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# Abstract

The charged FENE-P dumbbell was developed and used to study the flow behavior of dilute polymer solution. The model is an extended model of the FENE-P model proposed by Peterlin where a non-linear spring was used as a connection between two dumbbell beads. In the charged FENE-P model, repulsive charges were included between the beads so as to incorporate the effect of charge repulsion between ionizable groups on the polymer. Each bead is assigned an effective charge that suits the polymer/solvent/counter-ion system so that correct degree of rest state expansion is obtained. A constitutive equation was derived for this model and was found to be the same as that for the FENE-P model proposed by Peterlin but with a different value for  $Z$ . Viscosity and first normal stress difference were obtained from the constitutive equation. A plot of viscosity was carried out and the results shows that viscosity drops as salinity increase and the onset of shear thinning is shifted to the right

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# 1 Introduction

The important of oil in the world economy cannot be overstated. It has been the mainstay of the world economy. Oil and natural gas combined, provide over half of the worlds energy. Though there have been renewable and sustainable energy initiatives, none of them have been able to contribute a significant amount of energy to the world. As a result, Methods of recovering oil have been a subject of scientific and engineering research for so many years. The application of primary and secondary recovering process (usually water flooding), leaves much oil in the reservoir and indeed in some non-homogeneous reservoir systems, as much as 70 percent of the original oil may still remain in the reservoir [K.S.Sorbie, 1991]. This calls for improved methods which are aimed at recovering some portion of the remaining oil. One of the most promising method of improved oil recovery according to Norwegian Petroleum Directorate on the Norwegian Continental Shelf (NCS), is polymer combined with low salinity water flooding [Directorate, 2017]. This technique involves adding of high molecular weight polymer to the injected water. This leads to increased apparent viscosity of water and thus, improves sweep efficiency and allows more oil to be recovered from the reservoir. The low salinity can help to improve the microscopic sweep and ensure that the required polymer concentration can be decreased with the reduced amount of salt [K.S.Sorbie, 1991]. Polymer liquids are macromolecules which do not obey the law of classical, or Newtonian fluid dynamics. They are non-Newtonian fluids which means that the shear stress and normal stresses cannot be found from simple relations. This complicates the modelling of such fluids. It is known that polymer may lose its high viscosity in salt water. At the present, even advanced polymer models do not take salinity into account.

For Newtonian fluids, the stress tensor has a modest form and can be calculated as long as the viscosity for the fluid is known. For non-Newtonian fluids, it is tough to calculate the stress tensor. It can be generated from constitutive equation which in turn must be derived from non-equilibrium thermodynamics [Bird et al., 1987a]

Industrial problems often involve simple steady state shearing flows. In such flows, the non-Newtonian viscosity is one of the most important characteristics of the fluid. Multiple correlations for this quantity have been proposed and more or less effectively employed [Stavland et al., 2013]. such generalized Newtonian fluid models are able to describe the relationship between pressure drop and volume flow rate of this fluid, but fail to explain the dynamics of non-Newtonian fluids in cases when the viscoelasticity of the fluid plays a crucial role. this includes time-dependent flows and flows in complex geometries, including porous media. The tensorial nature of the constitutive equations has been generally overlooked at least in application for many decades.

Nonlinear differential and integral models [Bird et al., 1987a], which are designed to describe arbitrary flow fields, are of great interest for non-Newtonian fluid dynamics. The most successful of these models are those that have atleast some basis in molecular dynamics [Bird et al., 1987b]. Important examples include the FENE-P dumbbell model for diluted polymer solution [Bird et al., 1980], the FENE-CR model for Boger fluids [Chilcott and Rallison, 1988], and the Phan-Thien-Tanner model for concentrated polymer solutions and polymer melts [Phan-Thien and Tanner, 1977]. The FENE-P dumbbell fluid model is one of the most appropriate for describing the polymer solutions used in EOR procedure [Wever et al., 2011].

## 1.1 Objective of Study

This Study is aimed at modeling a charged dumbbell model of diluted polymer solutions that can be used to describe flows in complex geometries and account for the impact of salinity. In this work, the polymer is represented by generalization of the nonlinear dumbbell model. In addition to the nonlinear spring, repulsive charges are included between the beads in an attempt to incorporate the effects of charge repulsion between ionizable groups on the polymer chain. Each bead is assigned an effective charge,  $q$ , that suits the polymer/solvent/counter-ion system so that the correct degree of rest state expansion is obtained. At the end of this work, a constitutive equation will be derived for this model that can be used to describe flow taking salinity into consideration.



## 2 Fluid Dynamics

Fluid flows conforms to the conservation laws for mass, momentum, and energy. These laws can be stated in differential form, applicable at a point. They can also be stated in the integral form, applicable to an extended region. [P.K.Kandu and I.R.Cohen, 1990]. In the integral form, the expression of the laws depend on whether they relate to a volume fixed in space, or to a material volume which consist of the same fluid particles and whose bounding surface moves with the fluid.

### 2.1 Conservation of Mass

Let us consider a volume fixed in space as in the figure below

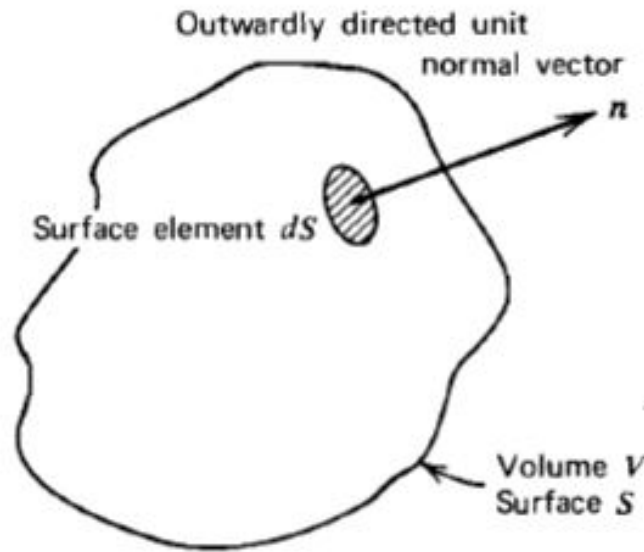


Figure 1: Control Volume Fixed in Space [Bird et al., 1987a]

where  $(\mathbf{n} \cdot \mathbf{v}) dS$  represents local volume flow out and

$(\mathbf{n} \cdot \rho \mathbf{v}) dS$  local mass flow rate out

Then

$$\frac{d}{dt} \int_V \rho dV = - \int_S (\mathbf{n} \cdot \rho \mathbf{v}) dS \quad (2.1)$$

Using Gauss' divergence theorem the surface integral is transform into a volume integral

$$\frac{d}{dt} \int_V \rho dV = - \int_V (\nabla \cdot \rho \mathbf{v}) dV \quad (2.2)$$

Rearranging the equation by bringing the time derivative inside the integral yields

$$\int_V \left[ \frac{\partial \rho}{\partial t} + (\nabla \cdot \mathbf{v}) \right] dV = 0 \quad (2.3)$$

$V$  is arbitrary, hence

$$\frac{\partial \rho}{\partial t} + (\nabla \cdot \rho \mathbf{v}) = 0 \quad (2.4)$$

Equation 2.4 is called the equation of Continuity

If  $\rho$ , is constant, then,

$$\nabla \cdot \mathbf{v} = 0 \quad (2.5)$$

In cartesian coordinate system, it can be represented as

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} = 0 \quad (2.6)$$

## 2.2 Conservation of Momentum

Considering the figure 1 above,

$(\mathbf{n} \cdot \mathbf{v}) dS$  represents local volume flow rate out

$(\mathbf{n} \cdot \mathbf{v}) \rho \mathbf{v} dS$  represents local momentum flux out due to macroscopic motion of the fluid

$$(\mathbf{n} \cdot \mathbf{v}) \rho \mathbf{v} dS = [\mathbf{n} \cdot \rho \mathbf{v} \mathbf{v}] dS$$

There is also momentum transport by molecular process

$[\mathbf{n} \cdot \boldsymbol{\pi}] dS$  represents local momentum flux out due to microscopic transport processes.

Here,  $\pi_{ij}$  is the flux of positive  $j$  momentum in  $i$  positive direction

Then,

$$\frac{d}{dt} \int_V \rho \mathbf{v} dV = - \int_S [\mathbf{n} \cdot \rho \mathbf{v} \mathbf{v}] dS - \int_S [\mathbf{n} \cdot \boldsymbol{\pi}] dS + \int_V \rho \mathbf{g} dV \quad (2.7)$$

where  $\mathbf{g}$  is the force per unit mass due to gravity. Using Gauss' divergence theorem the surface integral is transform into a volume integral

$$\frac{d}{dt} \int_V \rho \mathbf{v} dV = - \int_V [\nabla \cdot \rho \mathbf{v} \mathbf{v}] dV - \int_V [\nabla \cdot \boldsymbol{\pi}] dV + \int_V \rho \mathbf{g} dV \quad (2.8)$$

Rearranging the equation by bringing the time derivative inside the integral yields

$$\int_V \left[ \frac{\partial}{\partial t}(\rho \mathbf{v}) + [\nabla \cdot \rho \mathbf{v} \mathbf{v}] + [\nabla \cdot \boldsymbol{\pi}] - \rho \mathbf{g} \right] dV = 0 \quad (2.9)$$

$V$  is arbitrary,

$$\frac{\partial}{\partial t}(\rho \mathbf{v}) = -[\nabla \cdot \rho \mathbf{v} \mathbf{v}] - [\nabla \cdot \boldsymbol{\pi}] + \rho \mathbf{g} \quad (2.10)$$

Equation 2.10 is the momentum equation (Newton's second law)

The component  $\pi_{ij}$  is the stress acting in the positive  $j$ -direction on a surface perpendicular to the  $i$  direction

Surface force term has the form,  $-\int_S \boldsymbol{\pi}_n dS$  where the vector  $\boldsymbol{\pi}_n dS$  is a vector describing the force exerted by the fluid on the negative side of  $dS$  onto the fluid on the positive side of  $dS$

$$\text{We get, } - \int_S \boldsymbol{\pi}_n dS = - \int_S [\mathbf{n} \cdot \boldsymbol{\pi}] dS$$

Therefore,  $\boldsymbol{\pi}_n = [\mathbf{n} \cdot \boldsymbol{\pi}]$ : force exerted by a fluid on a surface.

Then,  $\pi_{ij} =$  (force per unit area) acting in positive  $j$ - direction onto a surface perpendicular to the  $i$ - direction.

$-\int [\mathbf{n} \cdot \boldsymbol{\pi}] dS$ : force of fluid outside  $V$  acting on the fluid inside  $V$  across  $S$ .

$\pi_{ij}$  is called the total stress tensor of the fluid. It is decomposed as follows

$$\boldsymbol{\pi} = p\boldsymbol{\delta} + \boldsymbol{\tau} \quad (2.11)$$

$\tau$  is called the anisotropic stress tensor. It vanishes at equilibrium i.e when there is no flow.  $p$  is the thermodynamical pressure [Bird et al., 1987a]

An equation specifying  $\tau$  is called constitutive equation of the fluid.

