Chapter 8. Polymeric liquids

- Behaviour of polymeric liquids
- Rheometry and material functions
- Non-Newtonian viscosity and the generalised Newtonian models
- Elasticity and the linear viscoelastic models
- The co-rotational derivatives and the nonlinear viscoelastic models
- Molecular theories for polymeric liquids

Behaviour of polymeric liquids

- Remarks:
  - Polymeric liquids
    \[ \frac{v_z}{v_{z,\text{max}}} = 1 - \left( \frac{r}{R} \right)^{1+\frac{1}{n}} \]
    \[ \frac{\langle v_z \rangle}{v_{z,\text{max}}} = \frac{(1/n) + 1}{(1/n) + 3} \]
  - \( n=1 \) for Newtonian liquids
  - Velocity profile of polymeric liquids suggests that viscosity depends on the velocity gradient

Behaviour of polymeric liquids

- Recoil after cessation of steady-state flow in a circular tube
Behaviour of polymeric liquids

- Normal stress effects. Rod climbing effect for polymeric liquids

- Siphoning continues to occur when the tube is raised above the surface

Rheometry and Material functions

- Material functions
  - Newtonian fluids: Viscosity
  - Non-Newtonian: several material functions

- Steady simple shear flow. $\dot{\gamma}$ is called the shear rate
Rheometry and Material functions

• Remarks for Steady simple shear flow
  – For Newtonian liquids, Normal stresses are all zero
  – For Non-Newtonian, the Normal stresses are not zero and are not equal
• Three material functions are defined
  – Non-Newtonian viscosity \( \eta \)
    \[ \tau_{yx} = -\eta \frac{dv_x}{dy} \]

Rheometry and Material functions

• Three material functions are defined …
  – First normal stress coefficient
    \[ \tau_{xx} - \tau_{yy} = -\Psi_1 \left( \frac{dv_x}{dy} \right)^2 \]
  – Second normal stress coefficient
    \[ \tau_{yy} - \tau_{zz} = -\Psi_2 \left( \frac{dv_x}{dy} \right)^2 \]

Rheometry and Material functions

• Material functions are a function of the stress rate
• There are several other material functions
• For Newtonian liquids
  \[ \eta = \mu \quad \Psi_1 = \Psi_2 = 0 \]

Non-Newtonian viscosity and the generalised Newtonian models

• Three levels
  – Generalised Newtonian models. Important in many industrial applications
  – Linear viscoelastic models. For system with small displacement gradient
  – Nonlinear viscoelastic models, include all the cases
Non-Newtonian viscosity and the generalised Newtonian models

- For Incompressible Newtonian fluids
  \[ \tau = -\mu [\nabla v + (\nabla v)^+] = -\mu \dot{\gamma} \]

- For the generalised Newtonian fluid model
  \[ \tau = -\eta [\nabla v + (\nabla v)^+] = -\eta \dot{\gamma} \quad \text{with } \eta = \eta(\dot{\gamma}) \]

Empirical Non-Newtonian viscosity function, \( \eta \)

- Simplest one. Two-parameter power law
  \[ \eta = m \dot{\gamma}^{n-1} \]

- Four-parameter Carreau equation
  \[ \frac{\eta - \eta_0}{\eta_0 - \eta_\infty} = [1 + (\lambda \dot{\gamma})^2]^{(n-1)/2} \]

Laminar flow of an incompressible Power law fluid in a circular tube

- Mass flow rate for a polymer liquid. Power law model

- Introducing \( \eta \) in the shear stress
  \[ \tau_{rz} = -\eta \frac{dv_z}{dr} \quad \Rightarrow \quad \tau_{rz} = -m \dot{\gamma}^{n-1} \frac{dv_z}{dr} \]

\[ \tau_{rz} = -m \left( -\frac{dv_z}{dr} \right)^{n-1} \frac{dv_z}{dr} = m \left( -\frac{dv_z}{dr} \right)^n \]

Laminar flow of an incompressible Power law fluid in a circular tube

- Relation shear stress and pressure difference
  \[ \tau_{rz} = \left( \frac{P_o - P_L}{2L} \right) r \]

- The shear stress becomes
  \[ m \left( -\frac{dv_z}{dr} \right)^n = \left( \frac{P_o - P_L}{2L} \right) r \]
Laminar flow of an incompressible Power law fluid in a circular tube

- Integrating
  \[ v_z = \left( \frac{(P_0 - P_L)R}{2 \text{mL}} \right)^{1/n} \frac{R}{(1/n) + 1} \left[ 1 - \left( \frac{r}{R} \right)^{(1/n) + 1} \right] \]

- Mass rate of flow
  \[ w = \frac{\pi R^3 \rho}{(1/n) + 3} \left( \frac{(P_0 - P_L)R}{2 \text{mL}} \right)^{1/n} \]

- It simplifies to Hagen-Poiseuille for Newtonian fluids

Elasticity and the linear viscoelastic models

- The Maxwell model
- The Jeffreys model
- The Generalised Maxwell model

Molecular theories for polymeric liquids

- Empirical relations require a lot of work.
- Molecular theories can help to formulate models for the polymeric liquids.
- Adjustable constants have to be determined by (Rheometric) experiments.

Molecular theories for polymeric liquids

- Theories. There are two classes
  - Network theories
  - Single-molecule theories

- Network theories
  - Developed to describe rubber behaviour
  - Extended to describe molten polymer, concentrated solutions
  - Assumptions about formations and rupturing of junctions are done
Network theories. A polymer network formed by temporary junctions (circles)

The single-molecule theories

- Developed to describe polymers in very diluted solutions
  - i.e., infrequent polymer-polymer interactions.
- Polymers are represented by “bead springs”
- Theory can extend to molten polymers and concentrated solutions

The single-molecule bead spring models.
  a) dilute polymer solutions
  b) polymer melt without solvent