Introduction to Rheology of complex fluids
Brief Lecture Notes

Nonlinear Viscoelasticity

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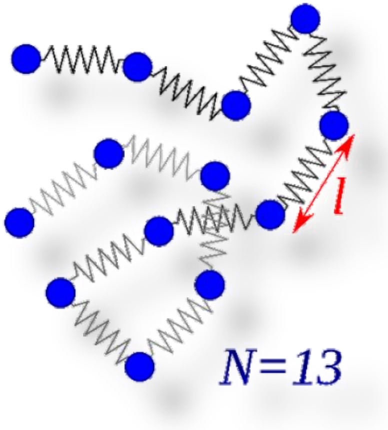

- Introductory Lecture
- Simple Flows
- Material functions & Rheological Characterization
- Experimental Observations
- Generalized Newtonian Fluids
- Generalized Linearly viscoelastic Fluids
- **Nonlinear Constitutive Models**

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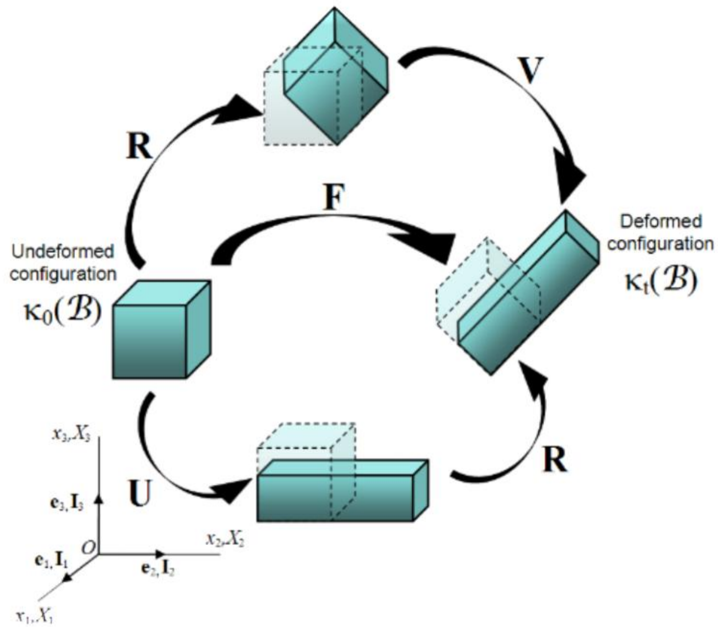

Nonlinear constitutive models: an overview

Macroscopic Constitutive models

$$\underline{\underline{\tau}} = \underline{\underline{\tau}}_p + \underline{\underline{\tau}}_s$$

$$\underline{\underline{\tau}}_s = 2\eta_s \underline{\underline{D}} = \eta_s \underline{\underline{\dot{\gamma}}}$$

$$\underline{\underline{\tau}} = \eta_s \underline{\underline{\dot{\gamma}}} + b_2 \overset{\nabla}{\underline{\underline{\dot{\gamma}}}} + b_{11} \underline{\underline{\dot{\gamma}}} \cdot \underline{\underline{\dot{\gamma}}}$$

Second-order fluid

$$\underline{\underline{\tau}} + \lambda_1 \overset{\nabla}{\underline{\underline{\tau}}} + \lambda_2 \left(\underline{\underline{\dot{\gamma}}} \cdot \underline{\underline{\tau}} + \underline{\underline{\tau}} \cdot \underline{\underline{\dot{\gamma}}} \right) + \lambda_3 tr(\underline{\underline{\tau}}) \underline{\underline{\dot{\gamma}}} + \lambda_4 \left(\underline{\underline{\tau}} : \underline{\underline{\dot{\gamma}}} \right) \underline{\underline{I}} =$$
$$\eta_o \left(\underline{\underline{\dot{\gamma}}} + \lambda_5 \overset{\nabla}{\underline{\underline{\dot{\gamma}}}} + \lambda_6 \underline{\underline{\dot{\gamma}}} \cdot \underline{\underline{\dot{\gamma}}} + \lambda_7 \left(\underline{\underline{\dot{\gamma}}} : \underline{\underline{\dot{\gamma}}} \right) \underline{\underline{I}} \right)$$

Oldroyd 8-constant

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Macroscopic Constitutive models

$$\underline{\underline{\tau}} = \underline{\underline{\tau}}_p + \underline{\underline{\tau}}_s$$

$$\begin{cases} \underline{\underline{\tau}}_s = 2\eta_s \underline{\underline{D}} \\ \underline{\underline{\tau}}_p + \lambda \overset{\nabla}{\underline{\underline{\tau}}}_p + \underline{\underline{F}}\left(\underline{\underline{D}}, \underline{\underline{\tau}}_p\right) = 2\eta_p \underline{\underline{D}} \end{cases}$$

$$\underline{\underline{F}}\left(\underline{\underline{D}}, \underline{\underline{\tau}}_p\right)$$

- $\underline{\underline{F}}\left(\underline{\underline{D}}, \underline{\underline{\tau}}_p\right) = \underline{\underline{0}}$ — Johnson-Segalman
- $\underline{\underline{F}}\left(\underline{\underline{D}}, \underline{\underline{\tau}}_p\right) = \alpha \underline{\underline{\tau}}_p \cdot \underline{\underline{\tau}}_p$ — Giesekus
- $\underline{\underline{F}}\left(\underline{\underline{D}}, \underline{\underline{\tau}}_p\right) = \alpha \underline{\underline{D}} : \underline{\underline{\tau}}_p \left(\underline{\underline{\tau}}_p + G\underline{\underline{I}}\right)$ — Larson
- $\underline{\underline{F}}\left(\underline{\underline{D}}, \underline{\underline{\tau}}_p\right) = \underline{\underline{0}} \quad \lambda = G/\eta_p\left(\sqrt{\underline{\underline{D}} : \underline{\underline{D}}}\right)$, $\quad \eta_p = \eta_p\left(\sqrt{\underline{\underline{D}} : \underline{\underline{D}}}\right)$ — Metzner

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Macroscopic Constitutive models

$$\underline{\underline{\tau}} = \underline{\underline{\tau}}_p + \underline{\underline{\tau}}_s$$

$$\underline{\underline{\tau}}_s = 2\eta_s \underline{\underline{D}}$$

$$\underline{\underline{\tau}}_p + \lambda \overset{\nabla}{\underline{\underline{\tau}}}_p + a\frac{\lambda}{\eta_p}\underline{\underline{\tau}}_p \cdot \underline{\underline{\tau}}_p = \eta_p \underline{\underline{\dot{\gamma}}}$$

Giesekus

$$\underline{\underline{\tau}}_p + \lambda \overset{\nabla}{\underline{\underline{\tau}}}_p = \eta_p \underline{\underline{\dot{\gamma}}} - \frac{2}{3}\lambda\left(\underline{\underline{\tau}}_p : \underline{\nabla}\underline{v}\right)\left(\underline{\underline{I}} + (1+\varepsilon)\frac{\lambda}{\eta_p}\underline{\underline{\tau}}_p\right)$$

Rolie-Poly

$$\underline{\underline{\tau}}_p + \lambda\left(\frac{\underline{\underline{\tau}}_p}{f(\underline{\underline{\tau}}_p)}\right)^{\nabla} = \frac{\eta_p}{f(\underline{\underline{\tau}}_p)}\underline{\underline{\dot{\gamma}}} - \eta_p \frac{D}{Dt}\left(\frac{1}{f(\underline{\underline{\tau}}_p)}\right)\underline{\underline{I}}$$

FENE-P

$$\underline{\underline{\tau}}_p + \lambda\left(\frac{\underline{\underline{\tau}}_p}{f(\underline{\underline{\tau}}_p)}\right)^{\nabla} = \eta_p \underline{\underline{\dot{\gamma}}}$$

$$f(\underline{\underline{\tau}}_p) = 1 + \frac{\lambda}{\eta_p L^2} tr(\underline{\underline{\tau}}_p)$$

FENE-CR

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PTT models

$$\underline{\underline{\tau}} = \underline{\underline{\tau}}_p + \underline{\underline{\tau}}_s \Rightarrow \begin{cases} \underline{\underline{\tau}}_s = 2\eta_s \underline{\underline{D}} \\ f\left(tr\underline{\underline{\tau}}_p\right)\underline{\underline{\tau}}_p + \lambda\left(\dfrac{D_\xi \underline{\underline{\tau}}_p}{Dt}\right) = 2\eta_p \underline{\underline{D}} \end{cases}$$

$$f\left(tr\underline{\underline{\tau}}_p\right) = \begin{cases} 1 + \dfrac{\varepsilon\lambda}{\eta_p} tr\left(\underline{\underline{\tau}}_p\right) & \text{Linear PTT} \\ 1 + \dfrac{\varepsilon\lambda}{\eta_p} tr\left(\underline{\underline{\tau}}_p\right) + \dfrac{1}{2}\left(\dfrac{\varepsilon\lambda}{\eta_p} tr\left(\underline{\underline{\tau}}_p\right)\right)^2 & \text{Quadratic PTT} \\ \exp\left(\dfrac{\varepsilon\lambda}{\eta_p} tr\left(\underline{\underline{\tau}}_p\right)\right) & \text{Exponential PTT} \end{cases}$$

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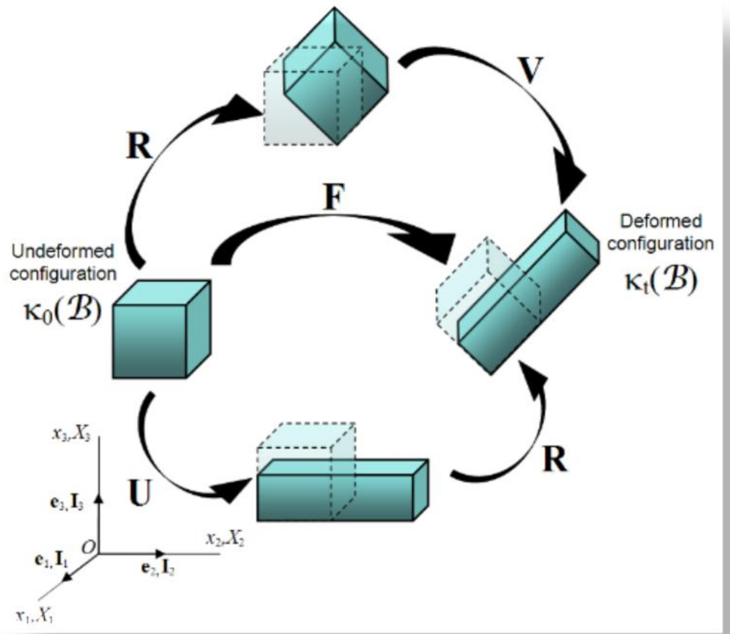