The constitutive equation for Newtonian fluids (experimentally established) [Bird et al., 1987a]

$$\tau = -\mu \left[ (\nabla \cdot \mathbf{v}) + (\nabla \mathbf{v})^T \right] + \left( \frac{2}{3}\mu - X \right) (\nabla \cdot \mathbf{v}) \delta \quad (2.12)$$

where  $\mu$  is the coefficient of viscosity

$X$  is the second, or dilational, or Bulk viscosity

For incompressible liquids,  $(\nabla \cdot \mathbf{v}) = 0$  and equation 2.11 becomes

$$\tau = -\mu \left[ (\nabla \cdot \mathbf{v}) + (\nabla \mathbf{v})^T \right] = \mu \dot{\gamma} \quad (2.13)$$

$\dot{\gamma}$  is called the rate of strain or Strain rate tensor

### 2.3 Wall/Pressure-driven Flow between Parallel Plates

Considering a pressure driven flow between parallel plates as shown in the figure below [Alexandrou, 2001]

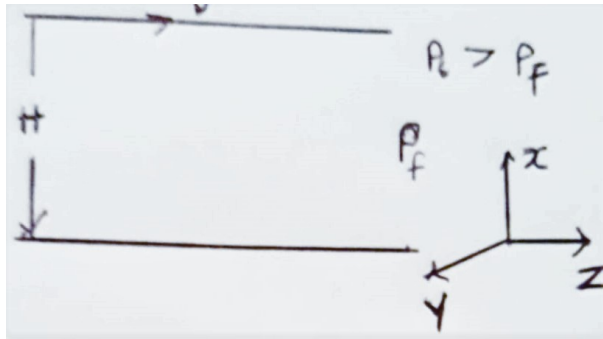


Figure 2: Pressure Driven Flow Between Parallel Plates

Laminar Planar Flow:

$$\mathbf{v} = (0, 0, v_z); \quad \frac{\partial}{\partial y} = 0 \quad (2.14)$$

Steady State:  $\frac{\partial}{\partial t} = 0$

From the equation of continuity,  $(\nabla \cdot \mathbf{v}) = 0$

$$\frac{\partial \mathbf{v}_x}{\partial x} = \frac{\partial \mathbf{v}_y}{\partial y} = 0$$

Therefore,

$$\frac{\partial \mathbf{v}_z}{\partial z} = 0, \quad \mathbf{v}_z = z(x) \quad (2.15)$$

Then

$$\dot{\gamma} = (\nabla \mathbf{v}) + (\nabla \mathbf{v})^T = \frac{d\mathbf{v}_z}{dx} \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}$$

Constitutive equation:

$$\tau = -\mu \frac{d\mathbf{v}_z}{dx} \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}$$

Therefore,  $\tau_{xz} = \tau_{zx} = -\mu \frac{d\mathbf{v}_z}{dx}$  all the rest are zeros

Momentum Equations:

$$-\frac{\partial}{\partial z} \tau_{xz} - \frac{\partial p}{\partial x} = 0; \quad \frac{\partial p}{\partial x} = 0 \quad \implies p = p(z) \quad (2.16)$$

$$-\frac{\partial p}{\partial y} = 0 \quad (2.17)$$

$$-\frac{\partial \tau_{xz}}{\partial x} - \frac{dp}{dz} = 0 \quad (2.18)$$

The first part of equation 2.17 is a function of  $x$  while the second part is independent of  $x$ . They are both considered as constants, we therefore have

$$\frac{dp}{dz} = \frac{p_f - p_i}{L} = -\mathcal{P} \quad (2.19)$$

where  $\mathcal{P}$  is a constant called pressure gradient

$$\frac{\partial \tau_{xz}}{\partial x} = \mathcal{P} \implies \tau_{xz} = \mathcal{P}x + A_1 \quad (2.20)$$

where  $A_1$  is a constant of integration

Therefore,

$$-\mu \frac{dv_z}{dx} = \mathcal{P}x + A_1 \quad (2.21)$$

$$\frac{dv_z}{dx} = -\frac{\mathcal{P}}{\mu}x + A_1 \quad (2.22)$$

$$v_z(x) = -\frac{\mathcal{P}}{2\mu}x^2 + A_1 \cdot x + A_2 \quad (2.23)$$

Applying boundary conditions:

$$v_z(0) = 0 \implies A_2 = 0$$

$$v_z(H) = v \implies A_1 = \frac{1}{H} \left[ v + \frac{\mathcal{P}}{2\mu}H^2 \right] = \frac{v}{H} + \frac{\mathcal{P}H}{2\mu}.$$

Therefore,

$$v_z(x) = \frac{\mathcal{P}}{2\mu} [Hx - x^2] + \frac{v_z}{H}x \quad (2.24)$$

If  $\mathcal{P} = 0$ ,  $\implies v_z(x) = \frac{v}{H}x$  linear velocity profile

if  $\mathbf{v} = 0$ ,  $\implies \mathbf{v}_z(x) = \frac{\mathcal{P}}{2\mu} [Hx - x^2]$  symmetric parabolic profile

Maximal velocity at  $\mathbf{v} = \frac{H}{2}$ :

$$\mathbf{v}_{max} = \mathbf{v}_z \left( \frac{H}{2} \right) = \frac{\mathcal{P}H^2}{8\mu} \quad (2.25)$$

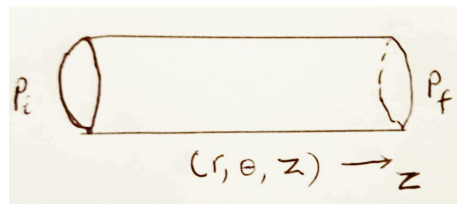
Average flow velocity:

$$\langle \mathbf{v} \rangle = \frac{1}{H} \int_0^H \mathbf{v}_z(x) dx = \frac{1}{H} \cdot \frac{\mathcal{P}}{2\mu} \left[ \frac{Hx^2}{2} \Big|_0^H - \frac{x^3}{3} \Big|_0^H \right] = \frac{\mathcal{P}H^2}{12\mu} \quad (2.26)$$

$$\langle \mathbf{v} \rangle = \frac{2}{3} \mathbf{v}_{max} \quad (2.27)$$

## 2.4 Poiseuille Flow: Laminar Steady-State Pressure Driven Flow in a Straight Circular Tube

For a flow through a straight circular tube,



[Alexandrou, 2001]

Figure 3: Pressure Driven Flow in a Straight Circular Tube

$$\mathbf{v} = (0, 0, \mathbf{v}_z)$$

$$\frac{\partial}{\partial \theta} = 0, \quad \frac{\partial}{\partial t} = 0$$

Continuity:

$$\frac{\partial \mathbf{v}_Z}{\partial z} = 0 \implies \mathbf{v}_Z = \mathbf{v}_Z(r) \quad (2.28)$$

Then,

$$\dot{\gamma} = (\nabla \mathbf{v}) + (\nabla \mathbf{v})^T = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix} \frac{dv_Z}{dr}$$

$$\tau = -\mu \frac{d\mathbf{v}_Z}{dr} \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}$$

$$\tau_{rz} = \tau_{zr} = -\mu \frac{dv_Z}{dr} \quad \text{the rest are 0}$$

Momentum Equations

$$-\frac{\partial}{\partial z} \tau_{rz} - \frac{\partial p}{\partial r} = 0 \implies \frac{\partial p}{\partial r} = 0 \quad (2.29)$$

$$-\frac{1}{r} \frac{\partial}{\partial r} (r \tau_{rz}) - \frac{\partial p}{\partial z} = 0 \quad (2.30)$$

The first part of equation 2.30 is a function of  $r$  while the second part is independent of  $r$ . therefore,  $p = p(z)$

Again,

$$-\frac{dp}{dz} = \mathcal{P} \implies \text{pressure gradient} \quad (2.31)$$

$$\frac{1}{r} \frac{d}{dr} [r \tau_{rz}] = \mathcal{P} \quad (2.32)$$

integrating equation 2.32 with respect to  $r$  yields

$$r \tau_{rz} = \frac{1}{2} \mathcal{P} r^2 + A_1 \quad (2.33)$$



where  $A_1$  is integration constant

$$\tau_{rz} = \frac{1}{2}\mathcal{P}r + \frac{A_1}{r} \quad (2.34)$$

no infinite stresses at  $r = 0 \implies A_1 = 0$

$$\tau_{rz} = \frac{1}{2}\mathcal{P}r \quad (2.35)$$

Therefore,

$$-\mu \frac{d\mathbf{v}_z}{dr} = \frac{1}{2}\mathcal{P}r \quad (2.36)$$

$$\frac{d\mathbf{v}_z}{dr} = -\frac{\mathcal{P}r}{2\mu} \quad (2.37)$$

Integrating equation 2.37 wrt  $r$  yields,

$$\mathbf{v}_z(r) = -\frac{\mathcal{P}r^2}{4\mu} + A_2 \quad (2.38)$$

$$\mathbf{v}_z(R) = 0 \implies \mathbf{v}_z(r) = \frac{\mathcal{P}}{4\mu} [R^2 - r^2] \quad (2.39)$$

Volume flow rate:

$$\begin{aligned} Q &= \int_0^R 2\pi r \mathbf{v}_z(r) dr = \frac{2\pi\mathcal{P}}{4\mu} \int_0^R (R^2 r - r^3) dr \\ &= \frac{\pi\mathcal{P}}{2\mu} \left[ \frac{R^4}{2} - \frac{R^4}{4} \right] = \frac{\pi R^4 \mathcal{P}}{8\mu} \end{aligned} \quad (2.40)$$

Equation 2.40 is the famous result of Hagen and poiseuille [Alexandrou, 2001][P.K.Kandu and I.R.Cohen, 19

If the cross sectional area of the tube is  $A = \pi R^2$  then the average flow velocity is given as

$$\langle \mathbf{v} \rangle = \frac{Q}{A} = \frac{\mathcal{P}R^2}{8\mu} \quad (2.41)$$

$$\mathbf{v}_{max} = 2 \langle \mathbf{v} \rangle \quad (2.42)$$

From equation 2.41,

$$Q = \frac{R^2}{8} \cdot \frac{A \cdot \mathcal{P}}{\mu} = K \cdot \frac{A \cdot \mathcal{P}}{\mu} \quad (2.43)$$

The viscosity of a Newtonian fluid can be determined knowing the measurement of  $Q$  and  $\mathcal{P}$ .

Its been found experimentally that for slow flows of Newtonian fluids, (in sandpacks originally) [Alexandrou, 2001][Batchelor, 1967]

$$Q = K \frac{A\mathcal{P}}{\mu} : \quad \text{Darcy's Law} \quad (2.44)$$

$K$  is a constant of the medium called permeability

For non-Newtonian fluids, the apparent or effective viscosity is defined as

$$\eta = K \frac{A\mathcal{P}}{Q} \quad (2.45)$$

### 3 Polymer

A polymer is a large molecule which are made up of small sample chemical units. These chemical units are also called structural units. In some polymer, each structural unit is connected to two other units forming a chain structure called a linear macromolecule or polymer while in other polymers, most structural units are connected to two or more other units forming a branched macromolecules. the figure below shows the representation of a linear and branched macromolecules respectively [Bird et al., 1987a].

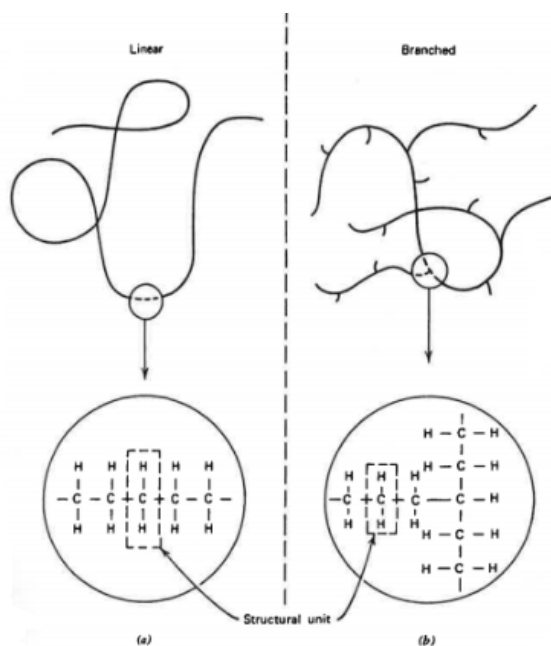


Figure 4: Symbolic Representations of Linear and Branched Polymer Molecules [Bird et al., 1987a]

Polymers can be distinguished into two different types, namely synthetic and natural (biological) polymers.

Synthetic polymers are built from a single structural unit can be referred to as homopolymer. Example of these are polyethylene, polyvinylchloride e.t.c. Polymer built from two or more different structural units are called copolymer.

