Microstructural studies for rheology

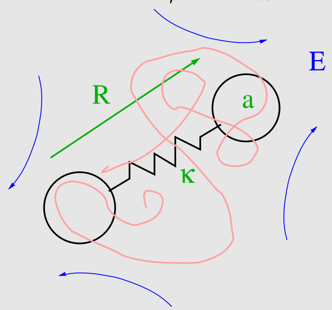
- Micro & macro views
- Einstein viscosity
- Rotations
- Deformations
- Interactions
- Polymers
- Others

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



- Flow distortion = Stokes drag = $6\pi\mu a(R\cdot\nabla U - \dot{R})$
  $a = \frac{1}{6}bN^{0.5} \to N^{0.6}$
- Resisted by entropic spring force = κR, $\quad \kappa = \frac{3kT}{Nb^2}$

Hence

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

Bead-and-Spring model of isolated polymer chain 2

- Adding Brownian motion of the beads: $A = \langle RR \rangle$

$$\overset{\nabla}{A} \equiv \frac{DA}{Dt} - A\cdot\nabla U - \nabla U^T\cdot A = -\frac{1}{\tau}\left(A - \frac{Nb^2}{3}I\right)$$

$$\sigma = -pI + 2\mu E + n\kappa A$$

with n number of chains per unit volume.

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

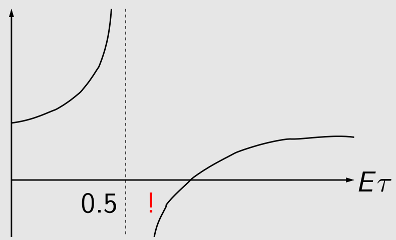
Rheological properties

Shear

- $\mu =$ constant, $N_1 \propto \gamma^2$, $N_2 = 0$.
- Distortion xy: $a\gamma\tau \times a$

Extension

- μ



- Distortion $\propto e^{(2E-\frac{1}{\tau})t}$
- For TDR: small shear and large extensional viscosities

Refinements

1. (boring) Spectrum of internal modes: Rouse 53, Zimm 56 with pre-averaged hydrodynamics
2. (boring) Polydisperse molecular weights
3. (important) Finite extensibility – to stop infinite growth $\propto e^{(2E-\frac{1}{\tau})t}$
   - Nonlinear spring force – inverse Langevin law

     $$F(R) = \frac{kT}{b}\mathcal{L}^{-1}\left(\frac{R}{Nb}\right) \quad \text{with} \quad \mathcal{L}(x) = \coth x - \frac{1}{x}$$

   - F.E.N.E approximation

     $$F(R) = \frac{kT}{Nb^2}\frac{R}{1 - R^2/L^2} \quad \text{with fully extended length} \quad L = Nb$$

   - FENE-P closure

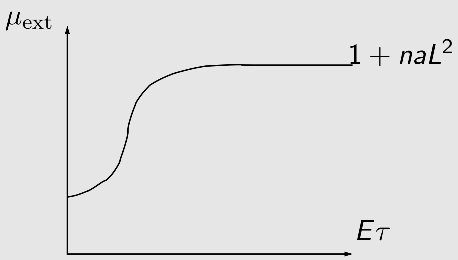
     $$\langle RR/(1 - R^2/L^2)\rangle = \langle RR\rangle/(1 - \langle R^2\rangle/L^2)$$

     but "molecular individualism"

FENE-P constitutive equation

$$\overset{\nabla}{A} = -\frac{1}{\tau}\frac{L^2}{L^2 - \text{trace}\, A}\left(A - \frac{a^2}{3}I\right)$$

$$\sigma = -pI + 2\mu E + n\kappa\frac{L^2}{L^2 - \text{trace}\, A}A$$

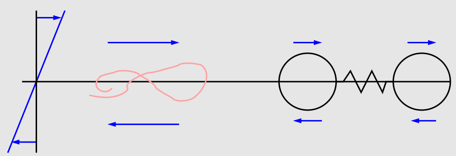


More refinements

4. Nonlinear bead friction
   Hydrodynamic drag increase with size $6\pi\mu(a \to R)$

   $$\mu_{\text{ext}} = 1 + nL^3 \qquad \text{and hysteresis}$$

5. Rotation of the beads – simple shear not so simple



Couple balance

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

inefficiency of straining

One more refinement

6. Dissipative stress – nonlinear internal modes
   Simulations show growing stretched segments

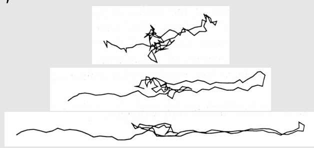
$$\text{segment length} \propto \frac{R^2}{L}, \quad \text{number} \propto \frac{L^2}{R^2}, \quad \text{dissipation} \propto \frac{R^4}{L}$$

$$\sigma = -pI + 2\mu\left(1 + n\frac{(\text{trace}\,A)^2}{L}\right)E + n\kappa\frac{L^2}{L^2 - \text{trace}\,A}A$$

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 $Et = 0.8,\ 1.6,\ 2.4$.

