Rheology of polymer solutions over a wide range of concentrations

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Background

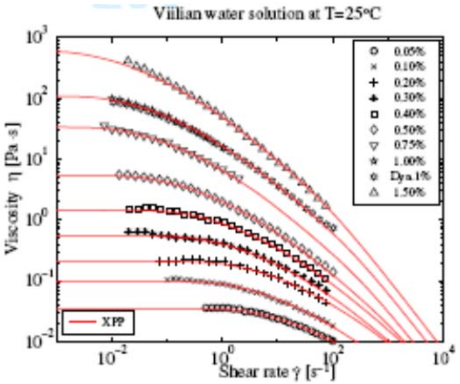
- Semi-flexible polymer solutions are of technological and nutritional significance in industrial applications:
  - Oil industry
  - Paints
  - Adhesives
  - Pharmaceuticals
  - Bacterial or extracellular polysaccharides for “safety” food.
  - Gelling agents/thickening effect in food products.
- Polymer solutions with high molecular weight can give rise to unusually high solution viscosities at relatively low concentrations (Morris, 1981).

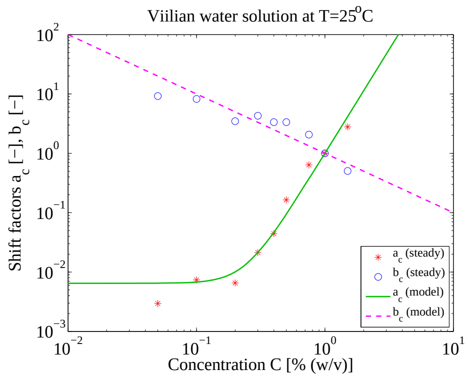
Background

- Semi-flexible polymer solutions with an entanglement network conformation show generally shear-thinning behaviour.
- Often described by General Viscous Fluid Models:
  - Cross model
  - Carreau model
  - Morris equation (Morris, 1990)
- Excellent description of steady state shear viscosity.
- Fail to describe other viscoelastic phenomena:
  - Time dependence.
  - Normal stresses in shear.
  - Different behaviour in shear and elongation.

Objectives

- Describe quantitatively the experimental rheological shear behaviour of semi-flexible aqueous polymer solutions over a broad range of concentrations with non-linear viscoelastic models using a single set of parameters.
- Develop predictive models to describe the concentration dependence of the relaxation spectrum.
- Test non-linear viscoelastic models on experimental data of random-coil polysaccharide solutions.

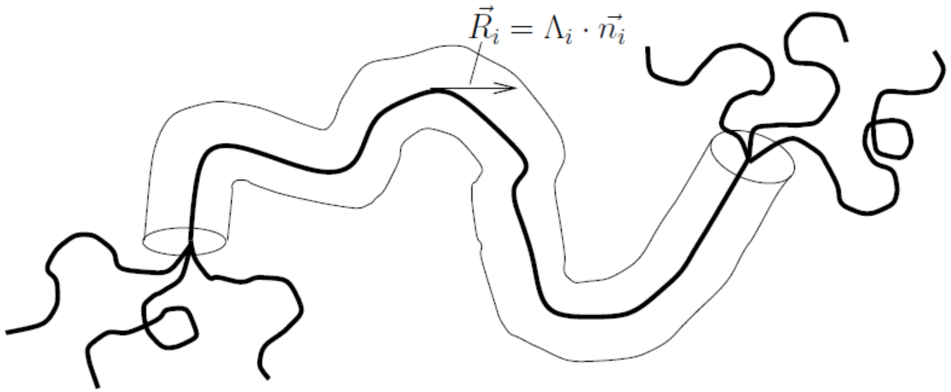




Tools

- Experimental rheological data:
  - Linear dynamic shear data.
  - Non-linear transient & steady state shear data.
  - Concentration range.
  - Non-linear transient & steady state extensional data.
  - Reversed flow data
- Constitutive models:
  - eXtended Pom-Pom (JoR '01, JNNFM '04)
  - Exponential PTT
  - Giesekus

Construction of constitutive equation



Connector vector: $\overrightarrow{R_i} = \Lambda_i \cdot \overrightarrow{n_i}$

Equation of motion: $\dot{\vec{R}} = \left(\vec{\nabla}\vec{u}\right)^T \cdot \vec{R} - \boldsymbol{B} \cdot \vec{R}$

Conformation tensor: $\boldsymbol{c} = \langle \vec{R}\vec{R} \rangle$

Stress tensor: $\boldsymbol{\sigma} = 3G\boldsymbol{c} = 3G\Lambda^2\boldsymbol{S} = \boldsymbol{\tau} + G\boldsymbol{I}$

Slip tensor $\boldsymbol{B}$: To be specified function of averaged (*i.e.* macroscopic) variables, such as **stress**, strain, or strain rate.

