Non-linear Viscoelasticity
FINITE STRAIN EFFECTS IN SOLIDS

Consider an elastic solid in shear:

$$\text{Shear Stress} \qquad \sigma(\gamma) = G\gamma$$

If we apply a shear in the opposite direction:

$$\text{Shear Stress} \qquad \sigma(-\gamma) = -G\gamma = -\sigma(\gamma)$$

This means that the shear stress is always an **odd function** of the strain.

$$\sigma(\gamma) = A_1\gamma + A_2\gamma^3 + \cdots$$

The normal stress difference does not depend on the direction of the shear strain.

$$\text{First Normal Stress Difference} \qquad N_1(\gamma) = N_1(-\gamma)$$

This means that the first normal stress difference is always an **even function** of the strain.

$$N_1(\gamma) = B_1\gamma^2 + B_2\gamma^4 + \cdots$$

Thus the first departures from linear viscoelasticity at small strains are:

$$\sigma(\gamma) = A_1\gamma + A_2\gamma^3$$

$$N_1(\gamma) = B_1\gamma^2$$

A true solid has $A_1 = B_1 = G$

$$\sigma = G\gamma \qquad\qquad\qquad (3\text{-}49)$$

$$N_1 = G\gamma^2 \qquad\qquad\qquad (3\text{-}50)$$

Non-linear Viscoelasticity
FINITE STRAIN EFFECTS IN SOLIDS

The first departure from linear viscoelasticity is the non-zero normal stress difference.

$$\text{Recoverable Strain} \qquad \gamma_\infty = \gamma = \frac{N_1}{\sigma} \qquad (3\text{-}51)$$

The **Lodge rubber-like liquid model** predicts

$$\text{Strain} \quad = \frac{N_1}{\sigma} \qquad \text{The Lodge-Meissner Relation} \qquad (3\text{-}35)$$

$$\text{Recoverable Strain} \qquad \gamma_\infty = \frac{N_1}{2\sigma} \qquad (3\text{-}52)$$

FINITE STRAIN RATE EFFECTS IN LIQUIDS

Consider a liquid sheared at a constant rate:

$$\text{Shear Stress} \qquad \sigma(\dot{\gamma}) = \eta \dot{\gamma}$$

If we apply the shear rate in the opposite direction:

$$\text{Shear Stress} \qquad \sigma(-\dot{\gamma}) = -\eta \dot{\gamma} = -\sigma(\dot{\gamma})$$

This means that the shear stress is always an **odd function** of the strain rate.

$$\sigma(\dot{\gamma}) = A_1 \dot{\gamma} + A_2 \dot{\gamma}^3 + \cdots$$

A_1 is simply the viscosity η_0.

$$\textbf{Apparent viscosity} \qquad \eta(\dot{\gamma}) \equiv \frac{\sigma(\dot{\gamma})}{\dot{\gamma}} = \eta_0 + A_2 \dot{\gamma}^2 + \cdots$$

The apparent viscosity is an even function since it is obtained by dividing two odd functions.

Non-linear Viscoelasticity
FINITE STRAIN EFFECTS IN LIQUIDS

The normal stress difference does not depend on the direction.

First Normal Stress Difference $\qquad N_1(\dot{\gamma}) = N_1(-\dot{\gamma})$

This means that the first normal stress difference is always an **even function** of the strain rate.

$$N_1(\dot{\gamma}) = B_1\dot{\gamma}^2 + B_2\dot{\gamma}^4 + \cdots$$

First Normal Stress Coefficient $\qquad \Psi_1 \equiv \dfrac{N_1}{\dot{\gamma}^2}$ $\qquad$ (3-39)

At low shear rates this is a constant

$$\Psi_{1,0} \equiv \lim_{\dot{\gamma}\to 0} \left[\Psi_1(\dot{\gamma})\right] = 2\int_0^\infty G(s)s\,ds \qquad (3\text{-}40)$$

$$\Psi_{1,0} = 2\eta_0^2 J_s^0 \qquad (3\text{-}42)$$

$$\Psi_{1,0} = 2\lim_{\omega\to 0}\left[\frac{G'}{\omega^2}\right] \qquad (3\text{-}43)$$

At low shear rates $\sigma > N_1$ with

$$\sigma = \eta_0\dot{\gamma} \quad \text{and} \quad N_1 = \Psi_{1,0}\dot{\gamma}^2$$

At what shear rate does $\sigma = N_1$?

$$\dot{\gamma} = \frac{\eta_0}{\Psi_{1,0}} = \frac{1}{2\eta_0 J_s^0} = \frac{1}{2\lambda}$$

For shear rates larger than $1/(2\lambda)$ nonlinearities are important.

Non-linear Viscoelasticity
SEPARABILITY AT LONG TIMES

For nonlinear stress relaxation at long times, the stress is separable into a strain dependent part and a time dependent part.

$$\sigma(t, \gamma) = \gamma h(\gamma) G(t) \tag{3-67}$$

The time dependent part is simply the linear viscoelastic stress relaxation modulus $G(t)$. The strain dependent part is known as the damping function $h(\gamma)$.

$$G(t, \gamma) = h(\gamma) G(t) \tag{3-68}$$

$$N_1(t, \gamma) = \gamma^2 h(\gamma) G(t) \tag{3-69}$$

$$h(\gamma) \leq 1$$

Physically, this means that extra relaxations all take place at short times.

