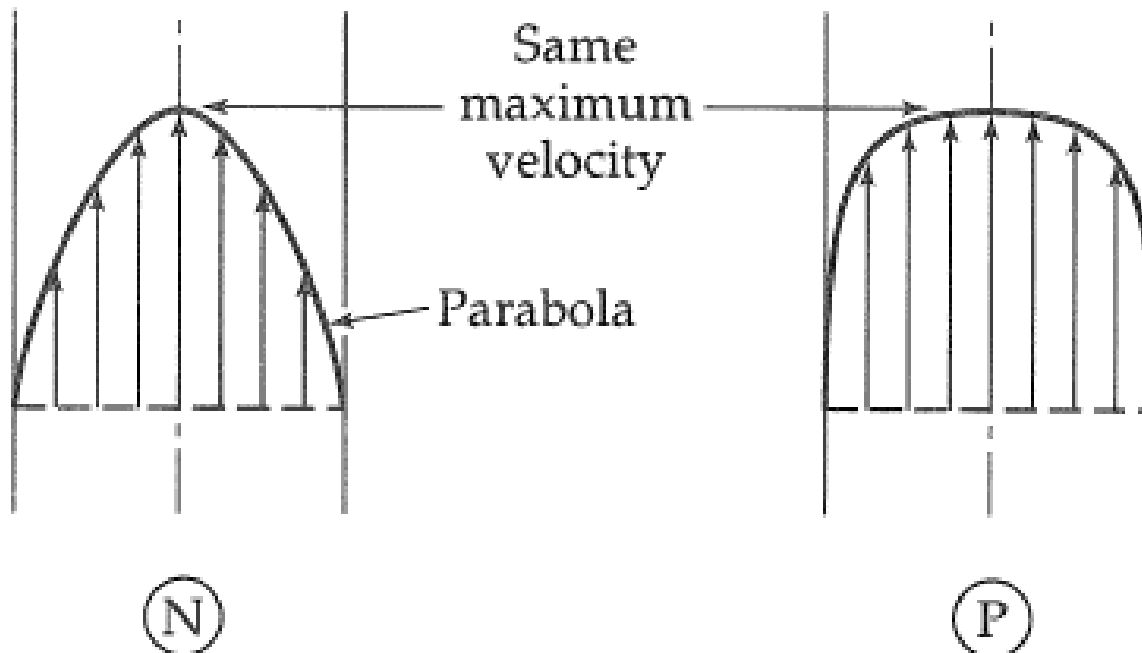


# Chapter 8. Polymeric liquids

- 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

- Laminar flow in a circular tube



# Behaviour of polymeric liquids

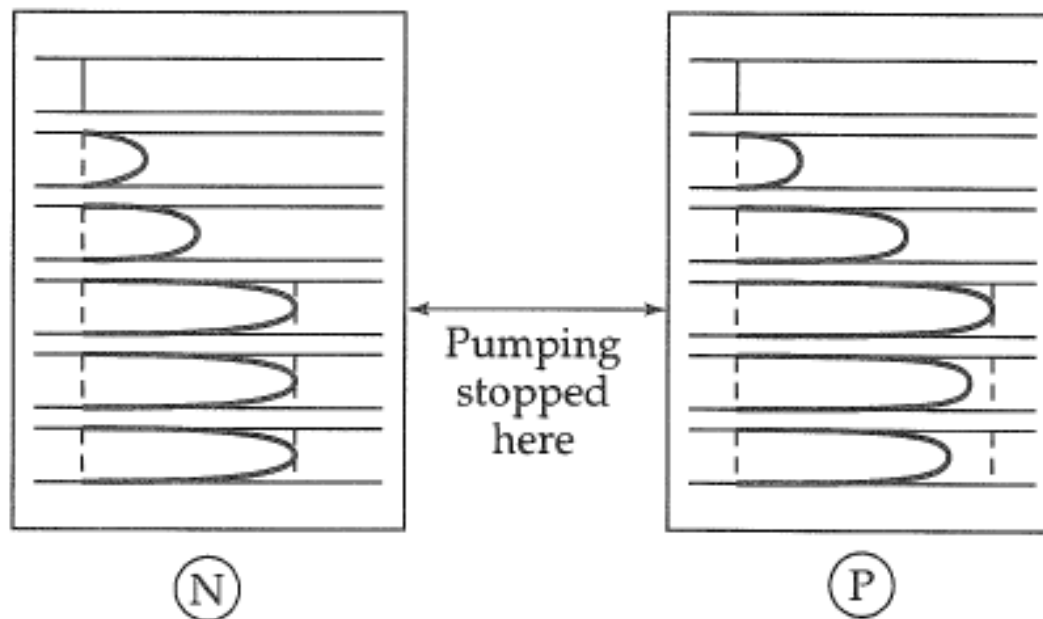
- Remarks:
  - Polymeric liquids

$$\frac{v_z}{v_{z,max}} = 1 - \left(\frac{r}{R}\right)^{1+\frac{1}{n}} \qquad \frac{\langle v_z \rangle}{v_{z,max}} = \frac{\frac{1}{n} + 1}{\frac{1}{n} + 3}$$

- $n=1$  for Newtonian liquids
- Velocity profile of polymeric liquids suggests that viscosity depends on the velocity gradient