Biological polymers contains a large number of different structural units in contrast to synthetic polymer. Examples of biological macromolecules are viruses, DNA molecules, protein, xanthan gum.

The molecular weight of a macromolecule is the product of the molecular weight of a structural unit and the number of structural units in the molecule. A polymer sample in which the molecular weight of all the macromolecules is the same is called monodisperse. In contrast, when they contains of many different weights, it is referred to as polydisperse.

Considering a polydisperse macromolecular sample compound of a number of monodisperse functions, the number average molecular weight is given as

$$\bar{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i} \quad (3.1)$$

The weight average molecular weight is given as

$$\bar{M}_w = \frac{\sum_i w_i M_i}{\sum_i w_i} = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \quad (3.2)$$

Where  $w_i = N_i M_i$

For monodisperse samples, these averages are equal ( $\bar{M}_n = \bar{M}_w$ ). But for Polydisperse samples,  $\bar{M}_n < \bar{M}_w$ . The ratio of the weight average molecular weight to the number average molecular weight is called heterogeneity index. [Bird et al., 1987a]

### 3.1 Polymer Rheology

Rheology invented by Professor Eugene Bingham in the 1920's was defined as the study of deformation and flow behavior in various materials. Examples of such materials are asphalt, lubricants, paints, plastics and rubber.[Staudinger, 1920]

### 3.2 Shear Viscosity

The viscosity of a fluid is defined as the measure of its resistance to flow when shear force is applied. Newton's law of viscosity states that the stress between adjacent fluid layers is proportional to the velocity gradient or shear rate between the two layers. The constant of proportionality of the ratio of the shear stress to the shear rate at a given temperature and pressure is called viscosity or apparent viscosity. The SI unit of viscosity is Pascal-Second ( $P \cdot s$ ). Expressed mathematically, [H.A.Barnes et al., 1989]

$$\tau = \eta \dot{\gamma} \quad (3.3)$$

where  $\tau$  is the shear stress

$\eta$  is the viscosity

$\dot{\gamma}$  is the shear rate

### 3.2.1 Factors that affects Viscosity of a Material

A lot of factors affects the viscosity of a fluid. Some of these factors are

1. Shear Rate
2. Temperature Variation
3. Pressure Variation

#### Shear Rate

Fluid will behave differently when shear is applied. Most fluids are dependent on the shear rate. For a Newtonian fluid the viscosity is constant as a function of shear rate. For non-Newtonian fluid, some fluid like polymer solution decreases in viscosity when shear rate increases while some other display the opposite behavior as their viscosity increases as shear rate increases.

#### Temperature variation

Temperature is one factor that also affects viscosity of liquid. The viscosity of Newtonian liquid decreases with increase in temperature. This can be express according to Arrhenius relationship as

$$\eta = Ae^{\frac{B}{T}} \quad (3.4)$$

Where T is the absolute temperature and A and B are constants of the liquid.

#### Pressure Variation

Pressure also affects the viscosity of a liquid. The viscosity of a liquid increases exponentially with isotropic pressure. Water is the only exception when it is below  $30^{\circ}C$ .

### 3.3 Newtonian Fluids

A fluid is a substance that deforms continuously when acted upon by a shearing stress of any magnitude. Most low molecular weight substances such as organic and inorganic liquids exhibit Newtonian flow characteristics. That is at constant temperature and pressure in simple shear, the shear stress ( $\tau$ ) is directly proportional to the velocity gradient. Fluids like water and oil that exhibit this characteristics are called Newtonian fluids. It can be expressed mathematically as

$$\tau_{ij} = \eta \left( \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) \quad (3.5)$$

where

$\tau_{ij}$  is the shear stress

$\eta$  is the viscosity

$\left(\frac{\partial v_1}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right)$  is the velocity gradient [Batchelor, 1967]

Newtonian behavior at constant temperature and pressure has the following characteristics

1. The only stress guaranteed in simple shear flow is the shear stress  $\tau$ , the two normal stress difference are zero.
2. The shear viscosity does not vary with velocity gradient or shear rate.
3. The viscosity is constant with respect to the time of shearing and the stress in the liquid falls to zero immediately the shearing is stopped.
4. The viscosities measured in different type of deformation are always in simple proportion to one another.

Fluids showing any iota of deviation from this is termed non-Newtonian Fluid. Non-Newtonian fluids are fluids in which the relationship between shear stress and shear rate is not constant. The viscosity of non-Newtonian fluids often changes as the shear rate is varied

One important characteristics of polymer liquids is that they display shear rate dependent or non-Newtonian viscosity. Various experiments were performed to illustrate this property. In one of the experiments, two tubes are filled with fluids, one Newtonian and the other polymeric fluid. they are chosen in such a way as to have low viscosity at very low shear rate.

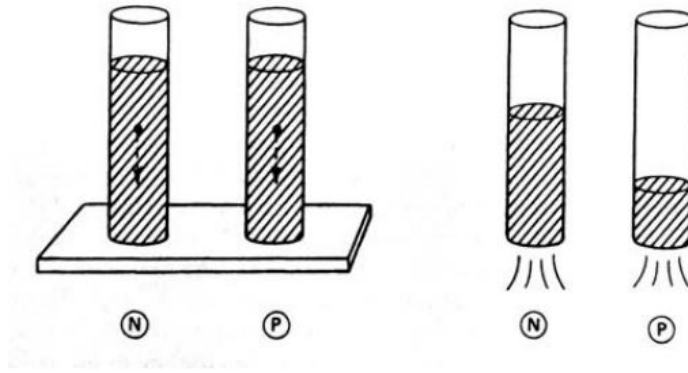


Figure 5: Tube flow and Shear Thinning [Bird et al., 1987a]

As shown in figure 5 above, it was observed that when the plate is removed from the bottom of the tubes and the fluid are allowed to flow out by gravity, the polymer fluid drain faster than the Newtonian fluid. This shows that the polymer liquid has a lower viscosity in high shear rate. This decrease in viscosity is referred to as shear thinning. [Bird et al., 1987a]

Another experiment that shows contrasting behavior between polymeric fluids and Newtonian fluids is the rod climbing experiment. This is shown in the figure below

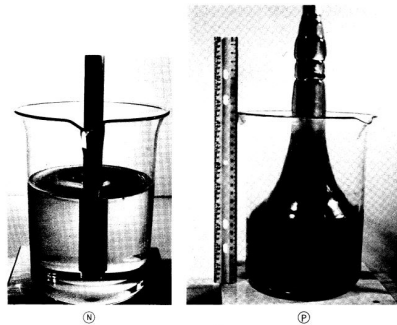


Figure 6: Rod Climbing Experiment [Bird et al., 1987a]

In this experiment, rotating rods are inserted into two beakers, each containing Newtonian and polymeric fluids. It is observed that the Newtonian liquid near the rotating rod is pushed outward by centrifugal force and there is a dip in the surface of the liquid near the rod. In contrast, in polymeric liquids, the polymer moves in the opposite direction towards the center of the beaker and climb up the rod. This effect is as a result of the elasticity in the fluid which generates a normal stress acting upwards, hence causing the fluid to climb. [Bird et al., 1987a][Weissenberg, 1947]

Another contrasting behavior between the duo can be observed in a typical syphoning experiment as shown in the figure below. [Bird et al., 1987a]

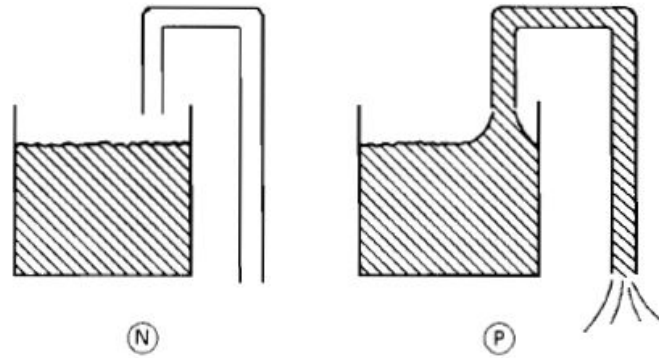


Figure 7: The Tubeless Siphon

For a Newtonian fluid when the tube is lifted up out of the fluid in the container, the flow immediately stops. But in the case of the polymeric fluid, the liquid continues to flow up and through the siphon.

There are several types of non-Newtonian flow behavior characterized by the way a fluid's viscosity change in response to variation in shear rate. The different behavior shown are

1. Shear Thinning Behavior
2. Shear Thickening Behavior
3. Bingham Plastic Behavior
4. Viscoplastic Behavior

### 3.3.1 Shear Thinning behavior

This is the behavior exhibits by a fluid or liquid when an increase in shear stress leads to decrease in shear rate. The shear thinning behavior is time independent. This kind of fluid contain components that can deform and rearrange to accommodate the flow. Examples of fluids that exhibit this kind of behavior are polymer solution, micelles, blood, detergent slurries e.t.c

### 3.3.2 Shear Thickening Behavior

In shear thickening behaviour, the fluid contains components that cannot deform or rearrange to accommodate flow. As the flow and deformation rate increases, they kind of become stuck or jammed together and not able to rearrange quickly enough to accommodate the flow leading to increase in viscosity. Examples of these are particle suspensions, corn starch in water.



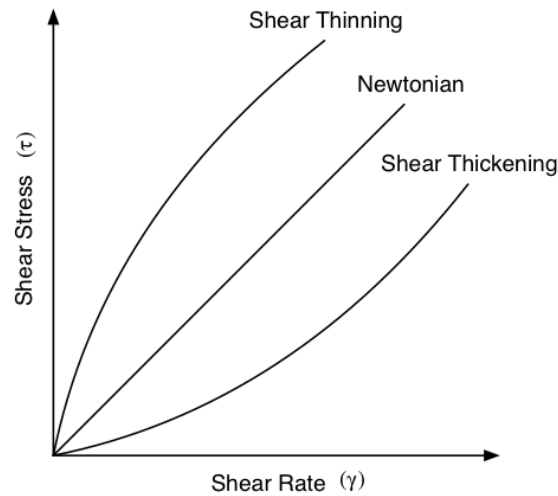


Figure 8: Shear Thinning and Thickening Behavior [Evans, 1998]

### 3.3.3 Bingham Plastic behavior

This type of non-Newtonian behavior is characterized by the existence of a threshold stress (called yield stress) which must be exceeded for flow to be initiated. Below this yield point, a flow can not be initiated. Examples of fluids that exhibit this kind of behavior are tooth paste, drilling mud, mayonnaise e.t.c. The figures below show graphical representation of this kind of behavior

### 3.3.4 Viscoplastic Behavior

This is another kind of behavior displays by non-Newtonian fluids. this behaviour is similar to the Bingham plastic but shows shear thinning behavior at stress levels exceeding yield point. The figure below shows graphically viscoplastic non-Newtonian behavior

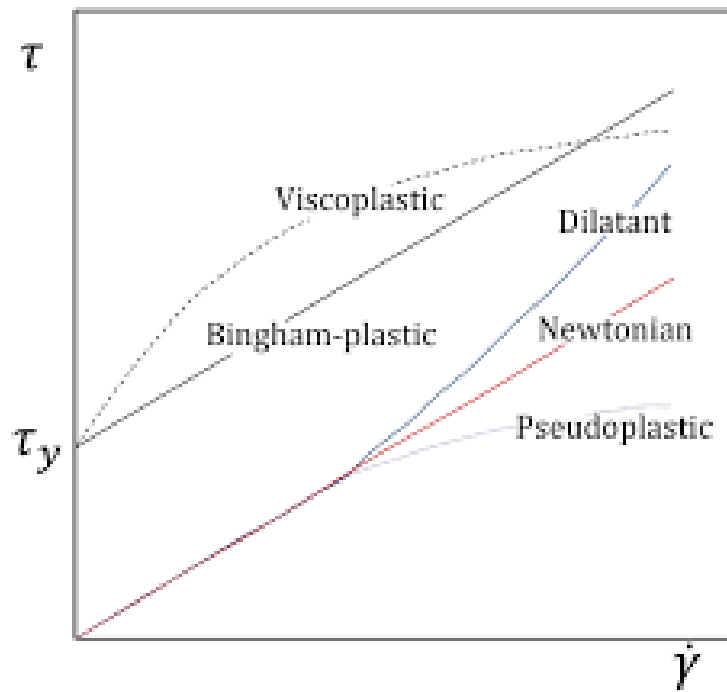


Figure 9: Bingham Plastic and ViscoPlastic Behavior [Evans, 1998]

### 3.4 Material Functions for Polymeric Liquids

Experiment on a Newtonian fluid yields a single material constant. This constant is called viscosity. Experiments performed on polymeric liquid produces a host of material function that depends on shear rate, frequency, time etc. Fluids can be classified by these material functions and they also help to determine constants in non-Newtonian constitutive equation. [Bird et al., 1987a]

There are two standard kind of flow patterns used in characterizing polymeric liquids. they are shear and shear free flow.

