Rheology
Theory and Applications
Course Outline

- Basics in Rheology Theory
- TA Instruments Rheometers
  - Instrumentation
  - Choosing a Geometry
- Rheology Experimental
  - Flow tests
  - Oscillation tests
  - Transient tests
- Applications of Rheology
  - Polymers
  - Yield stress and thixotropy of structured fluids
Basics in Rheology Theory
Rheology: An Introduction

Rheology: The study of the flow and deformation of matter. Rheological behavior affects every aspect of our lives.
Basic Material Behaviors

- **Water**: Viscous Liquids
  - Flow
  - Viscosity = \( \frac{\text{Stress}}{\text{Strain Rate}} \)

- **Oil**: Viscous Liquids
  - Flow

- **Soap**
  - Flow & Deformation

- **Egg white**: Viscoelastic
  - Flow & Deformation

- **Polymer Melt**: Viscoelastic
  - Flow & Deformation

- **Ceramic**
  - Deformation

- **Metal**: Elastic Solids
  - Deformation
  - Modulus = \( \frac{\text{Stress}}{\text{Strain}} \)
Rheology: An Introduction

- Rheology is the study of flow and deformation of matter
  - The word ‘Rheology’ was coined in the 1920s by Professor E C Bingham at Lafayette College
- Flow is a special case of deformation
- The relationship between stress and deformation is a property of the material

\[
\frac{\text{Stress}}{\text{Shear rate}} = \text{Viscosity}
\]

\[
\frac{\text{Stress}}{\text{Strain}} = \text{Modulus}
\]
Elastic Behavior of an Ideal Solid

Hooke’s Law of Elasticity: Stress = Modulus \cdot Strain

\[ \sigma = E \cdot \gamma \]
Viscous Behavior of an Ideal Liquid

Newton’s Law: stress

\[ \sigma = \eta \cdot \dot{\gamma} \]

\( \eta \) = coefficient of viscosity \cdot shear rate
Viscoelasticity Defined

Range of Material Behavior

Liquid Like--------- Solid Like

*Ideal Fluid* ----- Most Materials ----- *Ideal Solid*

*Purely Viscous* ----- *Viscoelastic* ----- Purely Elastic

**Viscoelasticity**: Having both viscous and elastic properties

- Materials behave in the linear manner, as described by Hooke and Newton, only on a small scale in stress or deformation.
Solid or Liquid?

- Long deformation time: pitch behaves like a highly viscous liquid
  - 9th drop fell July 2013
- Short deformation time: pitch behaves like a solid

Started in 1927 by Thomas Parnell in Queensland, Australia

Time-Dependent Viscoelastic Behavior

T is short [< 1s]  T is long [24 hours]
Importance of Rheological Measurements

- Investigating molecular structure
- Guide and troubleshooting processing
- Evaluate product performance
Basic Parameters and Units

Stress = Force / Area [Pa, or dyne/cm\(^2\) ]
  \(\sigma\) = shear stress

Strain = Geometric Shape Change [no units]
  \(\gamma\) = shear strain

Strain Rate or Shear Rate = Velocity Gradient [1/s]
  \(\dot{\gamma}\) = shear strain rate

Modulus = Stress / Strain [Pa or dyne/cm\(^2\) ]
  \(G\) = Shear Modulus

Compliance = Strain / Stress [1/Pa or cm\(^2\)/dyne]
  Typically denoted by \(J\)

Viscosity = Stress / Strain Rate [Pa·s or Poise]
  Denoted by \(\eta\)

\[ S.I. \ units \times 10 = c.g.s. \ units \]
TA Instruments Rheometers
Types of Rheometers

- Rotational (Shear) Rheometers
  - ARES-G2 and ARES (Strain Control – SMT)
  - DHR or AR (Stress Control – CMT)
  - Closed Die Cavity Rheometer (Strain Control – SMT)

- Solids (Tensile/Bending) Rheometers
  - RSA-G2 and RSA (Strain Control – SMT)
  - DMA 850/Q800 (Stress Control – CMT)

**SMT**: *Separate* Motor and Transducer (Dual-Head)

**CMT**: *Combined* Motor and Transducer (Single Head)
Rotational Rheometers by TA

ARES G2
- Controlled Strain
- Dual Head
- SMT

DHR
- Controlled Stress
- Single Head
- CMT
Rotational Rheometer Designs

**Dual head or SMT**
- **Separate motor & transducer**
  - Transducer
  - Direct Drive Motor
  - Sample
  - Measured Torque (Stress)
  - Applied Strain or Rotation

**Single head or CMT**
- **Combined motor & transducer**
  - Non-Contact Drag Cup Motor
  - Static Plate
  - Displacement Sensor
  - Measured Strain or Rotation
  - Applied Torque (Stress)

Note: With computer feedback, DHR and AR can work in controlled strain/shear rate, and ARES can work in controlled stress.
Closed Die Cavity Rheometer by TA

Measured Torque (Stress)

Applied Strain or Rotation

Direct Drive Motor

RPA Elite, RPA Flex and MDR

Controlled Strain SMT or Dual Head
How do Rheometers Work?

• The study of **stress** and **deformation** relationship

\[
\begin{align*}
\text{Shear stress} \quad & \sigma = \frac{F}{A} \\
\text{Shear strain} \quad & \gamma = \frac{\Delta x}{y_0} \\
\text{Shear rate} \quad & \dot{\gamma} = \frac{1}{y_0} \cdot \frac{dx(t)}{dt}
\end{align*}
\]

\[
\begin{align*}
\frac{\text{Stress}}{\text{Shear rate}} &= \text{Viscosity} \\
\frac{\text{Stress}}{\text{Strain}} &= \text{Modulus}
\end{align*}
\]
How do Rheometers Work?

- In a rheological measurement, stress, strain and strain rate (shear rate) are all calculated signals.
- The raw signals behind the scene are torque, angular displacement and angular velocity.

Fundamentally, a rotational rheometer will apply or measure:

1. Torque (Force)
2. Angular Displacement
3. Angular Velocity
Measured parameter: torque

- Torque (M) is a measure of how much a force (F) acting on an object causes that object to rotate.
  - The object rotates about an axis, called the pivot point
  - The distance (r) from the pivot point to the point where the force acts is called the moment arm
  - The angle (θ) at which the force acts at the moment arm

\[ M = r \cdot F \cdot \sin \theta = r \cdot F \]
(for θ = 90° as shown)
Calculated parameter: stress

• Shear stress is calculated from the torque and geometry stress constant

\[ \sigma = M \cdot K_\sigma \]

- \( \sigma \) = shear stress (Pa or Dyne/cm\(^2\))
- \( M \) = torque (N\( \cdot \)m or gm\( \cdot \)cm)
- \( K_\sigma \) = stress constant

• The stress constant, \( K_\sigma \), is dependent on measurement geometry and/or initial sample dimensions
Measured parameter: angular displacement

- Angular displacement (θ) is the angle, in radians, through which an object moves on a circular path.

  - s = arc length (or linear displacement)
  - r = radius of a circle
  - Conversion: degrees = radians \cdot \frac{180}{\pi}

\[ \theta = \frac{s}{r} \]
Calculated parameter: strain

- Strain is a measure of deformation representing the angular displacement relative to a reference length.

\[ \gamma = \theta \cdot K_\gamma \]

- \( \gamma \) = shear strain (no units)
- \( \theta \) = angular displacement (radians)
- \( K_\gamma \) = strain constant

- The strain constant, \( K_\gamma \), is dependent on measurement geometry and/or initial sample dimensions.
- Calculate percent strain (\( \gamma\% \)) by multiplying strain by 100.
Equation for modulus

\[ G = \frac{\sigma}{\gamma} = \frac{M \cdot K_{\sigma}}{\theta \cdot K_{\gamma}} \]

- **Material function**
- **Constitutive equation**
- **Measured signals**
- **Geometry constants**
Measured parameter: angular velocity

- Angular velocity ($\Omega$) is the change in angular displacement ($\theta$) per unit time of measurement.