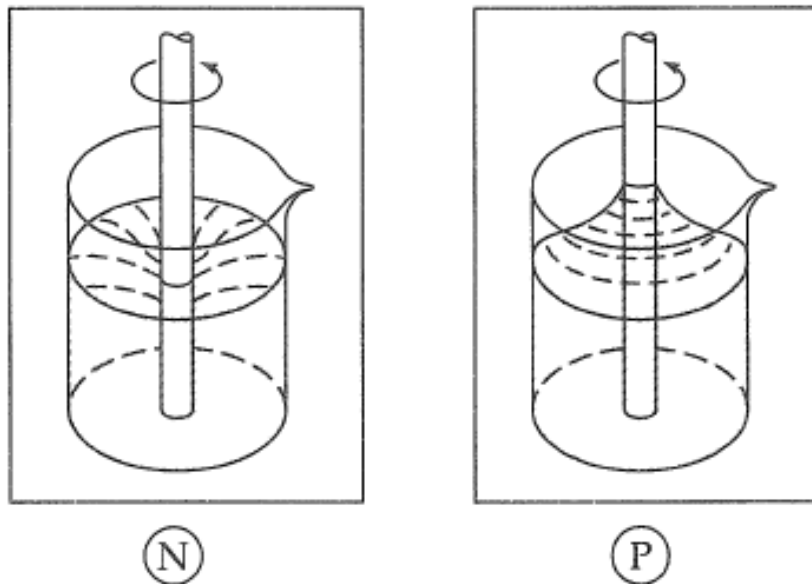
# Behaviour of polymeric liquids

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



# Behaviour of polymeric liquids

- Normal stress effects. Rod climbing effect for polymeric liquids

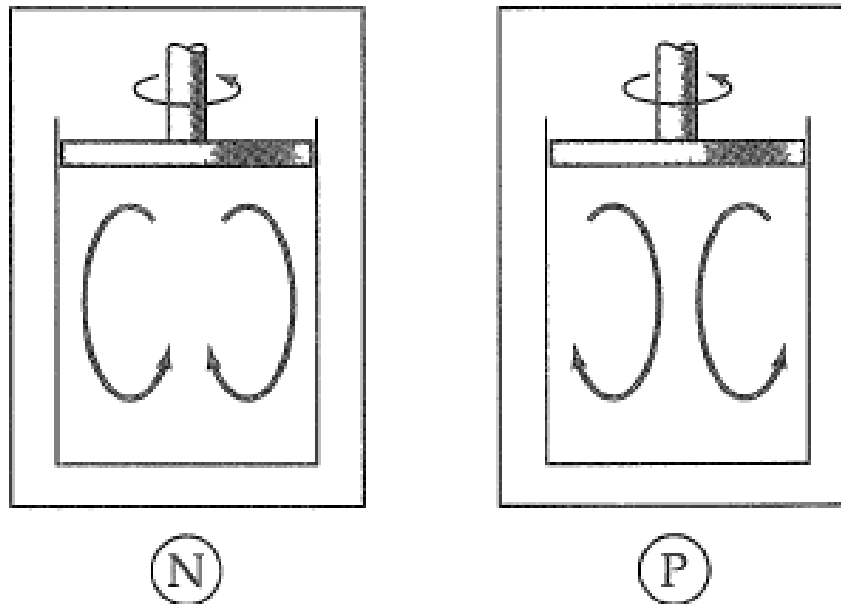


"Transport Phenomena" 2nd ed.,  
R.B. Bird, W.E. Stewart, E.N. Lightfoot