#### 3.4.1 Shear Flow

The velocity for a simple shear flow is given by:

$$v_x = \dot{\gamma}_{yx}y$$

$$v_y = v_z = 0$$

Here the velocity gradient which can be a function of time  $\dot{\gamma}$  is called the shear rate. It is independent of time for steady shear flow. This kind of flow is found in polymer processing operations like injection molding and extrusion. [Bird et al., 1987a]

### 3.4.2 Shearfree Flow

The velocity field for a simple shear free flow are given as:

$$v_x = -\frac{1}{2}\dot{\epsilon}(1+b)x$$

$$v_y = -\frac{1}{2}\dot{\epsilon}(1-b)y$$

$$v_z = +\dot{\epsilon}z$$

if  $b = 0$  and  $\dot{\epsilon} > 0$ , we have elongational or extensional flow

$b = 0$  and  $\dot{\epsilon} < 0$ , we have a biaxial stretching flow

$b = 1$ , we have a planar elongational flow.

Shearfree flow are found in many polymer processing operations for example, film blowing, vacuum thermoforming, fibre spinning [Bird et al., 1987a]

### 3.4.3 Stress Tensor for Shear Flow

For Newtonian liquids, only the shear stress  $\tau_{yx}$  is non zero in the shear flow. In non-Newtonian flow, it is assumed that all four independent components of the stress tensor may be non zero. The total stress tensor for a simple shearing flow is

$$\boldsymbol{\pi} = p\boldsymbol{\delta} + \boldsymbol{\tau} = \begin{pmatrix} p + \tau_{xx} & \tau_{yx} & 0 \\ \tau_{yx} & p + \tau_{yy} & 0 \\ 0 & 0 & p + \tau_{zz} \end{pmatrix}$$

The important quantities in these are:

$$\tau_{yx} \quad \implies \text{Shear Stress}$$

$$\tau_{xx} - \tau_{yy} \quad \implies \text{First Normal Stress Difference (FNSD)}$$

$$\tau_{yy} - \tau_{zz} \quad \implies \text{Second Normal Stress Difference (SNSD)}$$

### 3.4.4 Stress Tensor for Shear Free Flows

For shearfree flow, the stress tensor is given as:

$$\boldsymbol{\pi} = P\boldsymbol{\delta} + \boldsymbol{\tau} = \begin{pmatrix} p + \tau_{xx} & 0 & 0 \\ 0 & p + \tau_{yy} & 0 \\ 0 & 0 & p + \tau_{zz} \end{pmatrix}$$

For incompressible flow, only two normal stress difference are of importance.

$$\tau_{zz} - \tau_{xx}$$

$$\tau_{yy} - \tau_{xx}$$

For elongational and biaxial flow,  $b = 0$

therefore  $\tau_{xx} - \tau_{yy} = 0$  which have only one normal stress to be determined.

### 3.4.5 Steady Shear Flow Material Function

The relevant material functions for non-Newtonian liquids can be expressed in the form below:

$$\tau_{yx} = -\eta(\dot{\gamma})\dot{\gamma}_{yx}$$

$$\tau_{xx} - \tau_{yy} = -\psi_1(\dot{\gamma})\dot{\gamma}_{yx}^2$$

$$\tau_{yy} - \tau_{zz} = -\psi_2(\dot{\gamma})\dot{\gamma}_{yx}^2$$

where  $\eta$  is the non-Newtonian viscosity,  $\psi_1$  and  $\psi_2$  are the first and second normal stress coefficients.  $\eta$ ,  $\psi_1$  and  $\psi_2$  can be referred to as viscometric function. For any viscometric flow, the three viscometric function completely describe the rheological behavior of a fluid. [Bird et al., 1987a]

Typical Behavior of the First Normal Stress Coefficient (FNCS)

- qualitative dynamic similar to  $\eta\dot{\gamma}$
- rate of decline of  $\psi$  is higher
- $\psi_1 > 0$
- $\psi_1 \rightarrow \psi_{1,0}$  at  $\dot{\gamma} \rightarrow \infty$

Typical Behavior of the Second Normal Stress Coefficient (SNCS)

- $\psi_2 < 0$
- $|\psi_2| \ll |\psi_1|$  but not zero although can mostly be neglected [Bird et al., 1987a]

### 3.4.6 Unsteady Shear Flow Material Function

#### 1. Small Amplitude Oscillatory Shear Flow,

Here,

$$\dot{\gamma}_{yx} = \dot{\gamma}^0 \cos \omega t \quad (3.6)$$

where  $\dot{\gamma}^0$  is so small that  $\tau_{yx}$  is linear in  $\dot{\gamma}$

$$\tau_{yx} = \eta'(\omega)\dot{\gamma}^0 \cos \omega t - \eta''(\omega)\dot{\gamma}^0 \sin \omega t \quad (3.7)$$

$$\tau_{yy} - \tau_{xx} = \psi_1^0 - \psi_1' \dot{\gamma}_0^2 \cos 2\omega t - \psi_1'' \dot{\gamma}_0^2 \sin 2\omega t \quad (3.8)$$

here  $\psi_1$  are all function of  $\omega$

For newtonian fluid,  $\tau_{yx}$  is in phase with  $\dot{\gamma}_{yx}$ . There are no normal stress difference as ( $\psi_1^0 = \psi_1' = \psi_1'' = 0$ ).

$$\tau_{yx} = -\mu \dot{\gamma}_0 \cos \omega t$$

For polymers,  $\tau_{yx}$  oscillates with  $\omega$  but not in phase with  $\dot{\gamma}_{yx}$ . The normal stresses oscillate with frequency  $2\omega$  about a non zero mean value.

#### 2. Stress Growth at Sudden Inception of Shear Flow

In sudden growth experiment, fluid sample are assumed to be at rest. it means at  $t = 0$ , the velocity gradient  $\dot{\gamma}_{xy} = 0$  and when  $t > 0$  the velocity gradient  $\dot{\gamma}_{xy} = \dot{\gamma}_0$ .

The material function for stress growth at sudden inception of shear flow are  $\eta^+(\dot{\gamma}_0, t)$ ,  $\psi_1^+(\dot{\gamma}_0, t)$ ,  $\psi_2^+(\dot{\gamma}_0, t)$ . They are defined in analogously to  $\eta$ ,  $\psi_1$  and  $\psi_2$  to describe the transient shear stress and normal stress difference. The plus sign superscript emphasis that a steady shear rate is applied for positive times [Bird et al., 1987a]

#### 3. Sudden Cessation of Simple Shear Flow Here the motion of fluid that is undergoing steady shear flow with shear rate $\dot{\gamma}_0$ is suddenly stopped at $t = 0$ so that $\dot{\gamma} = 0$ at $t \geq 0$ . The decay of the steady shear flow stresses to zero is observed. The relaxing stresses can be described by the stress relaxation material function $\eta^-(t, \dot{\gamma}_0)$ , $\psi_1^-(t, \dot{\gamma}_0)$ , $\psi_2^-(t, \dot{\gamma}_0)$ which are used in similar way as the viscometric function. The superscript minus sign is a reminder that the steady

shear flow occurred for negative times [Bird et al., 1987a]

### 3.5 Generalized Newtonian Fluid Model

Generalized Newtonian fluid is a fluid for which the shear stress is a function of shear rate at a particular time. The generalized Newtonian fluid does not describe normal stress difference, time dependent phenomena and it applies only to shear stress in steady shear flow. The generalized Newton fluid model that are generally used are Power law model . It has been used by engineers to solve specific flow and and heat transfer problems. [Bird et al., 1987a][H.A.Barnes et al., 1989]

#### 3.5.1 Power Law Model

The Power law model is a type of generalized Newtonian fluid model for which shear stress  $\tau$  is given as [Bird et al., 1987a]

$$\tau = m\dot{\gamma}^n \quad (3.9)$$

where

$m$  is the consistency

$\dot{\gamma}$  is the shear rate measured in per second

$n$  is the behavior index

The power law model can also be expressed as:

$$\eta(\dot{\gamma}) = m\dot{\gamma}^{n-1} \quad (3.10)$$

where  $\eta$  represents apparent or effective viscosity as a function of shear rate. When

$n = 1, \quad m = \mu \quad \implies$  Newtonian

$n < 1, \quad \implies$  shear thinning

$n > 1, \quad \implies$  Shear thickening

The power law has a limitation as it does not as it does not describe the portion of viscosity curve where  $\dot{\gamma} = 0$  and where  $\eta = \eta_0$ .

#### 3.5.2 Carreau-yasuda Model

Carreau fluid model is a type of generalized Newtonian fluid model where viscosity ( $\eta$ ) depends upon shear rate  $\dot{\gamma}$  by the following equation [Bird et al., 1987a][Carreau, 1968]

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = [1 + (\lambda\dot{\gamma})^a]^{\frac{n-1}{a}} \quad (3.11)$$

where

$\eta_0 =$  viscosity at zero shear rate

$\eta_\infty =$  viscosity at infinite shear rate

$\lambda =$  relaxation time

$n =$  power index

At low shear rate ( $\dot{\gamma} \ll \frac{1}{\lambda}$ ) Carreau fluid behaves like Newtonian fluid and at high shear rate ( $\dot{\gamma} \gg \frac{1}{\lambda}$ ) as power law fluid. [Bird et al., 1987a]

### 3.6 Non-linear Viscosity Constitutive Equations

Constitutive equations or rheological equation of state are equations that relates stress and deformation variables. An example of constitutive equation for Newton's viscous liquid is

$$\tau = \eta \dot{\gamma} \quad (3.12)$$

For some decades now, several constitutive equations have been proposed for polymeric fluids. Among the surviving ones which have been proposed for time- dependent flows are

#### 1. The Oldroyd 8 -Constant Model

This model was proposed by Oldroyd in 1958. It is an empirical expression that is linear in the stress tensor, but contains allowable terms quadratic in velocity gradient and all allowable products of stresses and velocity gradients. it has be renowned for developing the numeric techniques for Non-Newtonian fluid dynamicssince it can give qualitatively correct results in a wide variety of flow situations, The constitutive equation is

$$\tau + \lambda_1 \tau_{(1)} + \frac{1}{2} \lambda_3 \{ \dot{\gamma} \cdot \tau + \tau \cdot \dot{\gamma} \} + \frac{1}{2} \lambda_5 (tr \tau) \dot{\gamma} + \frac{1}{2} \lambda_6 (\tau \cdot \dot{\gamma}) \delta = -\eta_0 [\dot{\gamma} + \lambda_2 \dot{\gamma}_{(1)} + \lambda_4 \{ \dot{\gamma} \cdot \dot{\gamma} \} + \frac{1}{2} \lambda_7 (\dot{\gamma} : \dot{\gamma}) \delta] \quad (3.13)$$

Where  $\dot{\gamma} = \nabla V + (\nabla V)^T$  is the rate of deformation tensor.  $\delta$  is the unit tensor. The subscript (1) indicates the first contravariant time derivative defined for a second ordered tensor  $\Lambda$  as follows

$$\Lambda_{(1)} = \frac{\delta \Lambda}{\delta t} + \{ \bar{V} \cdot \nabla \Lambda \} - \{ \nabla V^T \cdot \Lambda \} - \{ \Lambda \cdot \nabla V \} \quad (3.14)$$