Conformation tensor $\underline{\underline{A}}$

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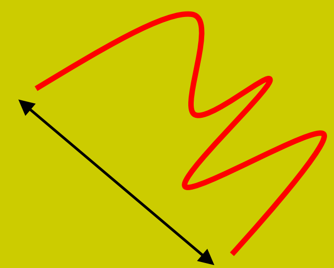
Conformation Tensor: $\underline{\underline{A}}=\langle \underline{R}\underline{R} \rangle$

$$\underline{\underline{A}} = \underline{\underline{c}} = \underline{r}\,\underline{r} = \langle \underline{R}\,\underline{R} \rangle = \begin{pmatrix} \langle R_x^2 \rangle & \langle R_x R_y \rangle & \langle R_x R_z \rangle \\ \langle R_y R_x \rangle & \langle R_y^2 \rangle & \langle R_y R_z \rangle \\ \langle R_z R_x \rangle & \langle R_z R_y \rangle & \langle R_z^2 \rangle \end{pmatrix}$$

Dyadic of End-to-End Vector

End-to-End Vector



$$\underline{R} = R_x \underline{e}_x + R_y \underline{e}_y + R_z \underline{e}_z$$

The more complex the configuration of a polymer chain, the more non-zero entries in $\underline{\underline{A}}$

Spherical Symmetry

$$\underline{\underline{c}} = \begin{pmatrix} \langle R_x^2 \rangle & 0 & 0 \\ 0 & \langle R_x^2 \rangle & 0 \\ 0 & 0 & \langle R_x^2 \rangle \end{pmatrix}$$

Cylindrical Symmetry

$$\underline{\underline{c}} = \begin{pmatrix} \langle R_x^2 \rangle & 0 & 0 \\ 0 & \langle R_y^2 \rangle \left(\neq \langle R_x^2 \rangle \right) & 0 \\ 0 & 0 & \langle R_z^2 \rangle \left(\neq \langle R_x^2 \rangle \right) \end{pmatrix}$$

Conformation Tensor ($\underline{\underline{A}}$) vs. Stress Tensor ($\underline{\underline{\tau}}_p$)

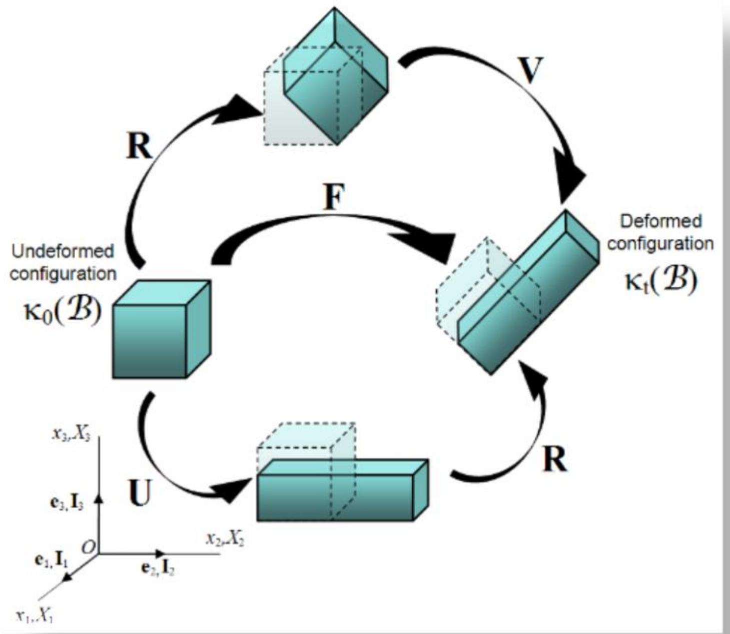
$$\underline{\underline{\tau}}_p = G\underline{\underline{A}}$$

The stress components are proportional to the 3D chain configuration. G is the shear modulus.

$$\underline{\underline{\tau}}_p = G\left(\underline{\underline{A}} - \underline{\underline{I}}\right)$$

But we have to define a reference (undeformed=random) state: $\underline{\underline{A}}=\underline{\underline{I}}$

$$G = nk_BT$$



Rheological Characterization Oldroyd-B

The constitutive model : Oldroyd-B

In conformation tensor form

$$\underline{\underline{\tau}}_p = G\underline{\underline{A}} \qquad (1)$$

$$\frac{\partial \underline{\underline{A}}}{\partial t} + (\underline{v} \cdot \underline{\nabla})\underline{\underline{A}} - \underline{\underline{A}} \cdot \underline{\nabla}\underline{v} - (\underline{\nabla}\underline{v})^T \cdot \underline{\underline{A}} = -\frac{1}{\lambda}\left(\underline{\underline{A}} - \underline{\underline{I}}\right) \qquad (2)$$

To express the constitutive relation in terms of stresses, eq. (1) should be solved in terms of conformation tensor $\underline{\underline{A}}$ (=$\underline{\underline{c}}$) and substituted in eq. (2).

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Governing equations for the flow of an Oldroyd-B fluid

$$\underline{\nabla} \cdot \underline{v} = 0$$

$$\rho\left(\frac{\partial \underline{v}}{\partial t} + \underline{v} \cdot \underline{\nabla}\underline{v}\right) = \underline{\nabla} \cdot \underline{\underline{\tau}}$$

$$\underline{\underline{\tau}} = -p\underline{\underline{I}} + \eta_s\left((\underline{\nabla}\underline{v}) + (\underline{\nabla}\underline{v})^T\right) + \underline{\underline{\tau}}_p$$

$$\underline{\underline{\tau}}_p = G\underline{\underline{A}}$$

$$\frac{\partial \underline{\underline{A}}}{\partial t} + (\underline{v} \cdot \underline{\nabla})\underline{\underline{A}} - \underline{\underline{A}} \cdot \underline{\nabla}\underline{v} - (\underline{\nabla}\underline{v})^T \cdot \underline{\underline{A}} = -\frac{1}{\lambda}\left(\underline{\underline{A}} - \underline{\underline{I}}\right)$$

Equations for the complete determination of both the velocity and the stress fields

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Simple Shear Flow

Let the velocity field equal to $\underline{v}(y,t) = \left(\dot{\varsigma}(t)y, 0, 0\right)$

$$\underline{\nabla}\underline{v}(y,t) = \begin{pmatrix} 0 & 0 \\ \dot{\varsigma}(t) & 0 \end{pmatrix}$$

The total stress tensor is given by the relation

$$\underline{\underline{\tau}} = \begin{pmatrix} -p & \eta_s\dot{\varsigma}(t) \\ \eta_s\dot{\varsigma}(t) & -p \end{pmatrix} + G\underline{\underline{A}}$$

The viscoelastic stresses are

$$\underline{\underline{\tau}}_p = G\underline{\underline{A}}$$

The conformation tensor is determined by

$$\frac{\partial}{\partial t}\begin{pmatrix} A_{xx} & A_{xy} \\ A_{yx} & A_{yy} \end{pmatrix} - \begin{pmatrix} \dot{\varsigma}(t)A_{xy} & 0 \\ \dot{\varsigma}(t)A_{yy} & 0 \end{pmatrix} - \begin{pmatrix} \dot{\varsigma}(t)A_{xy} & \dot{\varsigma}(t)A_{yy} \\ 0 & 0 \end{pmatrix} = -\frac{1}{\lambda}\begin{pmatrix} A_{xx}-1 & A_{xy} \\ A_{yx} & A_{yy}-1 \end{pmatrix}$$

Steady Simple Shear Flow

The total stress tensor is $\underline{\underline{\tau}} = \begin{pmatrix} -p & \eta_s \dot{\gamma}_o \\ \eta_s \dot{\gamma}_o & -p \end{pmatrix} + G\underline{\underline{A}}$

The viscoelastic stress is $\underline{\underline{\tau}}_p = G \begin{pmatrix} A_{xx} & A_{xy} \\ A_{yx} & A_{yy} \end{pmatrix}$

And the conformation tensor is

$$-\begin{pmatrix} \dot{\gamma}_o A_{xy} & 0 \\ \dot{\gamma}_o A_{yy} & 0 \end{pmatrix} - \begin{pmatrix} \dot{\gamma}_o A_{xy} & \dot{\gamma}_o A_{yy} \\ 0 & 0 \end{pmatrix} = -\frac{1}{\lambda} \begin{pmatrix} A_{xx} - 1 & A_{xy} \\ A_{yx} & A_{yy} - 1 \end{pmatrix}$$

Steady Simple Shear Flow

Which results into

$$\begin{cases} A_{yy} = 1 \\ A_{xy} = \dot{\gamma}_o \lambda \\ A_{xx} = 1 + 2\dot{\gamma}_o^2 \lambda^2 \end{cases}$$

$$\underline{\underline{\tau}}_p = G \begin{pmatrix} A_{xx} & A_{xy} \\ A_{yx} & A_{yy} \end{pmatrix} = G \begin{pmatrix} 1 + 2\dot{\gamma}_o^2 \lambda^2 & \dot{\gamma}_o \lambda \\ \dot{\gamma}_o \lambda & 1 \end{pmatrix}$$

The total stress tensor

$$\underline{\underline{\tau}} = \begin{pmatrix} -p + G + 2G\dot{\gamma}_o^2 \lambda^2 & (\eta_s + G\lambda)\dot{\gamma}_o \\ (\eta_s + G\lambda)\dot{\gamma}_o & -p + G \end{pmatrix}$$

The viscosity is:

$$\eta = \eta_s + G\lambda$$

The First Normal Stress Difference is:

$$N_1(\dot{\gamma}_o) = \tau_{xx} - \tau_{yy} = 2G\lambda^2\dot{\gamma}_o^2$$

Oscillatory Simple Shear Flow (SAOS)

