Microstructural studies for rheology

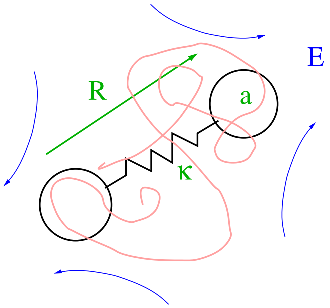
- Micro & macro views
- Einstein viscosity
- Rotations
- Deformations
- Interactions
- Polymers
- Others

Polymers

- Single polymer
  - Bead-and-spring model
  - Refinements
  - FENE-P constitutive equation
  - Unravelling a polymer chain
  - Kinks model
  - Brownian simulations
- Entangled polymers
  - rheology
  - Refinements
  - pom-pom

Bead-and-Spring model of isolated polymer chain

– simplest, only gross distortion, Kuhn & Kuhn 1945, Kramers 1946



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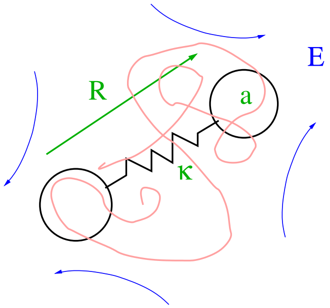

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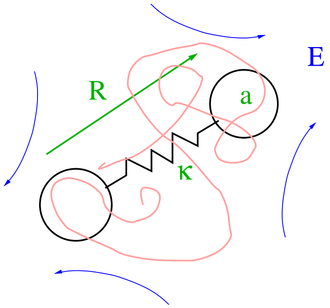

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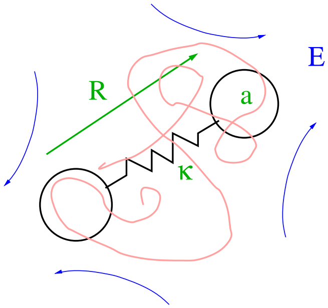

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Hence

$$\dot{R} = R\cdot\nabla U - \frac{1}{2\tau}R \quad \text{with} \quad \tau = 0.8kT/\mu(N^{1/2}b)^3$$

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– Oldroyd-B constitutive equation with UCD time derivative $\overset{\nabla}{A}$

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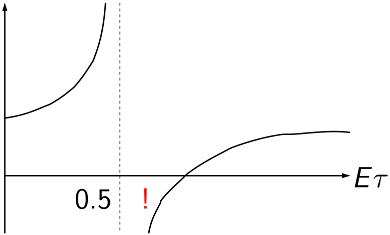

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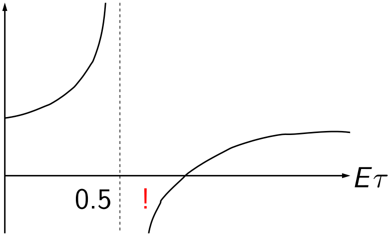

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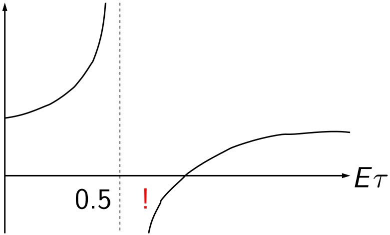

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- For TDR: small shear and large extensional viscosities

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but "molecular individualism"

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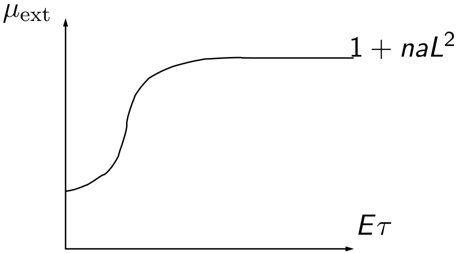

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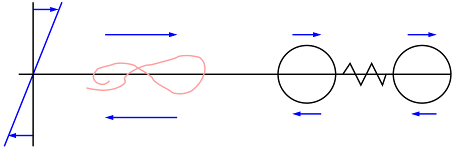

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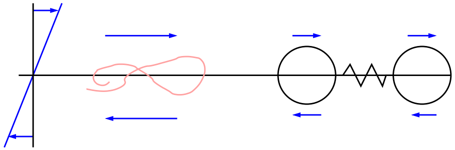