Non-linear Viscoelasticity
SEPARABILITY AT LONG TIMES

$$G(t, \gamma) = h(\gamma)G(t, 0) \qquad (3\text{-}68)$$

$$N_1(t, \gamma) = \gamma^2 h(\gamma)G(t, 0) \qquad (3\text{-}69)$$

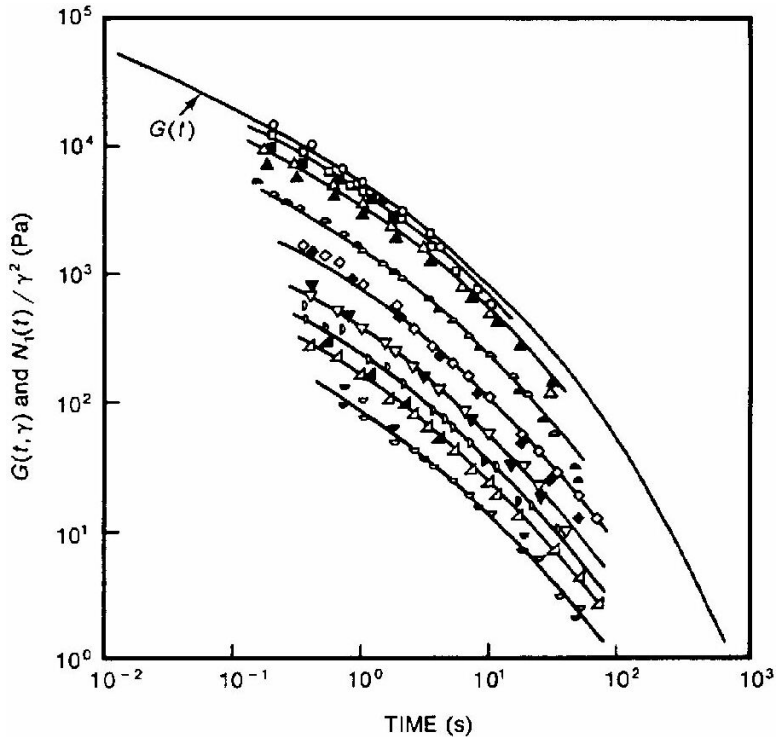$$G(t, \gamma) = \frac{N_1(t, \gamma)}{\gamma^2}$$

Figure 1: Strain dependence of relaxation modulus $G(t)$ (open symbols) and N_1/γ^2 (filled symbols) for low density polyethylene. Strain varies from $\gamma = 0.2$ (top) to $\gamma = 30.9$ (bottom).

Non-linear Viscoelasticity
SEPARABILITY AT LONG TIMES

Damping function $\qquad h(\gamma) = \dfrac{G(t,\gamma)}{G(t,0)}$
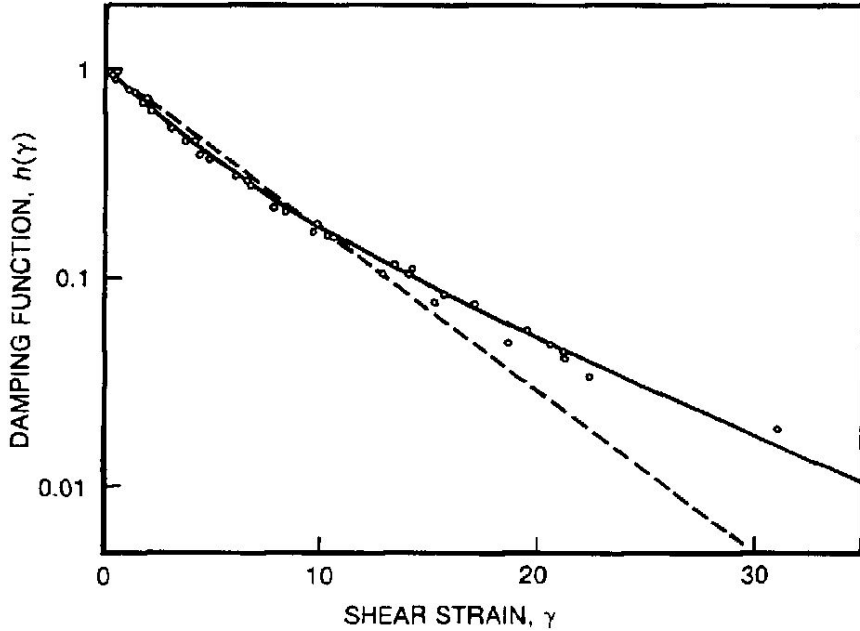
Figure 2: Damping function $h(\gamma)$ for the low density polyethylene melt of Figure 1.