  - Note: linear velocity $V = \Delta s/\Delta t$

  \[
  \Omega = \frac{\Delta \theta}{\Delta t}
  \]

  - $\Omega$ = angular velocity (radians/s)
  - $\theta$ = angular displacement (radians)
  - $t$ = time (s)
Calculated parameter: shear rate

• Shear rate is calculated from the angular velocity and geometry strain constant

\[ \dot{\gamma} = \Omega \cdot K_\gamma \]

- \( \dot{\gamma} \) = shear rate (s\(^{-1}\))
- \( \Omega \) = angular velocity (radians/s)
- \( K_\gamma \) = strain constant

• The strain constant, \( K_\gamma \), is dependent on measurement geometry and/or initial sample dimensions
Equation for viscosity

\[ \eta = \frac{\sigma}{\dot{\gamma}} = \frac{M \cdot K_\sigma}{\Omega \cdot K_\gamma} \]

Material function
Constitutive equation
Measured signals
Geometry constants
Five Important Rheometer Specifications

- Torque range
- Angular Resolution
- Angular Velocity Range
- Frequency Range
- Normal Force
# Discovery Hybrid Rheometer Specifications

<table>
<thead>
<tr>
<th>Specification</th>
<th>HR-3</th>
<th>HR-2</th>
<th>HR-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bearing Type, Thrust</td>
<td>Magnetic</td>
<td>Magnetic</td>
<td>Magnetic</td>
</tr>
<tr>
<td>Bearing Type, Radial</td>
<td>Porous Carbon</td>
<td>Porous Carbon</td>
<td>Porous Carbon</td>
</tr>
<tr>
<td>Motor Design</td>
<td>Drag Cup</td>
<td>Drag Cup</td>
<td>Drag Cup</td>
</tr>
<tr>
<td>Minimum Torque (nN.m) Oscillation</td>
<td>0.5</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>Minimum Torque (nN.m) Steady Shear</td>
<td>5</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Maximum Torque (mN.m)</td>
<td>200</td>
<td>200</td>
<td>150</td>
</tr>
<tr>
<td>Torque Resolution (nN.m)</td>
<td>0.05</td>
<td>0.1</td>
<td>0.1</td>
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<tr>
<td>Minimum Frequency (Hz)</td>
<td>1.0E-07</td>
<td>1.0E-07</td>
<td>1.0E-07</td>
</tr>
<tr>
<td>Maximum Frequency (Hz)</td>
<td>100</td>
<td>100</td>
<td>100</td>
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<tr>
<td>Minimum Angular Velocity (rad/s)</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Maximum Angular Velocity (rad/s)</td>
<td>300</td>
<td>300</td>
<td>300</td>
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<tr>
<td>Displacement Transducer</td>
<td>Optical encoder</td>
<td>Optical encoder</td>
<td>Optical encoder</td>
</tr>
<tr>
<td>Optical Encoder Dual Reader</td>
<td>Standard</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Displacement Resolution (nrad)</td>
<td>2</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Step Time, Strain (ms)</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Step Time, Rate (ms)</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Normal/Axial Force Transducer</td>
<td>FRT</td>
<td>FRT</td>
<td>FRT</td>
</tr>
<tr>
<td>Maximum Normal Force (N)</td>
<td>50</td>
<td>50</td>
<td>50</td>
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<tr>
<td>Normal Force Sensitivity (N)</td>
<td>0.005</td>
<td>0.005</td>
<td>0.01</td>
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<tr>
<td>Normal Force Resolution (mN)</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
</tr>
</tbody>
</table>

## DHR - DMA mode (optional)

<table>
<thead>
<tr>
<th></th>
<th>HR-1</th>
<th>HR-2</th>
<th>HR-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Motor Control</td>
<td>FRT</td>
<td>FRT</td>
<td>FRT</td>
</tr>
<tr>
<td>Minimum Force (N) Oscillation</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Maximum Axial Force (N)</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Minimum Displacement (µm) Oscillation</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Maximum Displacement (µm) Oscillation</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Displacement Resolution (nm)</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Axial Frequency Range (Hz)</td>
<td>1 x 10⁻⁵ to 16</td>
<td>1 x 10⁻⁵ to 16</td>
<td>1 x 10⁻⁵ to 16</td>
</tr>
</tbody>
</table>
# ARES-G2 Rheometer Specifications

## Force/Torque Rebalance Transducer (Sample Stress)

<table>
<thead>
<tr>
<th>Transducer Type</th>
<th>Force/Torque Rebalance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transducer Torque Motor</td>
<td>Brushless DC</td>
</tr>
<tr>
<td>Transducer Normal/Axial Motor</td>
<td>Brushless DC</td>
</tr>
<tr>
<td>Minimum Torque (µN.m) Oscillation</td>
<td>0.05</td>
</tr>
<tr>
<td>Minimum Torque (µN.m) Steady Shear</td>
<td>0.1</td>
</tr>
<tr>
<td>Maximum Torque (mN.m)</td>
<td>200</td>
</tr>
<tr>
<td>Torque Resolution (nN.m)</td>
<td>1</td>
</tr>
<tr>
<td>Transducer Normal/Axial Force Range</td>
<td>0.001 to 20</td>
</tr>
<tr>
<td>Transducer Bearing</td>
<td>Groove Compensated Air</td>
</tr>
</tbody>
</table>

## Driver Motor (Sample Deformation)

<table>
<thead>
<tr>
<th>Maximum Motor Torque (mN.m)</th>
<th>800</th>
</tr>
</thead>
<tbody>
<tr>
<td>Motor Design</td>
<td>Brushless DC</td>
</tr>
<tr>
<td>Motor Bearing</td>
<td>Jeweled Air, Sapphire</td>
</tr>
<tr>
<td>Displacement Control/ Sensing</td>
<td>Optical Encoder</td>
</tr>
<tr>
<td>Strain Resolution (µrad)</td>
<td>0.04</td>
</tr>
<tr>
<td>Minimum Angular Displacement (µrad) Oscillation</td>
<td>1</td>
</tr>
<tr>
<td>Maximum Angular Displacement (µrad) Steady Shear</td>
<td>Unlimited</td>
</tr>
<tr>
<td>Angular Velocity Range (rad/s)</td>
<td>1 x 10⁻⁶ to 300</td>
</tr>
<tr>
<td>Angular Frequency Range (rad/s)</td>
<td>1 x 10⁻⁷ to 628</td>
</tr>
<tr>
<td>Step Change, Velocity (ms)</td>
<td>5</td>
</tr>
<tr>
<td>Step Change, Strain (ms)</td>
<td>10</td>
</tr>
</tbody>
</table>

## Orthogonal Superposition (OSP) and DMA modes

<table>
<thead>
<tr>
<th>Motor Control</th>
<th>FRT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum Transducer Force (N) Oscillation</td>
<td>0.001</td>
</tr>
<tr>
<td>Maximum Transducer Force (N)</td>
<td>20</td>
</tr>
<tr>
<td>Minimum Displacement (µm) Oscillation</td>
<td>0.5</td>
</tr>
<tr>
<td>Maximum Displacement (µm) Oscillation</td>
<td>50</td>
</tr>
<tr>
<td>Displacement Resolution (nm)</td>
<td>10</td>
</tr>
<tr>
<td>Axial Frequency Range (Hz)</td>
<td>1 x 10⁻⁵ to 16</td>
</tr>
</tbody>
</table>
Geometry Options

- Concentric Cylinders: Very Low to Medium Viscosity
- Cone and Plate: Very Low to High Viscosity
- Parallel Plate: Very Low Viscosity to Soft Solids
- Torsion Rectangular: Solids

Water to Steel
Assess material to test

- Geometry - material of construction, size and surface
- In general, lower viscosity use larger diameter or larger contact area and higher viscosity or more solid-like smaller diameter
- Consider:
  - Volume requirements
  - Particle size, settling or mixing necessary
  - Loading procedure for structured substances (Pre-shear)
  - Evaporation – seal sample edge, solvent trap, or RH accessory
  - Surface slip and edge fracture

Cones and Plates

Concentric Cylinders (or Cups) and Rotors (or Bobs)

Smooth, Sandblasted, and Cross hatched
Parallel Plate

**Strain Constant:** \[ K_\gamma = \frac{r}{h} \]

(to convert angular velocity, rad/sec, to shear rate, 1/sec, at the edge or angular displacement, radians, to shear strain (unitless) at the edge. The radius, \( r \), and the gap, \( h \), are expressed in meters)

**Stress Constant:** \[ K_\sigma = \frac{2}{\pi r^3} \]

(to convert torque, N\( \cdot \)m, to shear stress at the edge, Pa, for Newtonian fluids. The radius, \( r \), is expressed in meters)
When to use Parallel Plates

- Low/Medium/High Viscosity Liquids
- Soft Solids/Gels
- Thermosetting materials
- Samples with large particles

- Samples with long relaxation time
- Temperature Ramps/ Sweeps
- Materials that may slip
  - Crosshatched or Sandblasted plates
- Small sample volume
Plate Diameters

As diameter decreases, shear stress increases

\[ \sigma = \frac{2M}{\pi r^3} \]
Plate Gaps

As gap height decreases, shear rate increases

\[ \dot{\gamma} = \Omega \frac{r}{h} \]
Effective Shear Rate varies across a Parallel Plate

- For a given angle of deformation, there is a greater arc of deformation at the edge of the plate than at the center.

\[ \gamma = \frac{dx}{h} \]

\( dx \) increases further from the center, \( h \) stays constant.