General and specific forms of slip tensor B

General form: $$\boldsymbol{B} = c_1\boldsymbol{\sigma} + c_2\boldsymbol{I} - c_3\boldsymbol{\sigma}^{-1}$$

Maxwell: $$\boldsymbol{B} = \frac{1}{2\lambda}\boldsymbol{I} - \frac{G}{2\lambda}\boldsymbol{\sigma}^{-1}$$

Giesekus: $$\boldsymbol{B} = \frac{\alpha}{2G\lambda}\boldsymbol{\sigma} + \frac{(1-2\alpha)}{2\lambda}\boldsymbol{I} - \frac{G(1-\alpha)}{2\lambda}\boldsymbol{\sigma}^{-1}$$

Phan-Thien Tanner: $$\boldsymbol{B} = -\xi\boldsymbol{D} + \frac{e^{(\varepsilon\,\mathrm{tr}(\boldsymbol{\tau})/G)}}{2\lambda}\boldsymbol{I} - \frac{Ge^{(\varepsilon\,\mathrm{tr}(\boldsymbol{\tau})/G)}}{2\lambda}\boldsymbol{\sigma}^{-1}$$

eXtended Pom-Pom (Verbeeten et al, JNNFM 117, 2004)**:**

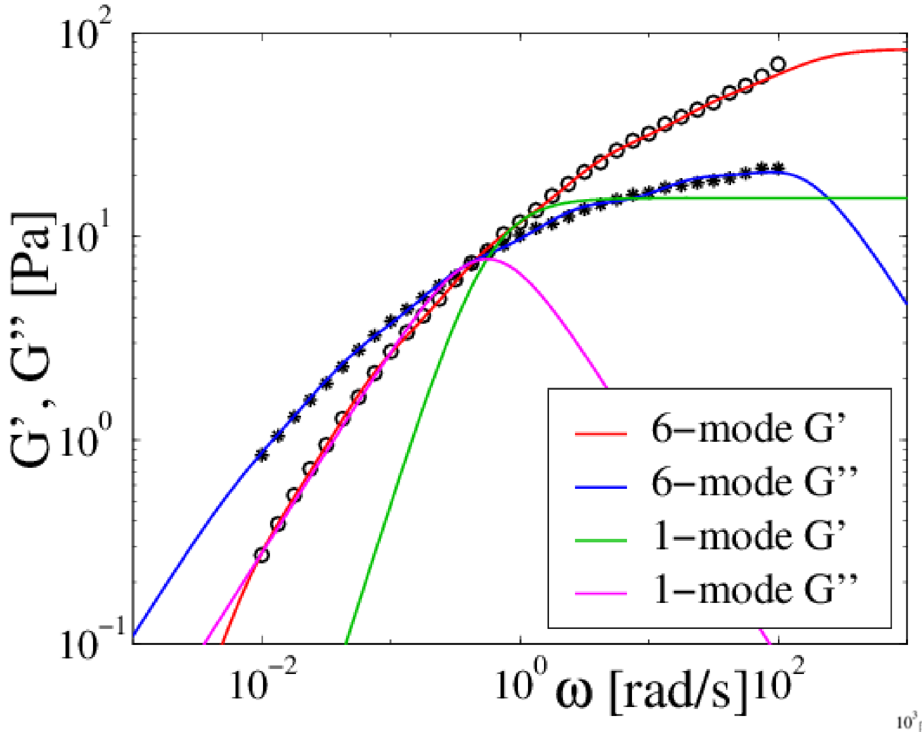
$$\boldsymbol{B} = \frac{\alpha}{2G\lambda}\boldsymbol{\sigma} + \left[\frac{1-\alpha-3\alpha\Lambda^4\,\mathrm{tr}(\boldsymbol{S}\cdot\boldsymbol{S})}{2\lambda\Lambda^2} + \frac{re^{\nu(\Lambda-1)}}{\lambda}\left(1-\frac{1}{\Lambda^2}\right)\right]\boldsymbol{I} - \frac{G(1-\alpha)}{2\lambda}\boldsymbol{\sigma}^{-1}$$

