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Polymeric Liquids

Non-Newtonian Liquids
A Brief Introduction to Rheology
(Class Notes)

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BRIEF CONTENTS

A. Material discussed in Class (Handouts)

A.1 General Introduction

For the Newtonian fluid, two material parameters are needed, coefficients of viscosity p and K, which depend on temperature, pressure, and composition, but not on the velocity gradients. The Newtonian Fluids are consider very easy to study because they have a constant viscosity. But not all fluids are Newtonian. Some of these structurally complex fluids include polymer solutions, polymer melts, soap solutions, suspensions, emulsions, pastes and some biological fluids. The mentioned fluids examples are classify in a separate group called Non-Newtonian fluids and its viscosity is not constant. Their viscosities depend strongly on the velocity gradients, and in addition they may display pronounced "elastic effects".

In dealing with Newtonian fluids the science of the measurement of viscosity is called viscometry and the instruments are called viscometers . To characterize non-Newtonian fluids we have to measure not only the viscosity, but the normal stresses and the viscoelastic responses as well. The science of measurement of these properties is called rheometry, and the instruments are called rheometers. The science of rheology includes all aspects of the study of deformation and flow of non-Hookean solids and non-Newtonian liquids.

A.2 Some important definitions

Newtonian Fluids are fluids for which the shearing stress is linearly related to the rate of shearing strain. (see Figure 1)

Non-Newtonian fluids are fluids which the shearing stress in not linearly related to the rate of shearing strain. Generally, non-Newtonian fluids emerge from Newtonian fluids that have experience changes in their viscosity. (see Figure 1)

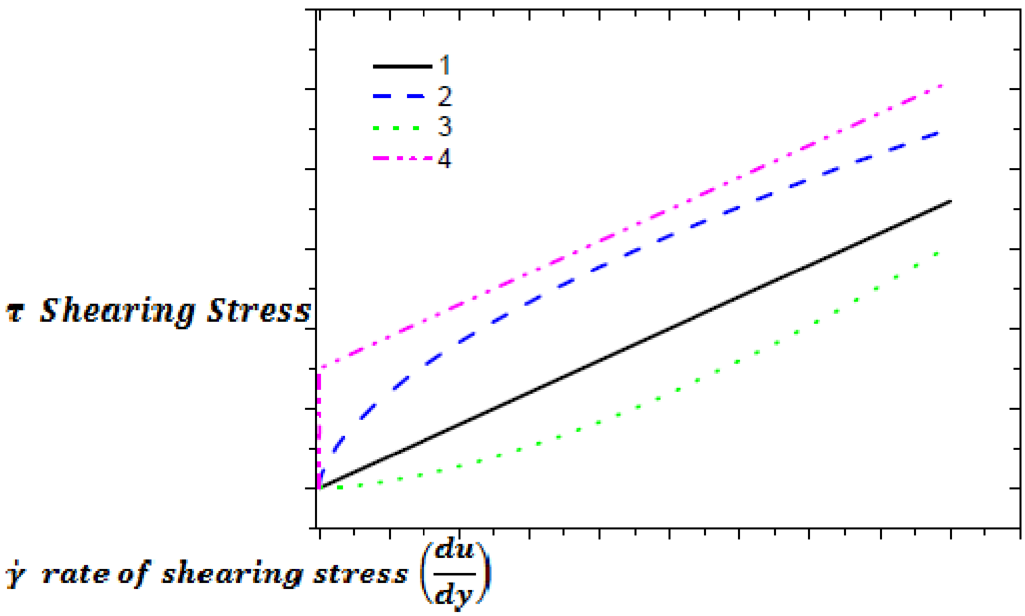


Figure 1: Representation of different fluids curves
Newtonian Fluid(1)   Non-Newtonian Fluids (2, 3 and 4)

Newtonian Fluid

Newton's law establishes the relationship between stress and deformation

Viscosity is constant

$$\tau = \eta \dot{\gamma}$$

Non-Newtonian Fluid

Viscosity is constant

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

Fluid mechanics is the field that study simpler fluids

Rheology is the study of deformation and flow of matter. This study the flow of complex fluids, such as: polymers, pastes, suspensions, foods, etc.

Shear thinning is the tendency of some materials to **decrease in viscosity** when driven to flow at **high shear rates**, such as by higher pressure drops

Shear thickening is the tendency of some materials to **increase in viscosity** when driven to flow at **high shear rates**

Some interesting videos to understand better the mentioned concepts

http://video.google.com/videoplay?docid=-9094972957848338868#

http://www.youtube.com/watch?v=3zoTKXXNQIU&NR=1&feature=fvwp

http://www.youtube.com/watch?v=f2XQ97XHjVw&NR=1

A.3 Modeling of Shear Thinning and Thickening

✓ **Power Law Model**: $\eta = m\dot{\gamma}^{n-1}$

m = m	**n = 1**	***Newtonian***
m	**n > 1**	***Shear Thickening, Dilatant***
m	**n < 1**	***Shear Thinning***

Some advantages of Power Law Model are that it is a simple method and is considered very success at predicting Q vs ΔP. Despite this, Power Law Meodel has disadvantages too. This model does not describe Newtonian Plateau at small shear rates.

- ✓ **Carreau-Yasuda Model**

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

a – affects the shape of the transition region

λ – time constant determines where it changes from constant to power law

n – describes the slope of the power law

$n_{o,}$ n_{oo} - describe plateau viscosities

Carreau-Yasuda Model have advantages and disadvantages like Power Law Model. One advantages is that using this model researchers can fits most data meanwhile some disadvantages are that contains only 5 parameters and do not give molecular insight into polymer behavior

A.4 Yield Stress

Bingham Model is used to calculate the yield stress that is the tendency of a material to flow only when stresses are above a treshold stress. This value can be calculate using the equation presented above

$$\eta(\dot{\gamma})=\begin{cases}\infty & \tau\le\tau_y\\ \mu_0+\dfrac{\tau_y}{\dot{\gamma}} & \tau\ge\tau_y\end{cases}$$

Ty = yield stress, always positive

μ_o = viscosity at higher shear rates

A.5 Elastic and Viscoelastic Effects

✓ Weissenberg Effect (Rod Climbing Effect)

– does not flow outward when stirred at high speeds

✓ Fluid Memory

– Conserve their shape over time periods or seconds or minutes

-- Elastic like rubber

-- Can bounce or partially retract

– Example: clay (plasticina)

✓ Viscoelastic fluids subjected to a stress deform

– when the stress is removed, it does not instantly vanish

– internal structure of material can sustain stress for some time

– this time is known as the relaxation time, varies with materials

– due to the internal stress, the fluid will deform on its own, even when external stresses are removed

– important for processing of polymer melts, casting, etc.

