Fluid Mechanics

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Apparent Viscosity
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Molecular Models:
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Viscosity
Recoverable Compliance
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Terminal Relaxation Time
Terminal Modulus
Plateau Modulus
  Entanglement Molecular Weight
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Apparent Viscosity
Polydispersity Effects
Branching Effects
Die Swell
Nonlinear Viscoelasticity

Stress is an Odd Function of Strain and Strain Rate
Viscosity and Normal Stress are Even Functions of Strain and Strain Rate
Lodge-Meissner Relation
Nonlinear Step Strain
   Extra Relaxation at Rouse Time
   Damping Function
Steady Shear
   Apparent Viscosity
      Power Law Model
      Cross Model
      Carreau Model
      Cox-Merz Empiricism
   First Normal Stress Coefficient
Start-Up and Cessation of Steady Shear
Nonlinear Creep and Recovery
Stress and Strain

SHEAR

Shear Stress \( \sigma \equiv \frac{F}{A} \)

Shear Strain \( \gamma \equiv \frac{l}{h} \)

Shear Rate \( \dot{\gamma} \equiv \frac{d\gamma}{dt} \)

Hooke’s Law \( \sigma = G\gamma \)

Newton’s Law \( \sigma = \eta\dot{\gamma} \)

EXTENSION

Tensile Stress \( \sigma \equiv \frac{F}{A} \)

Extensional Strain \( \varepsilon \equiv \frac{\Delta l}{l} \)

Extension Rate \( \dot{\varepsilon} \equiv \frac{d\varepsilon}{dt} \)

Hooke’s Law \( \sigma = 3G\varepsilon \)

Newton’s Law \( \sigma = 3\eta\dot{\varepsilon} \)
Viscoelasticity

APPARENT VISCOSITY

\[ \eta \equiv \frac{\sigma}{\dot{\gamma}} \]

1. Apparent Viscosity of a Monodisperse Polystyrene.
Oversimplified Models

MAXWELL MODEL

Stress Relaxation \[ \sigma(t) = \sigma_0 \exp(-t/\lambda) \]
\[ G(t) = G_0 \exp(-t/\lambda) \]

Creep \[ \gamma(t) = \gamma_0(1 + t/\lambda) \]
\[ J(t) = J_s^0(1 + t/\lambda) = J_s^0 + t/\eta \]

Oscillatory Shear \[ G'(\omega) = \omega \lambda G''(\omega) = \frac{G_0(\omega \lambda)^2}{1 + (\omega \lambda)^2} \]

The Maxwell Model is the simplest model of a VISCOELASTIC LIQUID.

VOIGT MODEL

Creep \[ \gamma(t) = \gamma_\infty[1 - \exp(-t/\lambda)] \]
\[ J(t) = J_\infty[1 - \exp(-t/\lambda)] \]

The Voigt Model is the simplest model of creep for a VISCOELASTIC SOLID.
Equations of Fluid Motion

CONTINUITY

Incompressible \( \nabla \cdot \vec{v} = 0 \)

Continuity is a differential equation describing conservation of mass.

NAVIER-STOKES

Slow Flows (no inertia, \( R_e < 1 \))

\[
\rho \frac{\partial \vec{v}}{\partial t} = -\nabla P + \rho \vec{g} + \eta \nabla^2 \vec{v}
\]

The Navier-Stokes equations are force balances (per unit volume).

DO NOT MEMORIZE CONTINUITY OR N-S EQUATIONS. IF NEEDED, I WILL GIVE THEM TO YOU.

YOU DO NEED TO KNOW HOW TO USE THEM TO SOLVE FOR PRESSURE AND VELOCITY DISTRIBUTIONS.