The conformation tensor is given by

$$\frac{\partial}{\partial t}\begin{pmatrix} A_{xx} & A_{xy} \\ A_{yx} & A_{yy} \end{pmatrix} - \begin{pmatrix} \dot{\varsigma}(t)A_{xy} & 0 \\ \dot{\varsigma}(t)A_{yy} & 0 \end{pmatrix} - \begin{pmatrix} \dot{\varsigma}(t)A_{xy} & \dot{\varsigma}(t)A_{yy} \\ 0 & 0 \end{pmatrix} = -\frac{1}{\lambda}\begin{pmatrix} A_{xx}-1 & A_{xy} \\ A_{yx} & A_{yy}-1 \end{pmatrix}$$

The rate of deformation equals

$$\dot{\varsigma}(t) = \alpha\omega\cos(\omega t)$$

If we assume that the flow starts at t = 0 s

$$\underline{\underline{A}} = \underline{\underline{I}}$$

All the chains are initially unstretched

By integrating in time we have

$$\frac{\partial A_{yy}}{\partial t} = -\frac{1}{\lambda}\left(A_{yy} - 1\right)$$

Which gives $A_{yy} = 1$

$$\frac{\partial A_{xy}}{\partial t} - \dot{\varsigma}(t) A_{yy} = -\frac{1}{\lambda} A_{xy}$$

$$\frac{\partial A_{xy}}{\partial t} - \alpha\omega\cos(\omega t) = -\frac{1}{\lambda} A_{xy}$$

$$\frac{\partial A_{xy}}{\partial t} + \frac{1}{\lambda} A_{xy} = \alpha\omega\cos(\omega t)$$

$$\frac{\partial}{\partial t}\left(A_{xy} e^{t/\lambda}\right) = \alpha\omega\cos(\omega t) e^{t/\lambda}$$

Thus,

$$A_{xy}=\frac{1}{1+\omega^2\lambda^2}\left(\alpha\omega\lambda\cos(\omega t)+\alpha\omega^2\lambda^2\sin(\omega t)-\alpha\omega\lambda e^{-t/\lambda}\right)$$

For t $\rightarrow\infty$ $\quad e^{-t/\lambda}<<1$

$$\tau_{xy}=\left(\eta_s+\frac{G\lambda}{1+\omega^2\lambda^2}\right)\dot{\gamma}(t)+\frac{G\omega^2\lambda^2}{1+\omega^2\lambda^2}\gamma(t)$$

$$G'(\omega)=\frac{G\omega^2\lambda^2}{1+\omega^2\lambda^2}$$

$$G''(\omega)=\eta_s+\frac{G\lambda}{1+\omega^2\lambda^2}$$

Steady 2D Extensional Flow

Let the velocity field be

$$\underline{v}(y,t)=(\dot{\varepsilon}_o x, -\dot{\varepsilon}_o y)$$

$$\underline{\nabla}\,\underline{v}(y,t)=\begin{pmatrix}\dot{\varepsilon}_o & 0\\ 0 & -\dot{\varepsilon}_o\end{pmatrix}$$

The total stress tensor is given by the relation

$$\underline{\underline{\tau}}=\begin{pmatrix}-p+2\eta_s\dot{\varepsilon}_o & 0\\ 0 & -p-2\eta_s\dot{\varepsilon}_o\end{pmatrix}+G\underline{\underline{A}}$$

The viscoelastic stresses are

$$\underline{\underline{\tau}}_p=G\underline{\underline{A}}$$

The conformation tensor

$$-\begin{pmatrix}\dot{\varepsilon}_o A_{xx} & -\dot{\varepsilon}_o A_{xy}\\ \dot{\varepsilon}_o A_{xy} & -\dot{\varepsilon}_o A_{yy}\end{pmatrix}-\begin{pmatrix}\dot{\varepsilon}_o A_{xx} & \dot{\varepsilon}_o A_{xy}\\ -\dot{\varepsilon}_o A_{xy} & -\dot{\varepsilon}_o A_{yy}\end{pmatrix}=-\frac{1}{\lambda}\begin{pmatrix}A_{xx}-1 & A_{xy}\\ A_{yx} & A_{yy}-1\end{pmatrix}$$

Hence,

$$\begin{cases} A_{xx} = \dfrac{1}{1-2\dot{\varepsilon}_o\lambda} \\ A_{xy} = 0 \\ A_{yy} = \dfrac{1}{1+2\dot{\varepsilon}_o\lambda} \end{cases}$$

The total stress tensor is

$$\underline{\underline{\tau}} = \begin{pmatrix} -p+2\eta_s\dot{\varepsilon}_o+G/(1-2\dot{\varepsilon}_o\lambda) & 0 \\ 0 & -p-2\eta_s\dot{\varepsilon}_o+G/(1+2\dot{\varepsilon}_o\lambda) \end{pmatrix}$$

The extensional Viscosity

$$\eta_e = \frac{\tau_{xx}-\tau_{yy}}{4\dot{\varepsilon}_o}$$

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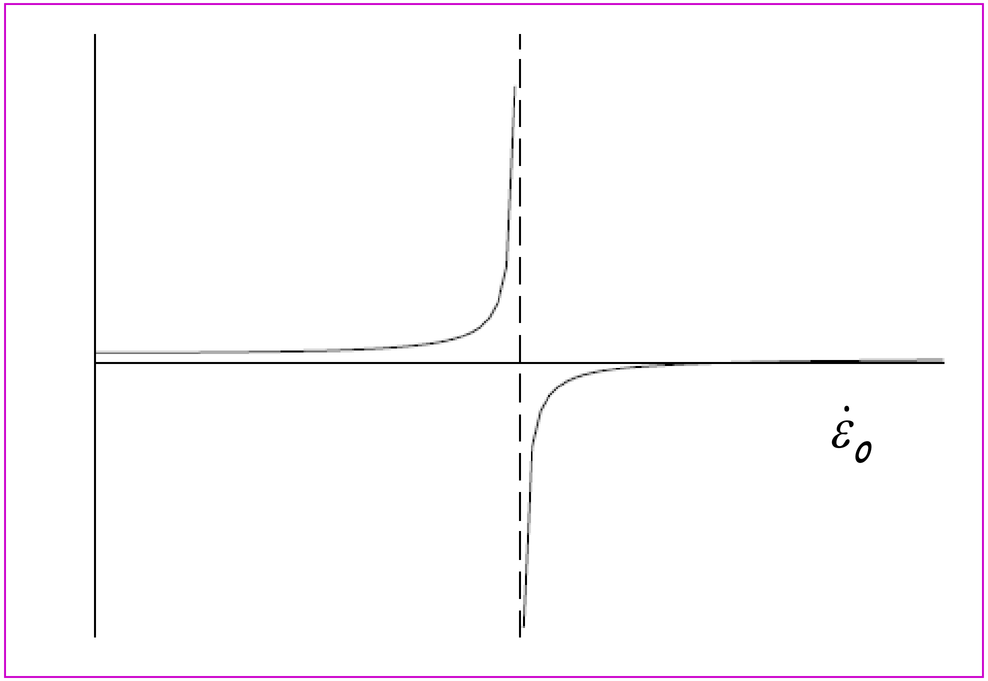
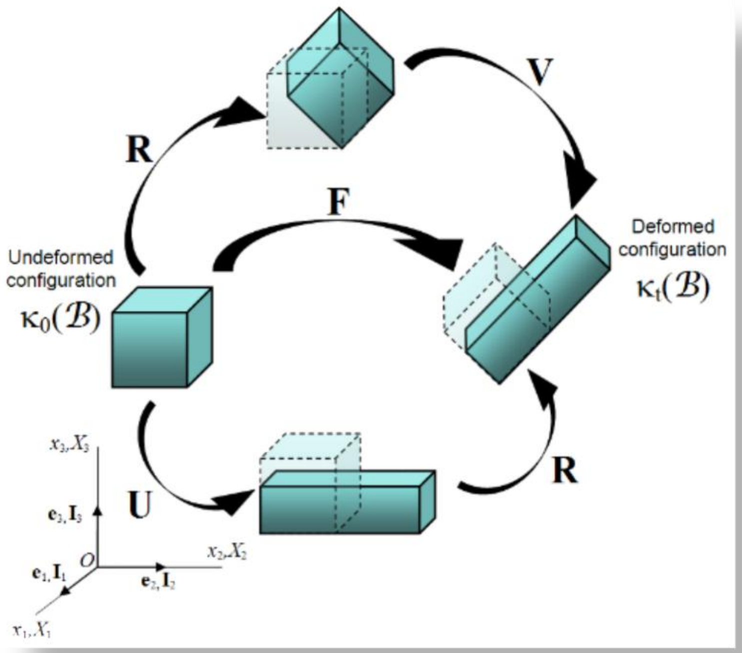
$$\eta_e = \eta + \frac{G\lambda}{1 - 4\dot{\varepsilon}_o \lambda^2}$$



$$\dot{\varepsilon}_o = \frac{1}{2\lambda}$$



Giesekus Model

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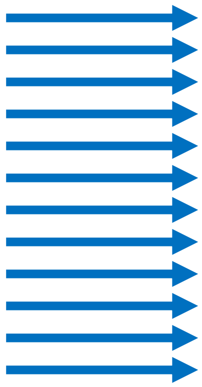
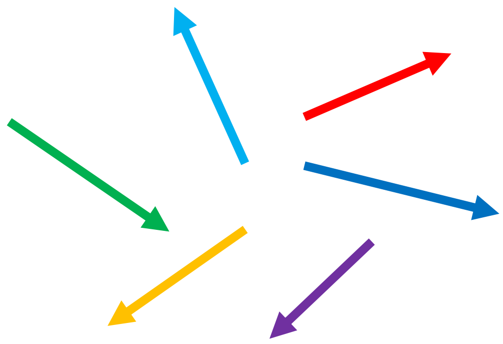
Anisotropic Drag Force