The eight constants are the zero-shear rate viscosity  $\eta_0$  and the time constant ( $\lambda_1, \dots, \lambda_7$ ). The model was renowned for numerical calculations because of Boger fluids. Quinzani et al. (1990) after careful rheological measurements has asked that the model be deemphasized as the Boger fluids are more complicated than the oldroyd B [Bird and Wiest, 1995]

## 2. The Giesekus Model

Giesekus developed a 3 constant model ( $\eta_0, \lambda_1, \alpha$ ) that is non linear based on molecular ideas. This model describes the power law regions for viscosity and normal- stress coefficients. It also gives concise description of elongational viscosity and the complex viscosity. The constitutive equation for this model is

$$\tau + \lambda_1 \tau_{(1)} - (\alpha \lambda_1 / \eta_0) \{\tau \cdot \tau\} = \eta_0 \dot{\gamma} \quad (3.15)$$

Bird & Wiest (1985) have given an alternative explanation of the Giesekus model and Wiest & Bird (1986) have studied the model further; they got the constitutive equation as the result of a mean-field theory that uses Hookean dumbbells as a model for the constituent polymers. Wiest (1989a) developed an extension of the model by using nonHookean springs; his model has been used by Iyengar & Co (1993) for studying film casting. [Bird and Wiest, 1995]

## 3. The Phan-Thien-tanner Model

The [Phan-Thien and Tanner, 1977] and [Phan-Thien, 1978] four-constant Model was derived from a network theory of polymer melts. This model is non-linear in stress. The constitutive equation for this model is given as

$$Y \tau + \lambda \tau_{(1)} + \frac{1}{\lambda} \varepsilon \lambda \{\dot{\gamma} \cdot \tau + \tau \cdot \dot{\gamma}\} = \eta_0 \dot{\gamma} \quad (3.16)$$

where Y is a function of the trace of the stress tensor.

$$Y = \exp[-\varepsilon(\frac{\lambda}{\eta_0})tr\tau] \approx 1 - \varepsilon(\frac{\lambda}{\eta_0})tr\tau \quad (3.17)$$

The second relation in equation 3.17 is valid for small  $tr\tau$  and it make the constitutive equation easier to use [Bird and Wiest, 1995].

## 4. The FENE (Finitely Extensible Non-linear Elastic) Dumbbell Model

The Fene dumbbell model constitutive equation results from a kinetic theory derivation. The polymer molecules is idealized as non elastic dumbbell in a diluted solution, where the solvent in this case is a Newtonian fluid with viscosity  $\eta_0$  and n represents the number of dumbbell per unit volume. This leads, after making the Peterlin approximation (in the expression for

the stress tensor the average of a ratio is replaced by the ratio of the averages), to

$$\tau = \eta_s \dot{\gamma} + \tau_p \quad (3.18)$$

where  $\tau_p$  is given as:

$$Z\tau_p + \lambda_H \tau_p^{(1)} - \lambda_H \left( \tau_p - \frac{b}{b+2} nKT\delta \right) \frac{D \ln Z}{Dt} = \left( \frac{b}{b+2} \right) nKT \lambda_H \dot{\gamma} \quad (3.19)$$

$\lambda_H$  is a time constant and  $Z$  is a function of the trace of the polymer contribution to the stress tensor

$$Z = 1 + \frac{3}{b} \left( \frac{b}{b+2} - \frac{tr \tau_p}{3nKT} \right) \quad (3.20)$$

The parameter  $b$  is a measure of the potential energy in the spring relative to the thermal energy. The Hookean dumbbell is obtained when  $b$  is infinite. This model is found useful because it allows for the possibility of describing the polymer stretching and orientation in various flow system. [Bird and Wiest, 1995][Peterlin, 1966]

## 4 Stress tesor of the Dumbbell model

In modelling of polymer solution, the polymer molecule is idealized as an elastic dumbbell with two identical beads of mass  $m$ . The two beads are connected by an elastic spring with a connector force  $F_c$  and a connector vector  $Q$  as shown in the figure below. The connector vector describes the overall orientation and internal configuration of the polymer. [Bird et al., 1987b]

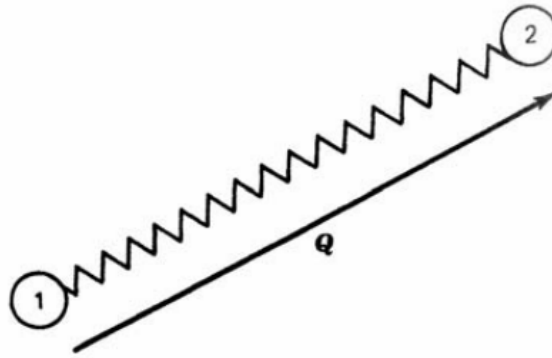


Figure 10: Dumbbells Connected to A Spring [Bird et al., 1987b]

In the dumbbell model, the following assumptions are made:

- The polymer solution is diluted
  - The solvent is a Newtonian fluid of viscosity  $\eta_s$
  - The velocity gradient does not change drastically at the distances of order of the polymer molecule size
1. Hydrodynamic drag force: This is the force of resistance, (Stokes-like) acting on the beads as they move through the solution. The force is taken to be proportional to the difference between the average bead velocity and the mass average velocity of the solution
  2. Brownian force: This is force acting on the beads due to thermal fluctuations in the liquid
  3. The Connector/Intra molecular force: This is the force acting in a bead which results from the spring in the dumbbell and it is presented as negative gradient of the potential energy of the spring
  4. External force: Apart from the forces mentioned above, another force that acts on the beads are external forces. Example of these kind of forces are electrical forces, gravitational force.

## 4.1 kramers' Approach

The total stress tensor of a dilute solution of dumbbell is given as

$$1. \boldsymbol{\pi} = p\boldsymbol{\delta} + \boldsymbol{\tau} = p\boldsymbol{\delta} + \boldsymbol{\tau}_s + \boldsymbol{\tau}_p = \boldsymbol{\pi}_s + \boldsymbol{\pi}_p$$

where,

$\boldsymbol{\tau}_s$  is tensor from the solvent

$\boldsymbol{\tau}_p$  is tensor from the polymer

$$\boldsymbol{\tau}_s = -\mu\dot{\boldsymbol{\gamma}} : \text{Newtonian}$$

where,

$\dot{\boldsymbol{\gamma}}$  is the rate of strain tensor and  $\boldsymbol{\delta}$  is the unit tensor

$$2. \boldsymbol{\pi}_p = \boldsymbol{\pi}_p^{(c)} + \boldsymbol{\pi}_p^{(e)} + \boldsymbol{\pi}_p^{(b)}$$

Where,

$\boldsymbol{\pi}_p^{(c)}$  is contribution from the connector

$\boldsymbol{\pi}_p^{(e)}$  is the contribution from external sources

$\boldsymbol{\pi}_p^{(b)}$  is the contribution from the beads

### 4.1.1 Contribution from the Connector

$$\boldsymbol{\pi}_p^{(c)} = -n \cdot \langle \mathbf{Q}\mathbf{F}_c \rangle \quad (4.1)$$

[Bird et al., 1987b]

where,

$$\mathbf{F}_c = F_c \frac{\mathbf{Q}}{Q}$$

$n = \text{Concentration}$

$F_c = \text{connector force}$

This contribution is symmetric

$\langle X \rangle$  is the phase space average of X

$$\langle X \rangle = \int X \psi(Q, t) dQ$$

$$\int \psi(\bar{Q}, t) dQ = 1$$

$\psi$  = normalized configuration distribution function [Bird et al., 1987b]

#### 4.1.2 Contribution from External Forces

The following is the contribution from external forces

$$\pi_p^{(e)} = \frac{n}{2} \langle \mathbf{Q}(\mathbf{F}_2^{(e)} - \mathbf{F}_1^{(e)}) \rangle \quad (4.2)$$

This contribution is not necessarily symmetric and its zero if there are no forces or if the same force acts on the bead

#### 4.1.3 Contribution from the Bead motion

The contribution from the bead motion assuming maxwellian velocity distribution is given as

$$\pi_p^{(b)} = 2nkT\delta \quad (4.3)$$

Combining the contributions from the solvent and polymer, one gets the stress tensor of a diluted solution of dumbbell without maxwellian velocity distribution as follows:

$$\pi = \pi_s = n \langle \mathbf{QF}_c \rangle + \frac{n}{2} \langle \mathbf{F}_2^{(e)} - \mathbf{F}_1^{(e)} \rangle + 2nkT\delta \quad (4.4)$$

Now there is need to get a similar equation for  $\tau$

By combining the equation of continuity for  $\psi$  and the equation of motion for  $\bar{Q}$ , it is possible to get an equation of change for  $\langle X \rangle$

In particular, for  $X \leftrightarrow QQ$

$$\frac{d}{dt} \langle \mathbf{Q}\mathbf{Q} \rangle - \{ \nabla \mathbf{V}^T \cdot \langle \mathbf{Q}\mathbf{Q} \rangle \} - \{ \langle \mathbf{Q}\mathbf{Q} \rangle \cdot \nabla \mathbf{V} \} = \frac{4}{\zeta} kT \boldsymbol{\delta} - \frac{4}{\zeta} \langle \mathbf{Q}\mathbf{F}_c \rangle \quad (4.5)$$

$\zeta$  = Hydrodynamic drag coefficient or

$$\langle \mathbf{Q}\mathbf{Q} \rangle_{(1)} = \frac{4}{\zeta} kT \boldsymbol{\delta} - \frac{4}{\zeta} \langle \mathbf{Q}\mathbf{F}_c \rangle$$

(1) is a short cut to oldroyd derivative

$$\boldsymbol{\Lambda}_{(1)} = \frac{\partial \boldsymbol{\Lambda}}{\partial t} + \{ \bar{\mathbf{v}} \cdot \nabla \boldsymbol{\Lambda} \} - \{ \nabla \mathbf{V}^T \cdot \boldsymbol{\Lambda} \} - \{ \boldsymbol{\Lambda} \cdot \nabla \mathbf{V} \} \quad (4.6)$$

In equilibrium or when there is no flow,

$$\langle \mathbf{Q}\mathbf{F}_c \rangle_{eq} = kT \boldsymbol{\delta}$$

$$P \boldsymbol{\delta} = P_s \boldsymbol{\delta} - nkT \boldsymbol{\delta} + 2nkT \boldsymbol{\delta} = P_s \boldsymbol{\delta} + nkT \boldsymbol{\delta} \quad (4.7)$$

Therefore,

$$\boldsymbol{\tau} = -\eta_s \dot{\boldsymbol{\gamma}} - n \langle \mathbf{Q}\mathbf{F}_c \rangle + nkT \boldsymbol{\delta} \quad \text{Kramer's form for the stress tensor}$$

$$\boldsymbol{\tau} = -\eta_s \dot{\boldsymbol{\gamma}} + \frac{n\zeta}{4} \langle \mathbf{Q}\mathbf{Q} \rangle_{(1)} \quad \text{Giesekus form for the stress tensor}$$

These forms can be used to obtain the following

- Constitutive Equation
- Viscometric functions
- Analytical solution for simple flows

## 4.2 Hookean Dumbbell

In the Hookean dumbbell model, the connecting spring is said to be linear elastic or Hookean. The connecting force is given as  $F_{(c)} = HQ$  [Bird et al., 1987b] where  $H$  is the spring constant.

