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# Chapter 3 Polymer Melt Rheology
## (Tadmor Chapter 6)

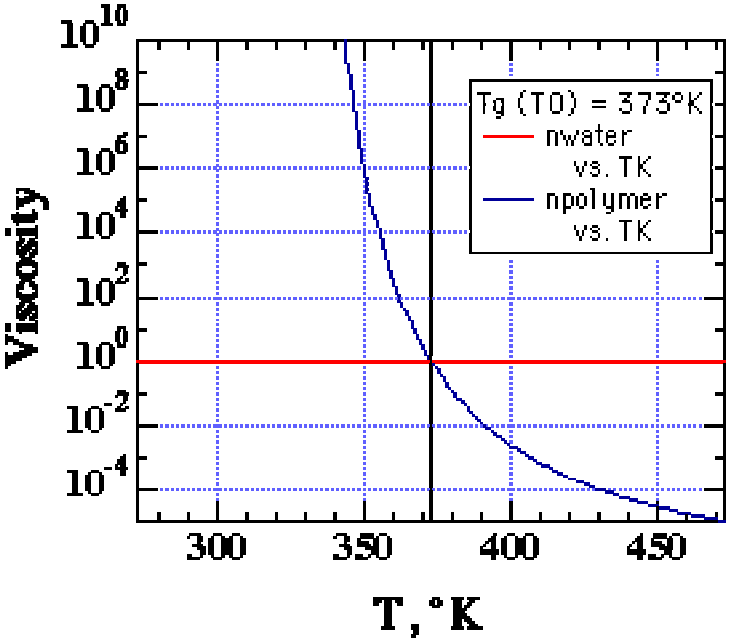
Tadmor's Chapter 6, is an overview of Non-Newtonian Rheology, which is basically taken from Bird, Armstrong, Hassager, "Dynamics of Polymeric Liquids" Volume 1 (of 2) Fluid Mechanics. (Volume 2 of this set deals with theory of melt viscosity and is a common reference but of little use for processing.)

The most important non-Newtonian effects in polymer melt flow are the **A)** temperature and **B)** shear rate dependence of viscosity.

**A)** First issue in chapter 6 is to compare the *temperature dependence* of Newtonian vs. polymeric fluids (See homework problem). A comparison of the Arrhenius behavior in eqn. 6.1.1 (pp. 147) and the WLF behavior of

$$\eta=\eta_0 \exp[-17.444(T-T_g)/\{51.6+(T-T_g)\}]$$

shows that the equations are similar (Arrhenius and WLF Functions). The thermal behavior is dramatically different as seen below in a semi-log plot.



**B)** The second issue in chapter 6 of Tadmor involves changes in the viscosity with shear rate (usually shear thinning behavior, see Chapter 1) and related issues of normal forces (Wiessenberg Effect and die swell). These issues are also related to the appearance of solid-like features (elastic component) to polymeric fluids including self-siphoning behavior, bubble shape, flow stabilization, fibrillation (ability to form fibers) and fluid memory effects. Several examples mostly from Bird Armstrong Hassager are given below. Most of these examples can be duplicated with common "structured" fluids such as molasses, shampoo or motor oil.

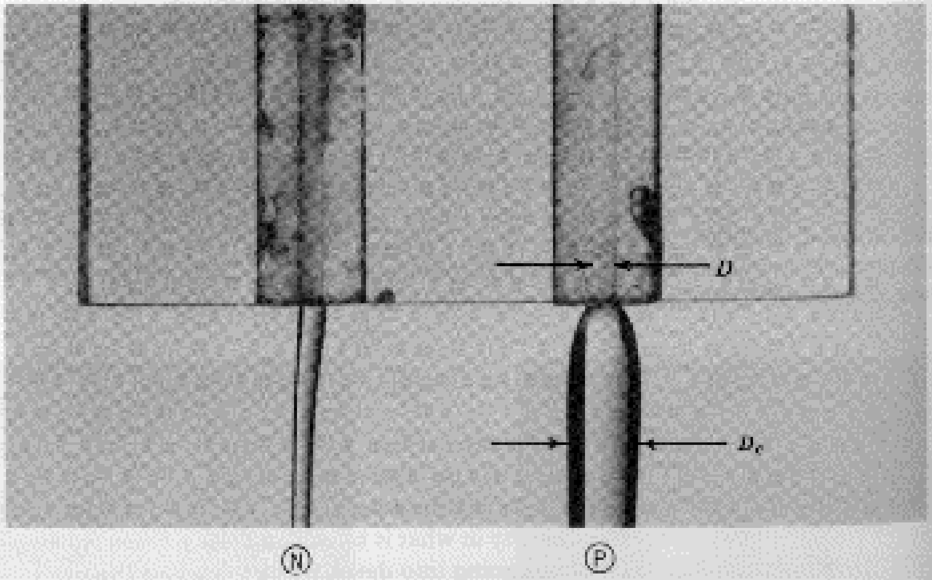
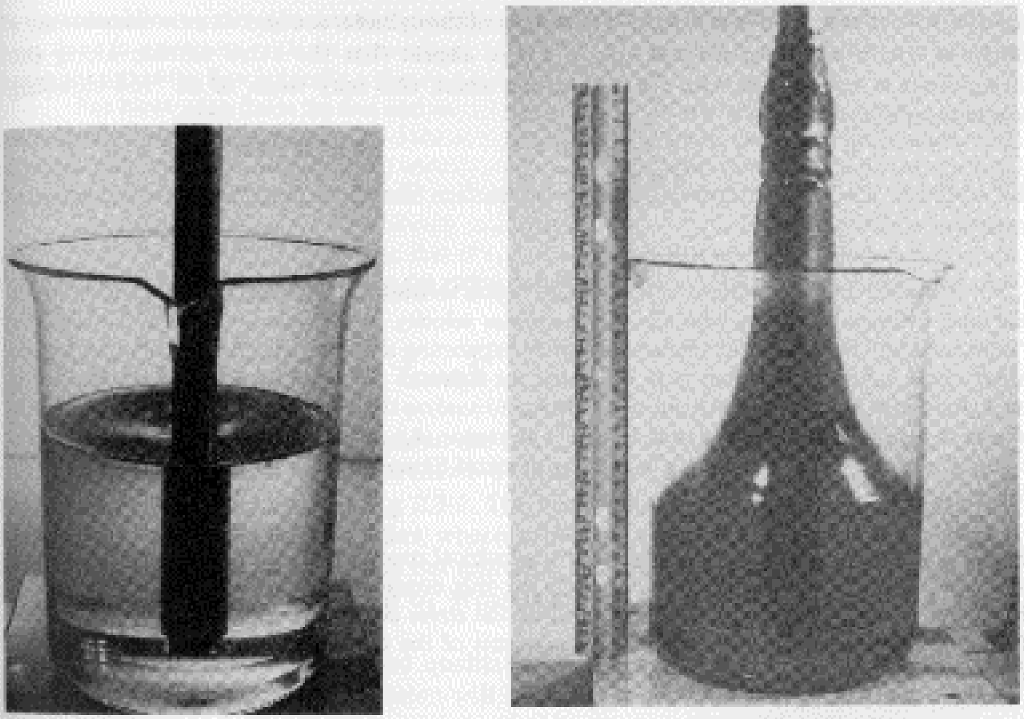


FIGURE 2.5-1. Behavior of fluids issuing from orifices. Ⓝ A stream of Newtonian fluid (silicone fluid) shows no diameter increase upon emergence from the capillary tube; Ⓟ a solution of 2.44 g of polymethylmethacrylate ($\bar{M}_n = 10^6$ g/mol) in 100 cm$^3$ of dimethylphthalate shows an increase by a factor of 3 in diameter as it flows downward out of the tube. [Reproduced from A. S. Lodge, *Elastic Liquids*, Academic Press, New York (1964), p. 242.]

