The kinetic theory approach to the rheology of polymer solutions

Dmitry Shogin

University of Stavanger
The National IOR Centre of Norway

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Polymer solutions

Polymer solutions are an example of non-Newtonian fluids:

- The viscous stress tensor \( \tau_{ij} \) describes the transfer of momentum in the fluid; knowledge of this tensor is required to construct and solve the equations of fluid dynamics.

- For Newtonian fluids, e.g. water and oil, \( \tau_{ij} \) is proportional to the velocity gradients:

\[
\tau_{ij} = \eta \left( \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right),
\]

where the viscosity \( \eta \) is a constant. Using this relation leads to the well-known Navier-Stokes equations of fluid dynamics.

- For non-Newtonian fluids it is essentially different.
Non-Newtonian viscosity

Polymer solutions demonstrate shear-thinning, dvs. viscosity drops as shear rate grows.
The normal stress

- Polymer solutions contract along the streamlines;
- Non-zero stress in a perpendicular direction is produced;
- In a flow between two parallel plates, a force is needed to hold the plates in place:

For Newtonian fluids, the normal stress is identically zero.
The "Rod-climbing" experiment

(a) Newtonian liquid
(b) Polymeric fluid

No normal forces  Normal forces dominate over centrifugal forces
The challenge

Many (very useful) correlations exist for the non-Newtonian viscosity. Why do we need an explanation based on the Kinetic theory?

- Non-Newtonian viscosity is not enough to describe a flow other than a simple shearing one.
- A physical model would predict the behaviour of the polymer solutions in different kinds of flows.
- Understanding of the underlying mechanism would predict the effects of temperature, polymer concentration, salinity of the solvent and other physical and chemical factors.
Introduction

The FENE Dumbbell Model

Analytical results

Ongoing experiments

What makes polymers so special?

**Polymers are macromolecules.**

They are constructed from one or several types of simple structural units (monomers) and may have an extremely high molecular weight (up to $10^5 - 10^7 \text{ g/mol}$).

**A huge amount of possible configurations.**

The molecules continuously change their configurations due to the thermal motion.

**Polydispersity.**

Typically, different polymer molecules do not have the same molecular weight.
The FENE Dumbbell Model
The Dumbbell model

A polymer molecule is represented by two spherical beads connected by an elastic spring. The polymer solution is assumed to be sufficiently dilute, and the solvent is an incompressible Newtonian fluid.
Molecular dynamics

**Forces acting on the beads:**
- Hydrodynamic drag (of Stokes type, with a coefficient $\zeta$);
- Brownian forces;
- The connector force from the spring;
- The inertial forces ($\text{mass} \times \text{acceleration}$);
- External forces;

The forces allow to calculate the configurational distribution function $\psi$ and the viscous stress tensor $\tau$. 
The viscous stress tensor

The contributions of the forces to the momentum transfer can be calculated:

\[
\tau = -\eta_s \dot{\gamma} - n\langle QF^{(c)} \rangle + nkT \delta
\]

or

\[
\tau = -\eta_s \dot{\gamma} + \frac{n\zeta}{4} \langle QQ \rangle_{(1)}.
\]

Some notations:

- \( \dot{\gamma} = \{ \nabla v \} + \{ \nabla v \}^T \) is the rate-of-strain tensor;
- Angle brackets denote the configuration-space average;
- \( \delta \) is the unit tensor.
The nonlinear connector force

- Hookean spring can be extended without limits: does not yield non-Newtonian fluid dynamics.
- A FENE (Finitely Elongated Nonlinear Elastic) spring is a working alternative:
  \[ F^{(c)} = \frac{HQ}{1 - (Q/Q_0)^2}. \]
- Nearly Hookean (with coefficient \( H \)) at small extensions...
- ...but strongly nonlinear at larger extensions;
- Finally, cannot be stretched beyond the length \( Q_0 \).
**The configurational distribution function**

### Known issues
- The configurational distribution function, $\psi$, is required to calculate the averages in $\tau_{ij}$;
- In equilibrium (no flow) the exact expression for $\psi$ is known;
- Out of equilibrium, $\psi$ can be found from a (partial differential) diffusion equation;
- The diffusion equation must be solved at each point of the flow - complicates the CFD procedures.
- Is there a way to go around this problem?
The Peterlin’s closure

The FENE-P assumption

\[ \left\langle \frac{QQ}{1 - Q^2/Q_0^2} \right\rangle \sim \frac{\langle QQ \rangle}{1 - \langle Q^2/Q_0^2 \rangle} + \varepsilon Q_0^2 \delta \]

The \( \varepsilon \)-containing term is introduced to improve the approximation. Here \( \varepsilon \) is a constant determined from the requirement that the trace of the above is true at equilibrium.

The closure allows to avoid determining \( \psi \) at each point of the flow by excluding the averages using mathematical transformations.
The constitutive equation for FENE-P dumbbells

\[ Z \tau_p + \lambda_H \tau_{p(1)} - \lambda_H \{ \tau_p - (1 - \varepsilon b) nkT \delta \} \frac{D \ln Z}{Dt} = -(1 - \varepsilon b) nkT \lambda_H \dot{\gamma} \]

\[ Z = 1 + \frac{3}{b} \left( 1 - \varepsilon b - \frac{\text{tr}(\tau_p)}{3nkT} \right). \]

**A two-parameter model**

- \( b = HQ_0^2 / kT \): a dimensionless parameter characterizing the degree of nonlinearity of the spring;
- \( \lambda_H = \zeta/4H \): a time parameter reflecting some typical timescale for configurational changes.

