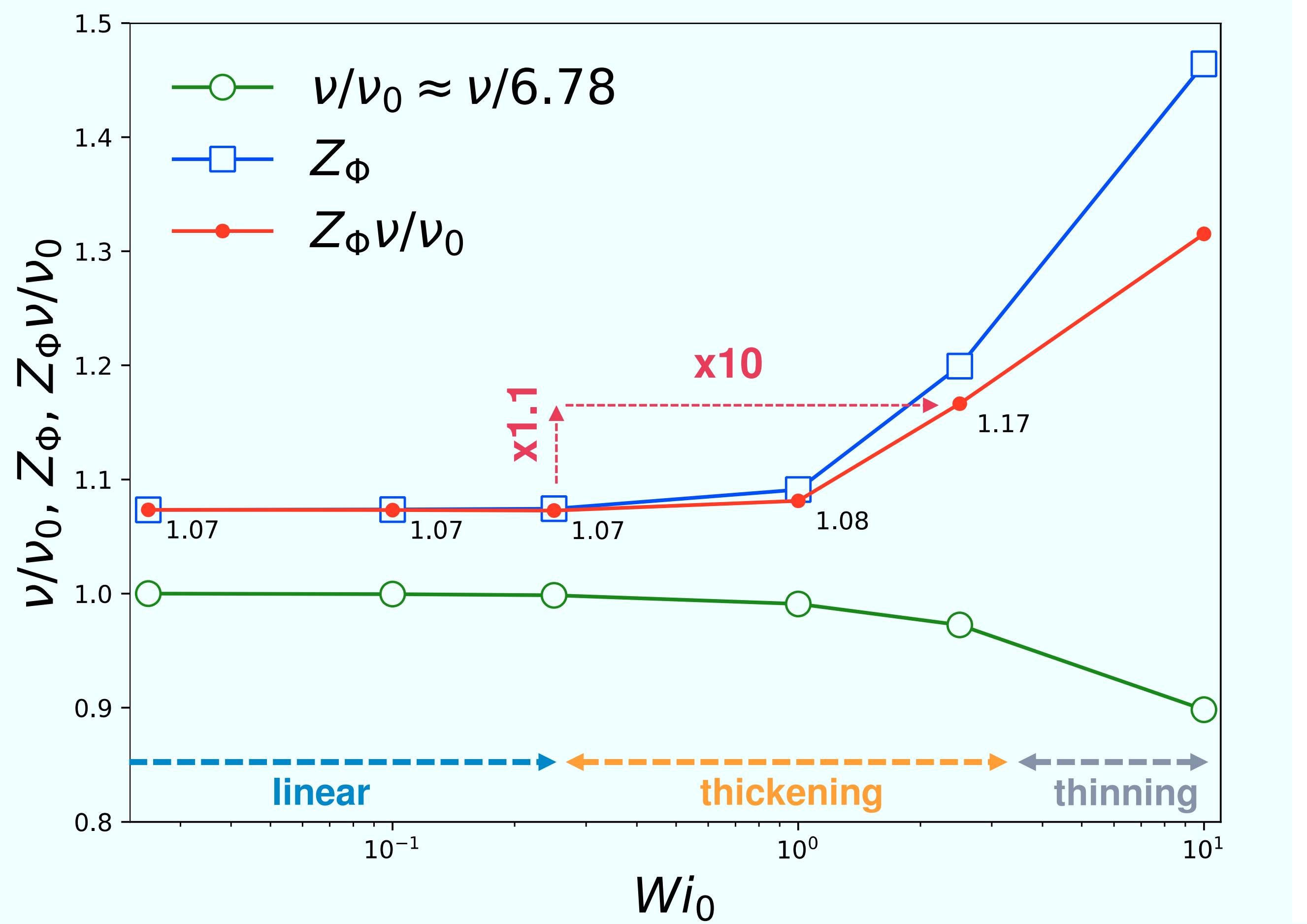
Shear thickening

Shear thinning

$f(Q)$: PDF of elastically active bridges with $Q = |\boldsymbol{Q}|$

$\Phi(Q)$: PDF of stress contribution of elastically active bridges with $Q = |\boldsymbol{Q}|$