The polymer contribution to the stress tensor for this model is given as

$$\boldsymbol{\tau}_p = -nH \langle \mathbf{Q}\mathbf{Q} \rangle + nkT\boldsymbol{\delta} \quad (4.8)$$

for Kramer's

$$\boldsymbol{\tau}_p = +\frac{n\zeta}{4} \langle \mathbf{Q}\mathbf{Q} \rangle_{(1)} \quad (4.9)$$

for Giesekus

To solve these equations, we need to get rid of the averages

Multiplying through (4.8) by  $\frac{\zeta}{4H}$  gives

$$\frac{\zeta}{4H} \boldsymbol{\tau}_p = -\frac{n\zeta}{4} \langle \mathbf{Q}\mathbf{Q} \rangle + \frac{nkT}{4H} \zeta \boldsymbol{\delta} \quad (4.10)$$

But,  $\lambda = \frac{\zeta}{4H}$  where  $\lambda$  is the time constant for the Hookean dumbbells

Equation 4.10 becomes,

$$\frac{n\zeta}{4} \langle \mathbf{Q}\mathbf{Q} \rangle = \lambda \boldsymbol{\tau}_p + nkT\lambda \boldsymbol{\delta} \quad (4.11)$$

Taking the oldroyd derivative of equation 4.11 yields,

$$\frac{n\zeta}{4} \langle \mathbf{Q}\mathbf{Q} \rangle_{(1)} = -\lambda \boldsymbol{\tau}_{p(1)} + nkT\lambda \boldsymbol{\delta}_{(1)} = -\lambda \boldsymbol{\tau}_{p(1)} + nkT\lambda \dot{\boldsymbol{\gamma}} \quad (4.12)$$

Substituting equation 4.12 into equation 4.9, we have

$$\boldsymbol{\tau}_p + \lambda \boldsymbol{\tau}_{p(1)} = nkT\lambda \dot{\boldsymbol{\gamma}} \quad (4.13)$$

Equation 4.13 is the rheological equation of state known as the constitutive equation for Hookean Dumbbell Model.

### 4.2.1 The Material Function For Steady Shear Flow

For steady shear flow between parallel plates,

$$\mathbf{v}_x = \dot{\gamma}y, \mathbf{v}_y = \mathbf{v}_z = 0$$

$$\boldsymbol{\tau}_p = \begin{bmatrix} \tau_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{xy} & \tau_{yy} & \tau_{yz} \\ \tau_{xz} & \tau_{yz} & \tau_{zz} \end{bmatrix} \quad (4.14)$$

$$\dot{\boldsymbol{\gamma}} = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \dot{\gamma} \quad (4.15)$$

$$\boldsymbol{\nabla} \mathbf{v} = (\partial_1 \mathbf{v}_j) = \left[ \frac{\partial \mathbf{v}_x}{\partial y} \equiv \partial_2 \mathbf{v}_1 \neq 0 \right] = \begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \dot{\gamma} \quad (4.16)$$

Applying transpose to equation 4.16 yields

$$\boldsymbol{\nabla} \mathbf{v}^T = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \dot{\gamma} \quad (4.17)$$

For steady shear flow,  $\boldsymbol{\tau}_{p(1)} : \frac{\partial}{\partial t} = 0$

$$\mathbf{v} \cdot \boldsymbol{\nabla} = \mathbf{v}_x \partial_x + \mathbf{v}_y \partial_y + \mathbf{v}_z \partial_z$$



For this case,  $\mathbf{v}_x \partial_x \cdot$ ,

$$\mathbf{v}_x \partial_x \tau_{\mathbf{p}} = 0$$

$$-\{\nabla \mathbf{V}^T \cdot \tau_{\mathbf{p}}\} = \begin{bmatrix} \tau_{xy} & \tau_{yy} & \tau_{yz} \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \dot{\gamma} \quad (4.18)$$

Applying transpose to equation 4,18 yields

$$-\{\tau_{\mathbf{p}} \cdot \nabla \mathbf{v}\} = \begin{bmatrix} \tau_{xy} & 0 & 0 \\ \tau_{yy} & 0 & 0 \\ \tau_{yz} & 0 & 0 \end{bmatrix} \dot{\gamma} \quad (4.19)$$

substituting equation 4.14-4.19 into the Hookean dumbbell constitutive equation yields

$$\begin{bmatrix} \tau_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{xy} & \tau_{yy} & \tau_{yz} \\ \tau_{xz} & \tau_{yz} & \tau_{zz} \end{bmatrix} + \lambda \begin{bmatrix} -2\tau_{xy} & \tau_{yy} & \tau_{yz} \\ -\tau_{yy} & 0 & 0 \\ -\tau_{yz} & 0 & 0 \end{bmatrix} \dot{\gamma} = -nkT\lambda \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \dot{\gamma} \quad (4.20)$$

from equation 4.20, the following below are extracted

$$\tau_{yy} = \tau_{yz} = \tau_{zz} = 0 \quad (4.21)$$

$$\tau_{xz} - \lambda\tau_{yz}\dot{\gamma} = 0 \quad (4.22)$$

$$\tau_{xx} - 2\lambda\tau_{xy}\dot{\gamma} = 0 \quad (4.23)$$

$$\tau_{xy} = -nkT\lambda\dot{\gamma} \quad (4.24)$$

From equation 4.23 and 4.24,

$$\tau_{xy} = -nkT\lambda\dot{\gamma} \quad (4.25)$$

$$\tau_{xx} = -2nkT\lambda^2\dot{\gamma}^2 \quad (4.26)$$

Dividing equation 4.25 by  $\dot{\gamma}$  and 4.26 by  $\dot{\gamma}^2$  yields

$$\eta(\dot{\gamma}) = -\frac{\tau_{xy}}{\dot{\gamma}} = nkT\lambda \quad (4.27)$$

$$\psi(\dot{\gamma}) = -\frac{\tau_{xx}}{\dot{\gamma}^2} = 2nkT\lambda^2 \quad (4.28)$$

$$\psi_2 = 0 \quad (4.29)$$

The Hookean dumbbell model does give us something non-Newtonian but its still not realistic. This is because the assumption on the connector force that is Hookean is too weak because it can be expanded without bound. This is the reason the Fene-P finitely extensible is introduced.

### 4.3 Fene-P Dumbbell Model

The name Fene stands for finitely elongated non linear elastic and the P stands for the closure proposed by Peterlin. It takes the dumbbell version of the Fene Model and assumed the peterline statistical closure for the restoring force. [Bird et al., 1987b][Peterlin, 1966]

To derive a constitutive equation for the stress tensor, one must specify the connector force. The finitely elongated non-linear elastic (FENE) spring obeys the Warner's law (Bird et al; 1980). At small extension, the spring is nearly Hookean, when further extended, it becomes strongly non-linear. The connector force grows rapidly, so that the spring cannot be stretched beyond some maximal length.

Introducing a non-linear force

$$F_c = \frac{HQ}{1 - \left(\frac{Q}{Q_0}\right)^2}$$

For kramer's,

$$\tau_p = -nH \left\langle \frac{QQ}{1 - \frac{Q^2}{Q_0^2}} \right\rangle + nkT\delta \quad (4.30)$$

For Giesekus,

$$\tau_p = \frac{n\zeta}{4} \langle QQ \rangle_{(1)} \quad (4.31)$$

A pre -averaging (closure) is need as it is not possible to solve without knowing  $\psi$

Peterlin's Closure :

$$\left\langle \frac{QQ}{1 - \frac{Q^2}{Q_0^2}} \right\rangle = \frac{\langle QQ \rangle}{1 - \left\langle \frac{Q^2}{Q_0^2} \right\rangle} + (\varepsilon Q_0^2 \delta) \quad (4.32)$$

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. [Bird et al., 1987b][Peterlin, 1966]

$$\text{Introducing } \lambda = \frac{\zeta}{4H}, \quad b = \frac{HQ_0^2}{kT}$$

Kramer's :

$$\tau_p = -nH \frac{\langle QQ \rangle}{1 - \left\langle \frac{Q^2}{Q_0^2} \right\rangle} - nH\varepsilon Q_0^2 \delta + nkT\delta \quad (4.33)$$

This is same as,

$$= -nH \frac{\langle QQ \rangle}{1 - \left\langle \frac{Q^2}{Q_0^2} \right\rangle} + (1 - \varepsilon b)nkT\delta \quad (4.34)$$

Taking the trace of equation 4.34 yields,

$$\text{tr}\tau_p = -nH \frac{\langle Q^2 \rangle}{1 - \langle \frac{Q^2}{Q_0^2} \rangle} + (1 - \varepsilon b)nkT \cdot 3 \quad (4.35)$$

Let  $x = \langle \frac{Q^2}{Q_0^2} \rangle$

Equation 4.35 becomes

$$\text{tr}\tau_p = \frac{nHQ_0^2x}{1-x} + 3(1 - \varepsilon b)nkT \quad (4.36)$$

Solving for x,

$$\frac{nkTb \cdot x}{1-x} = 3(1 - \varepsilon b)nkT - \text{tr}\tau_p \quad (4.37)$$

And equation 4.37 becomes

$$\frac{x}{1-x} = \frac{3}{b} \left( (1 - \varepsilon b) - \frac{\text{tr}\tau_p}{3nkT} \right) = Z - 1$$

Where  $Z = \frac{1}{1-x}$

$1-x = \frac{1}{Z}$  and  $x = 1 - Z^{-1}$

Therefore, equation 4.34 becomes

$$\tau_p = -nHZ \langle \mathbf{Q}\mathbf{Q} \rangle + (1 - \varepsilon b)nkT\delta \quad (4.38)$$

$$\tau_p = -\frac{n\zeta}{4} \langle \mathbf{Q}\mathbf{Q} \rangle_{(1)}$$

which implies that

$$\langle \mathbf{Q}\mathbf{Q} \rangle_{(1)} = -\frac{4\tau_p}{n\zeta} \quad (4.39)$$

Taking the oldroyd derivative of equation 4.38 yields,

$$\tau_{p(1)} = -nH (Z \langle \mathbf{Q}\mathbf{Q} \rangle)_{(1)} - (1 - \varepsilon b)nkT\dot{\gamma} \quad (4.40)$$

taking the material derivative of  $(Z \langle \mathbf{Q}\mathbf{Q} \rangle)_{(1)}$  yields

$$(Z \langle \mathbf{Q}\mathbf{Q} \rangle)_{(1)} = \frac{D}{Dt}(Z \langle \mathbf{Q}\mathbf{Q} \rangle) - \{\nabla v^T \cdot Z \langle \mathbf{Q}\mathbf{Q} \rangle\} - \{Z \langle \mathbf{Q}\mathbf{Q} \rangle \cdot \nabla v\} \quad (4.41)$$

Factorizing the left right side of equation 4.41 yields

$$\frac{D}{Dt}(Z \langle \mathbf{Q}\mathbf{Q} \rangle) - Z \{ \{ \nabla v^T \cdot \langle \mathbf{Q}\mathbf{Q} \rangle \} + \{ \langle \mathbf{Q}\mathbf{Q} \rangle \cdot \nabla v \} \} = \quad (4.42)$$

further derivative of the first term of equation 4.22 yields

$$\frac{DZ}{Dt} \langle \mathbf{Q}\mathbf{Q} \rangle + Z \frac{D \langle \mathbf{Q}\mathbf{Q} \rangle}{Dt} - Z \{ \{ \nabla v^T \cdot \langle \mathbf{Q}\mathbf{Q} \rangle \} + \{ \langle \mathbf{Q}\mathbf{Q} \rangle \cdot \nabla v \} \} \quad (4.43)$$

The first two terms of equation 4.43 is rewritten and applying equation 4.39 yields

$$\frac{DZ}{Dt} \langle \mathbf{Q}\mathbf{Q} \rangle + Z \langle \mathbf{Q}\mathbf{Q} \rangle_{(1)} = \frac{DZ}{Dt} \langle \mathbf{Q}\mathbf{Q} \rangle - 4Z \frac{\tau_p}{n\zeta} \quad (4.44)$$

$$\langle \mathbf{Q}\mathbf{Q} \rangle = \frac{1}{nHZ} [-\tau_p + (1 - \varepsilon b)nkT\delta] \quad \text{from Kramer's}$$

$$\tau_p_{(1)} = -nH \left[ \frac{Dz}{Dt} \langle \mathbf{Q}\mathbf{Q} \rangle - z \cdot \frac{4\tau_p}{n\zeta} \right] - (1 - \varepsilon b)nkT\dot{\gamma} \quad (4.45)$$