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Steady shear flow

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Steady shear flow

- The constitutive equation reduces to algebraic form;
- The viscous stress tensor has only two independent components;
- Exact analytical expressions for these components can be obtained;
- Two material functions, the non-Newtonian viscosity and the First normal stress coefficient, can be extracted:

\[ \tau_{yx} = \tau_{xy} = -\eta(\dot{\gamma})\dot{\gamma} \quad \tau_{xx} - \tau_{yy} = -\Psi_1(\dot{\gamma})\dot{\gamma}^2. \]
Steady shear flow

**Viscosity: the impact of $b$**

![Graph showing shear viscosity alteration of $b$ at $\lambda=0.01$](image)

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The kinetic theory approach to the rheology of polymer solutions
Steady shear flow

**Viscosity: the impact of $\lambda_H$**

![Shear viscosity graph](image)

Shear viscosity. Alteration of $\lambda$ at $b=50$
Steady shear flow

**First normal stress coefficient: the impact of** $b$

![Graph showing the variation of first normal stress coefficient with $b$ at $\lambda=0.01$.](image-url)
First normal stress coefficient: the impact of $\lambda_H$

![Graph showing the impact of $\lambda_H$ on first normal stress](image_url)
Analytical expansions

1. At very low shear rates:

\[ \eta \to \eta_s + nkTb\lambda_H \frac{1}{b+5}; \]
\[ \Psi_1 \to nkTb\lambda_H^2 \frac{(b+2)}{(b+5)^2}. \]

2. At high shear rates:

\[ \eta - \eta_s \approx nkTb \left( \frac{\lambda_H}{2(b+2)^2} \right)^{1/3} (\dot{\gamma})^{-2/3}; \]
\[ \Psi_1 \approx nkTb \left( \frac{2\lambda_H^2}{b+2} \right)^{1/3} (\dot{\gamma})^{-4/3}. \]
Steady shearfree flows

The velocity field is given by

\[ v_x = -\frac{1}{2} \dot{\epsilon} x, \quad v_y = -\frac{1}{2} \dot{\epsilon} y, \quad v_z = \dot{\epsilon} z; \]

- \( \dot{\epsilon} \) is the elongation rate;
- \( \dot{\epsilon} > 0 \): elongational flow;
- \( \dot{\epsilon} < 0 \): biaxial stretching.
Steady shearfree flows

- The viscous stress tensor is diagonal:

\[ \mathbf{\tau} = \text{diag}(\tau_{xx}, \tau_{xx}, \tau_{zz}); \]

- Characterized by the normal stress difference

\[ \tau_{zz} - \tau_{xx} = -\tilde{\eta}(\dot{\epsilon})\dot{\epsilon}; \]

- \( \tilde{\eta}(\dot{\epsilon}) \) is called the elongational (Trouton, extensional) viscosity;
- For Newtonian fluids, \( \tilde{\eta} = 3\eta \) and is constant.
Steady shearfree flows

**Extensive viscosity: Elongational flow**

\[
\frac{\bar{\eta} - 3 \eta_s}{3 n k T (1 - e b)}
\]

![Graph](image.png)

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The kinetic theory approach to the rheology of polymer solutions
Extentional viscosity: Biaxial stretching

\[ \frac{\bar{\eta} - 3 \eta_s}{3 n kT (1 - \epsilon b)} \]

\[ b = 50, \lambda = 0.01 \]
Steady shearfree flows

Analytical expansions

1. At very low elongation rates:

\[ \bar{\eta} \rightarrow 3\eta_s + 3nkTb\lambda_H \frac{1}{b + 5}, \]

2. At high elongation rates:

For \( \dot{\varepsilon} \rightarrow +\infty \): \( \bar{\eta} \rightarrow 3\eta_s + 2nkTb\lambda_H; \)

For \( \dot{\varepsilon} \rightarrow -\infty \): \( \bar{\eta} \rightarrow 3\eta_s + \frac{1}{2}nkTb\lambda_H. \)
Ongoing experiments
Rotational rheometer

Data obtained are the viscosity and the first normal stress coefficient as functions of the shear rate.
Specimen

- Flopaam 5115 SH polymer ($M_m \approx 15 \times 10^6$ g/mol);
- Different concentrations;
- In salt (NaCl) water of different salinity;
- At different temperatures.
Objectives

- Determine the actual values of $b$ and $\lambda_H$ for the polymer solutions of interest;
- Estimate the accuracy of the FENE-dumbbell model;
- Check the theoretically predicted dependence of the material functions on the polymer concentration and temperature;
- Investigate the model parameters $b$ and $\lambda_H$ as functions of the salinity of the brine;
- **Ultimately** – be able to simulate the flows of polymers dissolved in salt water brines through the pores of different geometries.
Thank you for attention!