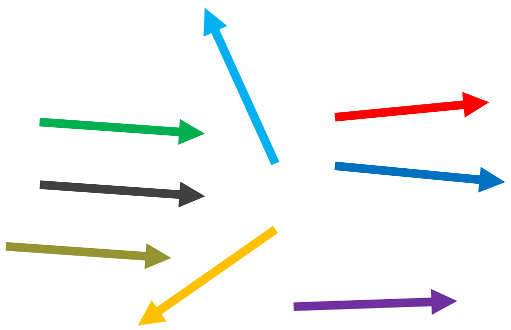
Flow field



Isotropy in chain mobility



Anisotropy in chain mobility



Anisotropic Drag Force

When a system is deformed, the space where a macromolecule deforms becomes anisotropic. This will lead to anisotropic drag force on it.

$$\underline{\underline{B}} \cdot \underline{\underline{\tau}}_p + \lambda \overset{\nabla}{\underline{\underline{A}}} = \underline{\underline{0}}$$

Mobility Tensor

Relaxation time

$$\overset{\nabla}{\underline{\underline{A}}} = \frac{\partial \underline{\underline{A}}}{\partial t} + \underline{v} \cdot \underline{\nabla} \underline{\underline{A}} - \left(\underline{\nabla} \underline{v} \right)^T \cdot \underline{\underline{A}} - \underline{\underline{A}} \cdot \underline{\nabla} \underline{v}$$

$$\underline{\underline{B}} = \underline{\underline{I}} + a\left(\underline{\underline{A}} - \underline{\underline{I}} \right)$$

a is a parameter that determines the degree of anisotropy in chain mobility

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The constitutive model in terms of conformation tensor

3-Constant Giesekus model. Relation is expressed in terms of the conformation tensor

$$a\left(\underline{\underline{A}}-\underline{\underline{I}}\right)^2+\left(\underline{\underline{A}}-\underline{\underline{I}}\right)+\lambda\overset{\nabla}{\underline{\underline{A}}}=\underline{\underline{0}}$$

$$\underline{\underline{\tau}}_p=G\left(\underline{\underline{A}}-\underline{\underline{I}}\right)$$

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The constitutive model in terms of stress tensor

3-Constant Giesekus model. Here expressed in terms of the polymeric stress tensor

$$\underline{\underline{\tau}}_p + \lambda \overset{\nabla}{\underline{\underline{\tau}}}_p + a \frac{\lambda}{\eta_o} \underline{\underline{\tau}}_p \cdot \underline{\underline{\tau}}_p = \eta_o \dot{\underline{\underline{\gamma}}}$$

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Material Properties

Steady Shear Flow

$$\frac{\eta}{\eta_o} = \frac{(1-f)^2}{1+(1-2a)f}$$

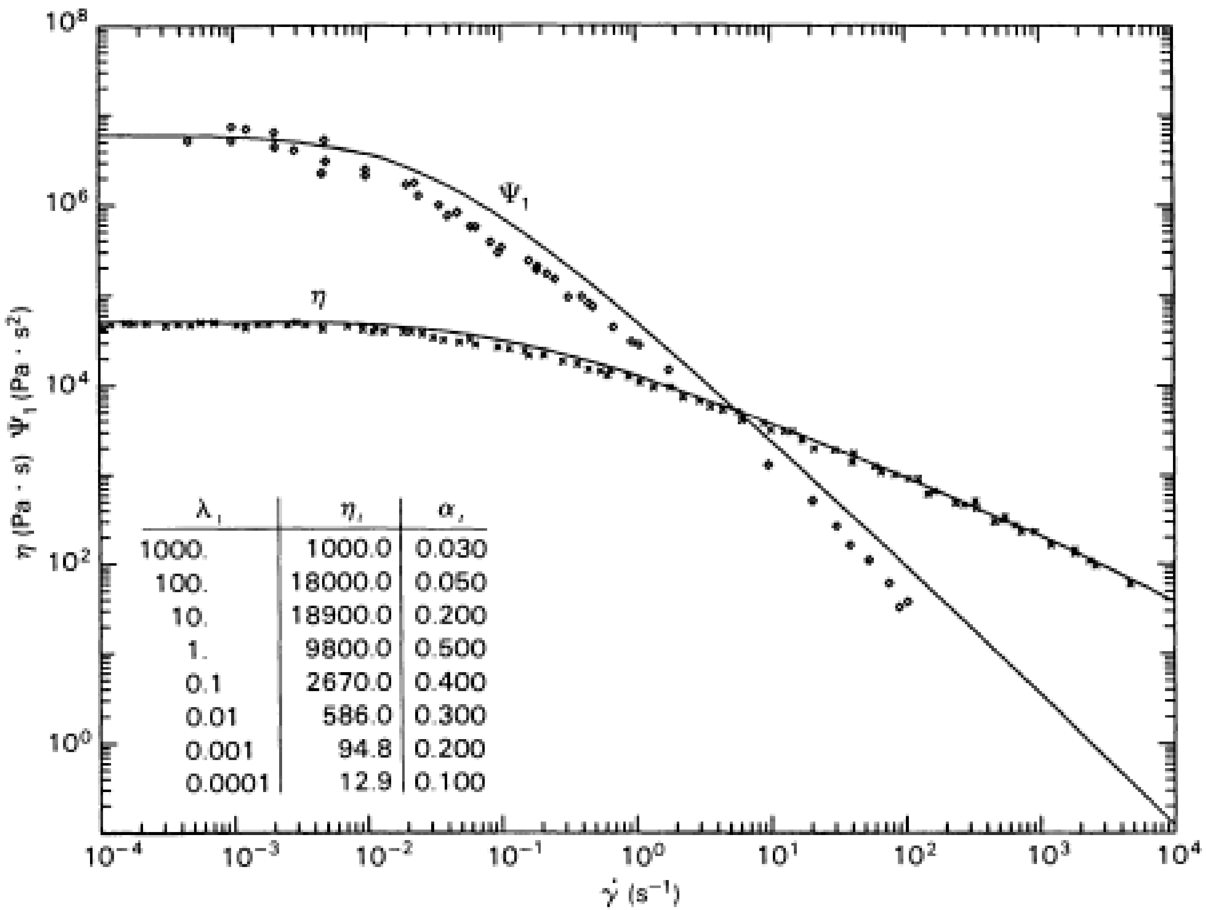
$$\frac{\Psi_1}{2\eta_o\lambda} = \frac{f(1-af)}{(1-f)a}\frac{1}{(\lambda\dot{\gamma}_o)^2}$$

$$\frac{\Psi_2}{\eta_o\lambda} = -f\frac{1}{(\lambda\dot{\gamma}_o)^2}$$

where

$$f = \frac{1-\chi}{1+(1-2a)\chi} \qquad \chi^2 = \frac{\left[1+16a(1-a)(\lambda\dot{\gamma}_o)^2\right]^{1/2}-1}{8a(1-a)(\lambda\dot{\gamma}_o)^2}$$

Material Properties: η & Ψ_1



λ_i	η_i	α_i
1000.	1000.0	0.030
100.	18000.0	0.050
10.	18900.0	0.200
1.	9800.0	0.500
0.1	2670.0	0.400
0.01	586.0	0.300
0.001	94.8	0.200
0.0001	12.9	0.100

Viscosity and first normal stress coefficient for an 8-mode Giesekus model as compared to experimental data for a low-density polyethylene melt

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Material Properties

Small
Amplitude
Oscillatory
Flow

$$\frac{\eta'}{\eta_o} = \frac{1}{1+(\lambda\omega)^2}$$

$$\frac{\eta''}{\eta_o} = \frac{\lambda\omega}{1+(\lambda\omega)^2}$$

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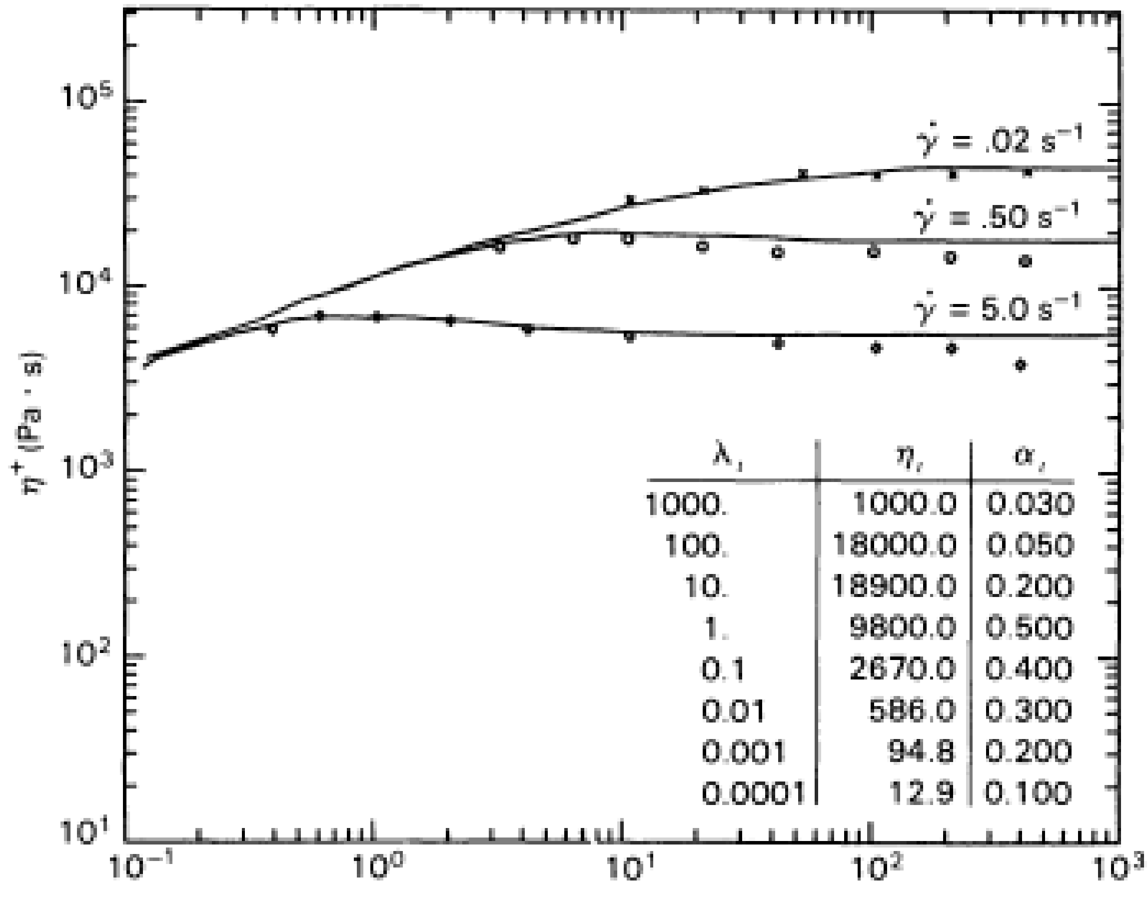
Startup shear Viscosity: η^+