Multiplying equation 4.45 by  $\lambda$  yields

$$Z\tau_p + \lambda\tau_p_{(1)} + \lambda nH \frac{DZ}{Dt} \langle \mathbf{Q}\mathbf{Q} \rangle = -(1 - \varepsilon b)nkT\lambda\dot{\gamma} \quad (4.46)$$

From equation 4.38,

$$nH \langle \mathbf{Q}\mathbf{Q} \rangle = -\frac{1}{Z} [\tau_p - (1 - \varepsilon b)nkT\delta] \quad (4.47)$$

Substituting equation 4.47 into equation 4.46 yields

$$Z\tau_p + \lambda\tau_p_{(1)} - \lambda [\tau_p - (1 - \varepsilon b)nkT\delta] \frac{D \ln Z}{Dt} = -(1 - \varepsilon b)nkT\lambda\dot{\gamma} \quad (4.48)$$

Equation 4.48 is called 'THE FENE-P CONSTITUTIVE EQUATION

Re-parametrization: [Shogin et al., 2017b][Shogin et al., 2017a]

The reason behind re-parametrization is to make a connection between the original parameter which are  $b$ ,  $\lambda$ ,  $\varepsilon$  to something which can easily define from experiment. Above all, it makes the equation looks nicer.

$$C_1 = \frac{b + 3(1 - \varepsilon b)}{b(1 - \varepsilon b)nkT\lambda} \quad C_2 = \frac{1}{b(1 - \varepsilon b)^2(nkT)^3\lambda} \quad C_3 = \frac{2}{(1 - \varepsilon b)nkT}$$

Divide equation 4.48 by  $(1 - \varepsilon b)nkT\lambda$ , yields

$$Z\boldsymbol{\tau}_p + \frac{C_3}{2}\boldsymbol{\tau}_p^{(1)} - \left\{ \frac{1}{2}C_3\boldsymbol{\tau}_p - \boldsymbol{\delta} \right\} \frac{D \ln z}{Dt} = -\dot{\gamma} \quad (4.49)$$

where the new  $Z = C_1 - \frac{2C_2}{C_3}tr(\boldsymbol{\tau}_p)$

### 4.3.1 Steady Shear Flow Material Functions for Fene-P

$$\mathbf{v}_x = \dot{\gamma}y, \quad \mathbf{v}_y = \mathbf{v}_z = 0, \quad \frac{\partial}{\partial t} = 0, \quad (\mathbf{v}\nabla) = 0$$

$$Z \begin{bmatrix} \tau_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{xy} & \tau_{yy} & \tau_{yz} \\ \tau_{xz} & \tau_{yz} & \tau_{zz} \end{bmatrix} + \frac{C_3}{2} \begin{bmatrix} -2\tau_{xy} & -\tau_{yy} & -\tau_{yz} \\ -\tau_{yy} & 0 & 0 \\ -\tau_{yz} & 0 & 0 \end{bmatrix} \dot{\gamma} = - \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \dot{\gamma}$$

$$\tau_{yy} = \tau_{yz} = \tau_{zz} = 0 \implies \psi_2 = 0 \quad \text{no second normal stress (SNS)}$$

$$\tau_{xz} = 0$$

$$Z\tau_{xx} - C_3\tau_{xy}\dot{\gamma} = 0, \quad \implies Z\tau_{xx} = C_3\tau_{xy}\dot{\gamma} \quad (4.50)$$

$$Z\tau_{xy} = -\dot{\gamma} \quad (4.51)$$

Dividing equation 4.50 by equation 4.51 yields

$$\frac{\tau_{xx}}{\tau_{xy}} = -C_3\tau_{xy} \quad (4.52)$$

$$\tau_{xx} = -C_3\tau_{xy}^2 \quad (4.53)$$

$$\psi_1 = C_3\eta^2$$

Using  $Z = C_1 - \frac{2C_2}{C_3}\tau_{xx}$ ,

$$Z = C_1 + 2C_2\tau_{xy}^2 \quad (4.54)$$

$$2C_2\tau_{xy}^3 + C_1\tau_{xy} + \dot{\gamma} = 0 \quad (4.55)$$

But,

$$\tau_{xy} = -\eta(\dot{\gamma})\dot{\gamma}$$

equation 4.55 becomes,

$$2C_2\dot{\gamma}^2\eta^3 + C_1\eta - 1 = 0 \quad (4.56)$$

At  $\dot{\gamma} = 0$ ,  $C_1\eta = 1$   $C_1 = \frac{1}{\eta_0}$

The only real solution yields viscosity as an explicit function of the local shear rate, which can be written as:

$$\eta(\dot{\gamma}) = \sqrt[3]{\frac{1}{4C_2\dot{\gamma}} \left[ \left( 1 + \sqrt{1 + \frac{2C_1^3}{27C_2\dot{\gamma}}} \right)^{1/3} + \left( 1 - \sqrt{1 + \frac{2C_1^3}{27C_2\dot{\gamma}}} \right)^{1/3} \right]} \quad (4.57)$$



## 5 Charged FENE-P Dumbbell Model

In the charged Fene-P dumbbell model, repulsive charges are included between the beads in an attempt to incorporate the effect of charge repulsion between ionizable groups on the polymer [Dunlap and Leal, 1984]. The connector force for this model is given as

$$F_c = \frac{HQ}{1 - \left(\frac{Q}{Q_0}\right)^2} - F_e \quad (5.1)$$

where  $F_e$  is the repulsive force containing the charges.

$$F_e = -\frac{1}{4\pi\epsilon_0} \cdot \frac{q^2}{R^2} = -\frac{E_1 Q}{Q^3} \quad (5.2)$$

where  $E_1 = \frac{q^2}{4\pi\epsilon_0}$

substituting equation 5.2 in equation 5.1 yields

$$F_c = \frac{HQ}{1 - \left(\frac{Q}{Q_0}\right)^2} - \frac{E_1 Q}{Q^3} \quad (5.3)$$

For Kramers:

$$\tau_p = -n \left\langle \frac{HQQ}{1 - \left(\frac{Q}{Q_0}\right)^2} - \frac{E_1 QQ}{Q^3} \right\rangle + nkT\delta \quad (5.4)$$

For Giesekus:

$$\tau_p = \frac{1}{4} n\zeta \langle \mathbf{QQ} \rangle_{(1)} \quad (5.5)$$

Applying peterlin's pre-averaging

$$\left\langle \frac{\mathbf{QQ}}{1 - \frac{Q^2}{Q_0^2}} \right\rangle \approx \frac{\langle \mathbf{QQ} \rangle}{1 - \left\langle \frac{Q^2}{Q_0^2} \right\rangle} \quad \text{and} \quad \left\langle \frac{\mathbf{QQ}}{Q^3} \right\rangle \approx \frac{\langle \mathbf{QQ} \rangle}{\langle Q^2 \rangle^{3/2}} \quad (5.6)$$

Let  $x = \left\langle \frac{Q^2}{Q_0^2} \right\rangle$  and  $\langle Q^2 \rangle = xQ_0^2$

Equation 5.4 becomes

$$\tau_p = -nH \frac{\langle \mathbf{QQ} \rangle}{1 - x} + \frac{nE_1 \langle \mathbf{QQ} \rangle}{Q_0^3 x^{3/2}} + nkT\delta \quad (5.7)$$

$$b = \frac{HQ_0^2}{kT} \text{ and } \lambda = \frac{\zeta}{4H}$$

Introducing energy electric and energy elastic where they are both given as

$$\text{Electric Energy} \sim \frac{q^2}{4\pi\epsilon Q_0} \quad \text{elastic energy} \sim HQ_0^2$$

$$\text{Energy ratio} = \frac{\text{ElectricEnergy}}{\text{ElasticEnergy}}$$

$$E = \frac{1}{4\pi\epsilon_0} \cdot \frac{q^2}{HQ_0^3} \quad (5.8)$$

Therefore,

$$E_1 = E \cdot HQ_0^3 \quad (5.9)$$

When  $E \rightarrow 0$ : The electric component component is negligible and the original uncharged FENE-P Dumbbell is recovered.

When  $E \rightarrow \infty$  or when ( $E \gg 1$ ): The repulsive forces dominate in the connecting force and the dumbbells tend to the rigid rod limit

Substituting equation 5.8 into equation 5.6 yields

$$\boldsymbol{\tau}_p = -nH \frac{\langle \mathbf{Q}\mathbf{Q} \rangle}{1-x} + nHE \frac{\langle \mathbf{Q}\mathbf{Q} \rangle}{x^{\frac{3}{2}}} + nkT\boldsymbol{\delta} \quad (5.10)$$

Factorizing equation 5.9 yields

$$\boldsymbol{\tau}_p = -nH \langle \mathbf{Q}\mathbf{Q} \rangle \cdot \left( \frac{1}{1-x} + \frac{E}{x^{3/2}} \right) + nkT\boldsymbol{\delta} \quad (5.11)$$

let

$$Z = \frac{1}{1-x} - E \cdot \frac{1}{x^{3/2}} \quad (5.12)$$

Equation 5.10 becomes

$$\boldsymbol{\tau}_p = -nHZ \langle \mathbf{Q}\mathbf{Q} \rangle + nkT\boldsymbol{\delta} \quad (5.13)$$

Equation 5.12 is same as equation 4.22 of the FENE-P Model and so, they have the same constitutive equation but with a different Z. The constitutive equation is therefore

$$Z\boldsymbol{\tau}_p + \lambda\boldsymbol{\tau}_p(1) - \lambda[\boldsymbol{\tau}_p - nkT\boldsymbol{\delta}] \frac{D \ln z}{Dt} = -nkT\lambda\dot{\gamma} \quad (5.14)$$

Taking the trace of equation 5.12

$$\text{tr}\tau_p = -nHZ \cdot Q_0^2 \cdot x^2 + 3nkT \quad (5.15)$$

$$\text{tr}\tau_p = -nKTb(Zx) + 3nkT \quad (5.16)$$

Dividing through by  $nkTb$  and solving for  $Z$  yields

$$Zx = \frac{3}{b} - \frac{\text{tr}\tau_p}{nkTb} = Z_0 - 1 \quad (5.17)$$

where  $Z_0$  is  $Z$  calculated in the original FENE-P Dumbbell model

$$Z_{FENE} = 1 + \frac{3}{b} - \frac{\text{tr}\tau_p}{nkTb} = Z_0 \quad (5.18)$$

Therefore,

$$Zx = \frac{3}{b} - \frac{\text{tr}\tau_p}{nkTb} = Z_0 - 1 \quad (5.19)$$

$$Zx = Z_0 - 1 \quad (5.20)$$

$$x = \frac{Z_0 - 1}{Z} \quad (5.21)$$

From equation 5.11,

$$Z = \frac{1}{1-x} - E \cdot \frac{1}{x^{3/2}}$$

Therefore,

$$Zx = Z_0 - 1 = \frac{x}{1-x} - E \cdot \frac{1}{x^{1/2}} \quad (5.22)$$

Equation 5.21 can be rewritten as

$$-1 + \frac{1}{1-x} - \frac{E}{x^{1/2}} = Z_0 - 1 \quad (5.23)$$

$$\frac{1}{1-x} - \frac{E}{x^{1/2}} = Z_0 \quad (5.24)$$

$$x = \frac{\langle Q^2 \rangle}{Q_0^2} \in (0, 1)$$

Introducing large  $X = \frac{1}{x}$ , in order to rewrite the equations so that they can easily be solved using Mathematica as the real solution can be found easily in mathematica.

equation 5.19 becomes

$$\frac{Z}{X} = Z_0 - 1 \quad (5.25)$$

and equation 5.23 becomes

$$\frac{1}{1-X} - E\sqrt{X} = Z_0 - 1 \quad (5.26)$$

Equation 5.25 can be solved half analytically by mathematica.