✓ Die Swell

– as a polymer exits a die, the diameter of liquid stream increases by up to an order of magnitude

– caused by relaxation of extended polymer coils, as stress is reduced from high flow producing stresses present within the die to low stresses, associated with the extruded stream moving through ambient air

B. Summary of Chapter 8: Polymeric Liquids (BSL Book)

B.1 Examples of the behavior of polymeric liquids

In this section we discuss several experiments that contrast the flow behavior of Newtonianand polymeric fluids.

Steady-State Laminar Flow in Circular Tubes

Even for the steady-state, axial, laminar flow in circular tubes, there is an important difference between the behavior of Newtonian liquids and that of polymeric liquids. For polymeric liquids, experimental data suggest that the following equations are reasonable:

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

where n is a positive parameter characterizing the fluid usually with a value less than unity. That is, the velocity profile is more blunt than it is for the Newtonian fluid, for which n = 1. It is further found experimentally that: $P_o - P_L \sim \omega^n$. The pressure drop thus increases much less rapidly with the mass flow rate than for Newtonian fluids, for which the relation is linear.

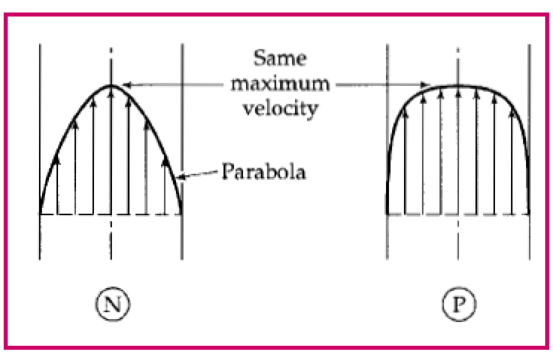


Figure 2 Laminar flow in a circular tube. (N = Newtonian liquid and P =polymeric liquid)

The Figure show typical velocity profiles for laminar flow of Newtonian and polymeric fluids for the same maximum velocity. This simple experiment suggests that the polymeric fluids have a viscosity that depends on the velocity gradient. For laminar flow in tubes of noncircular cross section, polymeric liquids exhibit secondary flows superposed on the axial motion. Recall that for turbulent Newtonian flows secondary flows are also observed-in Fig. 5.1-2 it is shown that the fluid moves toward the corners of the conduit and then back in toward the center. For laminar flow of polymeric fluids, the secondary flows go in the opposite direction-from the corners of the conduit and then back toward the walls.' In turbulent flows the secondary flows result from inertial effects, whereas in the flow of polymers the secondary flows are associated with the "normal stresses."

Recoil after Cessation of Steady-State Flow in a Circular Tube

We start with a fluid at rest in a circular tube and, witha syringe; we "draw" a dye line radially in the fluid as shown in Fig. 8.3. Then we pump the fluid and watch the dye deform For a Newtonian fluid the dye line deforms into a continuously stretching parabola but for a polymeric liquid the dye line deforms into a curve that is more blunt than a parabola.

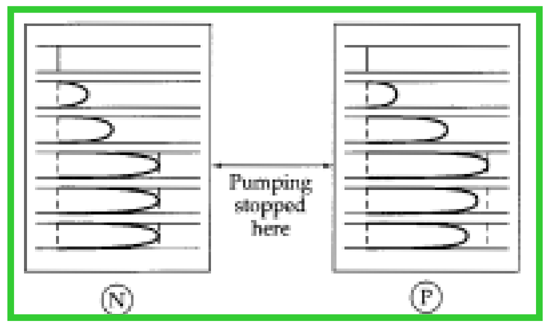


Figure 8.3

"Normal Stress" Effects

Other differences in the behavior of the Newtonian and polymeric liquids appear in the normal stress effects.

A rotating road in a beaker of a **Newtonian fluid** cause the fluid to undergo a tangential motion, but when it is on steady state the fluid surface is lower near the rotating rod. These happen because the centrifugal forces cause the fluid to move radially toward the beaker wall. For a **polymeric liquid,** the fluid move toward the rotating rod and at steady state occur the **Weissenberg rod-climbing effect** to the fluid.

Different experiments were performed, some of them were:

- Put a rotating disk on the surface of a fluid in a cylindrical container.
    - For a Newtonian liquid, the rotating disk causes the fluid to move in a tangential direction (“primary flow”), but the fluid will move slowly outward toward the cylinder wall because of the centrifugal force and then moves downward and then back up along the cylinder axis. (This flow is weaker than the primary flow and is termed “secondary flow”).
    - For a polymeric liquid, the fluid also develop a primary tangential flow with a weak radial and axial secondary flow, but the latter goes in a direction **opposite** to that seen in the Newtonian fluid.
- Let a liquid flow down a tilted, semi-cylindrical trough.
    - For a Newtonian fluid, the liquid surface is flat, except for the meniscus effects at the outer edges.
    - For polymeric liquids, the liquid surface is found to be slightly convex, the effect is small but reproducible.
- Operation of a simple siphon.
    - For a Newtonian fluid, the removal of a siphon tube from the liquid means that the siphoning action ceases.
    - For a polymeric liquid, the siphoning can continue even when the siphon is lifted several centimeters above the liquid surface, this is called the tubeless siphon effect.
- A long cylindrical rod, with its axis in the z-direction, is made to oscillate back and forth in the x direction with the axis parallel to the z axis
    - For a Newtonian fluid, a secondary flow is induced whereby the fluid moves toward the cylinder from above and below and moves away to the left and right.