Wagner Damping Function $\qquad h(\gamma) = \exp(-n\gamma) \qquad n = 0.14 \qquad$ (3-72)

Osaki Damping Function $\qquad h(\gamma) = a\exp(-n_1\gamma) + (1-a)\exp(-n_2\gamma)$
$$(3\text{-}73)$$

Non-linear Viscoelasticity
EXTRA RELAXATION AT SHORT TIMES

$$G(t, \gamma) = h(\gamma)G(t, 0) \tag{3-68}$$
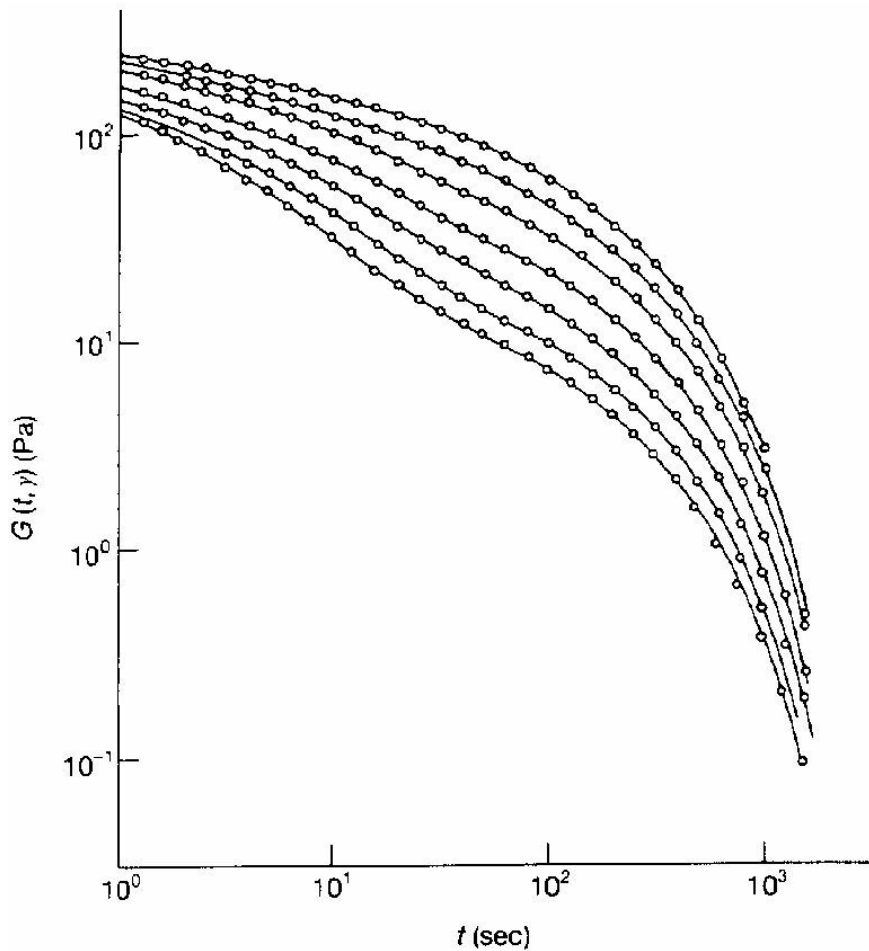
Figure 3: Nonlinear relaxation modulus $G(t)$ for a 6% polystyrene solution at 30°C.

Non-linear Viscoelasticity
EXTRA RELAXATION AT SHORT TIMES
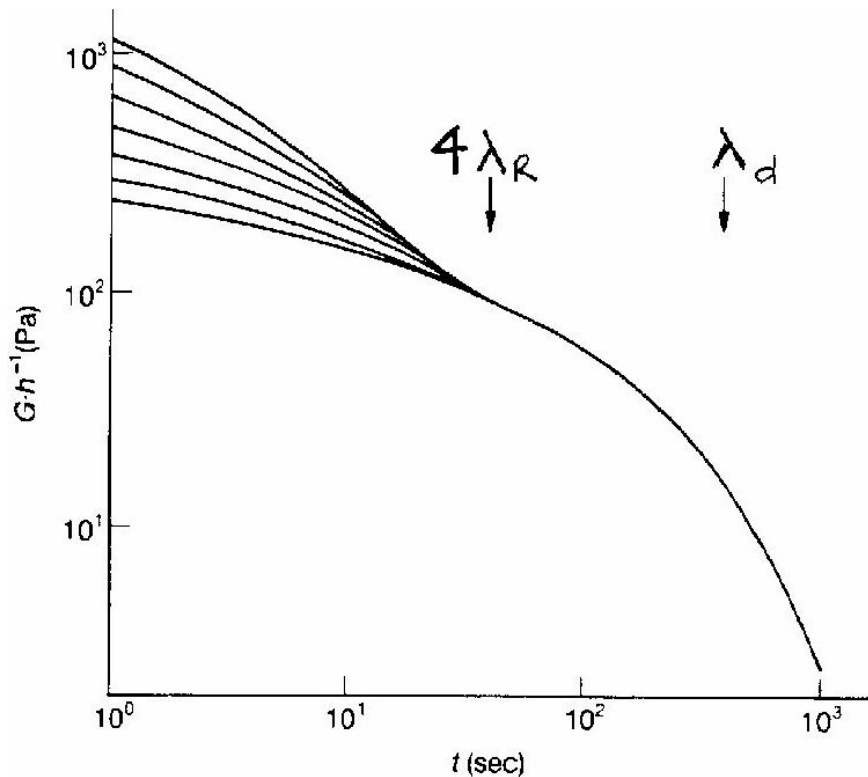
$$G(t, 0) = \frac{G(t, \gamma)}{h(\gamma)}$$

Figure 4: Reduced nonlinear relaxation modulus $G(t, \gamma)/h(\gamma)$, calculated from the polystyrene solution data of Figure 3.