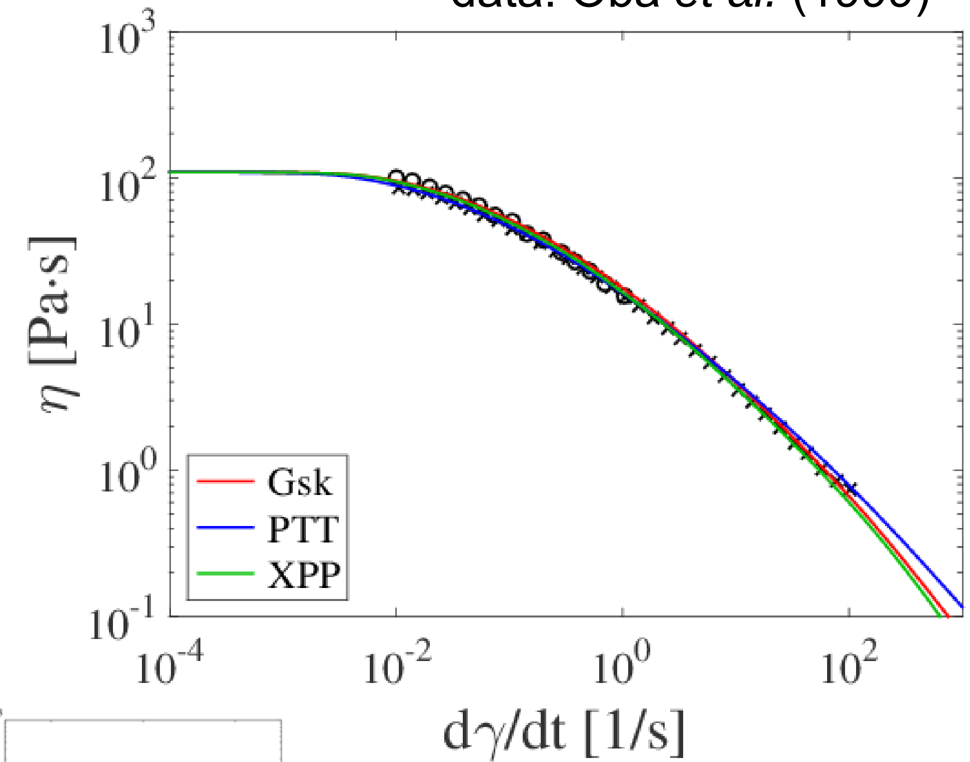
Rheometric performance: *single concentration*

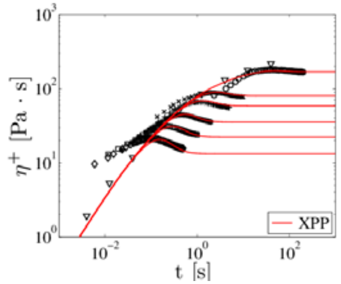
1.0% Viilian solution in water, T=25ºC:

(Aqueous solution of phosphopolysaccharide 'viilian' from *Lactococcus lactis* subspecies *cremoris* SBT 0495)

data: Oba *et al.* (1999)