λ_i	η_i	α_i
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0.0001	12.9	0.100

Comparison of η+ calculated by an 8-mode Giesekus model with experimental data for a low-density polyethylene melt

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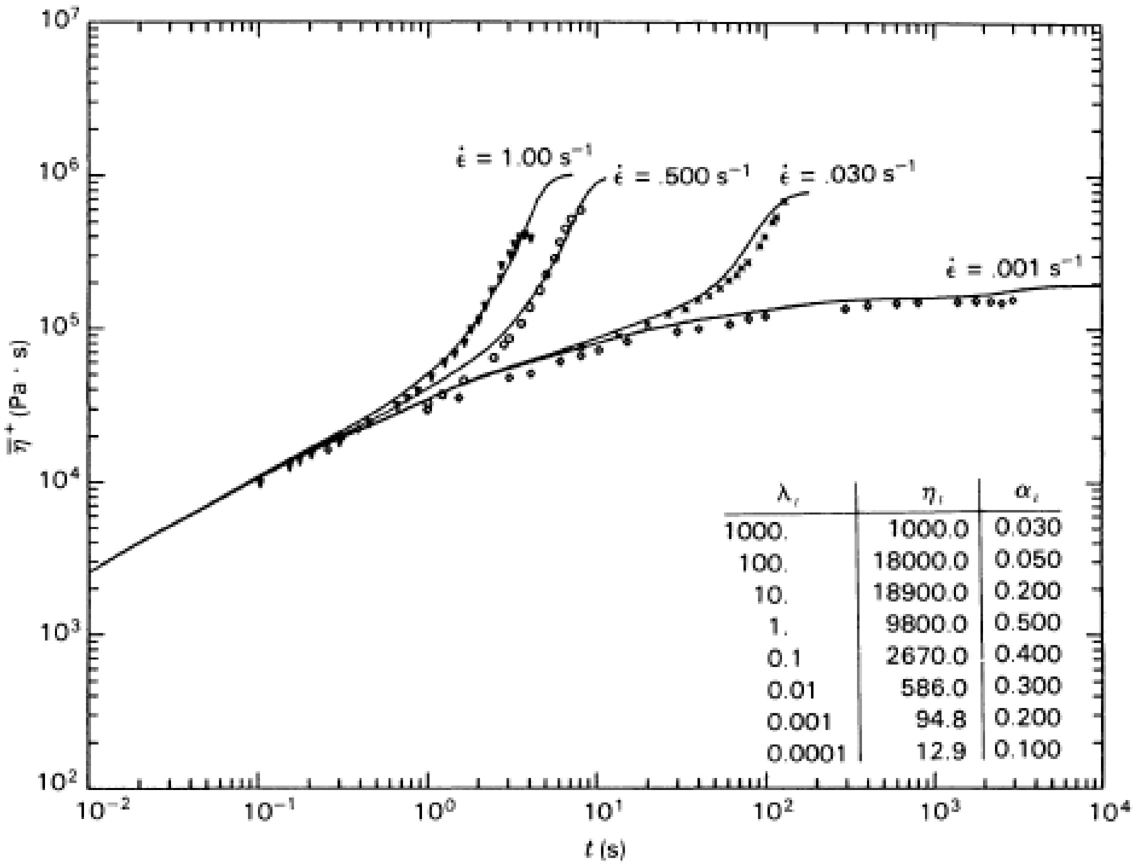
Material Properties

Steady Extensional Viscosity

$$\frac{\bar{\eta}}{3\eta_o} = \frac{1}{6a}\left(3 + \frac{1}{\lambda\dot{\varepsilon}}\sqrt{1 - 4(1-2a)\lambda\dot{\varepsilon} + 4(\lambda\dot{\varepsilon})^2} - \sqrt{1 + 2(1-2a)\lambda\dot{\varepsilon} + (\lambda\dot{\varepsilon})^2}\right)$$

Startup elongational Viscosity: $\tilde{\eta}^+$



Comparison of $\tilde{\eta}^+$ calculated by an 8-mode Giesekus model with experimental data for a low-density polyethylene melt

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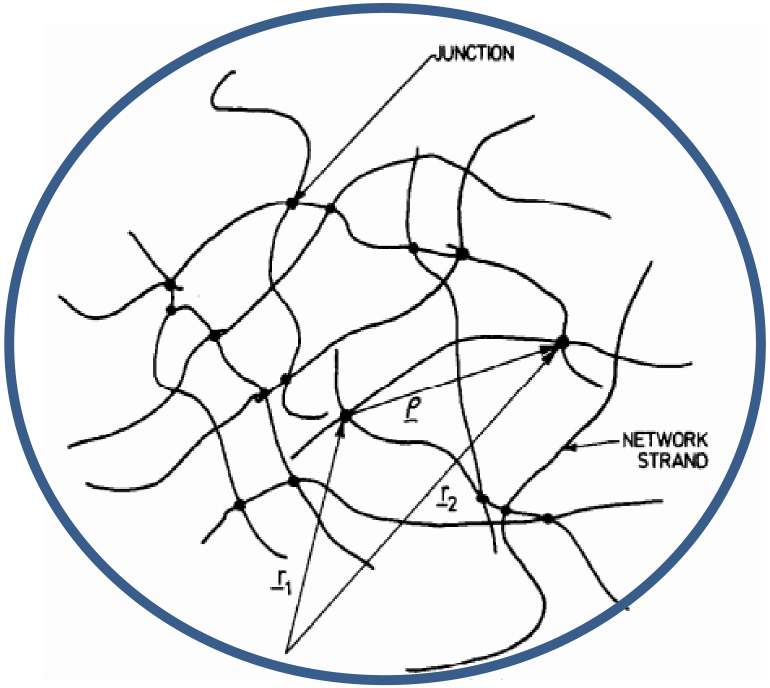
Phan-Tien & Tanner (PPT) model (based on network theory)

Typical network of polymer solutions



$$\overset{\nabla}{\underline{\underline{\tau}}} = \dot{\underline{\underline{\tau}}} - \underline{\underline{D}} \cdot \underline{\underline{\tau}} - \underline{\underline{\tau}} \cdot \underline{\underline{D}}^T$$

$\lambda = \eta / G$ is the relaxation time, ∇ over a variable indicates the upper convected time-derivative

$$\overset{\nabla}{\underline{\underline{\tau}}} + \underline{F_c}\left(\underline{\underline{\tau}}, \underline{\underline{D}}\right) + \frac{\underline{F_d}\left(\underline{\underline{\tau}}\right)}{\lambda} \cdot \underline{\underline{\tau}} = 2G\underline{\underline{D}}$$

$\underline{F_c}$ introduces non-affine motion of the polymer strands

$\underline{F_d}$ correlates with the creation and the destruction of junctions between the strands

<u>Affine motion</u>: The deformation characterizing the material at the macroscopic level is similar to its microscopic motion

The Phan Tien Tanner (PPT) model: the functions

Comments:

- The parameter $0 \le \xi \le 2$ alters the time derivative.
- For the limits, $\xi = 0$ and $\xi=2$, the upper and lower convected time derivative are obtained.
- With $\xi=1$ the co-rotational time derivative results

$$\underline{F}_c\left(\underline{\underline{\tau}}, \underline{\underline{D}}\right) = \xi \underline{\underline{D}} \cdot \underline{\underline{\tau}} - \xi \underline{\underline{\tau}} \cdot \underline{\underline{D}}^T$$

- In general the functional dependence is such that it accelerates stress decay rate at higher stresses and approaches zero at least quadratically when strains (i.e. stress divided by the modulus) approach zero.

- $\underline{F}_d$ or f, the relaxation time of the model is made a non-linear function of the extra stress tensor scaled with a modulus.

$$\underline{F}_d(\underline{\underline{\tau}}) = \exp(\varepsilon/G\, I_\tau)$$

- Predicts a maximum in the elongational viscosity before reaching extensional thinning at higher elongational rates

$$\underline{F}_d(\underline{\underline{\tau}}) = 1 + \varepsilon/G\, I_\tau$$

- Predicts extensional thickening behavior after which a plateau is reached at higher elongational rates

ℓ- PPT model: material functions

Predicts:

- Shear thinning behavior for shear viscosity and normal stress difference
- The elongational viscosities become bounded.
- For $\xi=0$, the second normal stress difference becomes zero.

Limitations:

- For $\xi\neq0$ spurious oscillations are predicted during start-up of shear flow.
- When $\xi=0$, similar predictions are obtained as the Giesekus model and no overshoot in the viscometric functions is predicted for start-up of shear

$$\eta_s = \beta\eta_0 + \frac{\eta_0(1-\beta)}{f},$$

$$N_1 = \frac{2\eta_0(1-\beta)\lambda_1\dot{\gamma}^2}{f^2},$$

$$N_2 = -\frac{\eta_0(1-\beta)\lambda_1\dot{\gamma}^2\xi}{f^2},$$

$$\eta_e = 3\beta\eta_0 + 3\eta_0(1-\beta)\left[\frac{f}{f^2 - f\lambda_1\dot{\varepsilon} - 2\lambda_1^2\dot{\varepsilon}^2}\right].$$

$N_2/N_1=-\xi/2$

Comments:

- The two parameters ξ, ε define the non-linear behavior.
- When $\varepsilon \ll \xi$ the behavior in shear flow is mainly determined by ξ, and ε serves to blunt the singularity in elongation that otherwise would be present.
- A single value of the slip parameter cannot fit both shear viscosity and first normal stress difference satisfactorily.