Single-point correction for the parallel plate geometry (0.76 radius)
Shear Rate is Normalized across a Cone

- The cone shape produces a smaller gap height closer to inside, so the shear on the sample is constant.

\[ \gamma = \frac{dx}{h} \]

\( h \) increases proportionally to \( dx \), \( \gamma \) is uniform.
Parallel Plate Stress Correction

- The parallel plate viscosity can be corrected through the Weissenberg-Rabinowitsch correction so that parallel plate data can be compared with cone and plate data.

\[ \sigma(R) = \frac{M}{2\pi R^3} \left[ 3 + \frac{d\ln M}{d\ln \dot{\gamma}_R} \right] \]
Cone and Plate

Strain Constant: \[ K_\gamma = \frac{1}{\beta} \]

(to convert angular velocity, rad/sec, to shear rate. 1/sec, or angular displacement, radians, to shear strain, which is unit less. The angle, \( \beta \), is expressed in radians)

Stress Constant: \[ K_\sigma = \frac{3}{2\pi r^3} \]

(to convert torque, N\cdot m, to shear stress, Pa. The radius, \( r \), is expressed in meters)
When to use Cone and Plate

- Very Low to High Viscosity Liquids
- High Shear Rate measurements
- Normal Stress Growth
- Unfilled Samples
- Isothermal Tests
- Small Sample Volume
Cone Diameters

As diameter decreases, shear stress increases

\[ \sigma = \frac{3}{2\pi r^3} M \]
Cone Angles

As cone angle decreases, shear rate increases

\[ \dot{\gamma} = \Omega \frac{1}{\beta} \]
Limitations of Cone and Plate

Typical Truncation Heights:
1° degree ~ 20 - 30 microns
2° degrees ~ 60 microns
4° degrees ~ 120 microns

Gap must be > or = 10 [particle size]!!
Correct Sample Loading – parallel plate and cone-plate

- **Under Filled sample:**
  Lower torque contribution

- **Over Filled sample:**
  Additional stress from drag along the edges

- **Correct Filling**
Concentric Cylinder

**Strain Constant:**

\[ \kappa_y = \frac{1 + \left( \frac{r_2}{r_1} \right)^2}{\left( \frac{r_2}{r_1} \right)^2 - 1} \]

(to convert angular velocity, rad/sec, to shear rate, 1/sec, or angular displacement, radians, to shear strain (unit less). The radii, \( r_1 \) (inner) and \( r_2 \) (outer), are expressed in meters)

**Stress Constant:**

\[ \kappa_\sigma = \frac{1}{4\pi l} \left[ 1 + \left( \frac{r_2}{r_1} \right)^2 \right] \]

(to convert torque, N\cdot m, to shear stress, Pa. The bob length, \( l \), and the radius, \( r \), are expressed in meters)

\( c_l \) is the face factor
Double Wall

- Use for very low viscosity systems (<1 mPas)

**Strain Constant:**

\[ K_{\gamma} = \frac{r_1^2 + r_2^2}{r_2^2 - r_1^2} \]

**Stress Constant:**

\[ K_{\sigma} = \frac{r_1^2 + r_2^2}{4\pi h \cdot r_2^2 \left( r_1^2 + r_3^2 \right)} \]
When to Use Concentric Cylinders

- Low to Medium Viscosity Liquids
- Unstable Dispersions and Slurries
- Minimize Effects of Evaporation
- Weakly Structured Samples (Vane)
- High Shear Rates
# Peltier Concentric Cylinders

## Concentric Cylinder Cup and Rotor Compatibility Chart

<table>
<thead>
<tr>
<th>Cup/Rotor</th>
<th>DIN</th>
<th>Recessed End</th>
<th>Starch Impeller</th>
<th>Vane</th>
<th>Wide Gap Vane</th>
<th>Double Gap</th>
<th>Helical Rotor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard (rad=15 mm)</td>
<td>⚫</td>
<td>⚫</td>
<td>⚫</td>
<td>⚫</td>
<td></td>
<td>⚫</td>
<td>⚫</td>
</tr>
<tr>
<td>Large Diameter (rad=22 mm)</td>
<td>⚫</td>
<td>⚫</td>
<td>⚫</td>
<td>⚫</td>
<td></td>
<td>⚫</td>
<td>⚫</td>
</tr>
<tr>
<td>Starch (rad=18.5 mm)</td>
<td>⚫</td>
<td>⚫</td>
<td>⚫</td>
<td>⚫</td>
<td></td>
<td>⚫</td>
<td>⚫</td>
</tr>
<tr>
<td>Grooved</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>⚫</td>
<td>⚫</td>
</tr>
<tr>
<td>Double Gap</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>⚫</td>
<td>⚫</td>
</tr>
<tr>
<td>Helical (rad=17 mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>⚫</td>
<td>⚫</td>
</tr>
</tbody>
</table>
Viscosity of Water

- Surface tension causes artifact shear thinning under low torque
- Secondary flow shows artifact shear thickening under high shear
- Use a large diameter geometry with a smaller gap

Diagram showing the relationship between viscosity and shear rate. The graph displays different data points for various conditions, indicating surface tension at low torques and secondary flows at high shear rates.
Torsion Rectangular

\[ K_Y = \frac{t}{l \left[ 1 - 0.378 \left( \frac{t}{w} \right)^2 \right]} \]

\[ K_T = \frac{3 + \frac{1.8}{w}}{(w \cdot t^2)} \]

**Advantages:**
- High modulus samples
- Small temperature gradient
- Simple to prepare

**Disadvantages:**
- No pure Torsion mode for high strains

Torsion cylindrical also available
Torsion and DMA Measurements

- Torsion and DMA geometries allow solid samples to be characterized in a temperature controlled environment.
  - Torsion measures $G'$, $G''$, and $\tan \delta$
  - DMA measures $E'$, $E''$, and $\tan \delta$
    - ARES G2 DMA is standard function (50 µm amplitude)
    - DMA is an optional DHR function (100 µm amplitude)

Rectangular and cylindrical torsion

DMA 3-point bending and tension (cantilever not shown)
# Geometry Overview

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Application</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cone/plate</td>
<td>fluids, melts viscosity &gt; 10mPas</td>
<td>true viscosities</td>
<td>temperature ramp difficult</td>
</tr>
<tr>
<td>Parallel Plate</td>
<td>fluids, melts viscosity &gt; 10mPas</td>
<td>easy handling, temperature ramp</td>
<td>shear gradient across sample</td>
</tr>
<tr>
<td>Couette</td>
<td>low viscosity samples &lt; 10 mPas</td>
<td>high shear rate</td>
<td>large sample volume</td>
</tr>
<tr>
<td>Double Wall Couette</td>
<td>very low viscosity samples &lt; 1mPas</td>
<td>high shear rate</td>
<td>cleaning difficult</td>
</tr>
<tr>
<td>Torsion Rectangular</td>
<td>solid polymers, composites</td>
<td>glassy to rubbery state</td>
<td>Limited by sample stiffness</td>
</tr>
<tr>
<td>DMA</td>
<td>Solid polymers, films, Composites</td>
<td>Glassy to rubbery state</td>
<td>Limited by sample stiffness (Oscillation and stress/strain)</td>
</tr>
</tbody>
</table>
Setting up Rheological Experiments
Flow Tests
Newtonian & Non-Newtonian Behavior