Non-linear Viscoelasticity
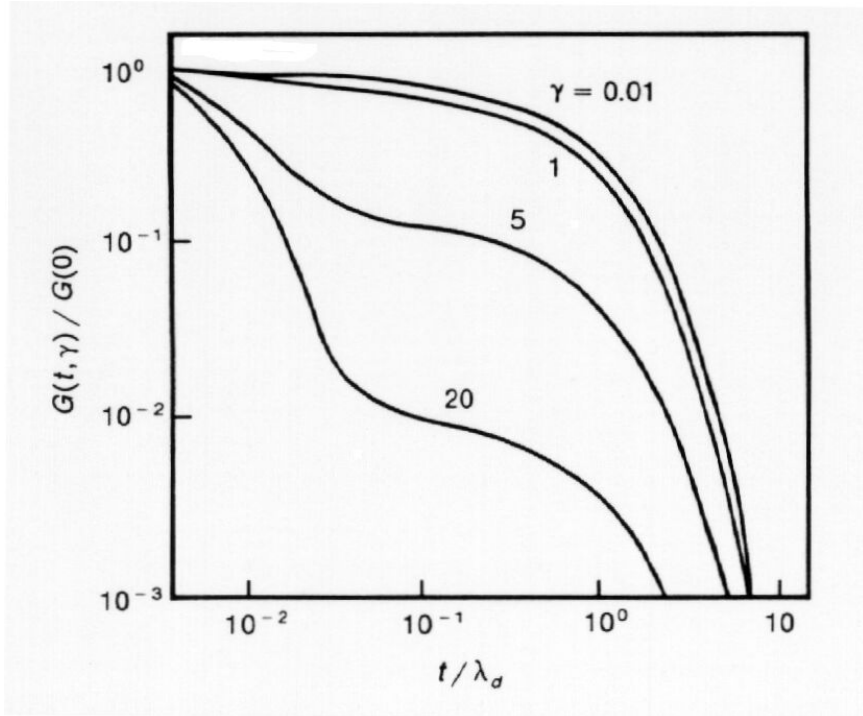# EXTRA RELAXATION AT SHORT TIMES

Figure 5: Theoretical nonlinear relaxation modulus at four strain levels.

Non-linear Viscoelasticity
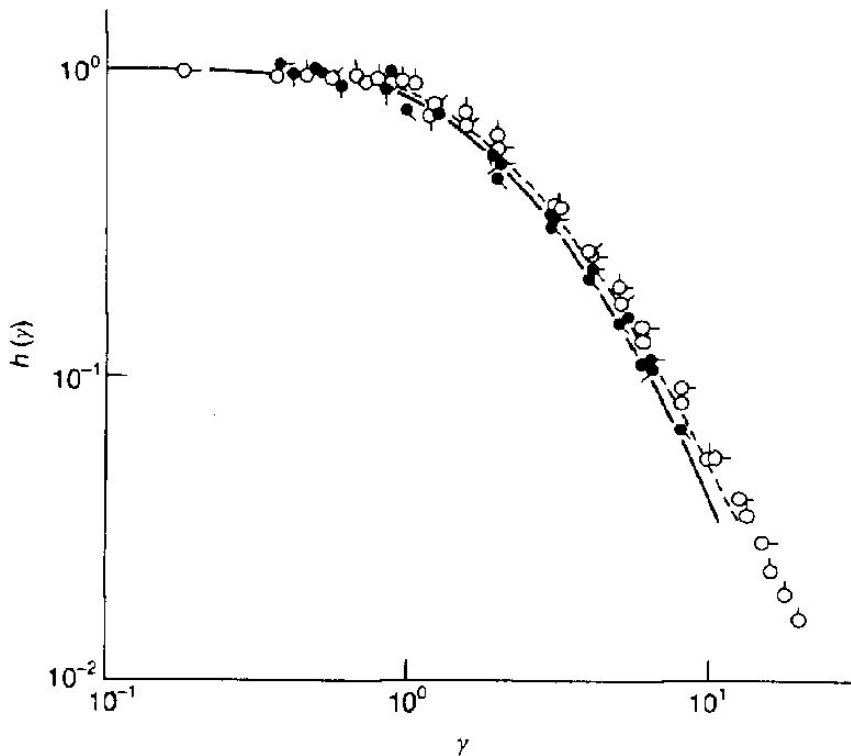## DAMPING FUNCTION FROM MOLECULAR THEORY

Figure 6: Damping function for polystyrene solutions of different concentrations and different molecular weights. Curves are predictions of the tube model.