- For the polymeric liquid, the induced secondary motion is in the opposite direction, the fluid moves inward from the left and right along the x axis and outward in the up and down direction along the y axis.

B.2 Rheometry and material functions

Polymeric liquids do not obey Newton's law of viscosity. Incompressible Newtonian fluids are described by only one material constant, the viscosity. But for non-Newtonian liquids can measure many different material functions. It is assumed that the polymeric liquids can be regarded as incompressible.

<u>Steady Simple Shear Flow</u>

We now consider this case where the velocity profile is given by $v_x = \dot{\gamma} y$:

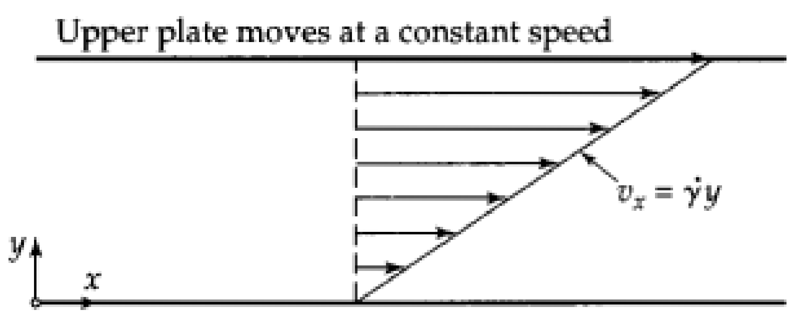


Figure 8.2-1

The normal stresses ($\tau_{xx}, \tau_{yy}, \tau_{zz}$) are nonzero and unequal for incompressible non-Newtonian fluids but they are zero for Newtonian fluids. For these fluids it's conventional to define three material functions:

$$\tau_{yx} = -\eta \frac{dv_x}{dy}$$

$$\tau_{xx} - \tau_{yy} = -\psi_1 \left(\frac{dv_x}{dy}\right)^2$$

$$\tau_{yy} - \tau_{zz} = -\psi_2 \left(\frac{dv_x}{dy}\right)^2$$

Where the following variables are all functions of $\dot{\gamma}$:

η = Non-Newtonian fluid viscosity.

ψ_1 = First normal stress coefficient.

ψ_2 = Second Normal Stress coefficient.

All these variables decrease by a big factor when the shear rate increases. When the fluid is made up of flexible macromolecules, η and ψ_1 are positive and ψ_2 is negative. A positive $\psi_1(\dot{\gamma})$ means that the fluid behaves as it when under tension in the flow direction and a negative $\psi_2(\dot{\gamma})$ means that the fluid is in tension in the transverse direction. For Newtonian fluids: η $=\mu$, $\psi_1 = 0, \psi_2 = 0$.

The positive ψ_1 is responsible for the Weissenberg rod-climbing effect. The tension created by the tangential flow pulls the fluid toward the rotating rod, overcoming the centrifugal force. Also, positive ψ_1 can explain qualitatively the secondary flows in the disk-and-cylinder experiment. The negative ψ_2 can explain the convex surface shape in the tilted-trough experiment.

<u>Small-Amplitude Oscillatory Motion:</u>

Small-amplitude oscillatory shear experiment (figure 8.2-2)

- Standard method for measuring the elastic response of a fluid.
- The top plate moves back and forth in sinusoidal fashion with tiny amplitude.
- The velocity profile will be linear if the plate spacing is extremely small and the fluid has very high viscosity.
- Linear velocity profile = $v_x = \dot{\gamma}^0 y \cos \omega t$; $\dot{\gamma}^0$ = amplitude of the shear rate excursion.

  Shear stress required to maintain the oscillatory motion:
  $\tau_{yx} = -\eta' \dot{\gamma}^0 \cos \omega t - \eta'' \dot{\gamma}^0 \sin \omega t$

Where η' and η'' are the components of the complex viscosity, $\eta^* = \eta' - i\eta''$. η' is the viscous response and η'' is the elastic response. Chemists use the curves of these variables to characterize polymers. For Newtonian fluids, $\eta' = \mu$ and $\eta'' = 0$.

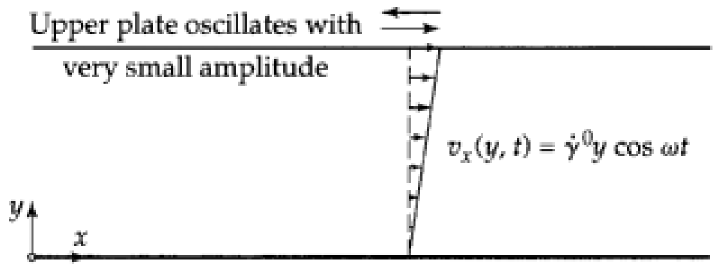


Figure 8.2-2

Steady State Elongational Flow:

A third experiment can be done which involves the stretching of the fluid. The velocity distribution is given by $v_z = \dot{\varepsilon} z$, $v_x = -\frac{1}{2}\dot{\varepsilon} x$ and $v_y = -\frac{1}{2}\dot{\varepsilon} y$. The quantity $\dot{\varepsilon}$ is called the elongation rate. The elongational viscosity $\bar{\eta}$,which depends on $\dot{\varepsilon}$, is defined by the following relation:

$$\tau_{zz} - \tau_{xx} = -\bar{\eta}\frac{dv_z}{dz}$$

This viscosity cannot be measured for all fluids. For Newtonian fluids, $\bar{\eta} = 3\mu$. This variables is sometimes called the Trouton viscosity.

Other reometric tests include stress relaxation after cessation of flow, stress growth at the inception of flow, recoil, and creep.