From Bird, Armstrong, Hassager, "Dynamics of Polymeric Liquids, Vol. 1"



Ⓝ Ⓟ

FIGURE 2.3-1. Fixed cylinder with rotating rod. Ⓝ The Newtonian liquid, glycerin, shows a vortex; Ⓟ the polymer solution, polyacrylamide in glycerin, climbs the rod. The rod is rotated much faster in the glycerin than in the polyacrylamide solution. At comparable low rates of rotation of the shaft, the polymer will climb whereas the free surface of the Newtonian liquid will remain flat. [Photographs courtesy of Dr. F. Nazem, Rheology Research Center, University of Wisconsin-Madison.]

From Bird, Armstrong, Hassager, "Dynamics of Polymeric Liquids, Vol. 1"

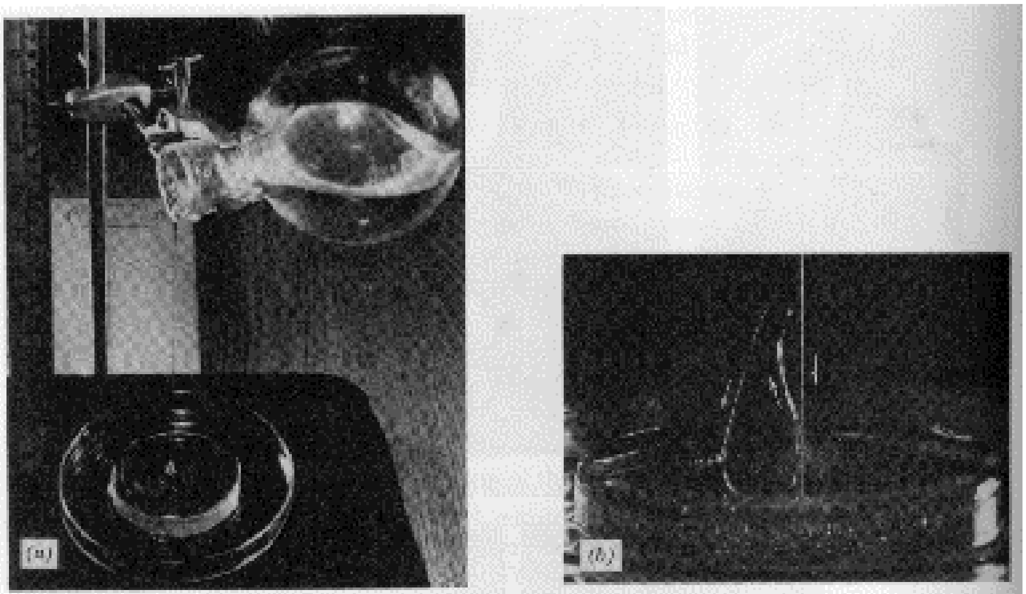


FIGURE 2.5-9. (*a*) A solution of 5.76 g of polyisobutylene ($M_v \doteq 10^6$) in 100 cm$^3$ of decalin is poured onto a shallow pool of the same liquid. (*b*) A filament of the liquid stream rebounds from the pool if the stream being poured has a sufficiently small diameter. [Reproduced from A. S. Lodge, *Elastic Liquids*, Academic Press, New York (1964), p. 251.]

From Bird, Armstrong, Hassager, "Dynamics of Polymeric Liquids, Vol. 1"

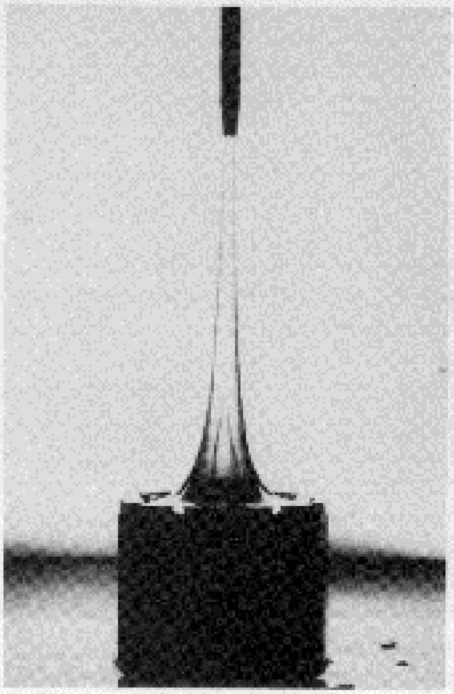


FIGURE 2.5-4. Fluid column in tubeless siphon experiment with the same polymer as in Fig. 2.5-3 Note the stable trapped bubble at the bottom of the column. [Reproduced from S. T. J. Peng and R. F. Landel in G. Astarita, G. Marrucci, and L. Nicolais, eds., *Rheology*, Vol. 2, Plenum Press, New York (1980), p. 388.]

From Bird, Armstrong, Hassager, "Dynamics of Polymeric Liquids, Vol. 1"

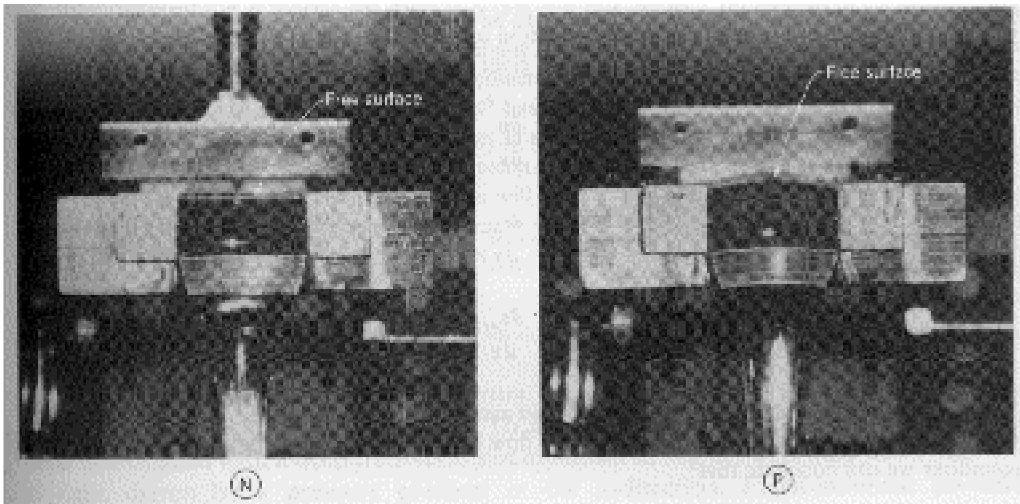


FIGURE 2.3-2. Tanner's tilted trough. A Newtonian liquid flowing down an inclined channel exhibits a flat free surface Ⓝ; the free surface of a polyisobutylene solution is convex Ⓟ. [Reproduced from R. I. Tanner, *Trans. Soc. Rheol.*, **14**, 483–507 (1970).]

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[6] R. I. Tanner, *Trans. Soc. Rheol.*, **14**, 483–507 (1970); R. I. Tanner, *Engineering Rheology*, Oxford University Press (1985), pp. 102–105.

[7] A. S. Wineman and A. C. Pipkin, *Acta Mech.*, **2**, 104–115 (1966).