Shear Rate Dependence of Isotropic Pre-factors

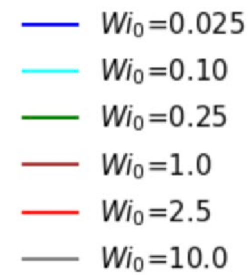


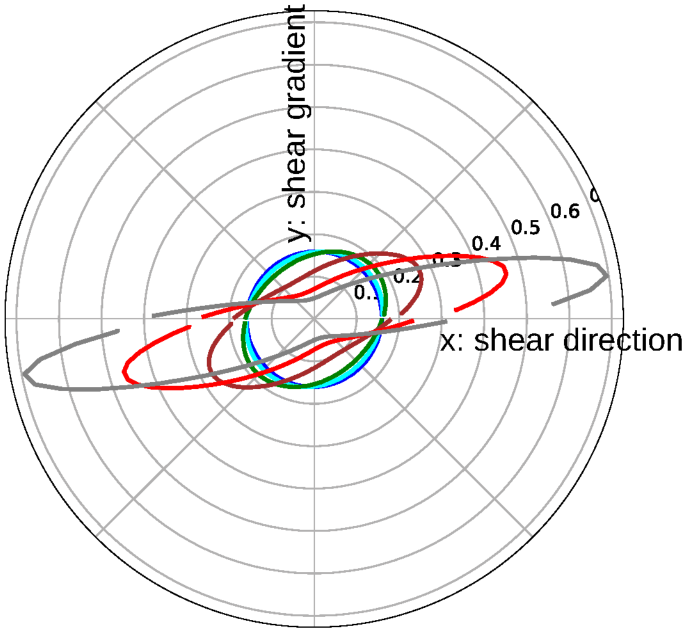
$\nu(\dot{\gamma})$: Number density of elastically active bridges

$Z_\Phi(\dot{\gamma})$: The isotropic contribution of finite extensibility

νZ_Φ: A measure of isotropic contributions of network elasticity to stress tensor