- Newtonian
  - Viscosity independent from shear rate and shear stress
  - Viscosity only changes with temperature

- Non-Newtonian
  - Viscosity is shear dependent
    - Decrease with shear – shear thinning
    - Increase with shear – shear thickening
  - Viscosity is time dependent
    - Decrease with time – Thixotropic
    - Increase with time – Rheopectic
# Viscosity Values

<table>
<thead>
<tr>
<th>Materials</th>
<th>Viscosity $\eta$ (Pa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air /Gas</td>
<td>0.00001</td>
</tr>
<tr>
<td>Water</td>
<td>0.001</td>
</tr>
<tr>
<td>Milk/ Coffee</td>
<td>0.01</td>
</tr>
<tr>
<td>Olive oil</td>
<td>0.1</td>
</tr>
<tr>
<td>Glycerol</td>
<td>1</td>
</tr>
<tr>
<td>Liquid Honey</td>
<td>10</td>
</tr>
<tr>
<td>Molasses</td>
<td>100</td>
</tr>
<tr>
<td>Polymer Melt</td>
<td>1000</td>
</tr>
<tr>
<td>Asphalt Binder</td>
<td>100,000</td>
</tr>
</tbody>
</table>
Newtonian Fluids

- Viscosity independent of shear rate and shear stress
- Examples: water, acetone, ethanol, glycol, glycerin, cooking oil etc.

\[ \text{Viscosity} = \frac{\sigma}{\dot{\gamma}} \]

Viscosity constant
Shear Thinning Fluids

- Viscosity decrease with shear rate and shear stress
- Examples:
  hand wash, paint, coating, shampoo….
Shear Thickening Fluids

- Viscosity increase with shear rate and shear stress
- Examples:
  - highly concentrated cornstarch slurry; mud slurry
**Time Dependent Fluids**

A rheopectic material becomes more viscous with increasing time of applied force.

A thixotropic material becomes more fluid with increasing time of applied force.

**Graph:**
- **X-axis:** Time
- **Y-axis:** Viscosity
- **Green Line:** Rheopectic
- **Blue Line:** Thixotropic

**Shear Rate = Constant**
Summary of Flow Diagrams

- Newtonian
- Bingham (Newtonian w/ yield)
- Pseudo-plastic (shear thinning)
- Bingham Plastic (shear thinning w/ yield)
- Newtonian
- Dilatant (shear thickening)

\[
\sigma = f(\dot{\gamma})
\]

\[
\text{Rate } (\dot{\gamma})
\]

\[
\text{Yield Stress } (\sigma_y)
\]

\[
\text{Stress } (\sigma)
\]
Rheological Methods

• Common rheological methods for measuring viscosity of liquids
  o Single rate/stress flow
  o Continuous rate/stress ramp
  o Stepped or steady state flow
  o Flow temperature ramp
Single Rate/Stress Test

- Isothermal temperature
- Constant rate vs. time
- Constant stress vs. time

USES
- Single point testing
- Scope the time for steady state under certain rate
Body Lotion: Single Rate Test

Sample: Body Lotion
Temperature: 25°C
Geometry: 40mm parallel plate
Gap: 1mm
Shear rate: 1.0 1/s
Viscosity: 68.1 Pa.s
Continuous Ramp

- Isothermal temperature
- Ramp stress or shear rate at a constant speed

USES

- Scouting viscosity over wide range of shear
- Measure yield stress
Viscosity of a Body Lotion

- Stress ramp from 0 to 200 Pa within 60 seconds.

![Graph showing the relationship between viscosity and shear rate.](Graph)

Data not collected under equilibrium
Measure Yield Stress of a Body Lotion

- Body lotion does not flow unless the applied stress exceeds a certain value – the yield point.
Stepped or Steady-State Flow

- Step stress or shear rate from low to high on a logarithmic scale.
- At each step, viscosity is measured when steady state has been reached.

**USES**

- Viscosity Flow Curves
- Yield Stress Measurements
Stepped or Steady-State Flow

- At each point, viscosity is measured at steady state
- Provides the most precise shear viscosity versus shear rate determination
DHR and ARES G2: Steady State Algorithm

Control variables:
- Shear rate
- Velocity
- Torque
- Shear stress

Steady state algorithm
Viscosity Curves of Various Fluids

![Viscosity Curves of Various Fluids](image)

- **Starch dispersion**
- **Peanut oil**
- **0.05% Poly-acrylamide solution**
- **PIB at 20°C**
- **Syrup**
- **Butter lotion**
- **Shower gel**
- **Polymer melt at 240°C**
## Typical Applications Shear Rates

<table>
<thead>
<tr>
<th>Process</th>
<th>Shear Rate (1/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sedimentation</td>
<td>$10^{-5} - 10^{-2}$</td>
</tr>
<tr>
<td>leveling and sagging</td>
<td>$10^{-2} - 1$</td>
</tr>
<tr>
<td>chewing, swallowing, dipping coating,</td>
<td>$1 - 10^2$</td>
</tr>
<tr>
<td>pipe flow, pumping, mixing, stirring</td>
<td>$1 - 10^3$</td>
</tr>
<tr>
<td>brushing, painting, extruding</td>
<td>$10^2 - 10^4$</td>
</tr>
<tr>
<td>milling, spraying, rubbing</td>
<td>$10^3 - 10^5$</td>
</tr>
<tr>
<td>high speed coating</td>
<td>$&gt;10^5$</td>
</tr>
</tbody>
</table>
Flow Temperature Ramp

- Constant shear stress or shear rate
- Ramp temperature

USES
- Measure the viscosity change vs. temperature

1-5°C/min.
Viscosity of Honey: Temperature Dependence

40m parallel plate
Gap: 1mm
Shear rate: 5 1/s
Heating rate: 3 °C/min
Setting up Rheological Experiments
Oscillatory Tests
Outline

- Understanding Oscillation
- Approach to Oscillation Experimentation
  - Stress and Strain Sweep
  - Time Sweep
  - Frequency Sweep
  - Temperature Ramp
  - Temperature Sweep (TTS)
Dynamic Oscillatory Tests

- Most commonly used tests in adhesive evaluations

- Apply a sinusoidal stress to the sample at a certain frequency
- Monitor sample response in strain deformation
- The shift between the input stress and output strain is the phase angle

\[
\text{Phase angle } \delta \\
\]

\[
\text{Strain, } \varepsilon \\
\]

\[
\text{Stress, } \sigma^* \\
\]
Dynamic Testing: Response for Classical Extremes

Purely Elastic Response (Hookean Solid)
\[ \delta = 0^\circ \]

Strain
Stress

Purely Viscous Response (Newtonian Liquid)
\[ \delta = 90^\circ \]

Strain
Stress

Viscoelastic Response
Phase angle \(0^\circ < \delta < 90^\circ\)
Viscoelastic Parameters

**The Modulus:** Measure of materials overall resistance to deformation.

**The Elastic (Storage) Modulus:**
Measure of elasticity of material. The ability of the material to store energy.

**The Viscous (loss) Modulus:**
The ability of the material to dissipate energy. Energy lost as heat.

**Tan Delta:**
Measure of material damping - such as vibration or sound damping.

\[
G^* = \left( \frac{\text{Stress}^*}{\text{Strain}} \right)
\]

\[
G' = \left( \frac{\text{Stress}^*}{\text{Strain}} \right) \cos \delta
\]

\[
G'' = \left( \frac{\text{Stress}^*}{\text{Strain}} \right) \sin \delta
\]

\[
\tan \delta = \left( \frac{G''}{G'} \right)
\]
Storage and Loss of a Viscoelastic Material

Dynamic measurement represented as a vector

\[ G^* = \left( G'^2 + G''^2 \right)^{1/2} \]
Complex Viscosity

- The viscosity measured in an oscillatory experiment is a **Complex Viscosity** much the way the modulus can be expressed as the complex modulus. The **complex viscosity** contains an elastic component and a term similar to the steady state viscosity.