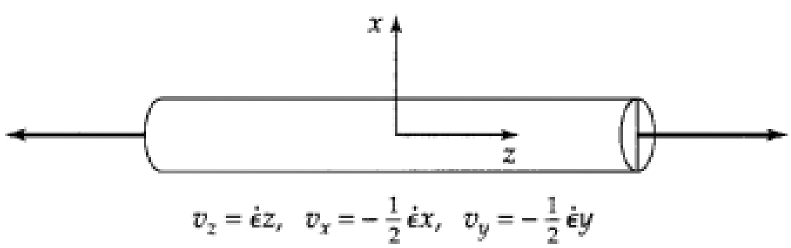


Figure 8.2-3

B.3 Non-Newtonian viscosity and the generalized Newtonian models

The generalized Newtonians models are primarily used to describe steady-state shear flows and have been widely used by engineers for designing flows systems. In this model we assume that the fluids are incompressible.

The generalized Newtonian models can describe only the non-Newtonian viscosity, and none of the normal stress effects, time-dependent effects, or elastic effects.

For incompressible Newtonian fluids the expression for the stress tensor is given by:

$$\tau = -\eta\gamma\,(\Delta\, v + (\Delta\, v)\,\dagger) = -\eta\boldsymbol{\gamma}$$

where:

$\gamma = \Delta\, v + (\Delta\, v)\,\dagger$ rate of strain tensor

The generalized Newtonian fluid model is obtained by simply replacing the constant viscosity μ by the non-Newtonian viscosity η, a function of the shear rate, which in general can be written as the magnitude of the rate-of-strain tensor $\gamma = \sqrt{\frac{1}{2}(\gamma:\gamma)}$

Therefore the generalized Newtonian fluid model is:

$$\tau = -\eta\,(\Delta\, v + (\Delta\, v)\,\dagger) = -\eta\boldsymbol{\gamma}$$

a. The simplest empiricism for $\boldsymbol{\eta}(\boldsymbol{\gamma})$ is the two-parameter power law

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

where:

m and n are constants characterizing the fluid.

n = 1 Newtonian

n > 1 shear thickening

n < 1 shear thinning

n – 1 is the slope of the log $\boldsymbol{\eta}$ vs. log $\boldsymbol{\gamma}$

b. A better curve fit for most data can be obtained by using the four-parameter Carreau equation

$$\frac{\eta - \eta\infty}{\eta 0 - \eta\infty} = [1 + (\lambda\gamma)^2]^{(n-1)/2}$$

Where:

η_0 = zero shear rate viscosity

$\eta\infty$ = infinite shear rate viscosity

λ = parameter with units of time

n = dimensionless parameter

Example:

Derive the expression for the mass flow rate of a polymer liquid, described by the power law model. The fluid is flowing in a long circular tube of radius R and length L, as a result of a pressure difference, gravity, or both.

Using the power law with the shear stress distribution equation for any fluid in developed steady flow in a circular tube, we obtain:

$$\tau = -m\gamma^{n-1}\frac{dv}{dr}$$

where:

$$\gamma = \sqrt{\frac{1}{2}(\gamma : \gamma)} = \sqrt{(\frac{dv}{dr})^2}$$

Now,

$$\tau = -m\left(-\frac{dv}{dr}\right)^{n-1}\frac{dv}{dr} = m\left(-\frac{dv}{dr}\right)^n$$

Combining the shear stress distribution and the above equation we get the differential equation for velocity,

$$m\left(-\frac{dv}{dr}\right)^n = \left(\frac{P0 - Pl}{2L}\right)r$$

After integrating the nth root of the equation, and applying the no-slip boundary condition at r = R, we get:

$$v = \left(\frac{(P0 - Pl)R}{2mL}\right)^{1/n} \frac{R}{\left(\frac{1}{n}\right) + 1}\left[1 - \left(\frac{r}{R}\right)^{\left(\frac{1}{n}\right)+1}\right]$$

When it is integrated over the cross section of the circular tube, we get:

$$w = \frac{\pi R^3 \rho}{\left(\frac{1}{n}\right) + 3}\left(\frac{(P0 - Pl)R}{2mL}\right)^{1/n}$$

Example 8.3-2 Flow of a Power Law Fluid in a Narrow Slit

Find the velocity distribution and the mass flow rate for a power law fluid flowing in the slit.

Solution:

The expression for the shear stress τ_{xz} as a function of position x in Eq. 2B.3-1 can be taken over here, since it does not depend on the type of fluid. The power law formula for τ_{xz} from Eq. 8.3-3 is:

$$\tau_{xz} = m\left(-\frac{dv_z}{dx}\right)^n \qquad \text{for } 0 \leq x \leq B \qquad (8.3\text{-}10)$$

$$\tau_{xz} = -m\left(\frac{dv_z}{dx}\right)^n \qquad \text{for } -B \leq x \leq 0 \qquad (8.3\text{-}11)$$

To get the velocity distribution for $0 \leq x \leq B$, we substitute τ_{xz} from Eq 8.3-10 into Eq. 2B.3-1 to get:

$$m\left(-\frac{dv_z}{dx}\right)^n = \frac{(\mathcal{P}_0 - \mathcal{P}_L)x}{L} \qquad 0 \leq x \leq B \qquad (8.3\text{-}12)$$

Integrating and using the no-slip boundary condition at x=B gives:

$$v_z = \left(\frac{(\mathcal{P}_0 - \mathcal{P}_L)B}{mL}\right)^{1/n} \frac{B}{(1/n)+1}\left[1 - \left(\frac{x}{B}\right)^{(1/n)+1}\right] \qquad 0 \le x \le B \qquad (8.3\text{-}13)$$

Since we expected the velocity profile to be symmetric about the midplane x=0, we can get the mass rate of flow as follows:

$$\begin{aligned} w = \int_0^W \int_{-B}^{B} \rho v_z dx\, dy &= 2\int_0^W \int_0^B \rho v_z dx\, dy \\ &= 2\left(\frac{(\mathcal{P}_0 - \mathcal{P}_L)B}{mL}\right)^{1/n} \frac{WB^2\rho}{(1/n)+1}\int_0^1 \left[1 - \left(\frac{x}{B}\right)^{(1/n)+1}\right] d\left(\frac{x}{B}\right) \\ &= \frac{2WB^2\rho}{(1/n)+2}\left(\frac{(\mathcal{P}_0 - \mathcal{P}_L)B}{mL}\right)^{1/n} \qquad (8.3\text{-}14) \end{aligned}$$

Experimental data on pressure drop and mass flow rate through a narrow slit can be used with Eq. 8.3-14 to determine the power law parameters.