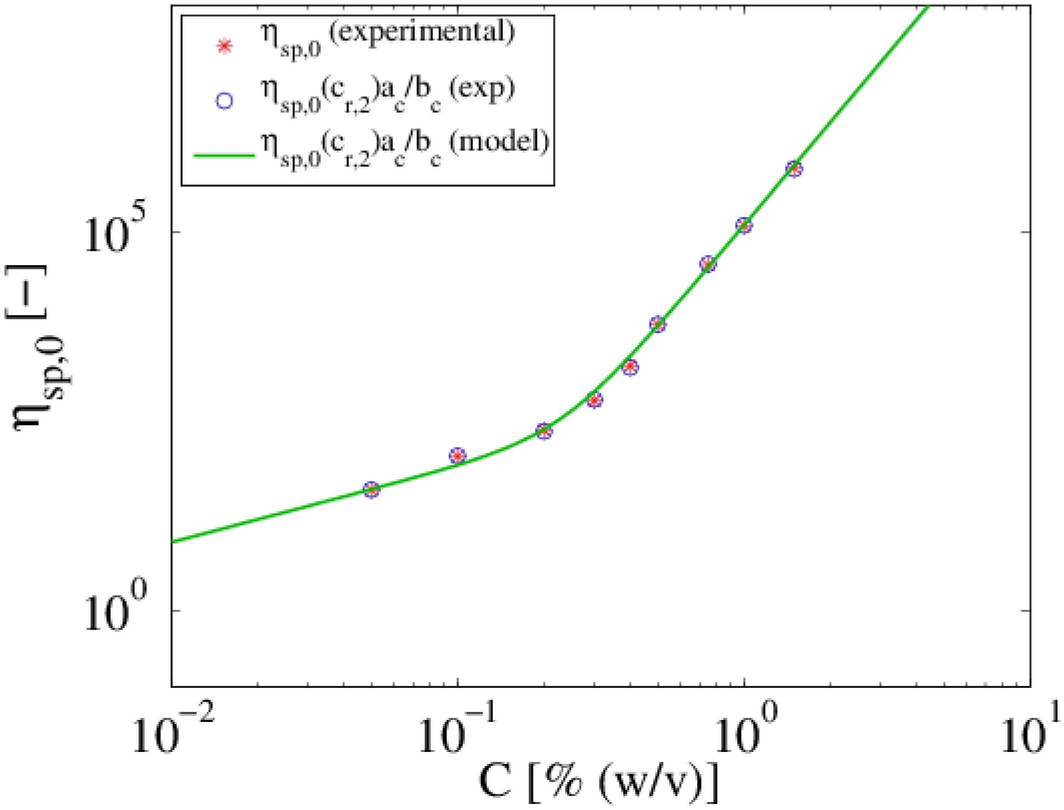


Concentration dependence

Zero-shear viscosity over entire concentration range:

Tuinier et al. (1999), Ren et al. (2003)

$$\eta_0(c) = \eta_s + (\eta_{r,1} - \eta_s)\left(\frac{c}{c_{r,1}}\right)^{n_1} + (\eta_{r,2} - \eta_s)\left(\frac{c}{c_{r,2}}\right)^{n_2}$$



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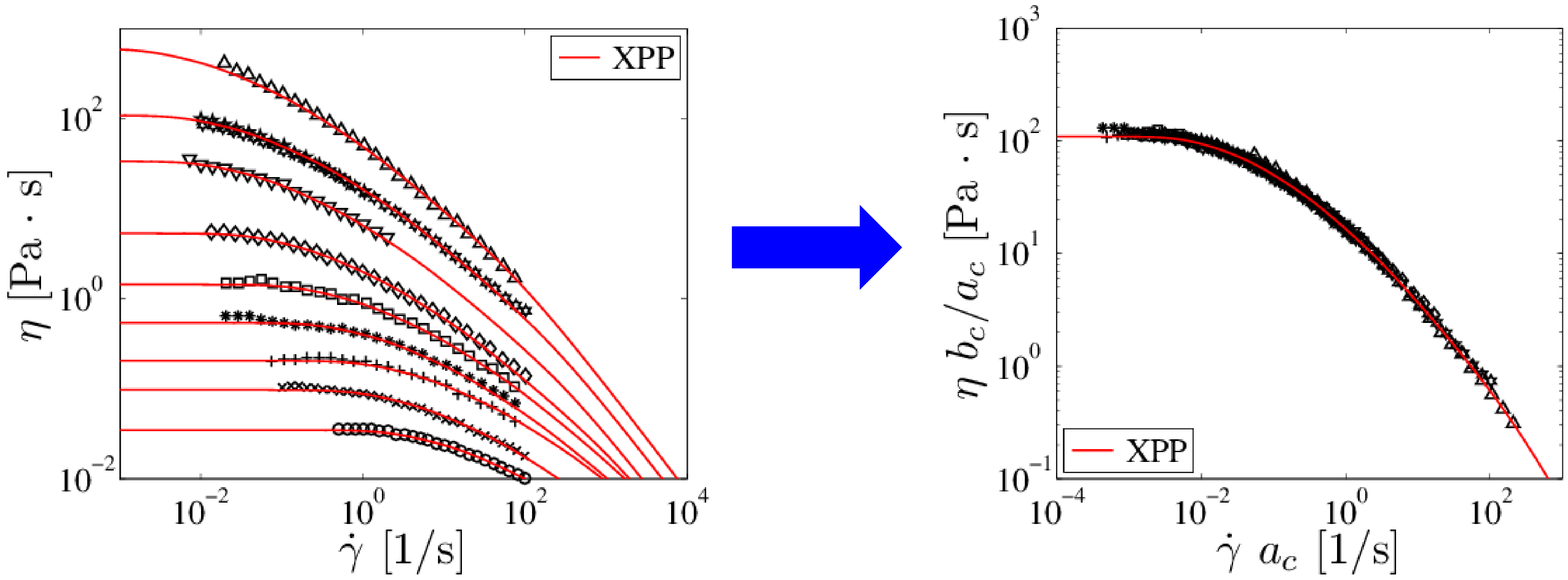
Shift factors to construct master curve:



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Shift factors to construct master curve:

$$\eta_0(c) = \eta_s + (\eta_{r,2} - \eta_s)\left\{k_1\left(\frac{c}{c_{r,1}}\right)^{n_1} + \left(\frac{c}{c_{r,2}}\right)^{n_2}\right\}$$

$$= \boxed{\eta_s + (\eta_{r,2} - \eta_s)\frac{a_c}{b_c}} = \eta_s + \left(\sum_{i=1}^{M} G_i\lambda_i - \eta_s\right)\frac{a_c}{b_c} \qquad k_1 = \frac{\eta_{r,1}-\eta_s}{\eta_{r,2}-\eta_s}$$

$$a_c = k_1\left(\frac{c_{r,2}}{c_{r,1}}\right)^{n_1} + \left(\frac{c}{c_{r,2}}\right)^{(n_2-n_1)}$$ → time-concentration superposition

$$\frac{1}{b_c} = \left(\frac{c}{c_{r,2}}\right)^{n_1}$$ → modulus-concentration superposition

Concentration dependence

Relaxation spectrum at a certain concentration:

$$\lambda_i(c) = \lambda_i\left(c_{r,2}\right) a_c$$

$$G_i(c) = G_i\left(c_{r,2}\right) / b_c$$

Construction of master curves (similar to time-temperature superposition):

$$\eta(\dot{\gamma} a_c, c_r) = \eta(\dot{\gamma}, c)\, b_c / a_c$$

$$G'(\omega a_c, c_r) = G'(\omega, c) b_c$$

$$G''(\omega a_c, c_r) = G''(\omega, c) b_c$$

Rheometric performance: *concentration range*

0.05% – 1.50% Viilian solution in water, T=25ºC:

(Aqueous solution of phosphopolysaccharide 'viilian' from *Lactococcus lactis* subspecies *cremoris* SBT 0495)

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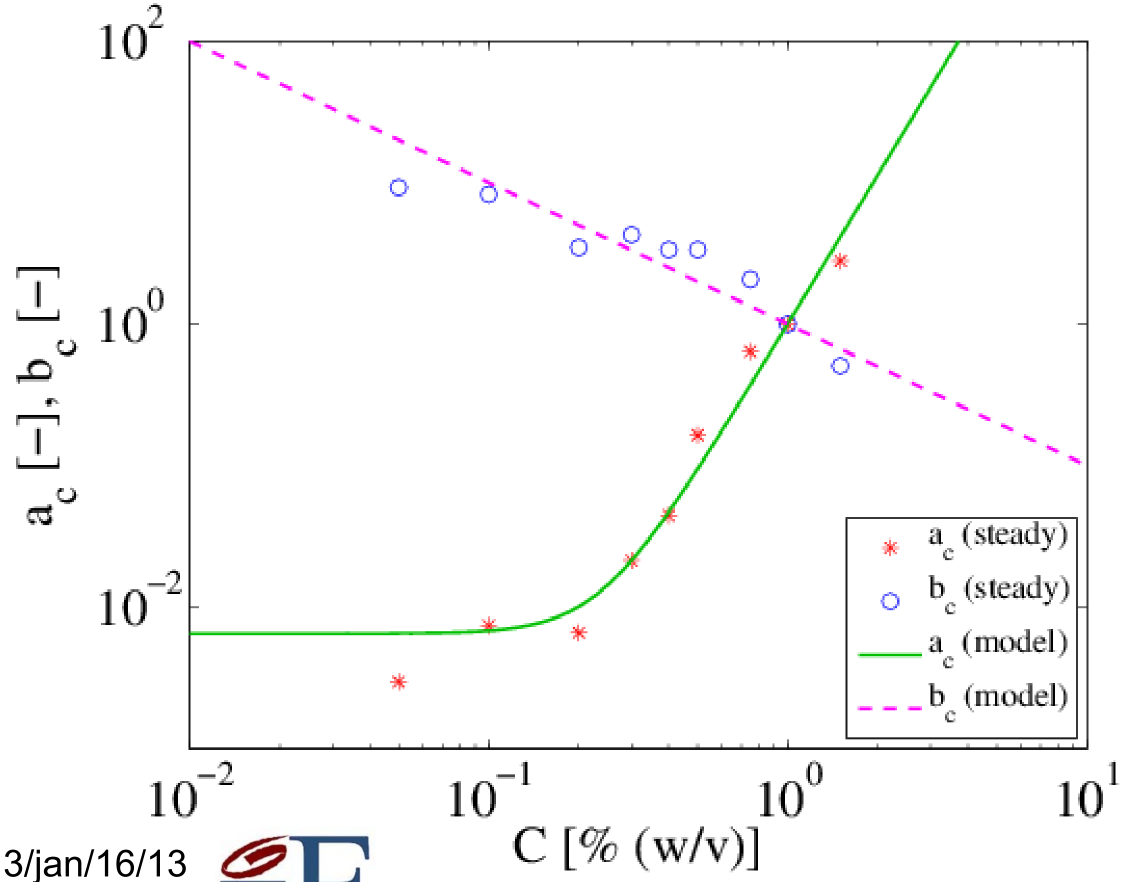