BOUNDARY CONDITIONS

1. NO SLIP at solid surfaces

2. No infinite velocities

MAXIMUM VELOCITY

for \( v_x = v_x(y) \), \( \frac{\partial v_x}{\partial y} = 0 \)

AVERAGE VELOCITY and VOLUMETRIC FLOW RATE

\[
v_{ave} = \frac{Q}{A} = \frac{1}{A} \int v_x dA
\]
Linear Viscoelasticity

Stress Relaxation Modulus

\[ G(t) \equiv \frac{\sigma(t)}{\gamma_0} \]

BOLTZMANN SUPERPOSITION: Add effects of many step strains to construct ANY linear viscoelastic deformation.

Viscosity

\[ \eta_0 = \int_0^\infty G(t) dt \]

Creep Compliance

\[ J(t) \equiv \frac{\gamma(t)}{\sigma} \]

Steady State Compliance

\[ J_s^0 = \lim_{t \to \infty} \left[ J(t) - \frac{t}{\eta_0} \right] \]

\[ J_s^0 = \frac{1}{\eta_0^2} \int_0^\infty G(t) t dt \]

Recoverable Compliance

\[ R(t) \equiv \frac{\gamma_r(t)}{\sigma} = J(t) - \frac{t}{\eta_0} \]

\[ J_s^0 = \lim_{t \to \infty} [R(t)] \]

Terminal Relaxation Time

\[ \lambda = \eta_0 J_s^0 = \frac{\int_0^\infty G(t) t dt}{\int_0^\infty G(t) dt} \]
Linear Viscoelasticity

OSCILLATORY SHEAR

apply strain \[ \gamma(t) = \gamma_0 \sin(\omega t) \]

measure stress \[ \sigma(t) = \gamma_0 \left[ G'(\omega) \sin(\omega t) + G''(\omega) \cos(\omega t) \right] \]

Loss Tangent \[ \tan(\delta) = \frac{G''}{G'} \]

Viscosity \[ \eta_0 = \lim_{\omega \to 0} \left[ \frac{G''(\omega)}{\omega} \right] \]

Steady State Compliance \[ J_s^0 = \lim_{\omega \to 0} \left[ \frac{G'(\omega)}{[G''(\omega)]^2} \right] \]
2. Storage and Loss Modulus Master Curves for Polybutadiene at Reference Temperature $T_0 = 25^\circ C$. 

\[ G'(\omega) \]

\[ G''(\omega) \]
6. Storage and Loss Moduli for Polystyrene $L_{15}$ with $M_w = 215000$. 
Linear Viscoelasticity

EFFECTS OF MOLECULAR STRUCTURE

7. Storage and Loss Moduli for Polystyrene with $M_w = 315000$ and $M_w/M_n = 1.8$. 
MOLECULAR THEORIES

ROUSE MODEL:

\[ D_R \sim \frac{1}{N} \quad \lambda_R \approx \frac{R^2}{D_R} \sim N^2 \quad G(\lambda_R) = \frac{\rho RT}{M} \quad \eta \approx \lambda_R G(\lambda_R) \sim N \]

\[ G(t) \sim t^{1/2} \quad \text{for } \lambda_N < t < \lambda_R \]

REPTATION MODEL:

Relaxation is simple Rouse motion up to the Rouse relaxation time of an entanglement strand.

\[ \lambda_e \sim N_e^2 \quad G(t) \sim t^{1/2} \quad \text{for } \lambda_N < t < \lambda_e \]

Plateau Modulus

\[ G_N^0 = \frac{\rho RT}{M_e} \]

\[ \lambda_d \approx \frac{L^2}{D_R} \sim N^3 \quad D \approx \frac{R^2}{\lambda_d} \sim \frac{1}{N^2} \quad \eta \approx \lambda_d G_N^0 \sim N^3 \]
Linear Viscoelasticity
TIME-TEMPERATURE SUPERPOSITION

Figure 1: (A) Isothermal Storage Modulus $G'(\omega)$ of a Polystyrene at Six Temperatures. (B) Storage Modulus Master Curve at Reference Temperature $T_0 = 150 \degree C$. 
Nonlinear Stresses

Shear Stress is an odd function of shear strain and shear rate.