From Bird, Armstrong, Hassager, "Dynamics of Polymeric Liquids, Vol. 1"

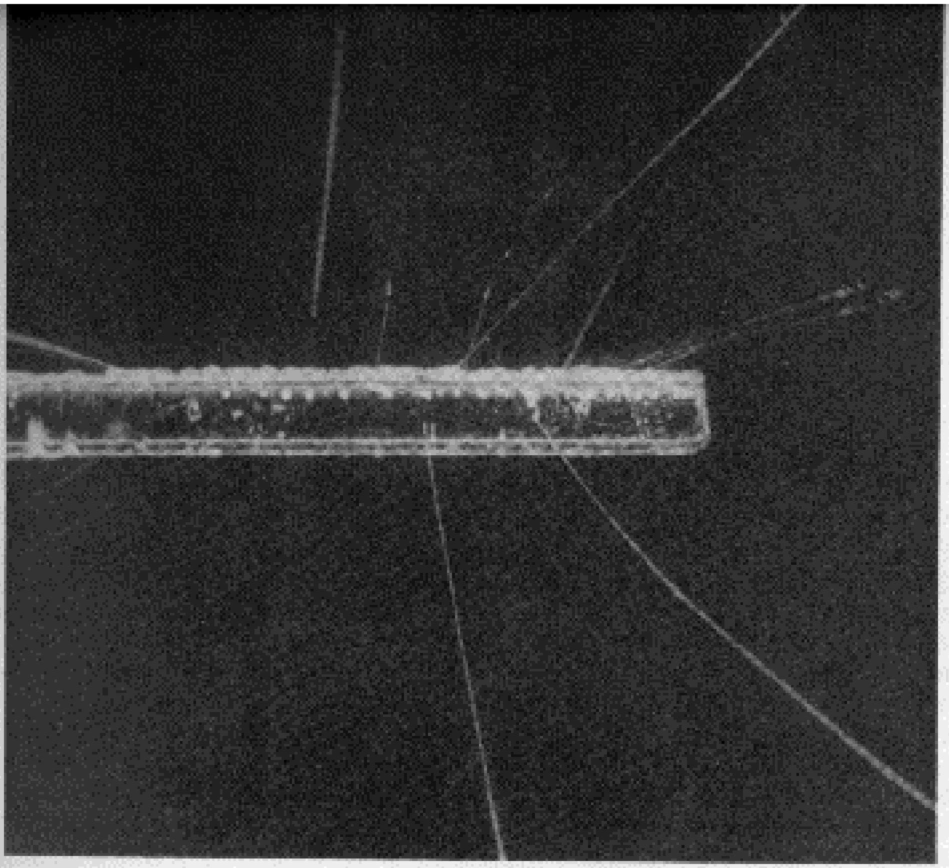


**FIGURE 2.5-10.** A solution of high molecular weight polyisobutylene in low molecular weight polyisobutylene forms fine, continuous streams emanating from a 6-mm glass rod. [Reproduced from B. J. S. Barnard and W. G. Pritchard, *Nature*, **250**, 215–216 (1974).]

From Bird, Armstrong, Hassager, "Dynamics of Polymeric Liquids, Vol. 1"

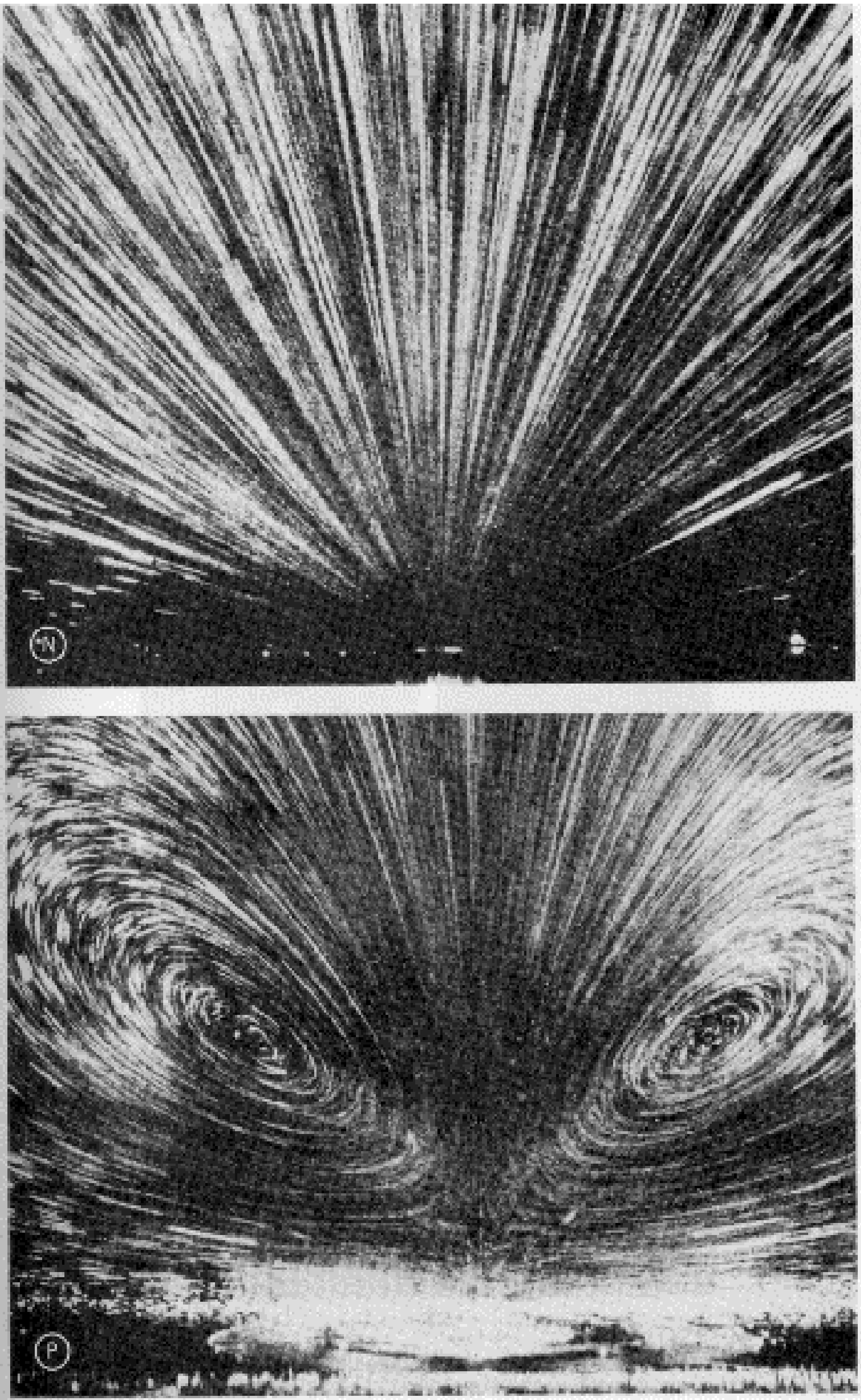


FIGURE 2.5-6. Velocity fields near a sudden contraction. The fluid moves from top to bottom in the photographs from a large reservoir into a small circular tube. Ⓝ The streamlines in glycerin are straight and all directed toward the exit; Ⓟ a 1.67% aqueous polyacrylamide solution shows a large toroidal vortex. [Photographs by H. Giesekus, given in A. B. Metzner, E. A. Uebler, and C. F. Chan Man Fong, *AIChE J.*, **15**, 750–758 (1969).]

From Bird, Armstrong, Hassager, "Dynamics of Polymeric Liquids, Vol. 1"

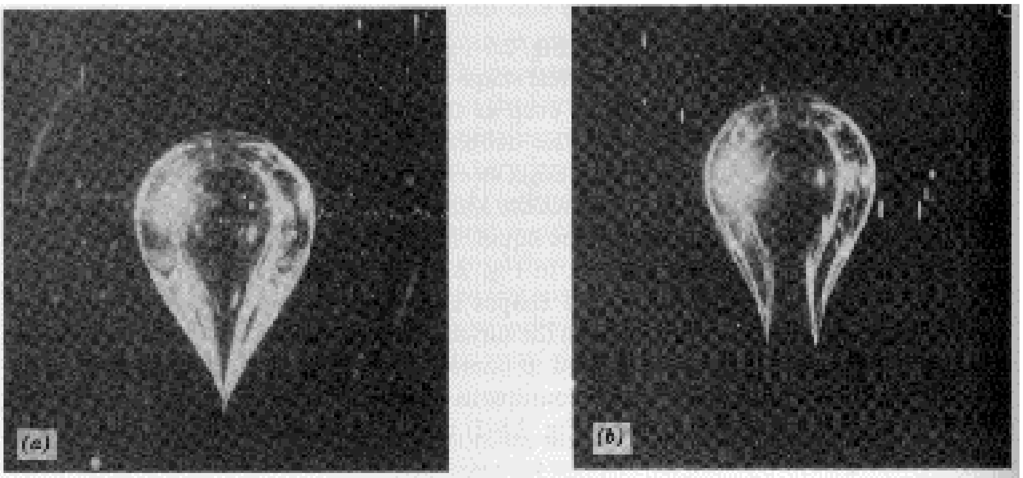


FIGURE 2.6-2. Highly distorted gas bubble of volume approximately 2100 mm$^3$ rising with velocity 10 mm/s in a polyacrylamide solution. The bubble is seen from two mutually perpendicular directions. Note that the bottom end is not axisymmetric. [Photographs by O. Persson, Instituttet for Kemiteknik, Danmarks tekniske Højskole, Danmark.]