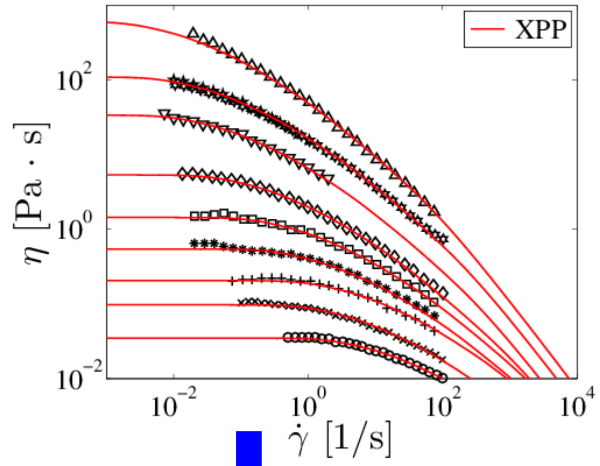

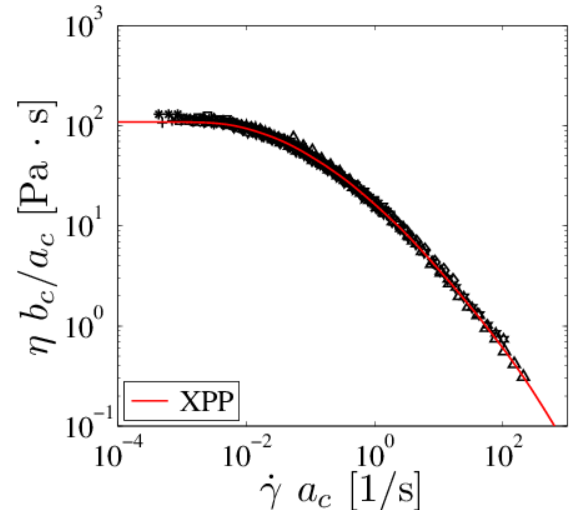

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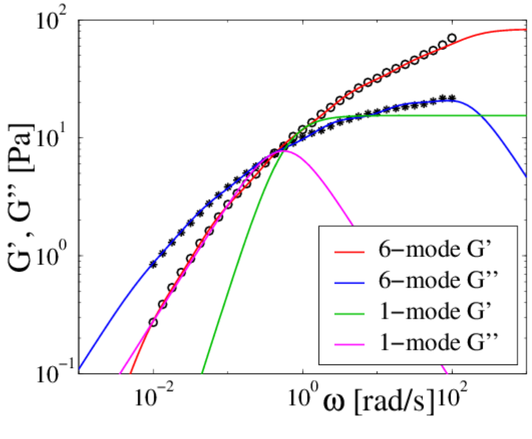