- The Complex viscosity is defined as:

\[ \eta^* = \eta' - i \eta'' \]

or

\[ \eta^* = G^*/\omega \]

Note: frequency must be in rad/sec!
Viscoelastic Spectrum for a Typical Amorphous Polymer

- **Glassy Region**: Very hard and rigid solid
- **Transition Region**: Stiff to Soft rubber
- **Rubbery Plateau Region**: Viscoelastic liquid
- **Terminal Region**

**Log E' (G') and E'' (G'') vs. Temperature**

- **Storage Modulus (E' or G')**
- **Loss Modulus (E'' or G'')**
Dynamic oscillation methods

- Stress, strain, or amplitude sweep
- Time sweep
- Frequency sweep
- Temperature ramp
- Temperature sweep (or step)
  - Time temperature superposition (TTS)
Strain, stress, or amplitude sweep

- The material response to increasing deformation amplitude is monitored at a constant frequency and temperature
- Determine LVR or yield stress
  - Tests assumes sample is stable
Creams/Lotions: Predict Stability

**Stability, phase separation of a cosmetic cream**

![Graph showing moduli G' & G'' for emulsions A and B](image)

- G' emulsion A
- G'' emulsion A
- G' emulsion B
- G'' emulsion B

Graph showing the strain percentage on the x-axis and the moduli G' & G'' in Pa on the y-axis.
Dynamic Strain Sweep: Material Response

LVR: Storage modulus independent of strain
Non-linear Region: modulus is a function of strain

\( E' \) or \( G' \)

\( \gamma_c = \text{Critical strain} \)

Strain (amplitude)
Frequency dependence of LVR

- LVR decreases with increasing frequency
- Modulus increases with increasing frequency

40% (G’ decreased by 5%)

25 mm parallel plates, 1 Hz, 30˚ C
Temperature Dependence of LVR

- In general, the LVR is shortest when the sample is in its most solid form.
Linear and Non-linear Viscoelasticity

LDPE Frequency Sweep 180°C

- Linear region: Sinusoidal excitation ➔ Sinusoidal response
- Linear region: Sinusoidal excitation ➔ Sinusoidal response
- Represented by fundamental in frequency domain

- Nonlinear region: Sinusoidal excitation ➔ Non-sinusoidal response
- Nonlinear region: Sinusoidal excitation ➔ Non-sinusoidal response
- Represented in frequency domain by fundamental and additional harmonics
Time sweep

- The material response is monitored at a constant frequency, amplitude, and temperature
- Determine stability (e.g. evaporation, degradation), thixotropy, and curing studies
  - Amplitude within LVR
Importance of Time Sweep

- Important, but often overlooked

- Determines if properties are changing over the time of testing
  - Complex Fluids or Dispersions
    - Drying or volatilization (use solvent trap)
    - Structure recovery
    - Thixotropy
  - Polymers
    - Degradation (inert purge)
    - Curing
Time Sweep on PEEK Melt - Thermal Stability

2000G time sweep at 400°C

Under N2 (Stable)

Under air (unstable)
Structure Recovery of a Paint

- Monitor the increase of the $G'$ or complex viscosity as function of time
- Thixotropic recovery can be described by the recovery time ($\tau$)
  - Rule out evaporation

$G'(t) = G'_o + (G'_\infty - G'_o)(1 - e^{t/\tau})$
Frequency sweep

• The material response to increasing frequency (rate of deformation) is monitored at a constant amplitude and temperature

• Determine stability over the expected duration of test
  ▪ Low frequencies = longer times
  ▪ Amplitude within LVR
Silly Putties have different characteristic relaxation times

Dynamic (oscillatory) testing can measure time-dependent viscoelastic properties more efficiently by varying frequency (deformation time)
Frequency Sweep - Time Dependent Viscoelastic Properties

Frequency at modulus crossover correlates with Relaxation Time
Differences in elasticity using frequency sweep

Mineral oil

PDMS

Skin cream

Hydrogel
Frequency Sweep: Material Response

Terminal Region
Rubbery Plateau Region
Transition Region
Glassy Region

Storage Modulus (E' or G')
Loss Modulus (E'' or G'')

log Frequency (rad/s or Hz)
log E' (G') and E'' (G'')
Inertial Effects

- What is Inertia?
  - **Definition**: That property of matter which manifests itself as a resistance to any change in momentum of a body
  - Instrument has inertia
  - Sample has inertia
Inertial Effects in Oscillation for DHR

- Inertia consideration
  - Viscosity limitations with frequency
  - Minimize inertia by using low mass geometries
  - Monitor inertia using Raw Phase in degree
  - When Raw Phase is greater than:
    - 150° degrees for AR series
    - 175° degrees for DHR series
    - This indicates that the system inertia is dominating the measurement signal. Data may not be valid

Raw Phase × Inertia Correction = delta
DHR Correction for Inertia

Waveforms at high frequencies

Access to raw phase angle only available with TA Instruments Rheometers!

Inertial Effects
Dynamic temperature ramp

- Linear heating rate is applied and the material response is monitored at a constant frequency and constant amplitude

- Common heating/cooling rate: 2-5 °C/min

- Amplitude within LVR
Temperature sweep (or step) - Single /Multi-Frequency

- Step and hold temperature then monitor material response
  - No thermal lag
- Common step: 5-10 degrees per step
- Amplitude within LVR
Dynamic Temperature Ramp or Sweep: Material Response

- Glassy Region
- Transition Region
- Rubbery Plateau Region
- Terminal Region

Graph showing:
- Log E' (G') and E'' (G'')
- Storage Modulus (E' or G')
- Loss Modulus (E'' or G'')

Temperature
Temperature Ramp of an Adhesive
Using Axial Force Control in a Temp Ramp Test

Sample expand, gap increase
Axial force: 0 +/- 0.2N
Adjusting strain and torque in temperature ramp

@ Low temperature:
A small strain is preferred.

@ High temperature:
A large strain is preferred.
DHR and AR: Non-iterative Sampling

Complex modulus $G'$ (Pa)

Temperature $T$ (°C)

Oscillation strain $\gamma$ (%)

Oscillation torque $T$ (μN.m)

0.1% 2 μN.m

Controlled Strain Advanced

Controlled strain type

Non-iterative sampling

Initial stress

Torque 10.0 μN.m

Lower torque limit 2.0 μN.m

Number of tries 4

Initial tolerance 0.5%

Store all tries as data points
ARES-G2 and DHR: Auto-Strain

![Diagram showing the auto-strain adjustment settings and the corresponding time, temperature, and torque graphs with strain and G' markers.]

- **Auto strain adjustment**
  - Mode: Enabled
  - Strain adjust: 30.0%
  - Minimum % strain: 0.01%
  - Maximum % strain: 2.0%
  - Torque: 10.0 μN.m
  - Maximum torque: 500.0 μN.m

- **Graphs**
  - Time
  - Temp
  - Torque
  - Strain
  - η or G'
  - Upper torque limit
  - Lower torque limit
TA Tech tips

Using Axial Force Control

Non-Iterative Sampling For Thermoset Rheology

Auto Strain using DHR w/ TRIOS v3.2 or higher

Auto-Strain Functionality when using the ARES-G2

Videos available at [www.tainstruments.com](http://www.tainstruments.com) under the Videos tab or on the TA tech tip channel of YouTube™ ([https://www.youtube.com/user/TATechTips](https://www.youtube.com/user/TATechTips))
Setting up Rheological Experiments
Transient Tests
Stress Relaxation Experiment

- Strain is applied to sample instantaneously (in principle) and held constant with time.
- Stress is monitored as a function of time $\sigma(t)$. 

![Graph showing strain over time](image)
Stress Relaxation Experiment

Response of Classical Extremes

**Elastic**
- Hookean Solid
- Stress for $t>0$ is constant

**Viscous**
- Newtonian Fluid
- Stress for $t>0$ is 0
Stress Relaxation Experiment

Response of ViscoElastic Material

Stress decreases with time starting at some high value and decreasing to zero.

- For small deformations (strains within the linear region) the ratio of stress to strain is a function of time only.
- This function is a material property known as the STRESS RELAXATION MODULUS, $G(t)$

$$G(t) = \sigma(t)/\gamma$$
Determining Strain For Stress Relaxation

- **Research Approach**, such as generation of a family of curves for TTS, then the strain should be in the linear viscoelastic region. The stress relaxation modulus will be independent of applied strain (or will superimpose) in the linear region.