let

$$F(\alpha, \beta)$$

be the only real solution of the equation

$$\frac{1}{X-1} - \beta\sqrt{X} = \alpha \quad (5.27)$$

It is assumed that  $\beta > 0$  and  $X > 1$

$$X = F(Z_0 - 1, E)$$

Then,

$$Z = (Z_0 - 1)X = (Z_0 - 1)F(Z_0 - 1, E) \quad (5.28)$$

$$Z = Z \left( b, \frac{\text{tr}\tau_p}{nkT}, E \right) \quad (5.29)$$

$Z$  is therefore a function of  $\frac{\text{tr}\tau_p}{nkT}$  as well as two model parameters  $b$  and  $E$

## 5.1 Steady Shear Flow Material Functions for Charged Fene-P

$$\mathbf{v}_x = \dot{\gamma}y, \quad \mathbf{v}_y = \mathbf{v}_z = 0, \quad \frac{\partial}{\partial t} = 0, \quad (\mathbf{v}\nabla) = 0$$

$$Z \begin{bmatrix} \tau_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{xy} & \tau_{yy} & \tau_{yz} \\ \tau_{xz} & \tau_{yz} & \tau_{zz} \end{bmatrix} + \lambda \begin{bmatrix} -2\tau_{xy} & -\tau_{yy} & -\tau_{yz} \\ -\tau_{yy} & 0 & 0 \\ -\tau_{yz} & 0 & 0 \end{bmatrix} \dot{\gamma} = -nkT\lambda \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \dot{\gamma}$$

$$\tau_{yy} = \tau_{yz} = \tau_{zz} = 0 \implies \psi_2 = 0 \quad \text{no second normal stress (SNS)}$$

$$\tau_{xz} = 0$$

$$Z\tau_{xx} = 2\lambda\tau_{xy}\dot{\gamma} \quad (5.30)$$

$$Z\tau_{xy} = -nkT\lambda\dot{\gamma} \quad (5.31)$$

Dividing equation 5.30 by equation 5.31 yields

$$\tau_{xx} = -\frac{2\tau_{xy}^2}{nkT} \quad (5.32)$$

The normal stress difference (FNSD)  $\tau_{xx} - \tau_{yy}$  is negative as expected, see [Bird et al., 1987a]

From their definitions, [Bird et al., 1987a], one obtains the distributions of non-Newtonian viscosity  $\eta$  and the first normal stress coefficient (FNSC)  $\psi$  across the flow

$$\psi_1 = \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}^2} = 2 \frac{\eta^2}{nkT} \quad (5.33)$$

$$Z = Z \left( \frac{\text{tr}\tau}{nkT}, b, E \right) \quad (5.34)$$

Introduce:  $\bar{\tau}_{ij} = \frac{\tau_{ij}}{nkT}$ , then,  $\frac{\text{tr}\tau}{nkT} = \text{tr}\bar{\tau}$

Therefore,

$$Z = Z(\text{tr}\tau, b, E) \quad (5.35)$$

Then,

$$Z\bar{\tau}_{xy} = -\lambda\dot{\gamma} \quad (5.36)$$

and

$$\bar{\tau}_{xx} = -2\bar{\tau}_{xy} \quad (5.37)$$

The trace of tau is given as

$$\text{tr}\bar{\tau} = \bar{\tau}_{xx} + \bar{\tau}_{yy} + \bar{\tau}_{zz} = \bar{\tau}_{xx} = -2\bar{\tau}_{xy} \quad (5.38)$$

since  $\bar{\tau}_{yy}$  and  $\bar{\tau}_{zz} = 0$

Therefore:

$$Z = Z(-2\bar{\tau}_{xy}, b, E) \quad (5.39)$$

$$Z(-2\bar{\tau}_{xy}, b, E) \bar{\tau}_{xy} = (\lambda\dot{\gamma}) \quad (5.40)$$

Plotting  $(\lambda\dot{\gamma})$  against  $\bar{\tau}_{xy}$  where  $(\lambda\dot{\gamma})$  is the dimensionless shear rate.

Normalizing the shear stress by multiply it by  $-\frac{b+3}{b}$  and dividing it by  $\bar{\dot{\gamma}}$ , we have

$$\frac{b+3}{bnkT\lambda} \cdot \eta(\dot{\gamma}) = -\frac{b+3}{b} \cdot \frac{\bar{\tau}_{xy}}{\bar{\dot{\gamma}}} \text{ against } (\lambda\dot{\gamma})$$

( $\eta_0, FENE - P = 1$ )

In FENE-P,  $\eta_0 = \frac{b}{b+3}nkT\lambda$

## 5.2 Conclusion

The charged FENE-P model was developed and was found to have the same constitutive equation with the FENE-P Model but a different  $Z$ . This was used to calculate the viscosity and first normal stress difference (Viscometric functions). A plot of the of  $\eta(\dot{\gamma})$  was made. The plots was normalized and the value of  $b$  was set to 150 and the value of  $E$ , 0.05, 0.1, 0.3, 0.7, 1, 3, 1000. The coloured solid lines represents the charged FENE-P model while the dashed line represent the FENE-P model. This model predicts viscosity drops as salinity increases and the onset of shear thinning is shifted to the right as salinity increases.

## 5.3 Recommendation

There are a lot to be done with this model as I propose the following

- There would be need for further investigation to find another material function.
- The model should be calibrated/tested against experiments
- It should also be used to solve for some flows like pipe flow
- it can also be generalized to a bead spring chain version
- To establish the connection between charge ( $E$ ) and the real salt concentration in the brine

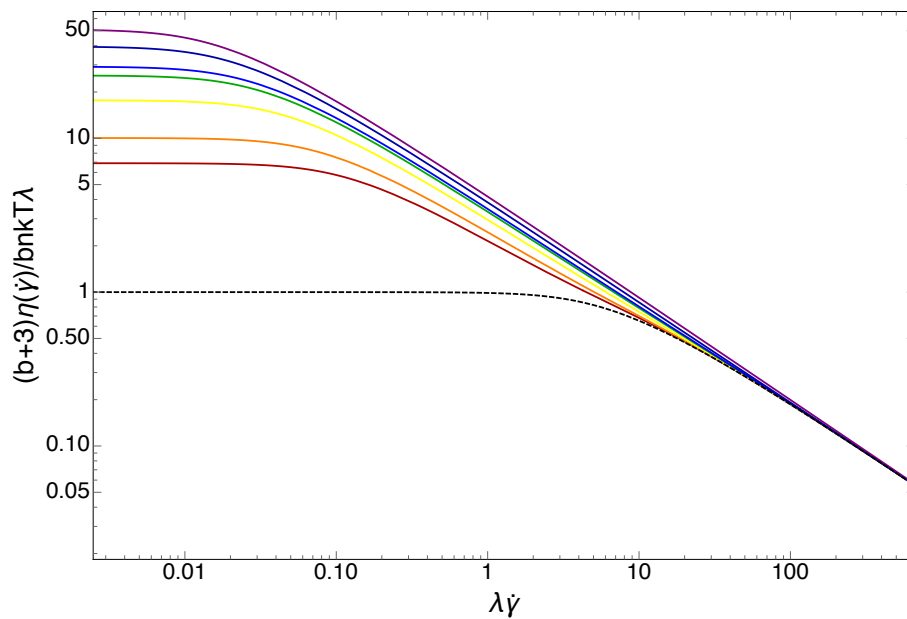


Figure 11: Charged FENE-P Viscosity Plot

## References

- [Alexandrou, 2001] Alexandrou, A. N. (2001). *Principles of Fluid Mechanics*. Prentice Hall, Upper Saddle River (NJ).
- [Batchelor, 1967] Batchelor, G. K. (1967). *An Introduction to Fluid Dynamics*. Cambridge University Press.
- [Bird et al., 1987a] Bird, R. B., Armstrong, R. C., and Hassager, O. (1987a). *Dynamics of Polymeric Liquids. Vol. 1. Fluid Mechanics*. John Wiley & Sons, Inc.
- [Bird et al., 1987b] Bird, R. B., Curtiss, C. F., Armstrong, R. C., and Hassager, O. (1987b). *Dynamics of Polymeric Liquids. Vol. 2. Kinetic Theory*. John Wiley & Sons, Inc.
- [Bird et al., 1980] Bird, R. B., Dotson, P. J., and Johnson, N. L. (1980). Polymer solution rheology based on a finitely extensible bead-spring-chain model. *J. Non-Newtonian Fluid Mech.*, 7:213–235.
- [Bird and Wiest, 1995] Bird, R. B. and Wiest, J. M. (1995). Constitutive equation for polymeric liquid. *Fluid mechanics*, 27:169–193.
- [Carreau, 1968] Carreau, P. J. (1968). *Rheological Equations from Molecular Network Theories*. PhD thesis, University of Wisconsin.
- [Chilcott and Rallison, 1988] Chilcott, M. D. and Rallison, J. M. (1988). Creeping flow of dilute polymer solutions past cylinders and spheres. *J. Non-Newtonian Fluid Mech.*, 29:381–432.
- [Directorate, 2017] Directorate, N. P. (2017). Immobile oil - positive prospects for producing more. *Norwegian Continental Shelf*, 1. Available online on NPD website.
- [Dunlap and Leal, 1984] Dunlap, P. N. and Leal, L. G. (1984). The charged dumbbell model for dilute polyelectrolyte solutions in strong flows. *Rheol. Acta*, 23:238–249.
- [Evans, 1998] Evans, G. (1998). Shear thinning vs shear thickening in associating fluids. *The Journal of chemical physics*, 108(4):1570–1577.
- [H.A.Barnes et al., 1989] H.A.Barnes, J.F.Hutton, and K.walters (1989). *An introduction to rheology*. Elsevier science, Amsterdam.
- [K.S.Sorbie, 1991] K.S.Sorbie (1991). *Polymer improved oil recovery*. Springer netherlands, New york.
- [Peterlin, 1966] Peterlin, A. (1966). Hydrodynamics of macromolecules in a velocity field with longitudinal gradient. *J. Polymer Sci. B: Polymer Letters*, 4(4):287–291.
- [Phan-Thien, 1978] Phan-Thien, N. (1978). A nonlinear network viscoelastic model. *J. Rheol.*, 22:259–283.
- [Phan-Thien and Tanner, 1977] Phan-Thien, N. and Tanner, R. I. (1977). A new constitutive equation derived from network theory. *J. Non-Newtonian Fluid Mech.*, 2:353–365.
- [P.K.Kandu and I.R.Cohen, 1990] P.K.Kandu and I.R.Cohen (1990). *Fluid mechanics*. Elsevier sciences, USA.



- [Shogin et al., 2017a] Shogin, D., Amundsen, P. A., Hiorth, A., and Madland, M. V. (2017a). Modeling the rheology of two-phase polymer flow. In *IOR Norway 2017*.
- [Shogin et al., 2017b] Shogin, D., Amundsen, P. A., Hiorth, A., and Madland, M. V. (2017b). Rheology of polymeric flows in circular pipes, slits and capillary bundles: analytical solutions from kinetic theory. In *IOR Norway 2017*.
- [Staudinger, 1920] Staudinger, H. (1920). Über polymerisation. *Berichte der deutschen chemischen Gesellschaft (A and B Series)*, 53(6):1073–1085.
- [Stavland et al., 2013] Stavland, A., Jonsbråten, H., and Strand, D. (2013). When will polymer viscosity be a design criterion for eor polymer flooding? In *IEA-EOR 34th Annual Symposium*, Stavanger, Norway.
- [Weissenberg, 1947] Weissenberg, K. (1947). A continuum theory of rheological phenomena. *Nature*, 159:310–311.
- [Wever et al., 2011] Wever, D. A. Z., Picchioni, F., and Broekhuis, A. A. (2011). Polymers for enhanced oil recovery: A paradigm for structure-property relationship in aqueous solution. *Progress in Polymer Science*, 36:1558–1628.