\[ \sigma(\gamma) = G\gamma + A_1\gamma^3 + \ldots \ldots \]

\[ \sigma(\dot{\gamma}) = \eta_0\dot{\gamma} + A_2\dot{\gamma}^3 + \ldots \ldots \]

Apparent viscosity is thus an even function of shear rate.

\[ \eta(\dot{\gamma}) \equiv \frac{\sigma(\dot{\gamma})}{\dot{\gamma}} = \eta_0 + A_2\dot{\gamma}^2 + \ldots \ldots \]

The first normal stress difference is an even function of shear strain and shear rate.

\[ N_1(\gamma) = G\gamma^2 + B_1\gamma^4 + \ldots \ldots \]

The first term comes from the Lodge-Meissner Relation

\[ \frac{N_1}{\sigma} = \gamma \]

\[ N_1(\dot{\gamma}) = \Psi_1^0\dot{\gamma}^2 + B_2\dot{\gamma}^4 + \ldots \ldots \]

First Normal Stress Coefficient is thus an even function of shear rate.

\[ \Psi_1 \equiv \frac{N_1(\dot{\gamma})}{\dot{\gamma}^2} = \Psi_1^0 + B_2\dot{\gamma}^2 + \ldots \ldots \]
SEPARABILITY AT LONG TIMES

\[ G(t, \gamma) = h(\gamma)G(t, 0) \]

\[ N_1(t, \gamma) = \gamma^2h(\gamma)G(t, 0) \]

\[ h(\gamma) \leq 1 \]
Steady Shear

Apparent Viscosity \( \eta \equiv \frac{\sigma}{\dot{\gamma}} \)

First Normal Stress Coefficient \( \Psi_1 \equiv \frac{N_1}{\dot{\gamma}^2} \)

Figure 4: Shear Rate Dependence of Viscosity and First Normal Stress Coefficient for Low Density Polyethylene.
Steady Shear

APPARENT VISCOITY MODELS

Power Law Model \[ \eta = \eta_0 |\lambda \dot{\gamma}|^{n-1} \]

Cross Model \[ \eta = \eta_0 \left[ 1 + |\lambda \dot{\gamma}|^{1-n} \right]^{-1} \]

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

MOLECULAR WEIGHT DEPENDENCES

\[ \eta_0 = KM_w^{3.4} \]

\[ \lambda = \frac{\eta_0}{G_N} \sim M_w^{3.4} \]

\[ \Psi_{1,0} = 2\eta_0^2 J_0 \sim M_w^{6.8} \]

THE COX-MERZ EMPIRICISM

\[ \eta(\dot{\gamma}) = |\eta^*(\omega)| \quad (\omega = \dot{\gamma}) \]
Nonlinear Viscoelasticity
START-UP OF STEADY SHEAR

Figure 5: Shear Stress Growth and Normal Stress Growth Coefficients for the Start-Up of Steady Shear of a Polystyrene Solution.

Start-up of nonlinear steady shear shows maxima in shear and normal stress growth functions, indicating extra short-time relaxation processes induced by the large shear rate.
Figure 6: Shear Stress Decay and Normal Stress Decay Coefficients for Cessation of Steady Shear Flow of a Polyisobutylene Solution.

Shear and normal stresses both decay FASTER at larger shear rates, consistent with long relaxation modes being replaced by shorter-time relaxation processes that are activated in steady shear.
Figure 7: Creep Compliance at a Linear Viscoelastic Stress $\sigma_1$ and two Nonlinear Stresses with $\sigma_3 > \sigma_2 > \sigma_1$.

As stress increases, the viscosity drops and the recoverable strain drops, consistent with large stresses inducing additional dissipation mechanisms.