Non-linear Viscoelasticity
SHEAR THINNING

Since large deformation activates *additional relaxation mechanisms*, the apparent viscosity and first normal stress coefficient *decrease* as shear rate increases.
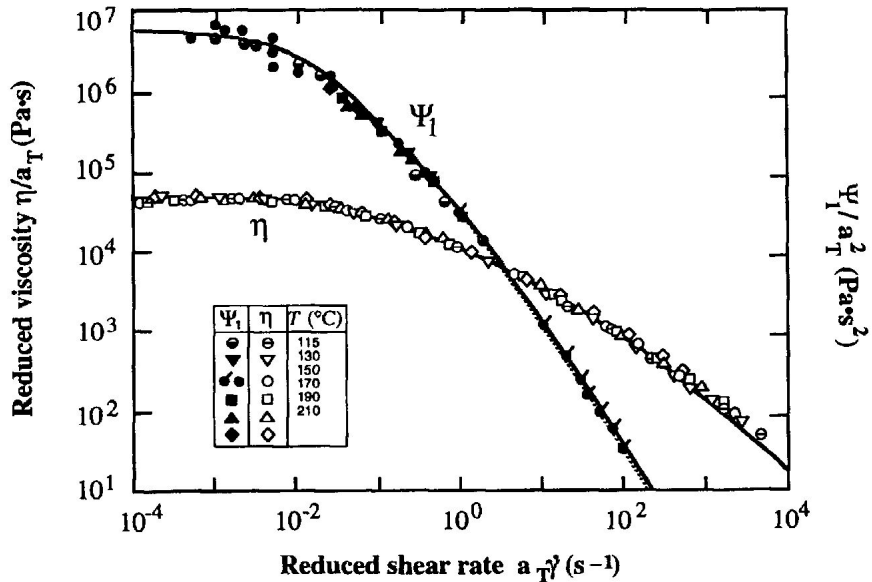

Figure 7: Shear rate dependence of viscosity and first normal stress coefficient for low density polyethylene.

Non-linear Viscoelasticity
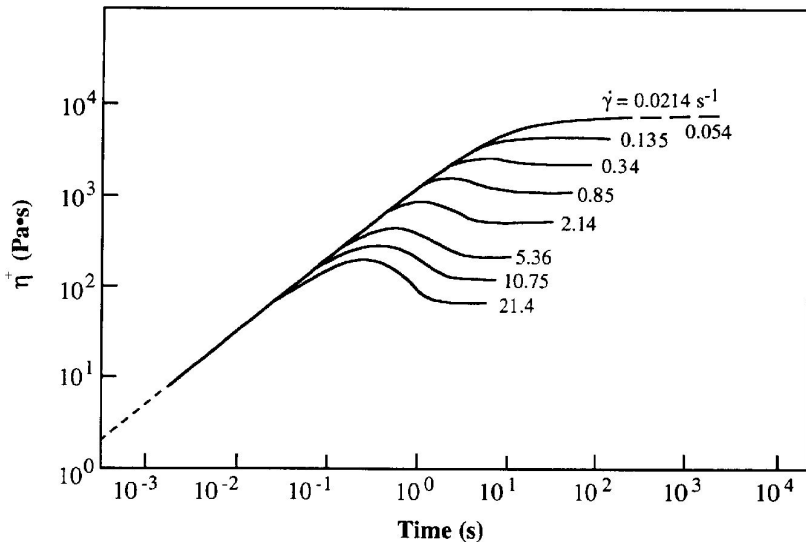## START-UP OF STEADY SHEAR

Figure 8: Start-up of steady shear for a 7.55% polybutadiene solution.

The overshoot indicates that short time relaxation processes are at work in steady shear as well as in stress relaxation.

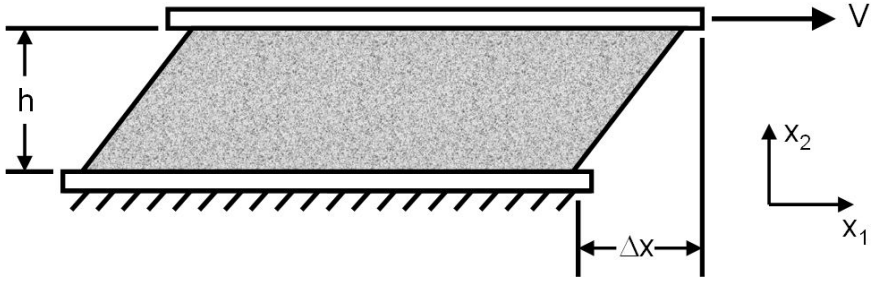# Non-linear Viscoelasticity
STEADY SHEAR

Figure 9: Steady simple shear flow.