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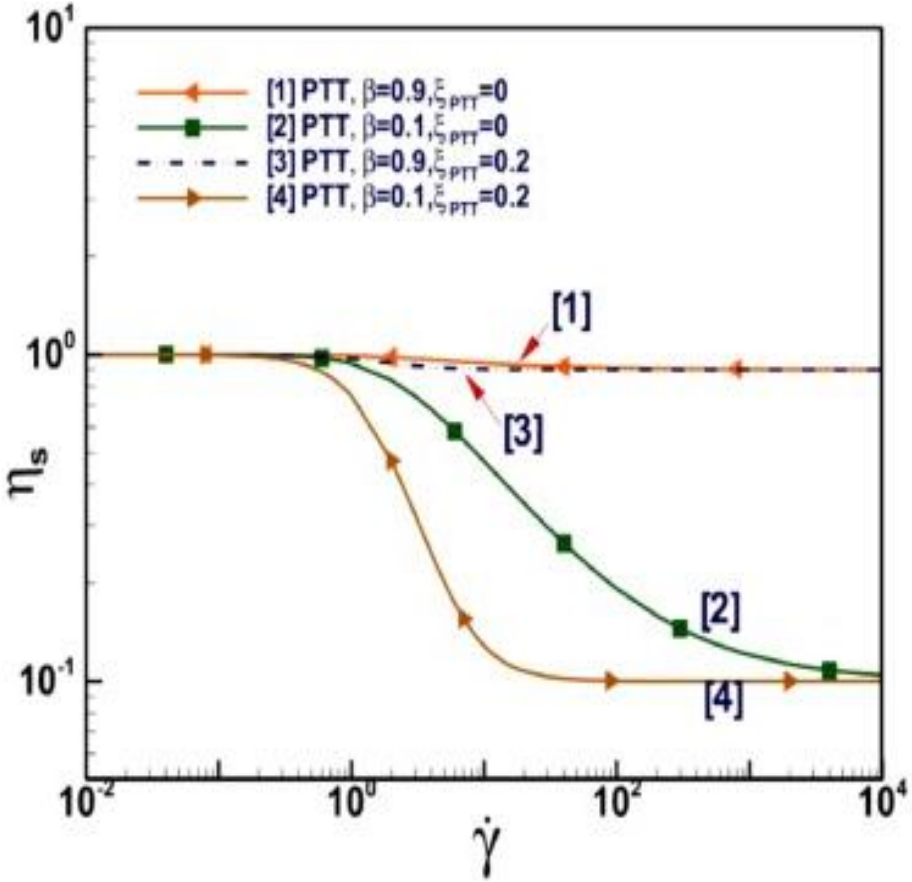
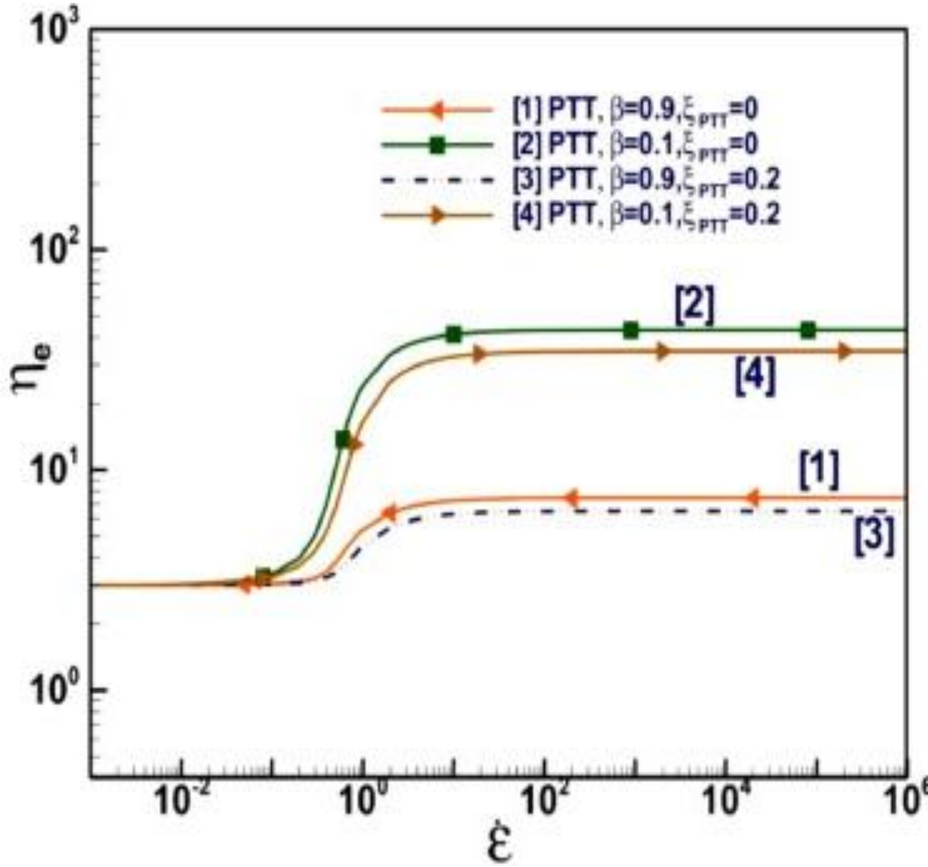
Material Properties for ℓ- PPT

Shear Viscosity



Extensional Viscosity



Material functions for PTT model with ε=0.04, ξ=0.0,0.2, $\beta = 0.9, 0.1$)

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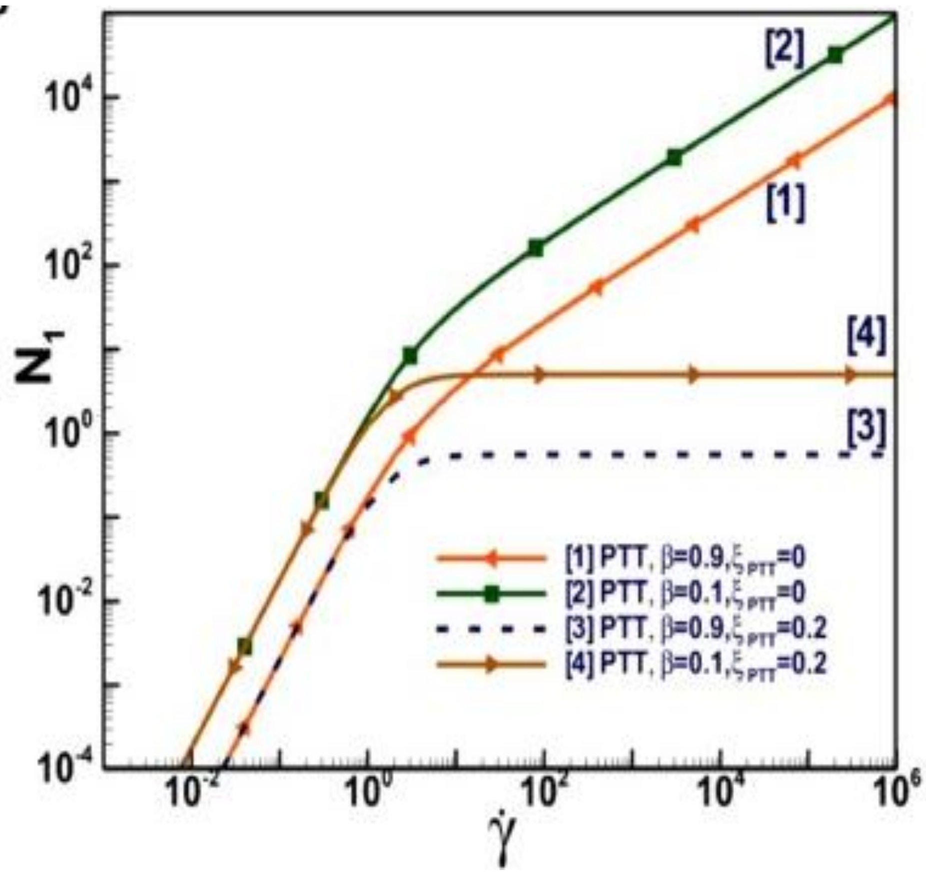
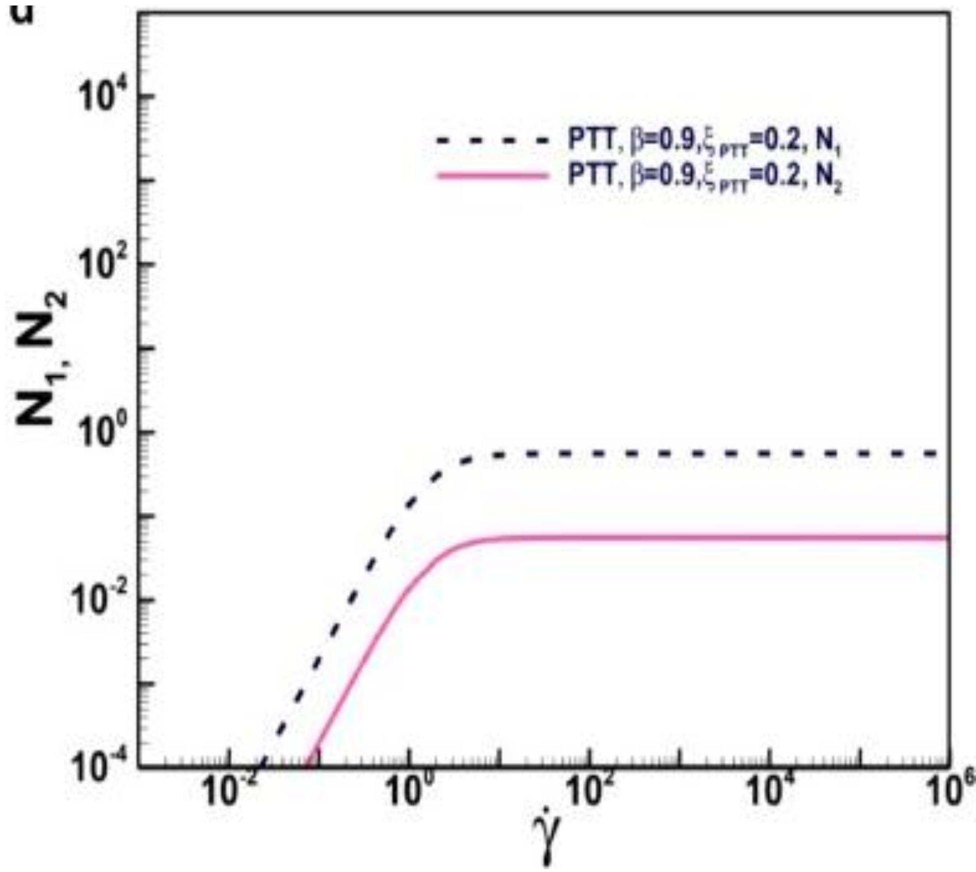
Material Properties for ℓ- PPT