Figure 8: Recoverable Compliance after Creep at Three Stress Levels (Increasing Creep Stress from Top to Bottom).
Rheometry

Couette Devices:
- Gap Loading vs. Surface Loading
- Controlled Stress vs. Controlled Strain
- Transducer (and Instrument) Compliance
- Cone & Plate
- Parallel Plate
- Eccentric Rotating Disks
- Concentric Cylinder
- Sliding Plates

Poiseuille Devices:
- Pressure Driven vs. Rate Driven
- Capillary Rheometer
  - Wall Shear Stress
  - Wall Shear Rate
  - Bagley End Correction
  - Cogswell Orifice Short-Cut
  - Rabinowitch Correction
- Slit Rheometer
- Melt Flow Index
- Die Swell
- Extrudate Distortion
Rheometry
ROTATIONAL AND SLIDING SURFACE RHEOMETERS

GEOMETRIES OF GAP LOADING INSTRUMENTS:

1. Cone and Plate

Figure 11: The Cone and Plate Rheometer.

2. Parallel Disks

Figure 12: The Parallel Disk Rheometer.
Rheometry
CAPILLARY RHEOMETER

Figure 1: The Capillary Rheometer.

Wall Shear Stress
\[ \sigma_w = R \left( -\frac{dP}{dz} \right) \]

Apparent Wall Shear Rate
\[ \dot{\gamma}_A = \frac{4Q}{\pi R^3} \]
Figure 5: Extrudate Swell after Exiting the Die Diminishes as the Die is Made Longer because the Memory of the Flow Contraction at the Entrance is Reduced.

With a specific polymer and die, die swell increases with increasing shear stress.
- Die swell increases as the die is shortened.
- Die swell increases as the molecular weight increases.
- Die swell increases as the molecular weight distribution is broadened, as it is particularly sensitive to the high molecular weight tail of the distribution.
Molecular Structure Effects

POLYDISPERSITY

Figure 21: Apparent Viscosity in Steady Shear for Polystyrene. Filled symbols have $M_w = 260000$ with $M_w/M_n = 2.4$. Open symbols have $M_w = 160000$ with $M_w/M_n < 1.1$.

Zero shear viscosity is simply a function of weight-average molecular weight.

$$\eta_0 = \begin{cases} 
K_1 M_w & \text{for } M_w < M_c \text{ (unentangled)} \\
K_2 M_w^{3.4} & \text{for } M_w > M_c \text{ (entangled)}
\end{cases}$$

Steady state compliance, and other measures of elasticity (such as first normal stress difference and die swell) are strong functions of polydispersity.

$$J_s^0 \sim \left( \frac{M_z}{M_w} \right)^a \quad \text{with } 2 < a < 3.7$$
Molecular Structure Effects

BRANCHING

Figure 22: Apparent Viscosity of Randomly Branched Polymers Compared to Linear Polymers.

Monodisperse entangled branched polymers have a stronger dependence of viscosity on molecular weight than linear polymers.

\[ \eta_0 \sim \exp \left( \nu \frac{M_b}{M_e} \right) \]

Monodisperse entangled branched polymers have steady state compliance increasing with molecular weight.

\[ J_s^0 = \frac{0.6M_b}{cRT} \]

\( M_b \) is the molecular weight of the star arm.

Randomly branched polymers have effects of both branching and polydispersity.
Injection Molding

Injection Molding Cycle
   Inject and pack mold
   Extrude next shot once gate solidifies
   Eject part once part solidifies

Injection Molding Economics
   Only inexpensive if we make many parts

Injection Molding Window

Poiseuille Flow in Runners and Simple Cavities
   Calculate injection pressure to fill mold
   Balance runner systems
   Calculate clamping force
Assumptions:
   Isothermal
   Newtonian

1
Extrusion

Extruder Characteristic:

\[ Q = \alpha N - \frac{\beta}{\mu} \Delta P \]

Die Characteristic:

\[ Q = \frac{K}{\mu} \Delta P \]

together, they determine the Operating Point

Pumping vs. Mixing:
Compression Ratio and Flow Restrictions
Pressure Distribution
Residence Time Distribution
Twin Screw Extrusion