Bridge Orientation Distribution



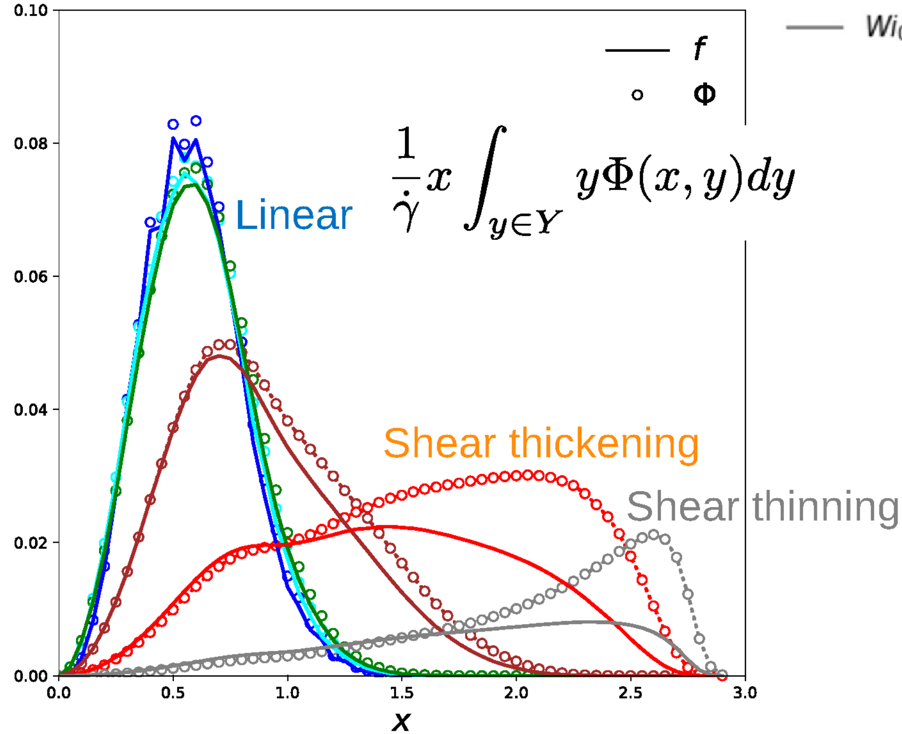


Orientation in shear (xy) plane

azimuthal angle

$$\phi \in [0, 2\pi)$$

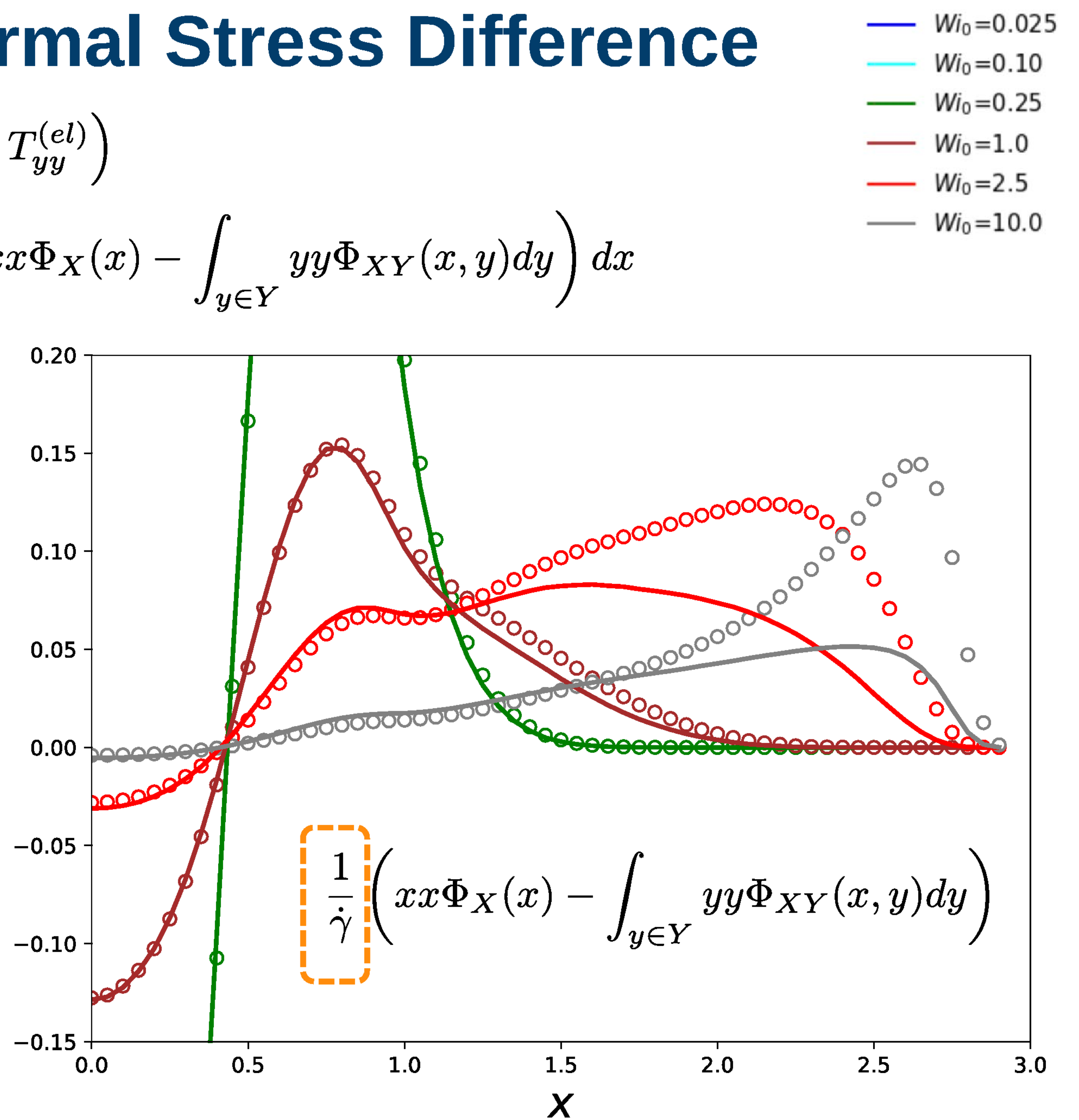
shear stress distribution along x



$$\eta^{(el)} = \frac{\alpha_G Z_\Phi \nu}{\dot{\gamma}} \int_{x \in X} x \left(\int_{y \in Y} y \Phi(x,y) dy \right) dx$$

Note: First Normal Stress Difference

$$\Psi_1^{(el)}(\dot{\gamma}) = \frac{\alpha_G Z_\Phi \nu}{\dot{\gamma}^2}\left(T_{xx}^{(el)} - T_{yy}^{(el)}\right)$$
$$= \frac{\alpha_G Z_\Phi \nu}{\dot{\gamma}^2}\int_{x\in X}\left(xx\Phi_X(x) - \int_{y\in Y} yy\Phi_{XY}(x,y)dy\right)dx$$



Conclusion and Remarks

- Park and Ianniruberto (2017): a realistic simulation method reproducing (i) single Maxwell relaxation, (ii) strain hardening in shear start-up, (iii) deviation of Cox-Merz rule, and (iv) shear thickening.
- In this study, we produce non-linear rheological data for $\tau_0 = 100\tau_m$ with the same results for (i-iv).
- Two normalized PDF are introduced to decouple elastic stress tensor into isotropic and directional parts: bridge vector distribution, $f(\boldsymbol{Q})$, and elastic force distribution, $\Phi(\boldsymbol{Q})$.
- Effect of an isotropic pre-factors can be negligible for the both of shear thickening and thinning regimes.
- The orientation of network strands is the main reason of the transition from shear thickening to shear thinning in terms of steady shear viscosity.

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