**Fig. 8.1-3.** The free surface of a liquid near a rotating rod. The polymeric liquid shows the Weissenberg rod-climbing effect.

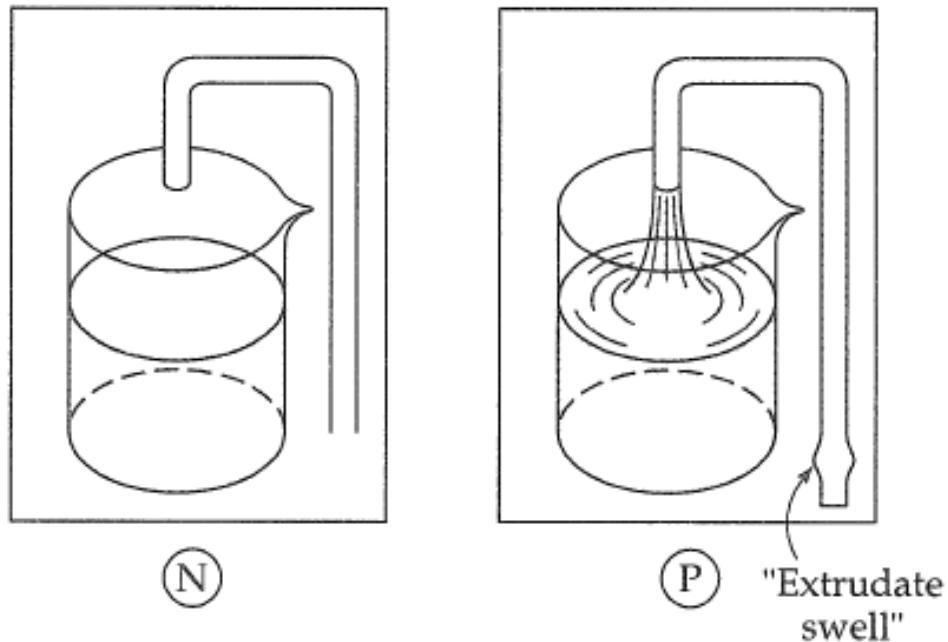
# Behaviour of polymeric liquids

- Normal stress effects. The secondary flows in a cylindrical container



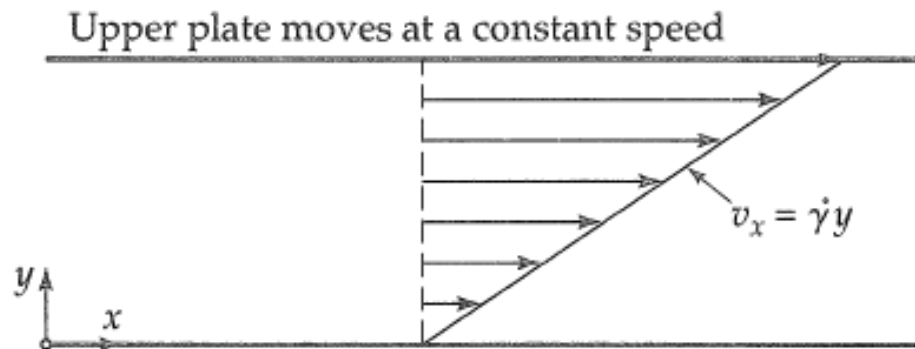
# Behaviour of polymeric liquids

- Siphoning continues to occur when the tube is raised above the surface (tubeless siphon effect)