Couple balance

$$\text{Afine} \quad \overset{\nabla}{A} \longrightarrow \text{non-affine} \quad \overset{\circ}{A} - \frac{\text{trace}\, A}{3 + \text{trace}\, A}(A\cdot E + E\cdot A)$$

inefficiency of straining

One more refinement

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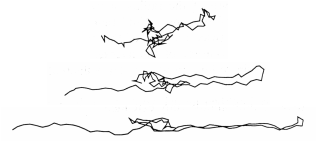
   Good for contraction flows

Unravelling a polymer chain in an extensional flow

Simulation of chain with $N = 100$ in uni-axial straining motion at strains $Et = 0.8$, 1.6, 2.4.



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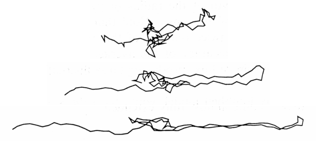

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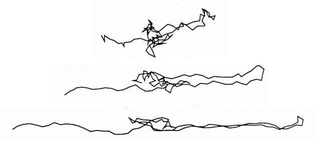

- Growing stretched segments
- Two ends not on opposite sides

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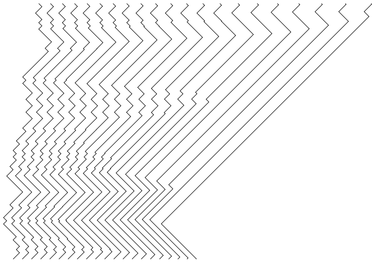
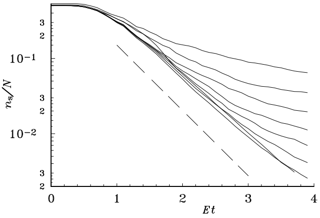


- Large gobble small

Kinks model 2



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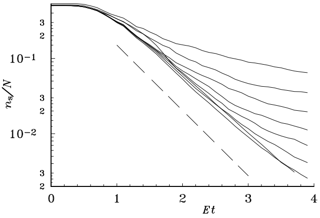

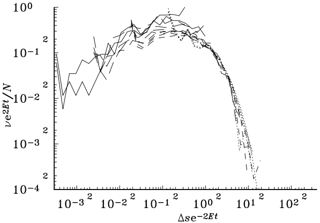

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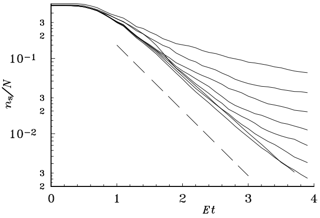

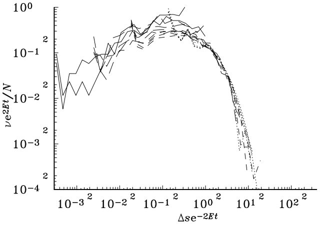

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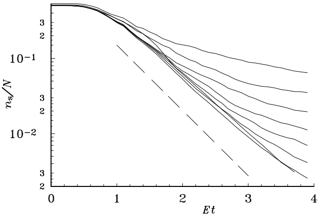

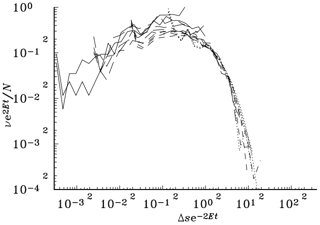

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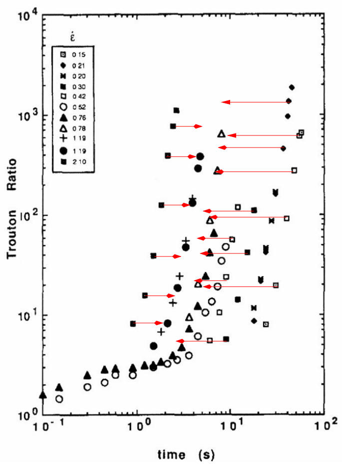
Evidence of a dissipative stress

Original data of Sridhar, Tirtaatmadja, Nguyen & Gupta 1991 plotted as viscosity as function of time