B.4 Elasticity and the linear viscoelastic models

In the generalizing Newton's law of viscosity nether time derivatives and time integrals were included in the discussion of the linear expression for the stress tensor in terms of the velocity gradients. The linear viscolelastic models, that we are about to explain, allowed the inclusion of both, time derivatives and integrals. These models still require a linear relationship between τ and γ.

Newton's expressions for the stress tensor for an incompressible vicious liquid along with Hooks analogous expression for the stress tensor for an incompressible elastic solid:

Newton: $$\boldsymbol{\tau} = -\mu(\nabla \mathbf{v} + (\nabla \mathbf{v})^\dagger) \equiv -\mu\dot{\boldsymbol{\gamma}} \qquad (8.4\text{-}1)$$

Hooke: $$\boldsymbol{\tau} = -G(\nabla \mathbf{u} + (\nabla \mathbf{u})^\dagger) \equiv -G\boldsymbol{\gamma} \qquad (8.4\text{-}2)$$

Where G is the elastic modulus and **u** is the displacement vector, which gives the distance and direction that a point in the solid has moved from its initial position as a result of the applied stresses. The quantity **γ** is called the infinitesimal strain tensor. The rate of strain tensor and the infinitesimal strain tensor are related by $\dot{\gamma} = \partial\gamma/\partial t$. The Hookean solid has a perfect memory; when imposed stresses are removed, the solid returns to its initial configuration. Hooks law is valid only for every small displacement gradients, ∇u. To better understand viscoelastic fluids we need to combine the ideas of the principal vicoelastic models.

The Maxwell Model:

The Maxwell model can be represented by a purely viscous damper and a purely elastic spring connected consecutively, as shown in the diagram. In this configuration, under an applied axial stress, the total stress, σ_{Total} and the total strain, ε_{Total} can be defined as follows:

$$\sigma_{Total} = \sigma_D = \sigma_S$$
$$\varepsilon_{Total} = \varepsilon_D + \varepsilon_S$$

where the subscript D indicates the stress/strain in the damper and the subscript S indicates the stress/strain in the spring. Taking the derivative of strain with respect to time, we obtain:

$$\frac{d\epsilon_{Total}}{dt} = \frac{d\epsilon_D}{dt} + \frac{d\epsilon_S}{dt} = \frac{\sigma}{\eta} + \frac{1}{E}\frac{d\sigma}{dt}$$

where E is the elastic modulus and η is the material coefficient of viscosity. This model describes the damper as a Newtonian fluid and models the spring with Hooke's law.

If we connect these two elements in parallel, we get a model of Kelvin-Voigt material.

In a Maxwell material, stress σ, strain ε and their rates of change with respect to time *t* are governed by equations of the form:

$$\frac{1}{E}\frac{d\sigma}{dt} + \frac{\sigma}{\eta} = \frac{d\epsilon}{dt}$$

or, in dot notation:

$$\frac{\dot{\sigma}}{E} + \frac{\sigma}{\eta} = \dot{\epsilon}$$

The equation can be applied either to the shear stress or to the uniform tension in a material. In the former case, the viscosity corresponds to that for a Newtonian fluid. In the latter case, it has a slightly different meaning relating stress and rate of strain.

The model is usually applied to the case of small deformations. For the large deformations we should include some geometrical non-linearity. For the simplest way of generalizing the Maxwell model, refer to the Upper Convected Maxwell Model.

The Jeffrey's Model:

The Maxwell model has a linear relation between the stresses and the velocity gradients, involving a time derivative of the stresses. One could also include a time derivative of the velocity gradients and still have a linear relation:

$$\tau + \lambda_1 \frac{\partial}{\partial t}\tau = -\eta_0\left(\dot{\gamma} + \lambda_2 \frac{\partial}{\partial t}\dot{\gamma}\right) \qquad (8.4\text{-}4)$$

The Jeffrey's model contains three constants: the zero shear rate viscosity and two time constants (λ_2 is called the retardation time).

We can add terms containing second, third and higher derivatives of the stress and rate of strain tensors with appropriate multiplicative constants, to get a still more general linear among the stress and the rate of strain tensors.

<u>The Generalized Maxwell Model</u>

Another way of generalizing Maxwell's original idea is to "superpose" equation of the form:

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

and write the generalized Maxwell model as

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

(this is a linear differential equation).

Using the empirical expression can be reduced to three the total number of parameters where: η_0=zero shear rate viscosity, λ=time constant, α=dimensionless constant.

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

Using condition that the fluid is at rest, integrating analytically:

$$\tau(t) = -\int_{-\infty}^{t} \left\{ \sum_{k=1}^{\infty} \frac{\eta_k}{\lambda_k} \exp[-(t-t')/\lambda_k] \right\} \dot{\gamma}(t')dt' = -\int_{-\infty}^{t} G(t-t')\,\dot{\gamma}(t')dt' \qquad (8.4\text{-}9)$$

Sometimes this expression is more convenient for solving viscoelastic problems than are the differential equations in

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

Depends on the motion with very small displacement gradients you can use linear viscoelastic models as Maxwell, Jeffrey and Generalized Maxwell.

The Generalized Maxwell model has been widely used for interpreting experimental data on liner viscoelasticity.