- **Application Approach**, mimic real application. Then the question is "what is the range of strain that I can apply on the sample?" This is found by knowing the Strain range the geometry can apply.
  - The software will calculated this for you.

\[
\gamma = K_\gamma \times \theta \quad (%\gamma = \gamma \times 100)
\]
Stress Relaxation and Linear Region

Stress Relaxation of PDMS, Overlay

G(t) (Pa)

200% strain
50% strain
10% strain

G(t)

200% strain is outside the linear region
Creep Recovery Experiment

- Stress is applied to sample instantaneously, \( t_1 \), and held constant for a specific period of time. The strain is monitored as a function of time (\( \gamma(t) \) or \( \varepsilon(t) \)).
- The stress is reduced to zero, \( t_2 \), and the strain is monitored as a function of time (\( \gamma(t) \) or \( \varepsilon(t) \)).
Creep Recovery Experiment

Response of Classical Extremes

**Elastic**
- Stain for \( t > t_1 \) is constant
- Strain for \( t > t_2 \) is 0

**Viscous**
- Stain rate for \( t > t_1 \) is constant
- Strain for \( t > t_1 \) increase with time
- Strain rate for \( t > t_2 \) is 0
Creep Recovery: Response of Viscoelastic Material

Strain rate decreases with time in the creep zone, until finally reaching a steady state.

In the recovery zone, the viscoelastic fluid recoils, eventually reaching an equilibrium at some small total strain relative to the strain at unloading.

Creep Recovery Experiment

- Creep Zone: $\sigma > 0$
- Recovery Zone: $\sigma = 0$ (after steady state)

Strain vs. time diagram with:
- $t_1$: Creep Zone
- $t_2$: Recovery Zone
- $\sigma/\eta$: Angle indicating the rate of creep
- Blue curve: Less Elastic
- Red curve: More Elastic
Creep Recovery: Creep and Recoverable Compliance

**Creep Zone**

- **Creep Compliance**
  \[ J(t) = \frac{\gamma(t)}{\sigma} \]

  The material property obtained from Creep experiments: Compliance = 1/Modulus (in a sense)

**Recovery Zone**

- **Recoverable Compliance**
  \[ J_r(t) = \frac{[\gamma_u - \gamma(t)]}{\sigma} \]

  Where \( \gamma_u \) = Strain at unloading
  \( \gamma(t) \) = time dependent recoverable strain

Determining Stress For Creep Experiment

- **Research Approach** - If you are doing creep on a polymer melt, and are interested in viscoelastic information (creep and recoverable compliance), then you need to conduct the test at a stress within the linear viscoelastic region of the material.

- **Application Approach** - If you are doing creep on a solid, you want to know the dimension change with time under a specified stress and temperature, then the question is "what is the max/min stress that I can apply to the sample?". This is found by knowing the Stress range the geometry can apply.

  - The software will calculate this for you.

  \[ \sigma = K_\sigma \times M \]
Creep and Recovery with Increasing Stress

Non linear effects can be detected in recovery before they are seen in the creep (viscosity dominates).
Creep Testing for Zero Shear Viscosity

\[ \text{Compliance (1/Pa)} \]

- **PE Blue curve**
  - y-intercept: $1.86010 \times 10^{-3}$
  - slope: $1.55770 \times 10^{-6}$
  - Viscosity = $6.42 \times 10^{-5}$ Pa·sec

- **PE Green curve**
  - y-intercept: $1.37996 \times 10^{-3}$
  - slope: $7.86877 \times 10^{-7}$
  - Viscosity = $1.27 \times 10^{-6}$ Pa·sec

Step time (s)
Programming Creep on an ARES-G2

- Set up a pre-test and get the sample information into the loop
- Stress Control Pre-test: frequency sweep within LVR

1: Conditioning Stress Control
   - Load Precomputed
   - Run and Calculate
     - Environmental Control
       - Temperature: 30 °C
       - Soak time: 60.0 s
     - Test Parameters
       - Strain %: 0.05 %
   - Save stress control PID file
     - Stress control PID file path: W:\2011\creepPIDfile.txt
   - Data acquisition

2: Step (Transient) Creep 25°C, 60s, 100Pa
ARES-G2 Stress Control Pretest

Pretest → Frequency Sweep from 2 to 200 rad/s → data analyzed in software to optimize Motor loop control PID constants

LDPE melt
Freq. Sweep
T = 190°C
Applications of Rheology
Polymers
Three main reasons for rheological testing:

- **Characterization**
  - MW, MWD, formulation, state of flocculation, etc.

- **Process performance**
  - Extrusion, blow molding, pumping, leveling, etc.

- **Product performance**
  - Strength, use temperature, dimensional stability, settling stability, etc.
Most Common Experiments on Polymers

- **Oscillation/Dynamic**
  - Time Sweep
    - Degradation studies, stability for subsequent testing
  - Strain Sweep – Find LVR
  - Frequency Sweep – $G'$, $G''$, $\eta^*$
    - Sensitive to MW/MWD differences melt flow can not see
  - Temperature Ramp/Temperature Step
    - Transitions, end product performance
  - TTS Studies

- **Flow/Steady Shear**
  - Viscosity vs. Shear Rate, mimic processing
  - Find Zero Shear Viscosity
  - Low shear information is sensitive to MW/MWD differences melt flow can not see

- **Creep and Recovery**
  - Creep Compliance/Recoverable Compliance are sensitive to long chain entanglement, elasticity
Know Your Sample – Polymers

- Polymer samples come in different forms (e.g. powder, flakes, pellets) and can be sensitive to environmental conditions
- Careful sample preparation techniques are required to prepare good test specimens for reproducible results
  - Molding a sample and punching discs
  - Handling powders, flakes
  - Controlling the environment
Loading Polymer Pellet Samples

1. Set Environmental System to test temperature.
2. Mount melt ring onto the lower plate and load pellets.
3. Bring the upper plate close to top of melt ring and close the oven.
4. After few minutes, open the oven, remove melt ring and go to trim gap.
5. After sample relaxes, open the oven and trim excess sample.
6. Close the oven and adjust gap to geometry/test gap.
Idealized Flow Curve – Polymer Melts

- First Newtonian Plateau
  \( \eta_0 = \text{Zero Shear Viscosity} \)
  \( \eta_0 = K \times MW^{3.4} \)

- Power Law Region

- Measure in Flow Mode

- Extend Range with Oscillation & Cox-Merz

- Extend Range with Time-Temperature Superposition (TTS) & Cox-Merz

- Second Newtonian Plateau

- Molecular Structure
- Compression Molding
- Extrusion
- Blow and Injection Molding

- \( \log \eta \)

- Shear rate (1/s)
Effect of HDPE Variations in Blow Molding

Blow Molding Polyethylene

No differences in MFI, Viscosity, or GPC!

M-2 produces heavier bottles in blow molding due to increased parison swell.
Edge Fracture

- Edge fracture is caused by the elasticity of the fluids.
- When shearing a viscoelastic material, a large normal stress difference (created from its elasticity) can lead to a crack formation at the geometry edge. This is called edge fracture.
- Results: decrease in viscosity
- To minimize edge fracture:
  - Decrease measurement gap
  - Use partitioned plate
Shear Thinning or Sample Instability?

When Stress Decreases with Shear Rate, it indicates that sample is leaving the gap.
The Cox-Merz Rule

- For materials that exhibit wall slip or edge fracture, one alternative way to obtain viscosity information over shear is to use the Cox-Merz rule.

- Cox-Merz “rule” is an empirical relationship. It was observed that in many polymeric systems, the steady shear viscosity plotted against shear rate is correlated with the complex viscosity plotted against frequency.

\[ \eta^* \text{ (Pa.s)} \sim \omega \text{ (rad/s)} \]

\[ \eta \text{ (Pa.s)} \sim \dot{\gamma} \text{ (1/s)} \]
Cox-Merz Transformation Benefit

The Cox-Merz transformation works primarily with polymer melts and polymer solutions.

![PDMS Flow Curves](image)

- Transformed curve
- Flow curve

Edge fracture
Melt Rheology: MW Effect on Zero Shear Viscosity

- Sensitive to Molecular Weight, MW
- For Low MW (no Entanglements) $\eta_0$ is proportional to MW
- For MW $> \text{Critical MW}_c$, $\eta_0$ is proportional to MW$^{3.4}$

\[ \eta_0 = K \cdot M_w \]

Influence of MW on Viscosity

The zero shear viscosity increases with increasing molecular weight. TTS is applied to obtain the extended frequency range.