From Bird, Armstrong, Hassager, "Dynamics of Polymeric Liquids, Vol. 1"

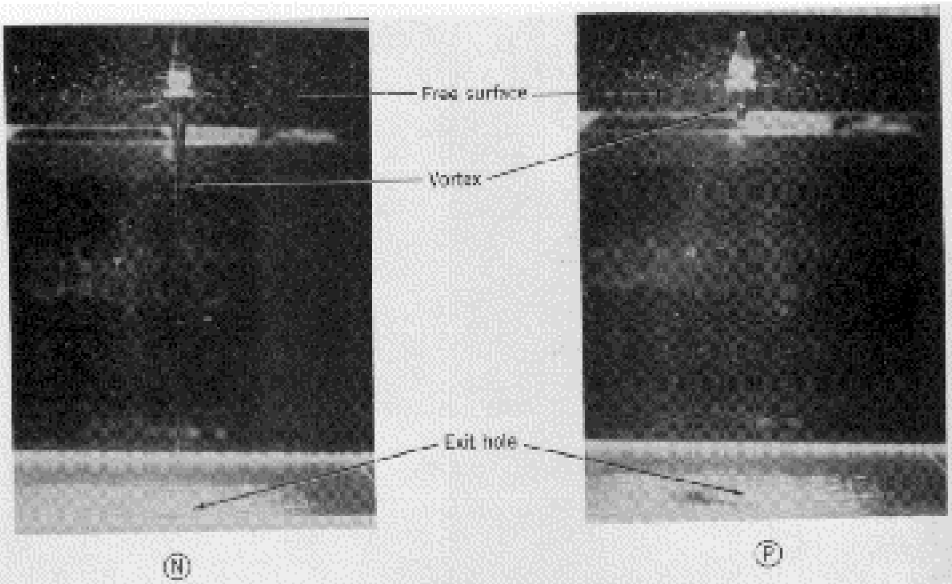


FIGURE 2.5-11. Vortex inhibition. Ⓝ shows the vortex that is formed as water drains form a tank, and Ⓟ shows the corresponding result after addition of a small amount of polymer to the water. A reflection of the vortex in the free surface of the liquid can be seen just above the vortex in both photographs. [Reproduced from photographs courtesy of Professor R. J. Gordon, Department of Chemical Engineering, University of Florida.]

From Bird, Armstrong, Hassager, "Dynamics of Polymeric Liquids, Vol. 1"

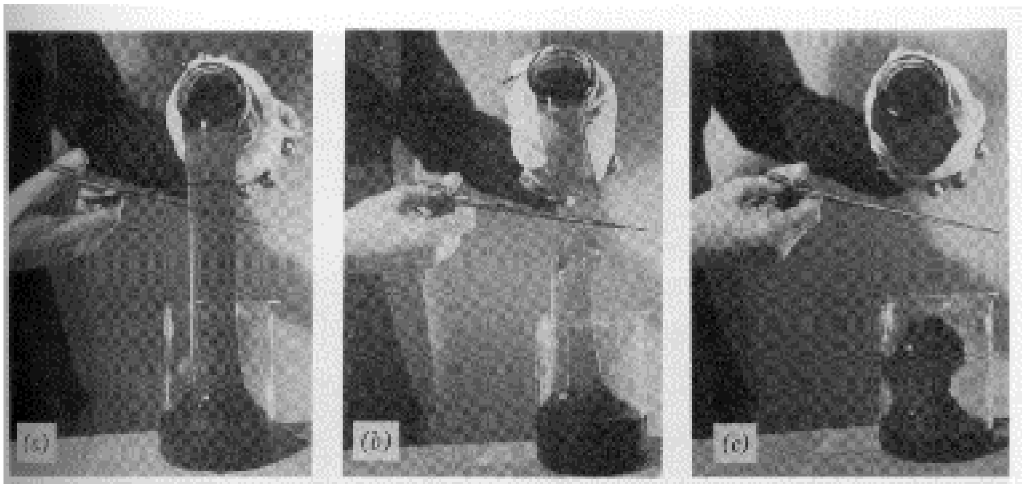


FIGURE 2.5-8. An aluminum soap solution, made of aluminum dilaurate in decalin and *m*-cresol, is (*a*) poured from a beaker and (*b*) cut in midstream. In (*c*), note that the liquid above the cut springs back to the beaker and only the fluid below the cut falls to the container. [Reproduced from A. S. Lodge, *Elastic Liquids*, Academic Press, New York (1964), p. 238. For a further discussion of aluminum soap solutions see N. Weber and W. H. Bauer, *J. Phys. Chem.*, **60**, 270–273 (1956).]

From Bird, Armstrong, Hassager, "Dynamics of Polymeric Liquids, Vol. 1"

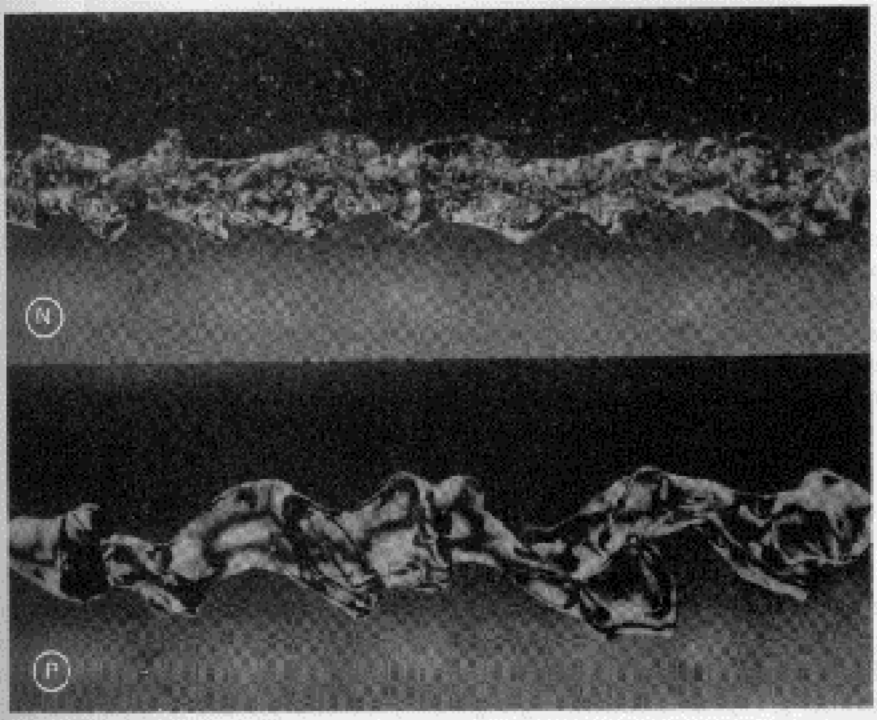


FIGURE 2.7-3. High-speed photographs of a jet 1 m from an orifice: Ⓝ pure water and Ⓟ 200 ppm solution of polyethyleneoxide in water. [Photographs courtesy of J. J. Taylor, Independent Consultant, Santa Barbara, CA, and J. W. Hoyt, Department of Mechanical Engineering, San Diego State University.]