Example 8.4-1: Small-amplitude oscillatory motion

Obtain an expression for the components of the complex viscosity by using the generalized Maxwell Model. The system is described in Fig 8.2-2

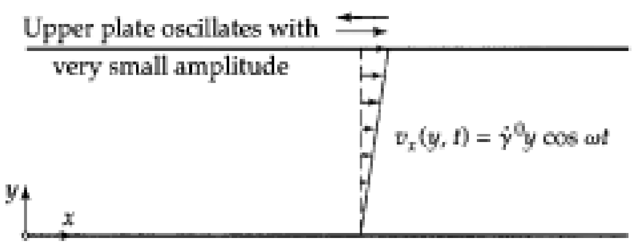


Fig. 8.2-2. Small-amplitude oscillatory motion. For small plate spacing and highly viscous fluids, the velocity profile may be *assumed* to be linear.

Solution:

Using yx-component of

$$\tau(t) = -\int_{-\infty}^{t} \left\{ \sum_{k=1}^{\infty} \frac{\eta_k}{\lambda_k} \exp[-(t-t')/\lambda_k] \right\} \dot{\gamma}(t')dt' = -\int_{-\infty}^{t} G(t-t')\,\dot{\gamma}(t')dt' \qquad (8.4\text{-}9)$$

For this problem is: $\dot{\gamma}_{yx}(t) = \dfrac{\partial v_x}{\partial y} = \dot{\gamma}^0 \cos \omega t$

Where ω is the angular frequency. When this is substitute into eqn 8.4-9 ;

$$\tau_{yx} = -\int_{-\infty}^{t} G(t - t')\dot{\gamma}^0 \cos \omega t' dt'$$

$$= -\dot{\gamma}^0 \int_0^{\infty} G(s) \cos \omega(t - s) ds$$

$$= -\dot{\gamma}^0 \left[\int_0^{\infty} G(s) \cos \omega s \, ds\right] \cos \omega t - \dot{\gamma}^0 \left[\int_0^{\infty} G(s) \sin \omega s \, ds\right] \sin \omega t$$

In which s=t-t'.

$$\eta'(\omega) = \int_0^{\infty} G(s) \cos \omega s \, ds$$

$$\eta''(\omega) = \int_0^{\infty} G(s) \sin \omega s \, ds$$

When the Generalized Maxwell expression for the relaxation modulus is introduced and the integrals are evaluated, we find that:

$$\eta'(\omega) = \sum_{k=1} \frac{\eta_k}{1 + (\lambda_k \omega)^2}$$

$$\eta''(\omega) = \sum_{k=1}^{\infty} \frac{\eta_k \lambda_k \omega}{1 + (\lambda_k \omega)^2}$$

Example 8.4-2 Unsteady viscoelastic flow near an oscillating plate

Using the Maxwell model obtain the attenuation and phase shift in the “periodic steady state”

Solution:

For the shearing floe, the equation of motion, written in terms of the stress tensor component gives:

$$\rho \frac{\partial v_x}{\partial t} = -\frac{\partial}{\partial y} \tau_{yx}$$

The Maxwell model in integral form is like eq 8.4-9, but with a single exponential

$$\tau_{yx}(y,t) = -\int_{-\infty}^{t} \left\{ \frac{\eta_0}{\lambda_1} \exp[-(t-t')/\lambda_1] \right\} \frac{\partial v_x(y,t')}{\partial y} dt'$$

Combining these two equations, we get

$$\rho \frac{\partial v_x}{\partial t} = \int_{-\infty}^{t} \left\{ \frac{\eta_0}{\lambda_1} \exp[-(t-t')/\lambda_1] \right\} \frac{\partial^2 v_x(y,t')}{\partial y^2} dt'$$

We postulated a solution of the form

$$v_x(y,t) = \Re\{v^0(y) e^{i\omega t}\}$$

Where $\upsilon^0(y)$ is complex. Substituting:

$$\begin{aligned} \rho \Re\{i\omega v^0 e^{i\omega t}\} &= \int_{-\infty}^{t} \left\{ \frac{\eta_0}{\lambda_1} \exp[-(t-t')/\lambda_1] \right\} \Re\left\{ \frac{d^2 v^0}{dy^2} e^{i\omega t'} \right\} dt' \\ &= \Re\left\{ \frac{d^2 v^0}{dy^2} e^{i\omega t} \int_0^{\infty} \frac{\eta_0}{\lambda_1} e^{-s/\lambda_1} e^{-i\omega s} ds \right\} \\ &= \Re\left\{ \frac{d^2 v^0}{dy^2} e^{i\omega t} \left[\frac{\eta_0}{1 + i\lambda_1 \omega} \right] \right\} \end{aligned}$$

Removing the real operator then gives an equation for $\upsilon^0(y)$

$$\frac{d^2 v^0}{dy^2} - \left[\frac{i\rho\omega(1 + i\lambda_1\omega)}{\eta_0} \right] v^0 = 0$$

Then if the complex quantity is set equal to $(\alpha+i\beta)^2$, the solution to the differential equation is;

$$v^0 = v_0 e^{-(\alpha+i\beta)y}$$

Multiplying this by $e^{i\omega t}$ and taking the real part

$$v_x(y,t) = v_0 e^{-\alpha y} \cos(\omega t - \beta y)$$

Quantities α and β depend on the frequency

$$\alpha(\omega) = \sqrt{\frac{\rho\omega}{2\eta_0}}\left[\sqrt{1 + (\lambda_1\omega)^2} - \lambda_1\omega\right]^{+1/2}$$

$$\beta(\omega) = \sqrt{\frac{\rho\omega}{2\eta_0}}\left[\sqrt{1 + (\lambda_1\omega)^2} - \lambda_1\omega\right]^{-1/2}$$