![Graph showing the relationship between zero shear viscosity and molecular weight.](image)

The high frequency behavior (slope -1) is independent of the molecular weight.

<table>
<thead>
<tr>
<th>SBR $M_w$ [g/mol]</th>
<th>130 000</th>
<th>230 000</th>
<th>320 000</th>
<th>430 000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero Shear Viscosity $\eta_0$ [Pa s]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Influence of MWD on Viscosity**

- A Polymer with a broad MWD exhibits non-Newtonian flow at a lower rate of shear than a polymer with the same $\eta_0$, but has a narrow MWD.
Influence of MW on $G'$ and $G''$

The $G'$ and $G''$ curves are shifted to lower frequency with increasing molecular weight.
Influence of MWD on $G'$ and $G''$

- The maximum in $G''$ is a good indicator of the broadness of the distribution.

Higher crossover frequency: lower $M_w$
Higher crossover Modulus: narrower MWD
(note also the slope of $G''$ at low frequencies – narrow MWD steeper slope)
Frequency sweep – polymer melt (ASTM D4440)

• Polymer Library software can be used to calculate MW and MWD

Analysis: MWD
Mn: 82,817 g/mol
Mw: 209,780 g/mol
Mz: 529,633 g/mol

Analysis: MWD
Mn: 53,623 g/mol
Mw: 129,984 g/mol
Mz: 314,199 g/mol

Polystyrene B
Polystyrene C

25 mm parallel plates
5.0% strain

João Maia: The Role of Interfacial Elasticity on the Rheological Behavior of Polymer Blends
Chris Macosko: Analyzing Molecular Weight Distribution w/ Rheology
Frequency Sweep-Terminal Regime

- The terminal regime in a frequency sweep result is sensitive to polymer structure.
- For a linear polymer:
  - $G''$: straight line with slope of -1;
  - $G'$: straight line with slope of -2

![Linear polymer (PS) TTS master curve at 180°C](image)
High MW Contributions

400,000 g/mol PS

400,000 g/mol PS
+ 1% 12,000,000 g/mol

400,000 g/mol PS
+ 4% 12,000,000 g/mol

Macosko, TA Instruments Users’ Meeting, 2015
Adhesive Tack Testing

- Tack testing method: ASTM D2979
- Use 8mm parallel plate, axial tensile at 0.1mm/sec
- The maximum force required to pull the plate away is defined as the sample’s tackiness.

[Graph showing comparison between Crosslinked PSA and Non-Crosslinked PSA]
Extensional Viscosity Measurements

- Non linear elongation flow is more sensitive for some structure elements (e.g. branching) than shear flows

- Many processing flows are elongation flows. Extensional viscosity measurements can be used to help predict processability
LLDPE (Low branching)

LLDPE, $T = 130\, ^\circ C$

- $0.01\, s^{-1}$
- $0.1\, s^{-1}$
- $1\, s^{-1}$
- $3\, s^{-1}$
- $10\, s^{-1}$
- [Steady Shear Viscosity * 3]

Warning: Overlay units don’t match
LDPE (High branching)

\[ \eta_e(t) \text{[Pa-s]} \]

<table>
<thead>
<tr>
<th>LDPE, T 150 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.003 s (^{-1})</td>
</tr>
<tr>
<td>0.01 s (^{-1})</td>
</tr>
<tr>
<td>0.03 s (^{-1})</td>
</tr>
<tr>
<td>0.1 s (^{-1})</td>
</tr>
<tr>
<td>0.3 s (^{-1})</td>
</tr>
<tr>
<td>1 s (^{-1})</td>
</tr>
<tr>
<td>3 s (^{-1})</td>
</tr>
<tr>
<td>10 s (^{-1})</td>
</tr>
<tr>
<td>30 s (^{-1})</td>
</tr>
</tbody>
</table>

[Steady Shear Viscosity * 3]
Thermosetting Polymers

- Thermosetting polymers are perhaps the most challenging samples to analyze on rheometers as they challenge all instrument specifications both high and low.

- The change in modulus as a sample cures can be as large as 7-8 decades and change can occur very rapidly.
Thermosets Analysis

- Monitor the curing process
  - Viscosity change as function of time or temperature
  - Gel time or temperature
- Test methods for monitoring curing
  - Isothermal time sweep
  - Temperature ramp
  - Combination profile to mimic process
- Analyze cured material’s mechanical properties (G’, G”, tan δ, T_g etc.)
Structural Development During Curing

Gel point
Curing Analysis: Isothermal Curing

Gel Point: \( G' = G'' \)
\( t = 330 \text{ s} \)

5 min

TA Instruments
Isothermal Curing

Tire Compound: Effect of Curing Temperature

G' (MPa) vs. Time (min) for different curing temperatures.
Temperature Ramp Curing

Surface Master® 905

- Crossover technique: Cubic / linear (Orche)
- Crossover modulus: 1188.26 Pa
- Crossover x value: 132.424 °C
- Min y: 5.474190e1 Pa.s
- At x: 122.507 °C

Storage modulus $G'$ (Pa)
Loss modulus $G''$ (Pa)
Complex viscosity $n^*$ (Pa.s)

Temperature $T$ (°C)
UV Curing

- Monitor UV curing: Dynamic time sweep
- Measure curing time with different formulations, UV intensity and temperature
- Measure cured adhesive modulus
Curing with Controlled Humidity

- Silicone adhesive curing under 25°C and 10%; 60% relative humidity
- Higher humidity, faster curing

![Graph showing storage modulus vs. step time for Silicone at 10% RH and Silicone at 60% RH.]
Testing Solids: Torsion and DMA

- Torsion and DMA geometries allow solid samples to be characterized in a temperature controlled environment
- Torsion measures $G'$, $G''$, and $\tan \delta$
- DMA measures $E'$, $E''$, and $\tan \delta$
  - DMA mode on ARES G2 (max 50 µm amplitude)
  - DMA mode on DHR (max 100 µm amplitude)

$$E = 2G(1 + v)$$

$v$ : Poisson’s ratio

Torsion rectangular and cylindrical clamps

DMA cantilever, 3-point bending and tension clamps
Dynamic Temp Ramp Test

- Measure moduli, tan δ and transitions
Applications of Rheology
Yield stress and thixotropy of structured Fluids
Structured Fluids

• A multiphase complex system consists of a continuous phase (e.g. water or oil) and a dispersed phase (solid, fluid, gas)
• Stabilizers or thickeners are added to form a weak three dimensional network structure
Properties of Structured Fluids

• Structured fluid properties
  - Non-Newtonian
  - Yield stress
  - Thixotropic
  - Viscoelasticity

![Diagram showing the properties of structured fluids](image-url)
Types of Structured Fluids

• Three categories
  o **Suspension** Solid particles in a Newtonian fluid
  o **Emulsion** Fluid in a fluid
  o **Foam** Gas in a fluid (or solid)

• Examples are:
  o Paints
  o Coatings
  o Inks
  o Adhesives
  o Personal Care Products
  o Cosmetics
  o Foods
Generalized Flow Curve for structured fluids

- **Brownian motion**
- **Random orientation**
- **Shear thinning**
- **Shear thickening**

\[ \log \eta \]

Shear field aligns particles along streamlines

Hydrodynamic interactions push particles out of alignment. Temporary hydro-clusters form, increasing the effective volume fraction and leading to shear thickening.

Shear thinning → Shear thickening

Trapped Continuous Phase Volume
What is Yield?

- Yield stress is a time dependent characteristic that is associated with many structured fluids such as Mayonnaise, Ketchup, hand lotion, hair gels, paints etc.

- A material that has yield does not flow unless the applied stress exceeds a certain value – yield point

- Yield stress is created in formulation by adding additional thickeners

- Yield helps stabilize complex fluids
  - Avoid sedimentation and increase shelf life
  - Reduce flow under gravity
  - Stabilize a fluid against vibration
How to Measure Yield

• Yield can be quantitatively measured on a rotational rheometer

• Common methods
  o Stress ramp
  o Stress sweep
  o Shear rate ramp
  o Dynamic stress/strain sweep

Note:
Yield behavior is a time dependent characteristic. Measured yield stress values will vary depending on experimental parameters
Yield Stress of a Body Lotion

- Stress ramp from 0 to 200 Pa in 60 seconds
- Yield is determined at the point where viscosity shows a peak

![Graph showing viscosity and shear rate as a function of stress.]