# Rheometry and Material functions

- Material functions
  - Newtonian fluids: Viscosity
  - Non-Newtonian: several material functions that describe the mechanical response of complex fluids
- 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 shear 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

$$\boldsymbol{\tau} = -\mu(\nabla\mathbf{v} + (\nabla\mathbf{v})^\dagger) \equiv -\mu\dot{\boldsymbol{\gamma}}$$

- For the generalised Newtonian fluid model

$$\boldsymbol{\tau} = -\eta(\nabla\mathbf{v} + (\nabla\mathbf{v})^\dagger) \equiv -\eta\dot{\boldsymbol{\gamma}} \quad \text{with } \eta = \eta(\dot{\boldsymbol{\gamma}})$$

# Empirical Non-Newtonian viscosity function, $\eta$

- Simplest one. Two-parameter power law

$$\eta = m\dot{\gamma}^{n-1}$$

- Four-parameter Carreau equation

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

# 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

$$\tau_{rz} = -m\dot{\gamma}^{n-1} \frac{dv_z}{dr}$$

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

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

- Relation shear stress and pressure difference

$$m \left( -\frac{dv_z}{dr} \right)^n = \left( \frac{\mathcal{P}_0 - \mathcal{P}_L}{2L} \right) r$$

- Integrating with no slip boundary condition

$$v_z = \left( \frac{(\mathcal{P}_0 - \mathcal{P}_L)R}{2mL} \right)^{1/n} \frac{R}{(1/n) + 1} \left[ 1 - \left( \frac{r}{R} \right)^{(1/n)+1} \right]$$

- Mass rate of flow  $w = \frac{\pi R^3 \rho}{(1/n) + 3} \left( \frac{(\mathcal{P}_0 - \mathcal{P}_L)R}{2mL} \right)^{1/n}$

- It simplify to Hagen-Poiseuille for Newtonian fluids when  $n=1$



# Elasticity and the linear viscoelastic models

$$\text{Newton: } \boldsymbol{\tau} = -\mu(\nabla \mathbf{v} + (\nabla \mathbf{v})^\dagger) \equiv -\mu \dot{\boldsymbol{\gamma}}$$

$$\text{Hooke: } \boldsymbol{\tau} = -G(\nabla \mathbf{u} + (\nabla \mathbf{u})^\dagger) \equiv -G \boldsymbol{\gamma}$$

- The Maxwell model

$$\boldsymbol{\tau} + \lambda_1 \frac{\partial}{\partial t} \boldsymbol{\tau} = -\eta_0 \dot{\boldsymbol{\gamma}}$$

- The Jeffreys model

$$\boldsymbol{\tau} + \lambda_1 \frac{\partial}{\partial t} \boldsymbol{\tau} = -\eta_0 \left( \dot{\boldsymbol{\gamma}} + \lambda_2 \frac{\partial}{\partial t} \dot{\boldsymbol{\gamma}} \right)$$

- The Generalized Maxwell model

$$\boldsymbol{\tau}(t) = \sum_{k=1}^{\infty} \boldsymbol{\tau}_k(t) \quad \text{where } \boldsymbol{\tau}_k + \lambda_k \frac{\partial}{\partial t} \boldsymbol{\tau}_k = -\eta_k \dot{\boldsymbol{\gamma}}$$