$$\text{Shear Strain} \qquad \gamma = \frac{\Delta x}{h} \qquad\qquad (1\text{-}10)$$

$$\text{Shear Rate} \qquad \dot{\gamma} = |\dot{\gamma}_{21}| = |\dot{\gamma}_{12}| = \frac{|V|}{h} \qquad\qquad (4\text{-}1)$$

$$\text{Stress Tensor} \qquad \sigma_{ij} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \\ \sigma_{21} & \sigma_{22} & \\ & & \sigma_{33} \end{bmatrix} \qquad\qquad (1\text{-}29)$$

$$\text{Shear Stress} \qquad \sigma \equiv |\sigma_{21}| = |\sigma_{12}| \qquad\qquad (4\text{-}2)$$

$$\text{Viscosity} \qquad \eta \equiv \frac{\sigma}{\dot{\gamma}} \qquad\qquad (4\text{-}5)$$

$$\text{First Normal Stress Difference} \qquad N_1 \equiv \sigma_{11} - \sigma_{22} \qquad\qquad (4\text{-}3)$$

$$\text{First Normal Stress Coefficient} \qquad \Psi_1 \equiv \frac{N_1}{\dot{\gamma}^2} \qquad\qquad (4\text{-}6)$$

$$\text{Second Normal Stress Difference} \qquad N_2 \equiv \sigma_{22} - \sigma_{33} \qquad\qquad (4\text{-}4)$$

$$\text{Second Normal Stress Coefficient} \qquad \Psi_2 \equiv \frac{N_2}{\dot{\gamma}^2} \qquad\qquad (4\text{-}3)$$

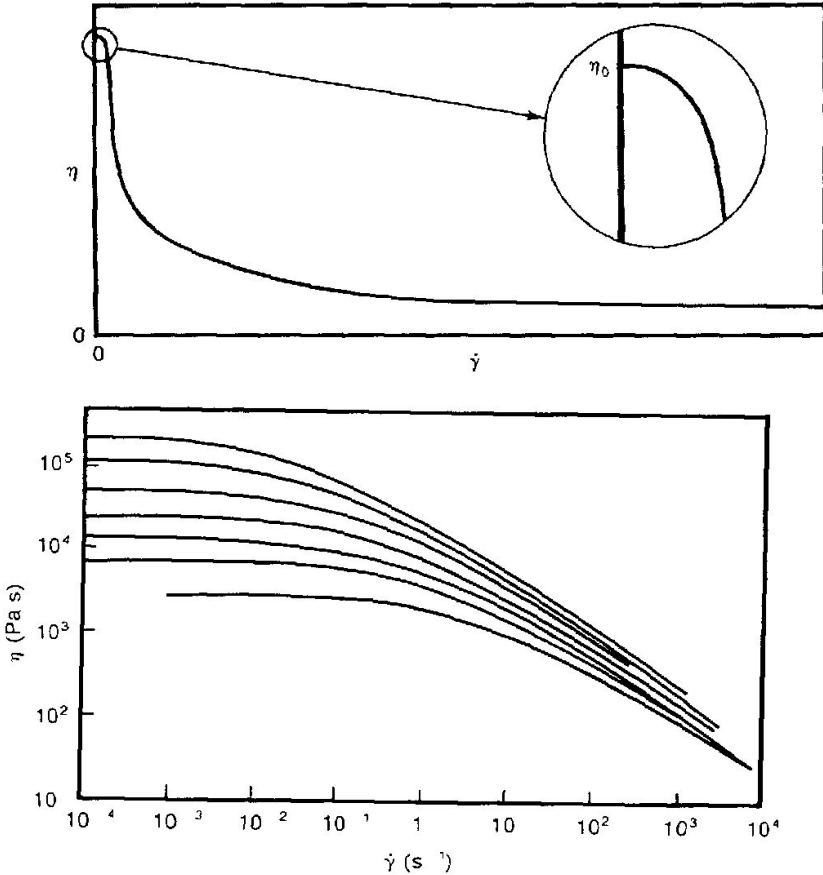# Non-linear Viscoelasticity
APPARENT VISCOSITY IN STEADY SHEAR

Figure 10: Shear rate dependence of apparent viscosity.

Shear thinning dominates the apparent viscosity at high rates.

Non-linear Viscoelasticity
APPARENT VISCOSITY MODELS

$$\text{Power Law Viscosity} \qquad \eta = K\dot{\gamma}^{n-1} \qquad (4\text{-}8)$$

n is the **power law index**.

$$\text{Shear Stress} \qquad \sigma = \eta\dot{\gamma} = K\dot{\gamma}^{n} \qquad (4\text{-}9)$$

Since we know that $\eta = \eta_0$ at $\dot{\gamma} = 1/\lambda$ (where shear thinning starts) we can write K in terms of η_0 and λ.

$$\text{Power Law Model} \qquad \eta = \eta_0 \left|\lambda\dot{\gamma}\right|^{n-1} \qquad (4\text{-}10)$$
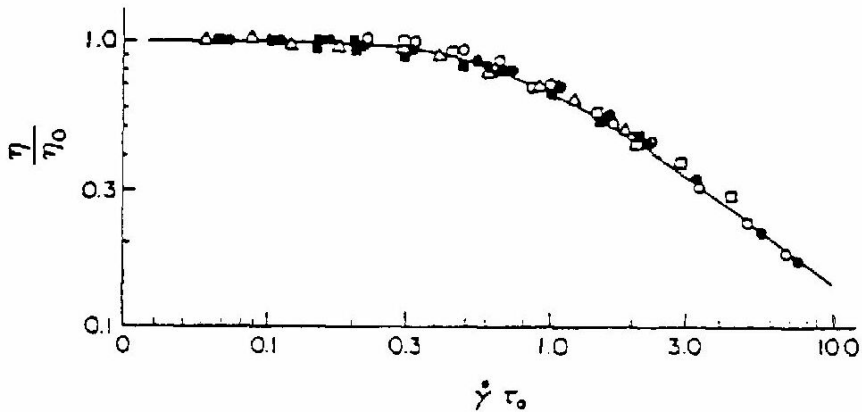