first normal stress-difference



second normal stress-difference



Material functions for PTT model (ε=0.04,ξ=0.0,0.2), $\beta = 0.9, 0.1$

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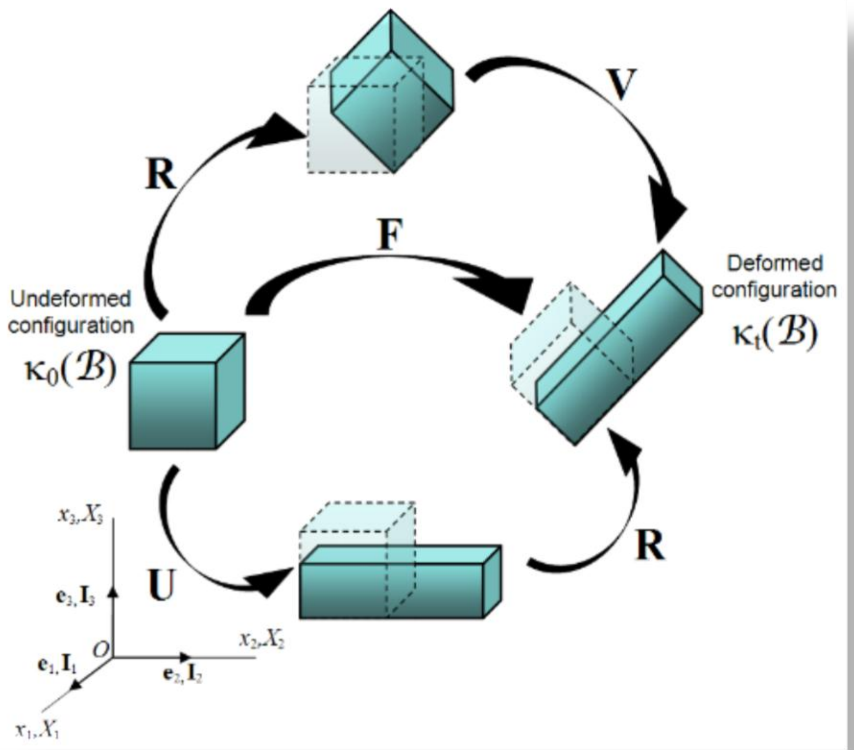
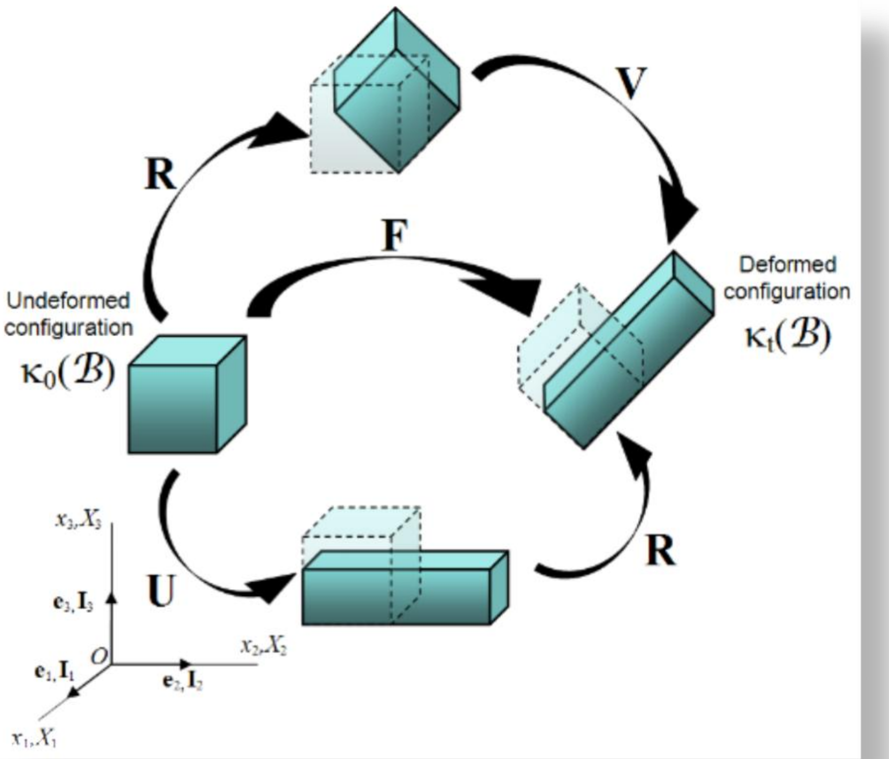


End of 4th lecture



FENE Constitutive models

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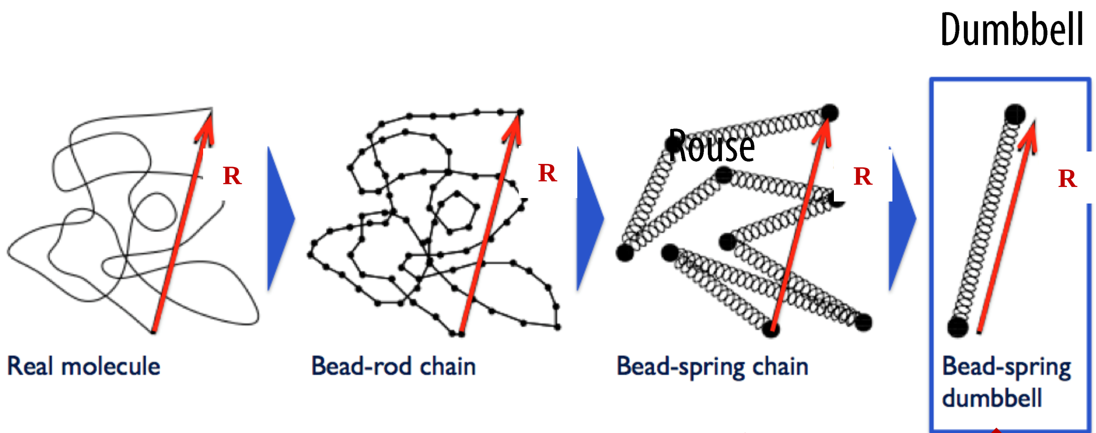
FENE Models



FENE stands for the finitely extensible nonlinear elastic model of a long-chained polymer. It simplifies the chain of monomers by connecting a sequence of beads with nonlinear springs.

$$\underline{F}^{(c)}(\underline{R}) = \frac{3k_B T}{\beta^2}\underline{R} = H\underline{R}$$

Hookean spring or entropic spring ⇨ Oldroyd-B model

$$\underline{F}^{(c)}(\underline{R}) = \frac{H\underline{R}}{1-(\underline{R}/R_{max})^2}$$

Warner's spring ⇨ FENE model

FENE Models

$$\underline{\underline{\tau}}_p = G\left(\left\langle \frac{\underline{R}\,\underline{R}}{1-\underline{R}^2/\underline{R}_{max}^2} \right\rangle - \underline{\underline{I}}\right)$$

FENE

$$\underline{\underline{\tau}}_p = G\left(\frac{\left\langle\underline{R}\,\underline{R}\right\rangle}{1-\left\langle\underline{R}^2\right\rangle/\underline{R}_{max}^2} - \underline{\underline{I}}\right)$$

FENE-P

$$\underline{\underline{\tau}}_p = G\left(\frac{\left\langle\underline{R}\,\underline{R}\right\rangle}{1-\left\langle\underline{R}^2\right\rangle/R_{max}^2} - \frac{R_{max}^2}{R_{max}^2-3}\underline{\underline{I}}\right)$$

FENE-CR

$$G = nk_BT$$

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FENE Chilcott-Rallison Model

$$\underline{\underline{\tau}}_p = \frac{\eta_s c f(tr\underline{\underline{A}})}{\lambda}\underline{\underline{A}}$$

If the dumbbell model is considered to have a maximum attainable length L. The force of the dumbbell is given by Warner law.

$$\frac{\partial \underline{\underline{A}}}{\partial t} + \underline{v}\cdot\underline{\nabla}\underline{\underline{A}} - \left(\underline{\nabla}\underline{v}\right)^T\cdot\underline{\underline{A}} - \underline{\underline{A}}\cdot\underline{\nabla}\underline{v} = \frac{f(tr\underline{\underline{A}})}{\lambda}\left(\underline{\underline{I}} - \underline{\underline{A}}\right)$$

$$f(tr\underline{\underline{A}}) = \frac{1}{1 - \frac{tr\underline{\underline{A}}}{R_{max}^2}}$$

$$c = \frac{\eta - \eta_s}{\eta_s}$$

Concentration

SAOS: relaxation modulus, G' & G''

$b = R^2_{max}$

FENE-P

relaxation modulus $$G_p\left(\left(t-t'\right)/\lambda\right) = \exp\left(-(t-t')(b+3)/\left(\lambda b\right)\right)$$

Loss moduli $$\frac{G''-\omega\eta_s}{nk_BT} = \frac{[(b+3)/b]\lambda\omega}{[(b+3)/b]^2+(\lambda\omega)^2}$$

Storage moduli $$\frac{G'}{nk_BT} = \frac{\left(\lambda\omega\right)^2}{[(b+3)/b]^2+(\lambda\omega)^2}$$

FENE-CR

relaxation modulus $$G_p\left(\left(t-t'\right)/\lambda\right) = \frac{b}{b-3}\exp\left(-(t-t')b/(b-3)\right)$$