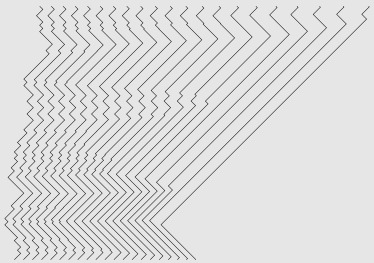


- Growing stretched segments
- Two ends not on opposite sides

Simplified 1D 'kinks' model

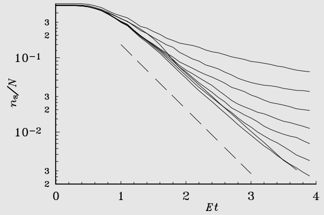
- $t = 0$: 1D random walk, N steps of ± 1
- $t > 0$: floppy inextensible string in $u = Ex$
- arc lengths satisfy

$$\dot{s}_i = \tfrac{1}{4}E(-s_{i+1} + 2s_i - s_{i-1})$$

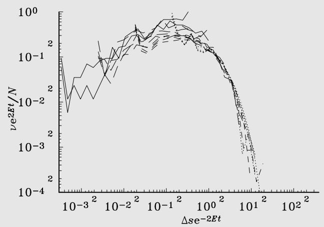


- Large gobble small

Kinks model 2



Number of segments $n(t)$



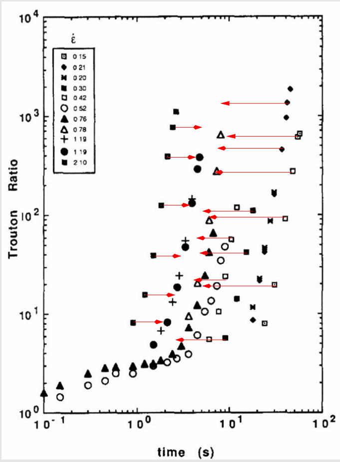
Distribution of lengths $\ell(t)$ scaled by e^{2Et}

Scalings

$$\begin{cases} n\ell = N \\ \sqrt{n}\ell = R = \sqrt{N}e^{Et} \end{cases} \longrightarrow \begin{cases} n = Ne^{-2Et} \\ \ell = e^{2Et} \end{cases}$$

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
2. Replace very stiff (fast) bonds with rigid + correction potential

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

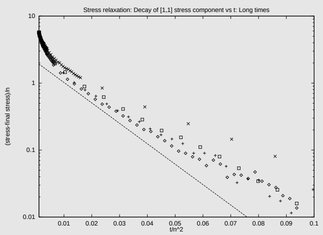
   where rigid constraints are $g^a(\mathbf{x}_1,\ldots,\mathbf{x}_N)=0$ and stiff spring energy $\frac{1}{2}|\nabla g^a|^2$
3. Stress by subtraction of large $\Delta t^{-1/2}$ term with zero average

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

Grassia, Nitsche & H 95

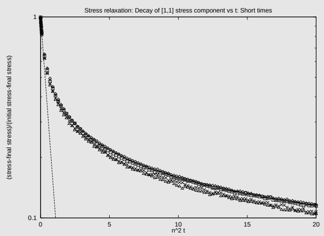
Relaxation of fully stretched chain

Long times - Rouse relaxation

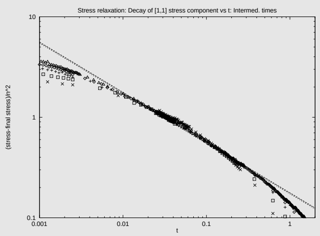


σ/N vs t/N^2 (Rouse)

Short times finite



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



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

Constitutive equation – options

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

$$\sigma = -pI + 2\mu E + GfA$$

- Oldroyd B $\quad f=1$
- FENE-P $\quad f = L^2/(L^2-\text{trace}\,A)$
- Nonlinear bead friction $\quad h=\sqrt{\text{trace}\,A/3}$
- New form of stress

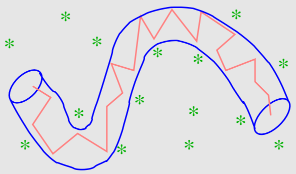
$$\sigma = -pI + 2\mu E + 2\mu_d(A:E)A + G\sqrt{\text{trace}\,AA}$$

  - Last term for finite stress when fully stretched
  - μ_d term ($\propto N^{-1/2}$) for enhanced dissipation

Good for positive pressure drops and large upstream vortices in contraction flows.

Reptation model of De Gennes 1971 – often reformulated

Chain moves in tube defined by topological constraints from other chains.