Figure 11: The power law only holds at high shear rates.

$$\text{Cross Model} \qquad \eta = \eta_0 \left[1 + \left|\lambda\dot{\gamma}\right|^m\right]^{-1} \qquad (4\text{-}11)$$

$$m = 1 - n \qquad (4\text{-}12)$$

$$\text{Carreau Model} \qquad \eta = \eta_0 \left[1 + (\lambda\dot{\gamma})^2\right]^{(n-1)/2} \qquad (4\text{-}14)$$

Non-linear Viscoelasticity
TEMPERATURE DEPENDENCE OF APPARENT VISCOSITY

Recall the temperature dependence of the stress relaxation modulus:

$$G(t, T) = b_T G\left(\frac{t}{a_T}, T_0\right)$$

The zero shear rate viscosity

$$\eta_0(T) = \int_0^\infty G(t, T) dt = b_T \int_0^\infty G\left(\frac{t}{a_T}, T_0\right) dt$$

Change integration variables $s = t/a_T$, so $ds = dt/a_T$.

$$\eta_0(T) = a_T b_T \int_0^\infty G(s, T_0) ds = a_T b_T \eta_0(T_0)$$

For the apparent viscosity

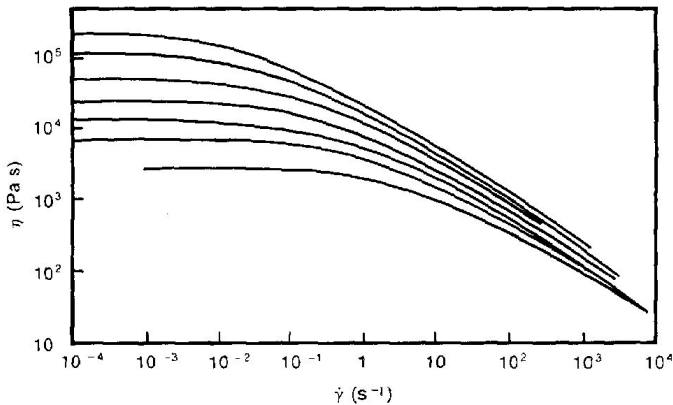$$\eta(\dot{\gamma}, T) = a_T b_T \eta(\dot{\gamma} a_T, T_0)$$

Figure 12: Apparent viscosity of low density Polyethylene at seven temperatures. From top to bottom: 115°C, 130°C, 150°C, 170°C, 190°C, 210°C, 240°C.

Non-linear Viscoelasticity
MOLECULAR WEIGHT DEPENDENCE OF VISCOSITY AND NORMAL STRESS COEFFICIENT

Zero Shear Rate Viscosity of monodisperse linear polymers:

$$\eta_0 = KM^{3.4} \tag{4-16}$$

Zero Shear Rate Viscosity of polydisperse linear polymers:

$$\eta_0 = KM_w^{3.4} \tag{4-17}$$

The weight average molecular weight has the following blending law:

$$M_w = w_1 M_1 + w_2 M_2 \tag{4-18}$$

where w_1 and w_2 are weight fractions.

Combining these three equations we get a blending rule for the zero shear rate viscosity.

$$\eta_0^{1/3.4} = w_1 \eta_{0,1}^{1/3.4} + w_2 \eta_{0,2}^{1/3.4} \tag{4-19}$$

Relaxation Time:

$$\lambda = \frac{\eta_0}{G_N^0} \sim M_w^{3.4}$$

First Normal Stress Coefficient:

$$\Psi_{1,0} = 2\eta_0^2 J_s^0 \tag{3-42}$$

Since J_s^0 is independent of M for entangled polymers,

$$\Psi_{1,0} \sim M_w^{6.8} \tag{4-32}$$

Since J_s^0 is nearly independent of T,

$$\frac{d \log \Psi_{1,0}}{dT} \cong 2 \left[\frac{d \log \eta_0}{dT} \right] \tag{4-35}$$

Non-linear Viscoelasticity
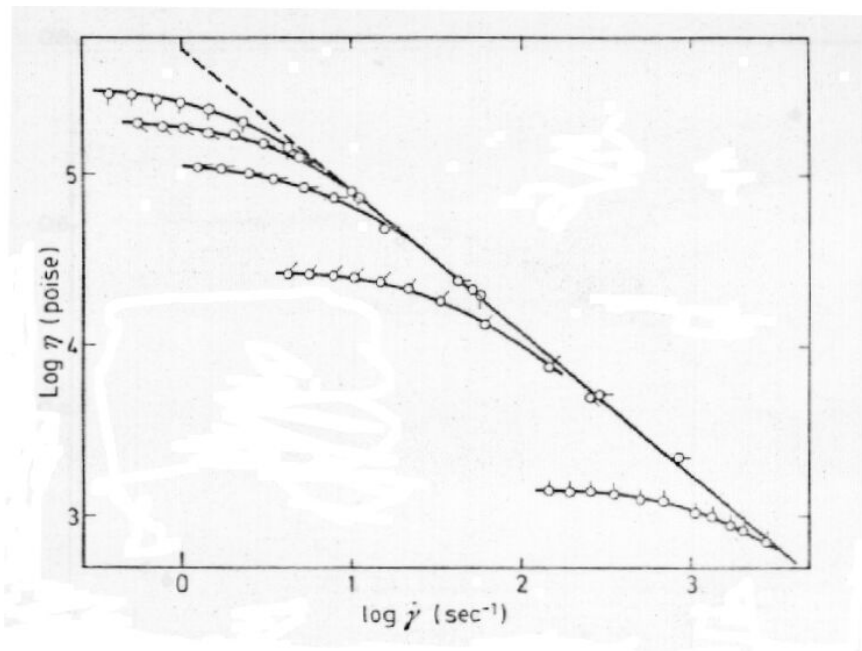## MOLECULAR WEIGHT DEPENDENCE OF APPARENT VISCOSITY