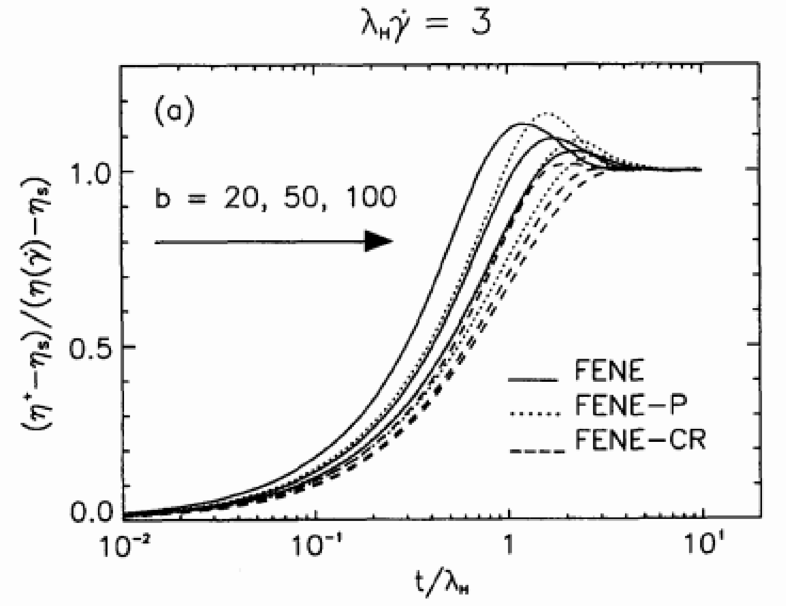
Loss moduli $$\frac{G''-\omega\eta_s}{nk_BT} = \frac{[b/(b-3)]^2\lambda\omega}{[b/(b-3)]^2+(\lambda\omega)^2}$$

Storage moduli $$\frac{G'}{nk_BT} = \frac{[b/(b-3)]\left(\lambda\omega\right)^2}{[b/(b-3)]^2+(\lambda\omega)^2}$$

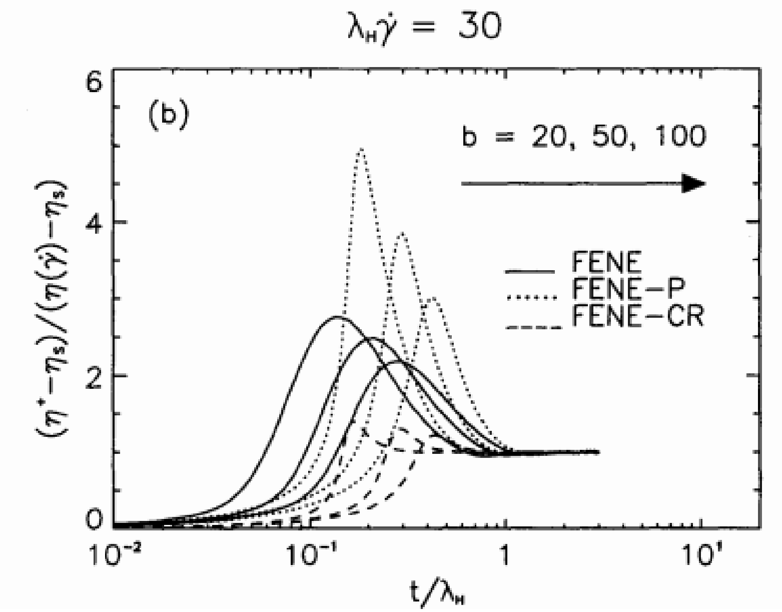
Startup shear flow: η^+

$b = R^2_{max}$

Low shear rate



High shear rate



Time evolution of η^+ after inception of shear flow for FENE, FENE-P and FENE-CR

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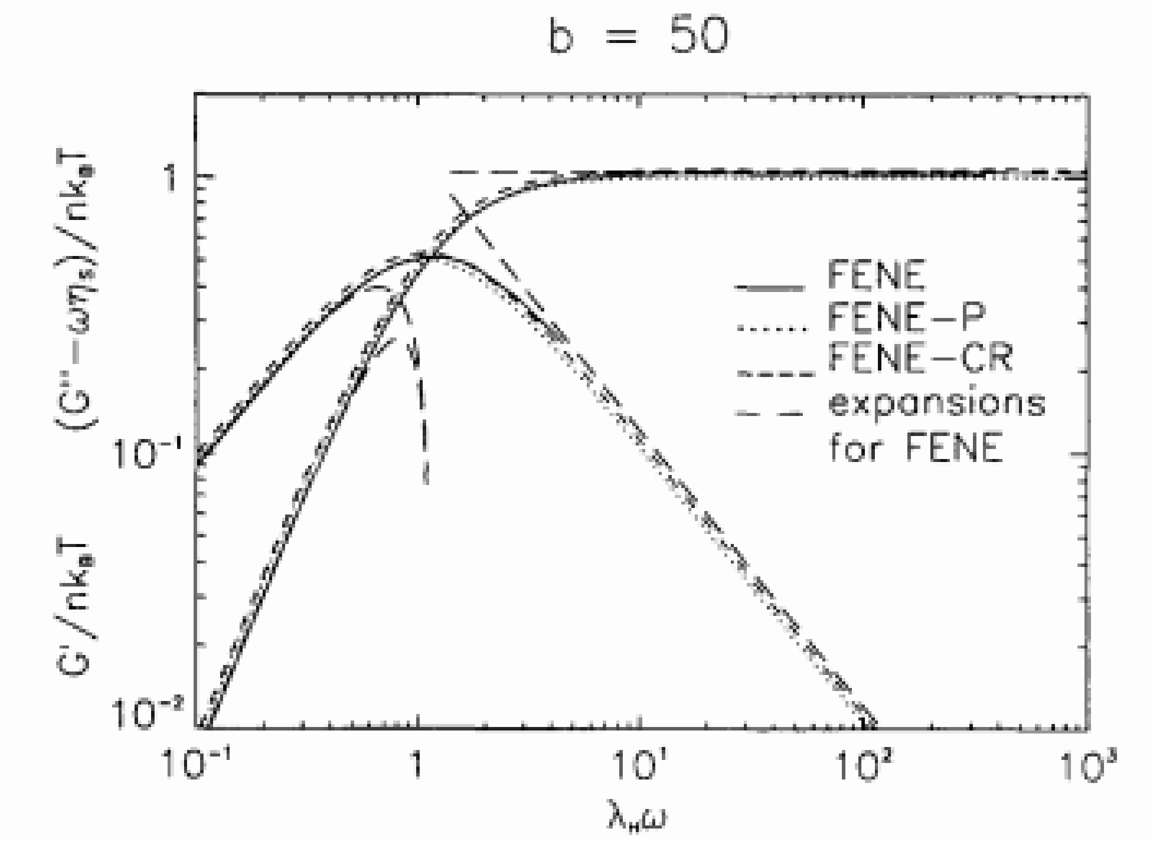
SAOS: G′ & G″

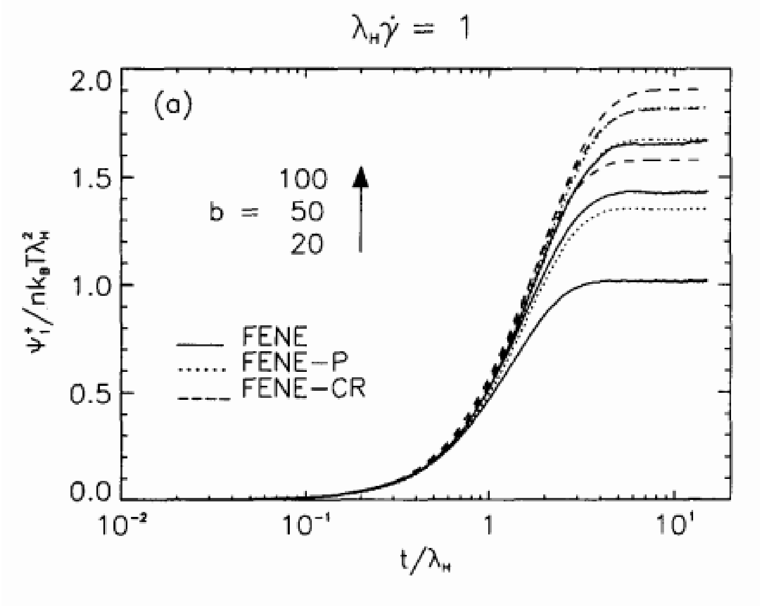
$b = R^2_{max}$



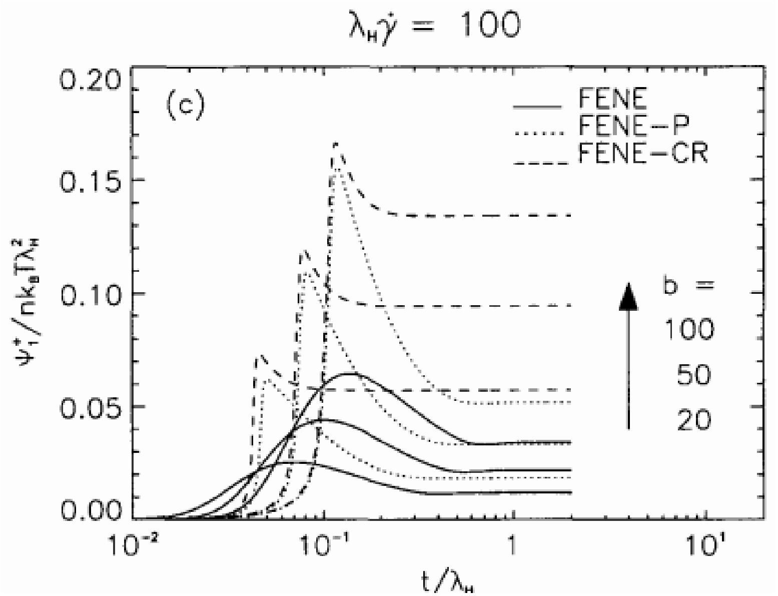
Startup shear flow: Ψ_1^+

$b=R^2_{max}$

Low shear rate



High shear rate



Time evolution of Ψ_1^+ after inception of shear flow for FENE, FENE-P and FENE-CR