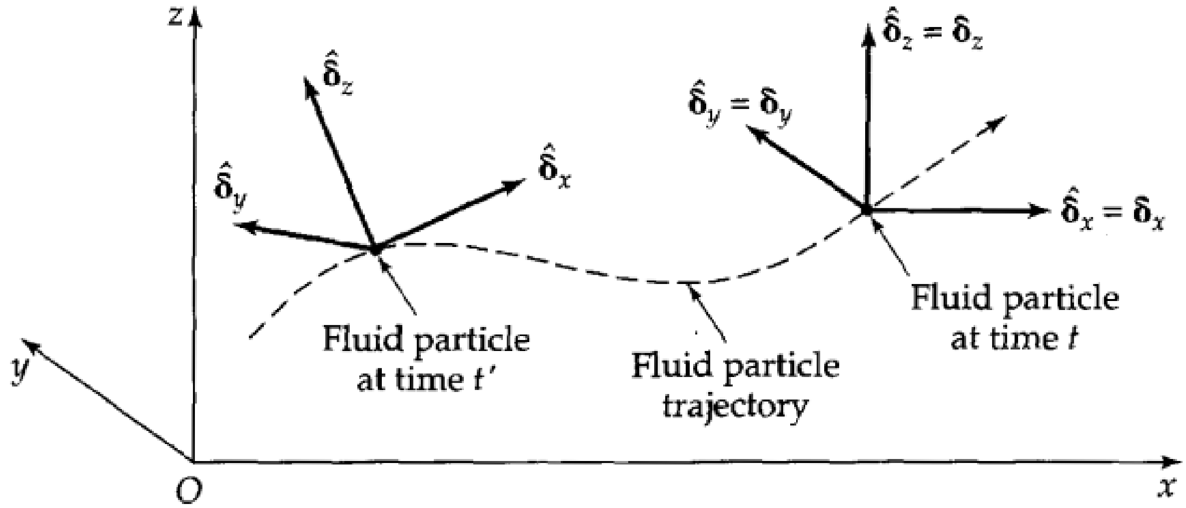
With increasing frequency, α decreases and β increase, this is because of the fluid elasticity. We also can see how elasticity affects the transmission of shear waves near an oscillating surface.

In example 8.4-1 the velocity profile is prescribed, and we have to derived an expression for the shear stress required to maintain the motion; the equation of motion was not used. In example 8.4-2 no assumption was made about the velocity distribution, and we derived the velocity distribution by using the equation of motion.

B.5 The corotational derivates and the nonlinear viscoelastic model

In this section we introduce the statement of the relation between the stress tensor and the kinematic tensors at a fluid particle. These tensors should be independent of the instantaneous orientation of that particle in space. For example, if you measure the stress-strain relation in a rubber band, it should not matter the direction that you are stretching the rubber.

To implement this statement is to introduce at each fluid particle a corotating coordinate frame. This orthogonal frame rotates with the local instantaneous angular velocity as it moves along with the fluid particle through space.



In the corotating coordinate system we can now write down a relation between the stress tensor and the rate-of-strain tensor. Write the Jeffrey's model and then add some additional nonlinear terms we obtain:

$$\hat{\boldsymbol{\tau}} + \lambda_1 \frac{\partial}{\partial t}\hat{\boldsymbol{\tau}} + \tfrac{1}{2}\mu_0(\text{tr}\,\hat{\boldsymbol{\tau}})\hat{\dot{\boldsymbol{\gamma}}} - \tfrac{1}{2}\mu_1\{\hat{\dot{\boldsymbol{\gamma}}}\cdot\hat{\boldsymbol{\tau}} + \hat{\boldsymbol{\tau}}\cdot\hat{\dot{\boldsymbol{\gamma}}}\} = -\eta_0\left(\hat{\dot{\boldsymbol{\gamma}}} + \lambda_2\frac{\partial}{\partial t}\hat{\dot{\boldsymbol{\gamma}}} - \mu_2\{\hat{\dot{\boldsymbol{\gamma}}}\cdot\hat{\dot{\boldsymbol{\gamma}}}\}\right)$$

In Eq. 8.5-1 μ_n & λ_n are constant and all has dimensions of time. Doing some mathematical corrections we can transform the tensor dot products components in the $\hat{x}\hat{y}\hat{z}$ frame to the xyz frame.

- ✓ ***Oldroyd 6-constant model***

$$\boldsymbol{\tau} + \lambda_1 \frac{\mathcal{D}}{\mathcal{D}t}\boldsymbol{\tau} + \tfrac{1}{2}\mu_0(\text{tr}\,\boldsymbol{\tau})\dot{\boldsymbol{\gamma}} - \tfrac{1}{2}\mu_1\{\boldsymbol{\tau}\cdot\dot{\boldsymbol{\gamma}} + \dot{\boldsymbol{\gamma}}\cdot\boldsymbol{\tau}\} = -\eta_0\left(\dot{\boldsymbol{\gamma}} + \lambda_2\frac{\mathcal{D}}{\mathcal{D}t}\dot{\boldsymbol{\gamma}} - \mu_2\{\dot{\boldsymbol{\gamma}}\cdot\dot{\boldsymbol{\gamma}}\}\right)$$

This model has no dependence on the local instantaneous orientation of the fluid particles in space. It should be emphasized that use of the corotating frame guarantees only that the instantaneous local rotation of the fluid has been subtracted off.

Another nonlinear viscoelastic model is the 3-constant Giesekus model, which contains a term that is quadratic in the stress components:

$$\boldsymbol{\tau} + \lambda\left(\frac{\mathcal{D}}{\mathcal{D}t}\boldsymbol{\tau} - \tfrac{1}{2}\{\boldsymbol{\tau}\cdot\dot{\boldsymbol{\gamma}} + \dot{\boldsymbol{\gamma}}\cdot\boldsymbol{\tau}\}\right) - \alpha\frac{\lambda}{\eta_0}\{\boldsymbol{\tau}\cdot\boldsymbol{\tau}\} = -\eta_0\dot{\boldsymbol{\gamma}}$$

- ✓ λ is a time constant

- ✓ η_0 is the zero shear stress viscosity
- ✓ α is a dimensionless parameter

This model gives reasonable shapes for most material functions, and the analytical expressions. They are summarized in Table, because terms are not particularly simple. Superpositions of Giesekus models can be made to describe the shapes of the measured material functions almost quantitatively. The model has been used widely for fluid dynamics calculations.