Replotted a function of strain = strain-rate×time

Improved algorithms for Brownian simulations

1. Mid-point time-stepping avoids evaluating $\nabla \cdot \mathbf{D}$
   Keep random force fixed in time-step, but vary friction

Grassia, Nitsche & H 95

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$$-kT \nabla \ln \sqrt{\det M^{-1}} \quad \text{with} \quad M^{-1\,ab} = \sum_{i \text{ beads}} m_i^{-1} \frac{\partial g^a}{\partial \mathbf{x}_i} \cdot \frac{\partial g^b}{\partial \mathbf{x}_i}$$

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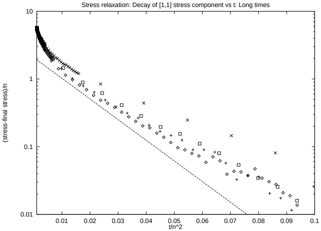
3. Stress by subtraction of large $\Delta t^{-1/2}$ term with zero average

$$\tfrac{1}{2}(x^n + x^{n+1})f^n \longrightarrow \tfrac{1}{2}\Delta x^n f^n$$

Grassia, Nitsche & H 95

Relaxation of fully stretched chain

Long times - Rouse relaxation



σ/N vs t/N^2 (Rouse)

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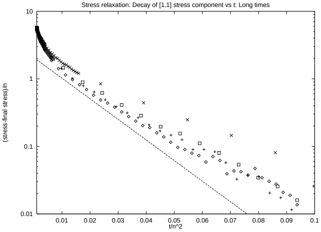

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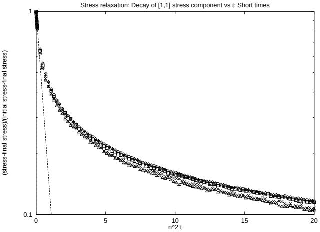

$\sigma/\frac{1}{3}N^3$ vs N^2t

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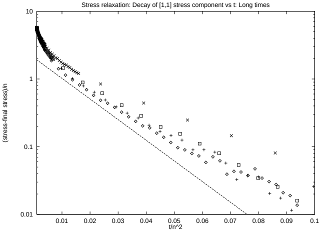

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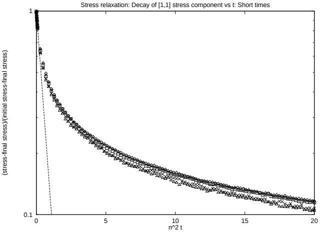

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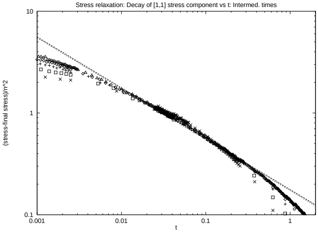

Intermediate times

$\sigma \sim kTN^2 t^{-1/2}$

Constitutive equation – options

$$\overset{\nabla}{A} = -\frac{1}{h\tau} f\,(A - I)$$

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- Nonlinear bead friction $\quad h = \sqrt{\operatorname{trace} A/3}$
- New form of stress

$$\sigma = -pI + 2\mu E + 2\mu_d (A : E) A + G \sqrt{\operatorname{trace} A} A$$

Constitutive equation – options

$$\overset{\nabla}{A} = -\frac{1}{h\tau} f \, (A - I)$$

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- Oldroyd B $\quad f = 1$
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Good for positive pressure drops and large upstream vortices in contraction flows.

Reptation model of De Gennes 1971 – often reformulated

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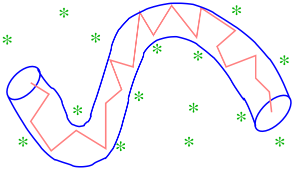

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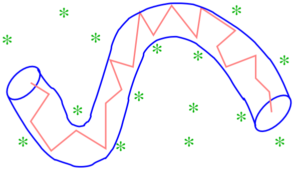

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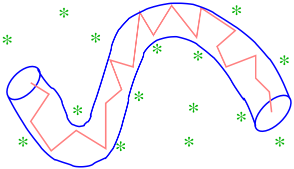