Figure 13: Apparent viscosity of monodisperse polystyrenes at 183°C. From top to bottom, $M = 242000$, $M = 217000$, $M = 179000$, $M = 117000$, $M = 48500$. Line has slope -0.82.

Non-linear Viscoelasticity
APPARENT VISCOSITY

At shear rates much larger than $1/\lambda$, the apparent viscosity cannot be measured in rotational rheometers. For $\dot{\gamma} > 1/\lambda$, the polymer tries to behave elastically (and leaves the gap).
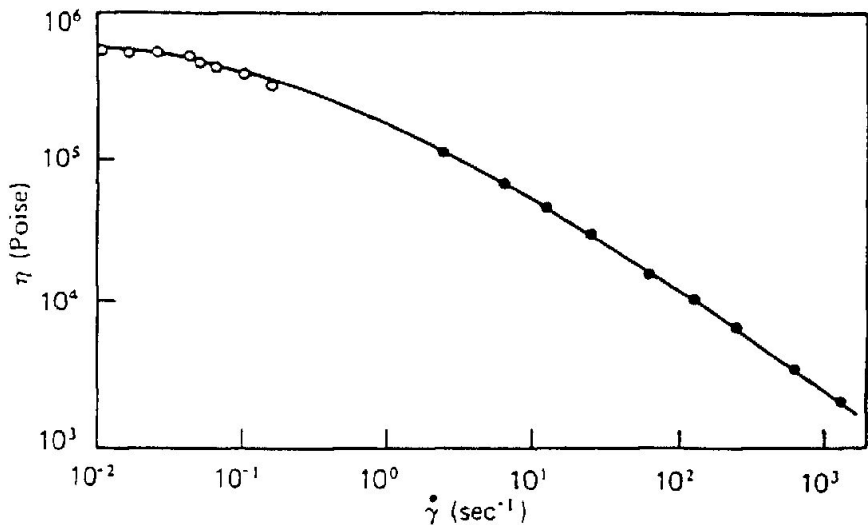

Figure 14: Apparent viscosity of a polystyrene melt. Open circles - cone and plate data. Filled circles - capillary data.

Non-linear Viscoelasticity
THE COX-MERZ EMPIRICISM

$$\eta(\dot{\gamma}) = |\eta^*(\omega)| \qquad (\omega = \dot{\gamma}) \qquad\qquad (4\text{-}41)$$

Can a linear viscoelastic property, $|\eta^*(\omega)|$, be related to a nonlinear one $\eta(\dot{\gamma})$?
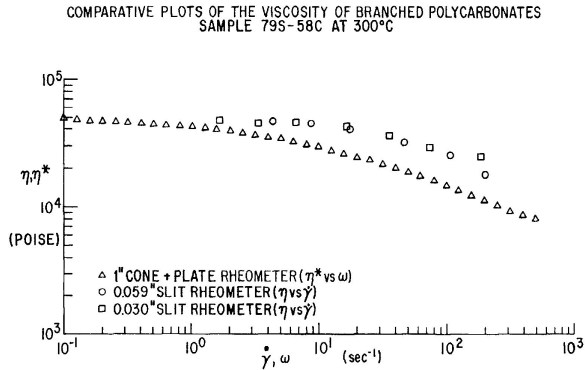

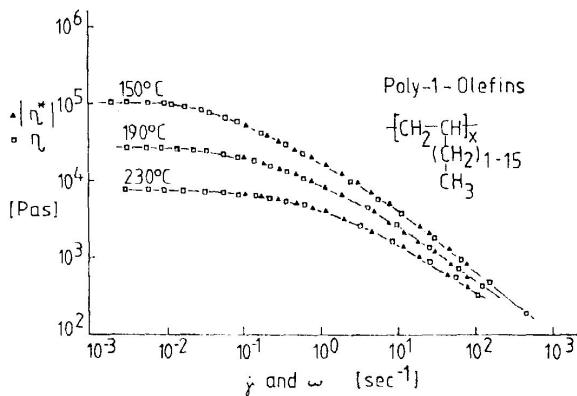Figure 15: Cox-Merz empiricism for a branched polycarbonate at 300°C.

Figure 16: Cox-Merz empiricism at three temperatures for linear polyolefins.