From Bird, Armstrong, Hassager, "Dynamics of Polymeric Liquids, Vol. 1"

# Constutive Equations for Polymer Flow

In order to deal with these effects a number of equations have been developed which describe some of these features. The primary reason for the vast diversity of equations which have been generated is that rheologists have developed different *frames of reference* to account for fluid elements which can be deformed in a flow. For example, if you consider a polymer chain as being deformed in a flow you will need a reference frame which follows a fluid element and describes its deformation. The main complication in dealing with these new frames of reference is converting from the machine or lab frame of reference to the new frame, doing calculations in the new frame and then converting back to the machine frame. These conversions are fairly complicated and we will not deal in detail with how they are carried out. (Bird Armstrong Hassager is a good source for reference frame conversions as is Christensen's "Theory of Viscoelasticity" 1982).

We do need to consider the generalities of these approaches in order to understand the source of the various equations used to describe non-Newtonian flow. To describe the flows shown in class we will need:

1. Tensors (we have normal forces)
2. A description of fluid memory (memory of stress/strain history)
3. Description of viscoelasticity.
4. Definition of various Reference Frames useful for the description of 2 and 3.

From an engineer's perspective the golden rule is *"If it ain't broke, don't fix it"* which translates into *always use the simplest equations that "work"*. If the Newtonian fluid equations are good enough, then use them. If you can live with a small modification of Newtonian fluids such as a power-law fluid, then do it.

Below is a list of terms useful in dealing with polymer flow and non-Newtonian rheology:

- Simple Fluids:
  Simple Fluids are fluids where the fluid elements are independent of each other. The simple fluid model is the basis of the *reference frames* listed below.
- Flow History:
  The accumulated strain history of fluid elements need be considered in a simple fluid. The strain history starts at an undeformed state and proceeds through all fluid deformations.

- Reference Frames:
  There are three reference frames that we need to consider:

  1. *Lab Frame*: This is the frame we have used to describe Newtonian flow. All other frames will need to be converted to this frame to yield useful results. The lab frame usually involves no flow history.The lab frame is also called the *substantial frame* or *viscometer frame*. The lab frame results in simple Newtonian-like constitutive equations:
     i. GNF-Generalized Newtonian Fluid, e.g. power-law fluid
     ii. If you account for time/memory *LVE Fluids or Maxwell Fluids*
  2. *Corotational Frame*: This is a frame that moves and rotates with a fluid element. The frame is fixed in size.
     i. *CEF Fluids* (Criminale-Ericksen-Filbey). These include time and memory effects.
        $\psi_1$ = f(gamma dot); $\psi_2$ = f(gamma dot); $\eta$ = f(gamma dot)
  3. *Codeformational Frame*: This is a frame that does what 2 does but also can change in unit size as the fluid element is deformed. (This leads to very complicated equations but can account for most situations). We won't consider these. Extremely complex equations.

## Simplest Assumption and Its Limitations

The simplest assumption for polymer flow is that the fluid is Newtonian and you the lab frame can be used. For a shear thinning fluid such as a polymer melt this requires ignoring the causes of a reduction in viscosity and treating a fluid at each shear rate as independent of the fluid at other shear rates. This approach can't account for normal forces, memory effects or elasticity. A typical viscosity versus rate of strain curve is shown below on a log/log plot. The generalized newtonian fluid assumption that the viscosity is fixed is clearly a poor assumption for a polymeric melt. In polymer processing it is the knee and power-law regimes that are of most importance.

If you ignore normal forces; memory effects; and elasticity, then simple equations for viscosity can be used by breaking down the log viscosity vs log shear rate plot into three regimes:

a. Newtonian regime

b. Transition regime.

c. Power-law fluid regime.

Consider polymer melt flow in an Extruder as an example of how and where this regime approach could be applied to a polymer processing operation:

1. Pellets/Melting: Bingham Fluid
2. Pressurization and Pumping: Transition Regime to Power-Law, Ellis Model/Carreau Model
3. High Shear in Die: Power-Law Fluid
4. Die Swell: CEF Fluid
5. Post Extrusion Processing: Linear Viscoelastic Equations, LVE Model

## Equation 6.3-1:
## Stress/Strain History of a Fluid Element (What is involved)

Equation 6.3-1 of Tadmor (p. 155) gives the Goddard expression for a simple fluid in a corotational frame as expanded in an integral series by Green and Rivlin among others:

$$\boldsymbol{\tau}(\mathbf{x},t) = -\int_{-\infty}^{t} G_1(t-t')\dot{\boldsymbol{\Gamma}}'\,dt' - \frac{1}{2}\int_{-\infty}^{t}\int_{-\infty}^{t} G_{11}(t-t',t-t'')[\dot{\boldsymbol{\Gamma}}'\cdot\dot{\boldsymbol{\Gamma}}'' + \dot{\boldsymbol{\Gamma}}''\cdot\dot{\boldsymbol{\Gamma}}']\,dt''\,dt' - \cdots \qquad (6.3\text{-}1)$$

This function is an indication of how complicated things can get when rheological equations are used to describe time history of fluid elements. Equation 6.3-1 is constructed by the following steps:

- Use a Corotational reference frame so the γ dot tensor is transformed by matrix manipulation in to Γ dot matrix.
- Then write time integrals of the strain to get the shear stress tensor, τ.

The parts of the equation are described by:

- **First integral** involves the integral over all time from -∞ to now, t, of strain using a constitutive parameter $G_1$, which is a tensor also.
- **Second integral** involves how the strain at time A effects the response at time B, i.e. if I stretched the fluid element at some point in history how does it effect the response at some other later time? This involves a second constitutive parameter $G_{11}$ which is also a tensor.
- **Other integrals** may be needed if three or higher number of points in time are related to each other... i.e. leading to $G_{111}$, $G_{1111}$ etc.

## Criminale-Ericksen-Filbey (CEF) Equation

The approach taken by CEF is to use expansions of the rate of strain in the corotational frame in derivatives of time and to truncate these derivatives in a fairly messy approach but one which justifies the use of power-law equations and equations for the first and second normal stress differences. This approach can also be used to justify LVE equations.

Equation 6.3-1 yields equation 6.3-5 for steady shear flows.

$$\boldsymbol{\tau} = -\eta\dot{\boldsymbol{\gamma}} - (\tfrac{1}{2}\Psi_1 + \Psi_2)\{\dot{\boldsymbol{\gamma}} \cdot \dot{\boldsymbol{\gamma}}\} + \frac{1}{2}\Psi_1 \frac{\mathscr{D}\dot{\boldsymbol{\gamma}}}{\mathscr{D}t} \qquad (6.3\text{-}5)$$

This is the CEF equation. The first term is related to the first integral of 6.3-1 and represents Generalized Newtonian Fluids. The second term is related to second integral of 6.3-1 and describes constitutive equations which parallel GNF equations for normal forces, i.e. gamma dot is squared instead of the first power for normal forces.

## Linear Viscoelastic (LVE) Equation

If only the first integral is retained in 6.3-1 the Goddard Miller (GM) equation can result which under small deformations, where the corotation frame becomes equivalent to the lab frame, the LVE equations result. One of these is the Maxwell constitutive equation:

$$\tau + \lambda_0 \, d\tau/dt = \eta_0 \, d\gamma; \qquad 6.3\text{-}9$$

Equation 6.3-9 describes a spring and a dashpot in series (elastic and viscous elements in series).

## Generalized Newtonian Fluids

The first term of equation 6.3-5 can also give rise to a *Generalized Newtonian Fluid* (Section 6.5 pp. 167) of which there are several types we will consider. We consider only the magnitude of $d\gamma/dt$ for GNF equations. An incompressible fluid under shear flow with no dependence of $\eta$ on the third invariant of $d\gamma/dt$, III. Each GNF equation is applicable only in a certain range of $d\gamma/dt$ and this must be specified with the equation parameters.