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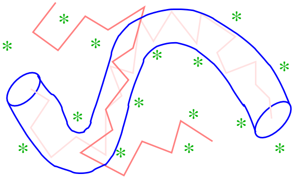
Modulus $G = nkT \longrightarrow \mu^* = G\tau_D \propto M^3$ (expts $M^{3.4}$)

Diffusion out of tube

At later time:



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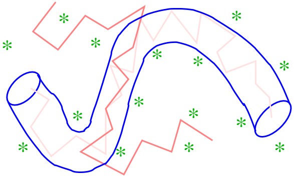

Fraction of original tube surviving

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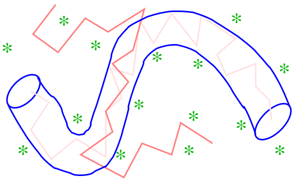

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Diffusion gives linear viscoelasticity $G' \propto \omega^{1/2}$

Doi-Edwards rheology 1978

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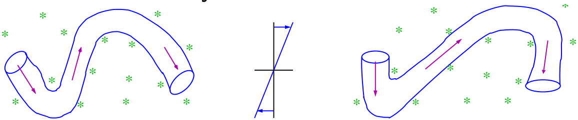
Deformation of the tube by a shear flow.



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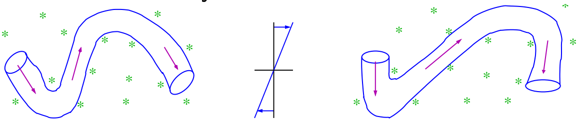

Unit segments of the tube **u** aligned by flow:

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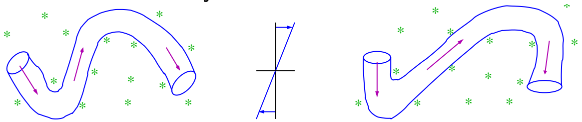

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surving tube segment tension

with relative deformation $\mathbf{A}^* = A(t)A^{-1}(t-s)$.

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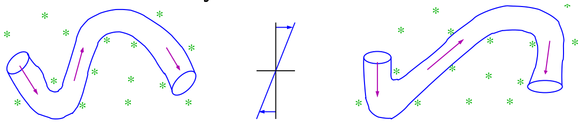

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A BKZ integral constitutive equation

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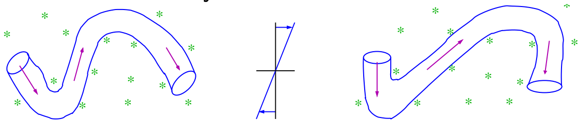

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Problem maximum in shear stress

Refinements

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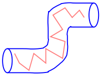
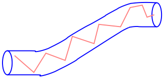
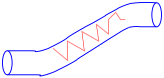


deform →



retract →



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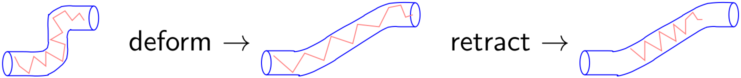

Chain returns in Rouse time to natural length $\longrightarrow$ loss of segments

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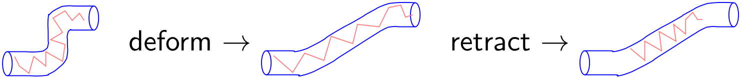

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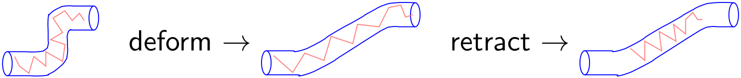

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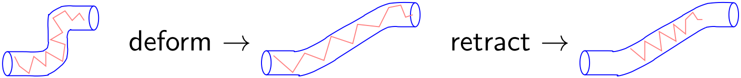

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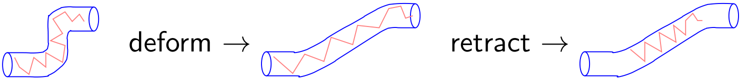

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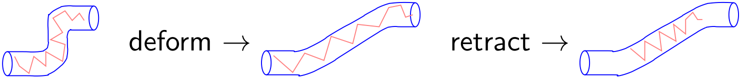

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6. Flow changes tube volume or cross-section