# The generalized Maxwell model

$$\tau(t) = \sum_{k=1}^{\infty} \tau_k(t) \quad \text{where } \tau_k + \lambda_k \frac{\partial}{\partial t} \tau_k = -\eta_k \dot{\gamma}$$

relaxation times  $\lambda_k$

Empirical expression reduces the number of parameters to 3.

$$\eta_k = \eta_0 \frac{\lambda_k}{\sum_j \lambda_j} \quad \text{and} \quad \lambda_k = \frac{\lambda}{k^\alpha}$$

$$\tau(t) = - \int_{-\infty}^t \left\{ \sum_{k=1}^{\infty} \frac{\eta_k}{\lambda_k} \exp[-(t-t')/\lambda_k] \right\} \dot{\gamma}(t') dt' = - \int_{-\infty}^t G(t-t') \dot{\gamma}(t') dt'$$

Relaxation modulus  
(fading memory)

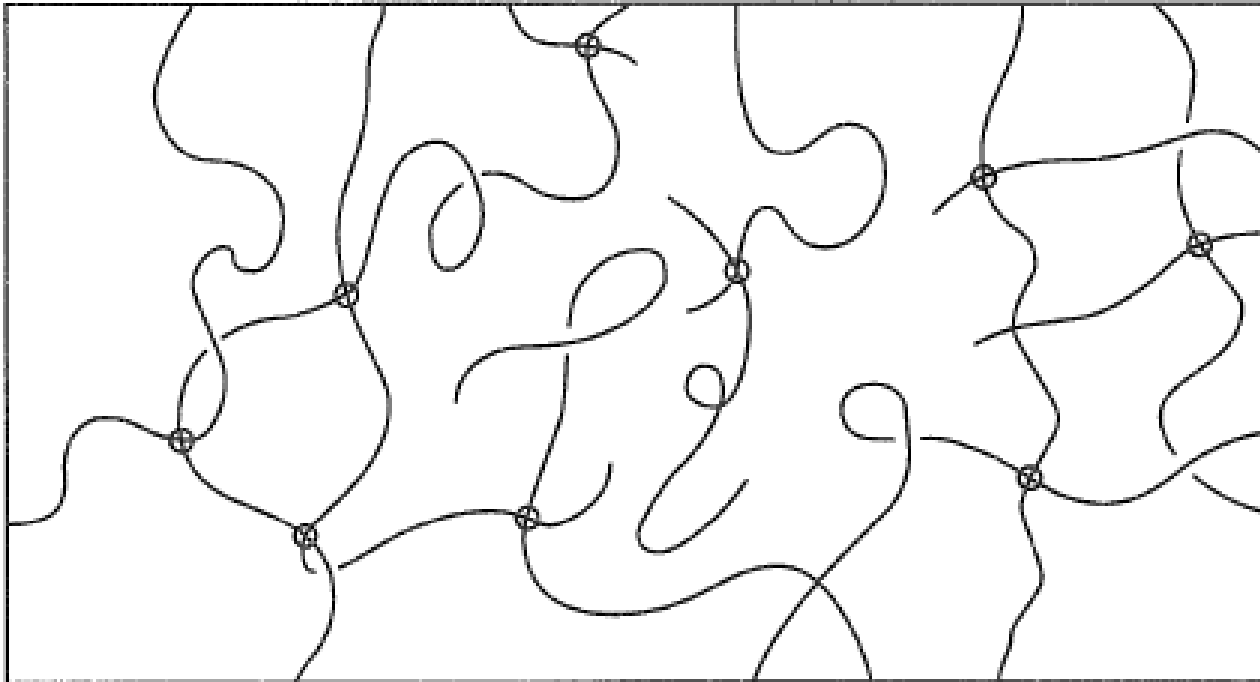
# Molecular theories for polymeric liquids

- Empirical relations require a lot of work.
- Molecular theories can help to formulate models for the polymeric liquids.
- Adjustable constant 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 represent by “bead springs”
- Theory can extent to molten polymers and concentrated solutions

The single-molecule bead spring models.

a) dilute polymer solutions

b) polymer melt without solvent