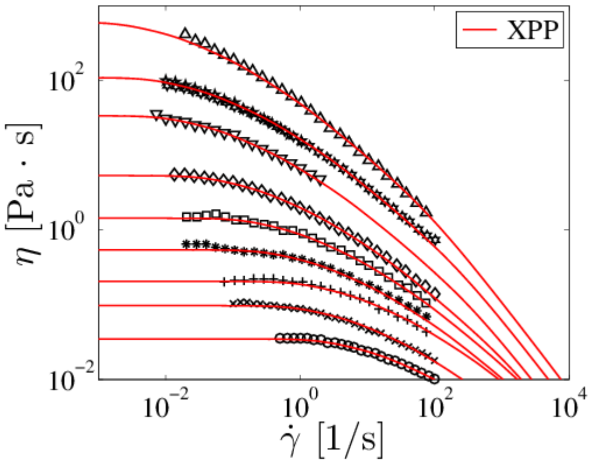

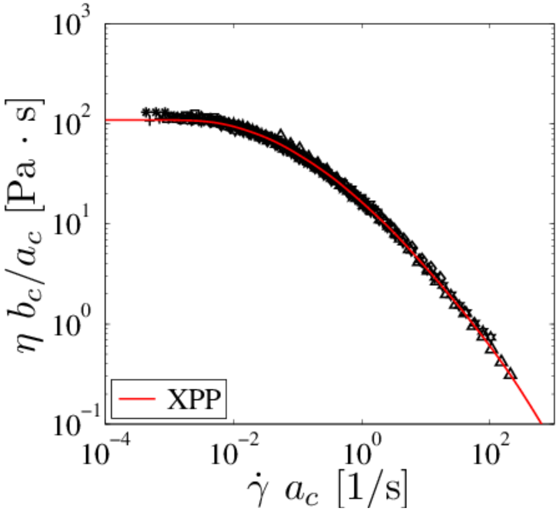

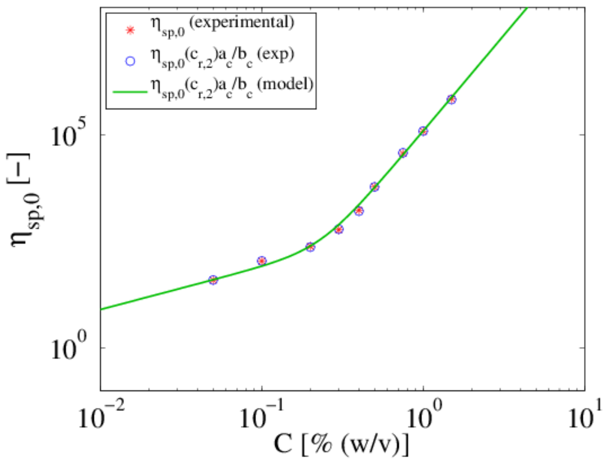

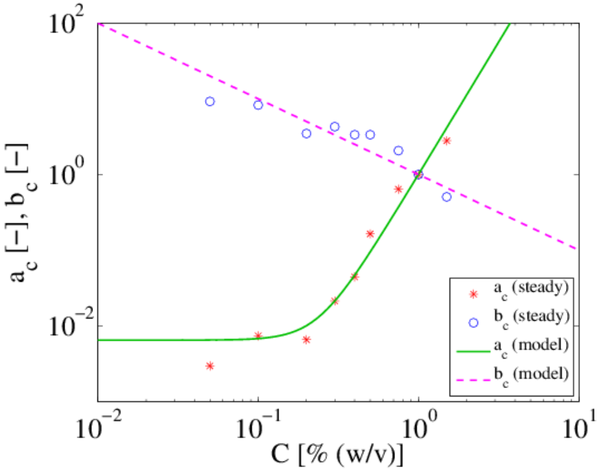

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Conclusions

- Non-linear viscoelastic models:
  - Quantitative prediction of linear viscoelastic, steady state shear, and transient start-up viscosity experimental data.
  - Qualitative prediction experimental first normal stress coefficient data for polysaccharide solution.
- Broad concentration range: dilute and semi-dilute region.
- Single set of parameters for flow problems over concentration and temperature range.
- FE simulations: non-linear viscoelastic models can improve predictive modelling of time-dependent complex flow problems for polymer melts and solutions.

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