Chain trapped in a fast shearing lattice

Lattice for other chains

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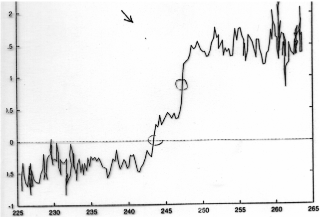
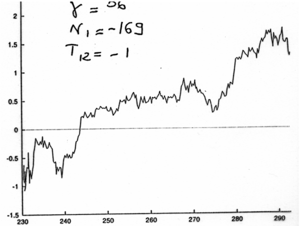


more shear $\rightarrow$



central section pulling chain out of arms

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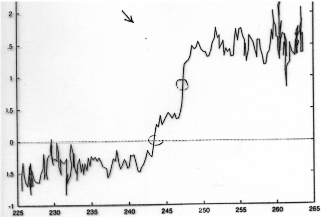

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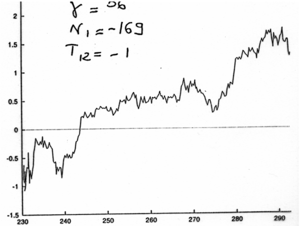
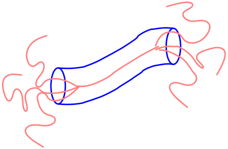


central section pulling chain out of arms → high dissipative stresses

Ianniruberto, Marrucci & H 98

Branched polymers – typical in industry



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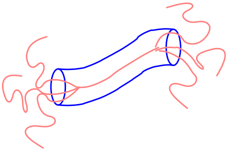

Very difficult to pull branches into central tube

$\mu \propto \exp(M_{\text{arm}}/M_{\text{entangle}})$

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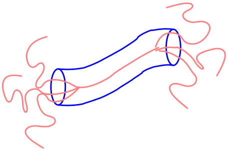

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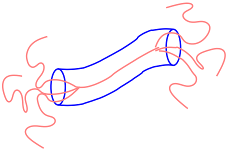

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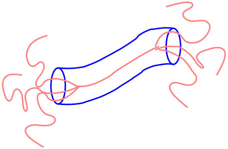

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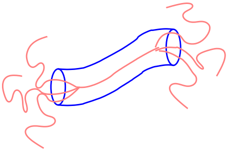

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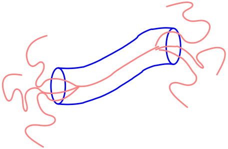

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with $\tau_O = \tau_{\text{arm}}(M_C/M_E)^3$ and $\tau_S = \tau_{\text{arm}}(M_C/M_E)^2$ and
$\tau_{\text{arm}} \cong \exp(M_{\text{arm}}/M_E)$ where $M_C = M_{\text{crossbar}}$ and $M_E = M_{\text{entanglement}}$.

Test of Pom-Pom model – Blackwell 2002

Fit: Linear Viscoelastic data and Steady Uni-axial Extension.

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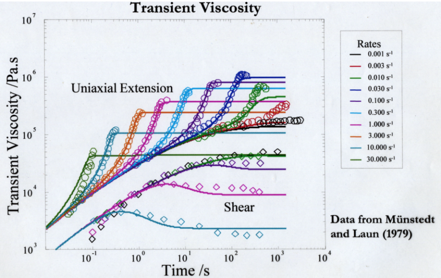

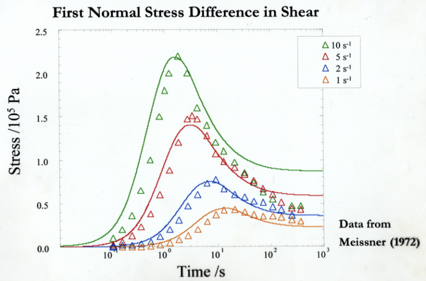

IUPAC-A data Müntedt & Laun (1979)

Polymers

- Single polymer
  - Bead-and-spring model
  - Refinements
  - FENE-P constitutive equation
  - Unravelling a polymer chain
  - Kinks model
  - Brownian simulations
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- Micro & macro views
- Einstein viscosity
- Rotations
- Deformations
- Interactions
- Polymers
- Others