Table 8.5-1 Material Functions for the Giesekus Model

Steady shear flow:

$$\frac{\eta}{\eta_0} = \frac{(1-f)^2}{1+(1-2\alpha)f} \quad \text{(A)}$$

$$\frac{\Psi_1}{2\eta_0\lambda} = \frac{f(1-\alpha f)}{\alpha(1-f)} \frac{1}{(\lambda\dot{\gamma})^2} \quad \text{(B)}$$

$$\frac{\Psi_2}{\eta_0\lambda} = -f\frac{1}{(\lambda\dot{\gamma})^2} \quad \text{(C)}$$

where

$$f = \frac{1-\chi}{1+(1-2\alpha)\chi} \quad \text{and} \quad \chi^2 = \frac{[1+16\alpha(1-\alpha)(\lambda\dot{\gamma})^2]^{1/2}-1}{8\alpha(1-\alpha)(\lambda\dot{\gamma})^2} \quad \text{(D, E)}$$

Small-amplitude oscillatory shear flow:

$$\frac{\eta'}{\eta_0} = \frac{1}{1+(\lambda\omega)^2} \quad \text{and} \quad \frac{\eta''}{\eta_0} = \frac{\lambda\omega}{1+(\lambda\omega)^2} \quad \text{(F, G)}$$

Steady elongational flow:

$$\frac{\bar{\eta}}{3\eta_0} = \frac{1}{6\alpha}\left[3 + \frac{1}{\lambda\dot{\varepsilon}}\left(\sqrt{1-4(1-2\alpha)\lambda\dot{\varepsilon}+4(\lambda\dot{\varepsilon})^2} - \sqrt{1+2(1-2\alpha)\lambda\dot{\varepsilon}+(\lambda\dot{\varepsilon})^2}\right)\right] \quad \text{(H)}$$

B.6 Molecular theory for polymeric liquids

The kinetic theories for polymers can be divided into 2 classes : *network theories* and *single-molecule theories*:

a) The network theories originally developed for describing rubber properties,
b) Single-molecule theories developed for describing polymer solutions in very dilute solutions.

Formula for a dilute solution of a polymer, modeled as an elastic dumbbell. The spring is nonlinear and finitely extensible with the force given by:

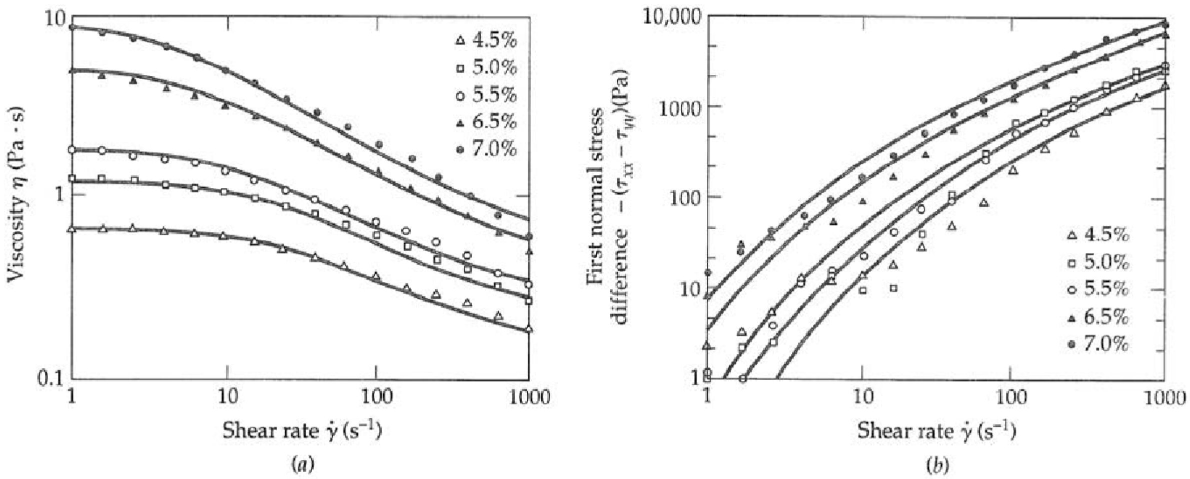
$$\mathbf{F}^{(c)} = \frac{H\mathbf{Q}}{1 - (Q/Q_0)^2}$$

Where H is a spring constant, Q is the end-to-end vector of the dumbbell representing the stretching and orientation of the dumbbell and Q_0 is the maximum elongation of the spring.
The following expression for the stress tensor is worked out using kinetic theory details. It is the sum of a Newtonian solvent and a polymer contribution:

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

$$\boldsymbol{\tau}_s = -\eta_s \dot{\boldsymbol{\gamma}}$$

$$Z\boldsymbol{\tau}_p + \lambda_H\left(\frac{\mathscr{D}}{\mathscr{D}t}\boldsymbol{\tau}_p - \tfrac{1}{2}\{\boldsymbol{\tau}_p \cdot \dot{\boldsymbol{\gamma}} + \dot{\boldsymbol{\gamma}} \cdot \boldsymbol{\tau}_p\}\right) - \lambda_H(\boldsymbol{\tau}_p - n\kappa T\boldsymbol{\delta})\frac{D \ln Z}{Dt} = -n\kappa T\lambda_H\dot{\boldsymbol{\gamma}}$$



Viscosity and first-normal-stress difference data for polymethylmethacrylate solutions.

C. References

Transport Phenomena, R. Byron Bird, Warren E. Stewart, Edwin N. Lightfoot Second Edition

Class Notes Inqu 4010 Professor Cordova Ph.D. August 9, 2010

http://www.youtube.com/watch?v=f2XQ97XHjVw&NR=1

http://www.youtube.com/watch?v=3zoTKXXNQIU&NR=1&feature=fvwp

http://video.google.com/videoplay?docid=-9094972957848338868#