1. Power-Law Fluid:

   $$\eta(d\gamma/dt) = m\,(d\gamma/dt)^{n-1}$$

   The n-1 power is a direct consequence of the first term in the CEF equation having a power of 1 for $d\gamma/dt$. m is the *consistency* and n is the *power-law index*. For a Newtonian fluid $n = 1$ and m is the viscosity. Typical values for n are given in appendix A and range from about 0.2 to close to 1. Power-law equations are for high strain rates. The power-law fluid model is a 2-parameter empirical constitutive equation.

2. Ellis Model:
   Both the Ellis and Carreau Models describe the knee part of the strain rate curve for viscosity. Ellis uses 3 parameters and Carreau uses 4 parameters (3 for polymer melts).
   The Ellis model is written in terms of $\tau$ and the Carreau in terms of $d\gamma/dt$.
   Values for the parameters are given in Appendix A for various polymers.
   Ellis:

   $$\eta_0/\eta(t) = 1 + (\tau/\tau_{1/2})^{\alpha-1}$$

   $\eta_0$ is the zero shear rate viscosity and $\tau_{1/2}$ is the value of $\tau$ where the viscosity is half that of $\eta_0$.

3. Carreau Model:

Equation 6.5-8 pp. 169

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

$\eta_\infty$ is the solvent viscosity for solutions or zero for polymer melts.

4. Bingham Fluid:
   For fluids that display a solid like behavior below a critical shear stress. Paints and Ketchup.

$$\eta(\dot{\gamma}) = \eta_0 + \frac{\tau_0}{\dot{\gamma}}$$

5. Constitutive Equations for Normal Forces (CEF):
   For Steady, Fully Developed Flow in a Tube, η follows one of the equations above and

$$N_1 = \Psi_1 \dot{\gamma}^2$$
$$N_2 = \Psi_2 \dot{\gamma}^2$$

## Application of Empirical Constitutive Equations to Describe Polymer Melt Flow

1. Newtonian, Low Shear Rate
2. Power-Law, High Shear Rate
3. Carreau Model (Transition in terms of rate of strain)
4. Ellis Model (Transition in terms of Shear stress)
5. Bingham Fluid (Yield stress behavior, ketchup)
6. CEF Normal Forces (die swell above for example)
7. LVE Solid-like behavior, i.e. elasticity and relaxation (elasticity in flow above).

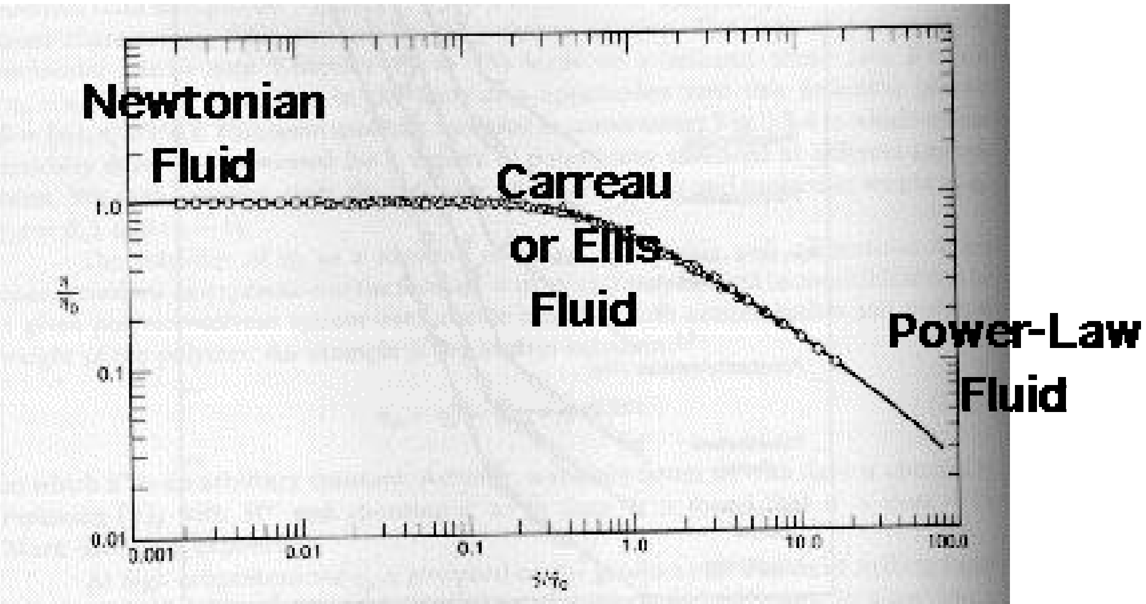


FIGURE 3.6-5. Composite plot of dimensionless viscosity $\eta/\eta_0$ versus dimensionless shear rate $\dot\gamma/\dot\gamma_0$ for several different concentrated polystyrene-*n*-butyl benzene solutions. Molecular weights varied from $1.6 \times 10^5$ to $2.4 \times 10^6$, concentrations from 0.255 to 0.55 g/cm$^3$, and temperatures from 303 to 333 K. [W. W. Graessley, *Adv. Polym. Sci.*, **16**, 1-179 (1974).]

Modified from Bird, Armstrong, Hassager, "Dynamics of Polymeric Liquids Vol. 1" (*Back to above*)

## Viscometric Flows

Next issue is how do you measure these things in a lab?

Also, what simple flows that can be produced in a lab can be used as standards for processing flows. i.e. we will always try to use VISCOMETRIC FLOWS as models for processing situations when possible.

**3 kinds of viscometer we will consider and their processing equivalents:**

Capillary Viscometer => Pipe flow or die flow

Couette Viscometer => Extruder or parallel plate flow

Cone and Plate Viscometer => No commonly used Processing Equivalent Flow

### Capillary Viscometer (Melt Flow Index, MFI)

Model Flow for Tube Flow and Flow in Injection Molding Runners, Extruder Die and the like

Figure 6.1 example 6.3 section 6.7 pp. 176

-Assume incompressible fluid, steady isothermal flow

-Use a cylindrical coordinate system, r, z, θ

-Assume $v_\theta = 0$, no θ dependence of velocity

-Assume $dv_z/dz = 0$ for Steady flow

-Assume $v_r = 0$, no radial flow

-The only velocity is $v_z(r)$

-Assume $\Delta P/\Delta r = 0$, $\Delta P/\Delta\theta = 0$, and $\Delta P/\Delta z$ has a value which drives the flow.

Consider the shear stress which is the force down the tube on a cylindrical fluid element of radius "r".

$$\tau_{rz}(r) = \frac{\Delta F_z}{\Delta A_{\text{perp to r}}}$$

The force at z = 0 is the inlet pressure times the area of a circular fluid surface perpendicular to flow. The same can be calculated at a non-zero value of z down stream. The area perpendicular to r is the circumference of a cylindrical element at r times the length of the tube.

$$F_0(r) = P_0(\pi r^2)$$
$$F_L(r) = P_L(\pi r^2)$$
$$\Delta F_z = (P_0 - P_L)\pi r^2$$
$$\Delta A_{\text{perp to r}} = 2L\pi r$$
$$\tau_{rz}(r) = \frac{\Delta \mathrm{Pr}}{2L}$$

The only point where the rate of strain can be calculated in the capillary is at the wall of the tube. The shear stress at the wall, then, needs to be calculated explicitly as this will be used to determine the viscosity. At the wall r=R and

$$\tau_{\text{wall}} = \frac{\Delta P}{2}\frac{R}{L}$$

usually $P_L = 0$ (gauge pressure)

The rate of strain at the wall under an assumption of a Newtonian model with no time effects is calculated from the flux out of the tube, Q. Q is obtained by measuring the mass which flows out of the capillary for a fixed length of time. Q is related to the velocity distribution by,

$$Q = \int_{r=0}^{r=R} dA\, v_z(r)$$

$$dA = 2\pi r\, dr$$

$$Q = 2\pi \int_{r=0}^{r=R} r\, v_z(r)\, dr$$

Use integration by parts to get

$$Q = 2\pi \left[ \left[ \frac{r^2 v_z(r)}{2} \right]_0^R - \int_0^R \frac{r^2}{2}\, dv_z \right]$$