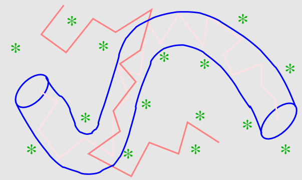
Chain disengages from tube by diffusing along its length

$$\tau_D = \frac{L^2}{D = kT/6\pi\mu L} \propto M^3$$

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

Diffusion out of tube

At later time:



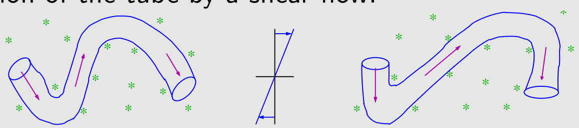
Fraction of original tube surviving

$$\sum_n \frac{1}{n^2} e^{-n^2 t/\tau_D}$$

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

Doi-Edwards rheology 1978

Deformation of the tube by a shear flow.



Unit segments of the tube $\mathbf{u}$ aligned by flow:

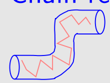
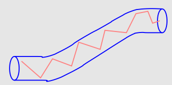
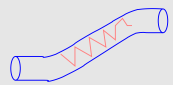
$$\mathbf{u} \longrightarrow \mathbf{A}\mathbf{u} \quad \text{with Finger tensor} \quad \mathbf{A}$$

Stress

$$\sigma(t) = n \int_0^\infty \underbrace{\sum_p \frac{1}{p^2} e^{-p^2 s/\tau_D}}_{\text{surving tube}} \underbrace{N_{\text{segements}} \frac{3kT}{a}}_{\text{segment tension}} a \left\langle \frac{\mathbf{A}^*\mathbf{u}\,\mathbf{A}^*\mathbf{u}}{|\mathbf{A}^*\mathbf{u}|^2} \right\rangle ds$$

with relative deformation $\mathbf{A}^* = A(t)A^{-1}(t-s)$.
A BKZ integral constitutive equation
Problem maximum in shear stress

Refinements

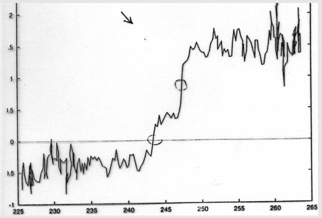
1. Chain retraction
    deform $\rightarrow$  retract $\rightarrow$ 
   Chain returns in Rouse time to natural length $\longrightarrow$ loss of segments
2. Chain fluctuations
3. Other chains reptate $\rightarrow$ release topological constraints
   "Double reptation" of Des Cloiseaux 1990. bimodal blends
4. 2 & 3 give $\mu \propto M^{3.4}$
5. Advected constraint release Marrucci 1996

$$\frac{1}{\tau_D} \longrightarrow \frac{1}{\tau_D} + \beta \nabla u : \langle uu \rangle$$

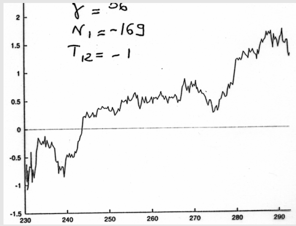
6. Flow changes tube volume or cross-section

Chain trapped in a fast shearing lattice

Lattice for other chains



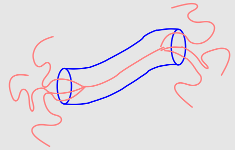
more shear →



central section pulling chain out of arms → high dissipative stresses

Ianniruberto, Marrucci & H 98

Branched polymers – typical in industry



Very difficult to pull branches into central tube
$\mu \propto \exp(M_{\text{arm}}/M_{\text{entangle}})$
Pom-Pom model of Tom McLeish and Ron Larson 1999

$$\text{Stress:} \quad \sigma = G\lambda^2 \mathbf{S}$$

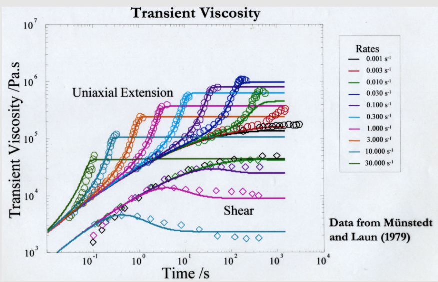
$$\text{Orientation:} \quad \mathbf{S} = \mathbf{B}/\text{trace}\mathbf{B} \qquad \overset{\nabla}{\mathbf{B}} = -\frac{1}{\tau_O}(\mathbf{B} - \mathbf{I})$$

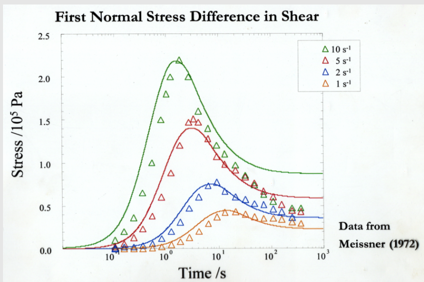
$$\text{Stretch:} \quad \dot{\lambda} = \nabla u : \mathbf{S} - \frac{1}{\tau_S}(\lambda - 1) \quad \text{while} \quad \lambda < \lambda_{\max}$$

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.
Predict: Transient Shear and Transient Normal Stress





IUPAC-A data Müntedt & Laun (1979)

Other microstructural studies

- Electro- and Magneto- -rheological fluids
- Associating polymers
- Surfactants - micells
- Aging materials
- GENERIC
- Modelling ‘Molecular individualism’ and closure problems