Assume no slip at wall, $v_z(R) = 0$, so first term is 0, and $dv_z = (dv_z(r)/dr)\, dr$ which is just the rate of strain times dr so:

$$Q = -\pi \int_{r=0}^{r=R} r^2 \dot{\gamma}_r(r)\, dr$$

$r^2 dr$ is converted to $\tau$ using formulas above, i.e. $r = 2\,L\,\tau_{zr}(r)/\Delta P$

and $dr = 2\,L\,/\Delta P\, d\tau_{zr}$, so,

$$Q = \frac{-4\pi L^3}{\Delta P^3} \int_{\tau=0}^{\tau=\tau_w} \tau_{zr}^{\,2} \dot{\gamma}_{zr}(r)\, d\tau_{zr} = \frac{-4\pi R^3}{\tau_w^3} \int_{\tau=0}^{\tau=\tau_w} \tau_{zr}^{\,2} \dot{\gamma}_{zr}\, d\tau_{zr}$$

This equation is differentiated with respect to $\tau_w$ to yield,

$$\dot{\gamma}_w = \frac{1}{\pi R^3} \left[ 3Q + \tau_w \frac{dQ}{d\tau_w} \right] = \frac{1}{\pi R^3} \left[ 3Q + \Delta P \frac{dQ}{d(\Delta P)} \right]$$

which is known as the Rabinowitsch equation (or Wissenberg-Rabinowitsch Equation).

The use of the Rabinowitsch equation requires a constitutive model for the fluid because of the last term in the equation above. For a Newtonian constitutive equation $Q=(\pi R^4 \Delta P)/(8\eta L)$ which is Pouiselle's Law. For a power-law constitutive equation where $\tau = m\,(d\gamma/dt)^n$, and $s = 1/n$, $Q = (\pi R^3)/(s + 3)\{R\Delta P/(2mL)\}^s$.

For capillary flow (flow in a tube)

$$\eta(\dot{\gamma}_{wall}) = \frac{\tau_{wall}}{\dot{\gamma}_{wall}}$$

$$\tau_{wall} = \frac{\Delta P}{2}\frac{R}{L}$$

$$\dot{\gamma}_{wall} = \frac{1}{\pi R^3}\left[3Q + \Delta P\frac{dQ}{d\Delta P}\right]$$

Limitations to capillary flow measurements included:

-Can't vary gamma dot very easily (at least not in MFI instrument).

-Can't measure normal stress differences.

-Can't perform dynamic experiments for LVE parameters.

-Need a model for viscosity versus rate of strain measurements.

The last term for the strain rate at the wall can not be determined with out a constitutive equation for the fluid in the capillary. For a power-law fluid,

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

the governing equation for a capillary viscometer (MFI) is:

$$Q = \left(\frac{n\pi R^3}{1+3n}\right)\left(\frac{R\Delta P}{2mL}\right)^{1/n}$$

For a Newtonian Fluid m = $\eta$, n = 1 and the above equation reduces to the Hagen-Poiseuille Equation for capillary flow.

**<u>Couette Viscometer (Brookfield Viscometer)</u>**

-can vary gamma dot easily

-can possibly measure first normal stress difference

-can't get second normal stress difference

-can do dynamically for LVE parameters

A Couette viscometer consists of a gap between two cylinders which move at a relative angular velocity, Ω. The radius of the inner cylinder is $R_i$ and the outer cylinder is $R_o$. The length of the cylinders contacting the fluid is L.

Locally, the Couette viscometer can be approximated as two parallel plates. The velocity of the fluid near the moving cylinder (plate) is the rotational velocity of the adjoining plate under the no-slip assumption. The velocity of the fluid near the static plate is 0 under the same assumption. The velocity profile across the gap of the viscometer is linear for a Newtonian fluid but can deviate significantly form linear for shear thinning fluids (power-law). The latter is due to the curvature of the Couette viscometer. For true infinite parallel plates the velocity profile is always linear and a single strain rate exists across the gap.

The θ-velocity at the outer, fixed cylinder is 0 and at the inner, rotating cylinder is $v_\theta(r=R_i) = R_i\Omega$. For a power-law fluid, $\eta = m(\dot{\gamma})^{n-1}$, the angular, θ, velocity profile for the Couette viscometer, as a function of "r", under the condition that the inner cylinder rotates at an angular velocity Ω and the outer cylinder is fixed, is:

$$v_\theta(r) = r\Omega\frac{1-\left(R_o/r\right)^{2/n}}{1-\left(R_o/R_i\right)^{2/n}}$$

where $R_o$ is the outer cylinder radius and $R_i$ is the inner cylinder radius.

The strain rate is the derivative of $v_\theta(r)$ with respect to r. At $r=R_o$ the strain rate has a simple form:

$$\dot{\gamma}_{Ro} = \frac{2\Omega}{n\left(1-\left(R_o/R_i\right)^{2/n}\right)}$$

For a Newtonian fluid the strain rate is given by:

$$\dot{\gamma}_{Newtonian}(r) = \frac{2\Omega R_i^2 R_o^2}{r^2\left(R_i^2 - R_o^2\right)}$$

The shear stress at $r=R_o$ is given by:

$$\tau_{Ro} = \frac{T}{2\pi R_o^2 L}$$

Where T is the torque and L is the submerged length of the cylinders. The power-law fluid parameters can be measured by variation in the angular velocity of the cylinder.

The main drawback to the Couette viscometer is that it does not display a constant velocity gradient across the gap.

These equations for the Couette viscometer can be adapted to model shear flow in an extruder.

## Cone and Plate Viscometer

-can vary gamma dot easily

-can bet both normal stress differences

-can do dynamically for LVE parameters

The cone and plate viscometer is composed of a shallow angle cone (1 to 3 degrees angle, β) and a flat plate. The cone is brought close to the plate with the gap filled by a fluid of interest. The cone is attached to a shaft which is rotated at an angular velocity Ω. The shear rate is constant across the gap and does not depend on a model for the fluid,

$$\dot{\gamma} = \frac{\Omega}{\beta}$$

The shear stress, t, is calculated from the torque, T, and the fluid contact radius (radius of the cone) $R_c$,

$$\tau = \frac{3T}{2\pi R_b^3}$$

The cone and plate viscometer is an ideal tool for characterization of non-Newtonian fluids since the rate of strain is constant across the gap and a model for the fluid is not needed to determine the viscosity, η = τ/(dγ/dt). The cone and plate viscometer, however, is not useful as a model for processing flows except for unusual processing equipment. The first normal stress difference can be measured from the upward pressure on the shaft or the downward pressure on the plate, $F_N$. The second normal stress difference can be measured through the used of pressure taps on the bottom plate. Most cone and plate rheometers are equipped for measurement of the first normal stress difference but not for the second normal stress difference measurement. The first normal stress difference is given by,

$$N_1 = \frac{2F_N}{\pi R_b^2}$$

## Elongational Flow (Fiber Spinning/Film Blowing)

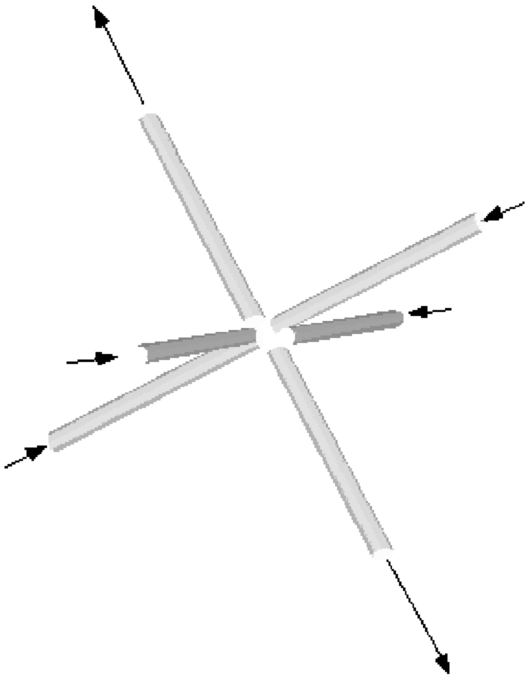
All of the discussion thus far has involved simple shear flow. Simple shear flow is useful to model flow in an extruder and mixing operations. However, many processing operations involve a different kind of flow where the fluid is stretched or elongated, i.e. elongational flow of a polymer melt. Operations such as blow molding of a parison to form a milk jug, film blowing and fiber drawing are some of the many processing operations that involve some form of elongational flow. Generally, elongational flows are nonuniform, non-isothermal and often involve a phase change to a semi-crystalline or solid state. Rheologists study elongational flow under ideal conditions which only approximate some of the conditions which occur in a processing operation. The reason for this is the complexity and difficulty of studying and modeling elongational flow.

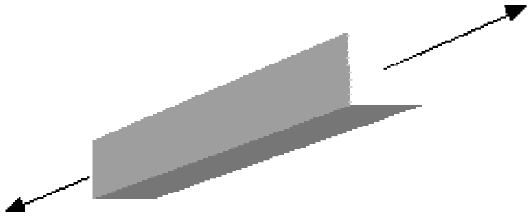
Elongational flow is similar to a tensile stress experiment performed on a solid sample. For an idealized, shear free flow, the rate of strain tensor has only diagonal components,

$$\underline{\underline{\dot{\gamma}}} = \begin{pmatrix} 2a_1 & 0 & 0 \\ 0 & 2a_2 & 0 \\ 0 & 0 & 2a_3 \end{pmatrix}$$

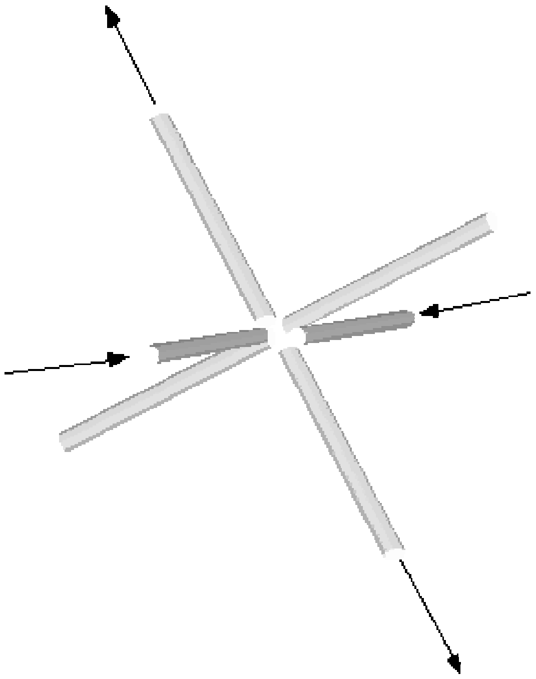
Essentially all polymer melts are incompressible so $a_1 + a_2 + a_3 = 0$. There are three simple types of elongational flow which can be modeled in a laboratory flow experiment by the flow condition at the intersection of 6 orthogonal tubes, or in a mechanical experiment by arrangements of tensile grips on a fluid element.

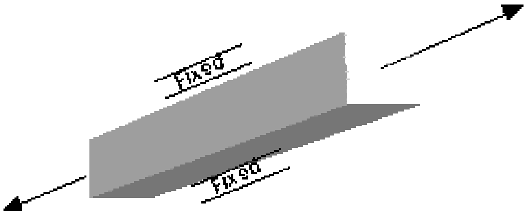
1) Simple Extentional or Elongational Flow: $a_1 = d\varepsilon/dt$; $a_2 = -1/2\ (d\varepsilon/dt)$; $a_3 = -1/2\ (d\varepsilon/dt)$



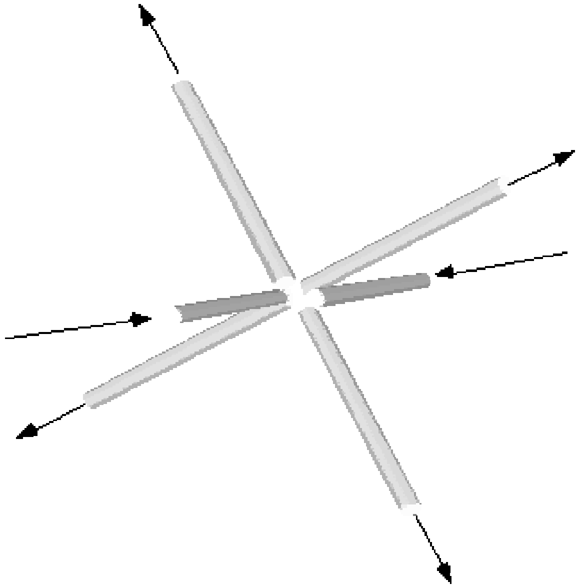


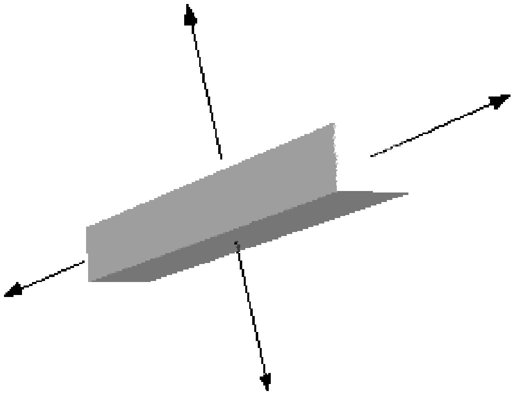
2) Planar Extensional or Elongational Flow: $a_1 = d\varepsilon/dt$; $a_2 = -d\varepsilon/dt$; $a_3 = 0$





3) Biaxial Extensional or Elongational Flow: $a_1 = d\varepsilon/dt$; $a_2 = d\varepsilon/dt$; $a_3 = -2\,(d\varepsilon/dt)$





Consider that you wish to create a simple elongational flow in a fluid element. In the x direction, the fluid element must be subjected to a strain rate $d\varepsilon/dt$ so that $v_x = dx/dt = x\, d\varepsilon/dt$. In terms of the length L in the x direction of a fluid element we have,

$$dL/dt = (d\varepsilon/dt)\, L(t)$$

At time 0, $L = L_0$ and at time "t", $L(t) = L_0 \exp(t\, d\varepsilon/dt)$. In order to obtain a constant rate of elongational strain in a tensile experiment the elongated length must exponentially increase in time! In any real processing operation this can not be achieved so processing operations involve variable strain rates.

**Trouton Viscosity:**

For steady elongational flow a constitutive parameter similar to viscosity relates the elongational stress difference (normal stress difference) to the elongational strain rate,

$$\tau_{11} - \tau_{33} = \bar{\eta}\dot{\varepsilon}$$

For a Newtonian fluid $\tau = \eta$ (**$d\gamma/dt$**) and under simple elongational flow,

$$\underline{\underline{\tau}} = \eta \begin{pmatrix} 2\dot{\varepsilon} & 0 & 0 \\ 0 & -\dot{\varepsilon} & 0 \\ 0 & 0 & -\dot{\varepsilon} \end{pmatrix}$$

so, $\tau_{11} - \tau_{33} = 3\eta\,(d\varepsilon/dt)$. For a Newtonian fluid or in the Newtonian plateau region, or a polymer melt, the Trouton viscosity is three times the Newtonian viscosity. The Trouton viscosity is a measure of the cohesivity of the melt or the melt strength. The Trouton viscosity is generally not strain rate dependent.

The ratio of the Trouton viscosity and the shear viscosity is 3 in the Newtonian regime for a power-law fluid and increases as the shear rate is increased since the Trouton viscosity is constant while the shear viscosity drops with increasing rate of strain. This ratio is called the melt strength and is an indication of the "spinnability" or "blowability" of a polymer melt.

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