- **Peak viscosity**: 1237 Pa.s
- **Yield stress**: 27.1 Pa
Fit Results with a Flow Models

- Fit the stress ramp curves with a mathematical flow model
- Three flow models to describe the yield behavior

**Bingham**
\[
\sigma = \sigma_y + \eta \dot{\gamma}
\]

**Herschel-Bulkley**
\[
\sigma = \sigma_y + K_B \dot{\gamma}^n
\]

**Casson**
\[
\sqrt{\sigma} = \sqrt{\sigma_y} + \eta_c \dot{\gamma}
\]
Yield Stress of Ketchup

- Stress ramp test on Ketchup
- Yield is computed by fitting the flow curve with a mathematical model

Yield stress = 56 Pa

Bingham Model:
\[ \sigma = \sigma_y + \eta \dot{\gamma} \]
Yield Stress of Orange Juice

- Shear rate ramp down from 500 to 0.001 1/s
- Yield is identified by the stress plateau

Yield stress = 0.017 Pa

Slope = -1
Yield Stress of a Toothpaste

- Steady state stress sweep from 10 Pa to 500 Pa
- Yield stress is determined by a sharp decrease in viscosity over a narrow range of applied shear stress
- Take the onset of viscosity vs. stress curve
Wall Slip – Artifact Yield

- Incidence of wall slip is often observed when testing structured fluids
- Wall slip shows artifact yield

Yield Stress Measurements on Toothpaste

\[\tau_y = 18 \text{ Pa}\]
\[\tau_y = 105 \text{ Pa}\]

Crosshatched plate
Smooth plate

Viscosity (Pa s)

Shear Stress (Pa)
Solutions To Minimize Wall Slip

• Diagnosis method
  o Running the same experiment at different gaps. For samples that don’t slip, the results will be independent of the gap

• Solutions
  o Use a grooved cup with vane or helical shape rotor geometry
  o Use a roughened surface geometry
Yield Stress of Mayonnaise

- Dynamic stress/strain sweep test on Mayonnaise
- Yield stress is signified at the onset of $G'$ vs. stress curve
- Yield determined by this method indicates the critical stress at which irreversible plastic deformation occurs

![Graph showing storage and loss modulus vs oscillation stress with a yield stress of 53.8 Pa](image-url)
What is Thixotropy?

• Thixotropy is a time-dependent shear thinning property, which is used to characterize structure change reversibility

• A thixotropic fluid takes a finite time to attain equilibrium viscosity when introduced to a step change in shear rate

• Thixotropy is a desired property for many applications such as:
  o Control sagging and levelling of paints
  o Start up of pipeline flow after rest
How to Measure Thixotropy

• Thixotropy can be quantitatively measured on a rotational rheometer

• Common methods
  - Stepped flow method
  - Stepped dynamic method
  - Stress ramp up and down method (Thixotropic loop)
  - Dynamic time sweep after pre-shear method

Note:
Thixotropic behavior is a time dependent characteristic. Measured thixotropy will vary depending on experimental parameters.
Stepped Flow Method

Experimental:
Step 1: Low Shear (e.g. 0.1 1/s), state of rest
Step 2: High Shear (e.g. 10 1/s), structural destruction
Step 3: Low Shear (e.g. 0.1 1/s), structural regeneration
Thixotropic Analysis of a Blue Paint

0.1 /s  10 /s  0.1 /s

Leveling problem
Good Performance
Sagging problem
Stepped Dynamic Method

Experimental:
Step 1: Dynamic time sweep within LVR, structure at rest
Step 2: Dynamic time sweep outside LVR, structural destruction
Step 3: Dynamic time sweep within LVR, structural regeneration
Good for measuring high viscosity samples
Blue Paint: Stepped Time Sweep

Storage modulus $G' (\text{Pa})$
Loss modulus $G'' (\text{Pa})$

Initial $G'$
Recoverable $G'$

$0.1\%$ $100\%$ $0.1\%$

$10^1$ $10^2$

Time $t$ (s)

$0$ $100$ $200$ $300$ $400$ $500$ $600$
Stress Ramp Up and Down Method

- Ramp shear stress linearly from zero up until sample flows, then ramp stress back down to zero.
- Thixotropic index is measured by taking the area between the up and down stress curves.
- TA Tech Tip:  [https://www.youtube.com/watch?v=8lZangOp1SY](https://www.youtube.com/watch?v=8lZangOp1SY)
Thixotropic Loop Testing on Foods

Mayonnaise, Yellow Mustard, and Ketchup

- 40mm sand blasted plate
- Gap: 1mm
- Ramp stress from 0-100-0 Pa
- Ramp up time: 60 sec
- Ramp down time: 60 sec

Thixotropy:
- Mayonnaise: 63.0 Pa/s
- Yellow Mustard: 714.4 Pa/s
- Ketchup: 1456.0 Pa/s
**Time Sweep After Pre-shear Method**

- Apply a constant shear (e.g. 10 or 100 1/s) for a certain time (e.g. 1 min.) to break down structure.
- Immediately start a time sweep within the linear region of the material to monitor structure recovery.
Blue Paint: Time Sweep After Pre-shear

- Monitor the increase of the $G'$ as a function of time.
- Thixotropic recovery is described by measuring the recovery time $(\tau)$

$$G'(t) = G'_0 + (G'_\infty - G'_0)(1 - e^{t/\tau})$$
TRIOS Help Menu

- Browse the contents list or search using the search tab.
- Access to Getting Started Guides also found through the help menu.
Instructional Videos

- From www.tainstruments.com click on Videos, Support or Training

See also: https://www.youtube.com/user/TATechTips
Instructional Video Resources

Quickstart e-Training Courses

Web based e-Training Courses

TA Instruments offers a variety of training opportunities via the Internet. e-Training opportunities include the following:

QUICKSTART e-TRAINING COURSES

QuickStart e-Training courses are designed to teach a new user how to set up and run samples on their analyzers. These 60-90 minute courses are available whenever you are. These pre-recorded courses are available to anyone at no charge. Typically these courses should be attended shortly after installation.

Contact Us for Web based e-Training Courses

Strategies for Better Data - Rheology

Rheology Quickstart e-Training Courses

Thermal Analysis

Part 1: Instrument Fundamentals and Sample Preparation

Part 2: Efficient and Effective Method Development

Part 3: Tips for Data Reduction and Presentation

IN THIS SESSION

This introductory session will introduce fundamental concepts of rheology and provide specific guidance for preparing the sample and instrument.

- Rheology Fundamentals: viscosity, modulus, stress, strain, viscoelasticity
- How a Rheometer Works
- Appropriate Geometry Selection
- Understanding Your Material and Preparing a Representative Sample

TA
TAINSTRUMENTS.COM
Avoid Testing Artifacts

• TA Webinar - Professor Randy H. Ewoldt
  
  [Link to TA Webinar]

About the Speaker

Randy H. Ewoldt is an Assistant Professor in the Department of Mechanical Science and Engineering at the University of Illinois at Urbana-Champaign. He has Ph.D. and S.M. degrees from MIT, and a B.S. degree from Iowa State, all in Mechanical Engineering. Before joining Illinois, he held a post-doctoral fellowship at the University of Minnesota. At Illinois, his research group studies rheology, fluid mechanics, and design of complex fluids; in particular, this includes yield stress fluids, polymer gels, biological materials, and large-amplitude oscillatory shear (LAOS) characterization. His work has been recognized by young investigator awards from NSF, ASME, 3M, DuPont, and The Society of Rheology.

What if I need help?

• TA Tech Tips
  ▪ [http://www.youtube.com/tatechtips](http://www.youtube.com/tatechtips)

• On-site training & e-Training courses - see Website

• TA Instruments Applications Helpline available from the TA website

• Service related queries
  - Email: servicehelpline@tainstruments.com
  - Ph: 302-427-4050

• Check out our Website
Thank You

The World Leader in Thermal Analysis, Rheology, and Microcalorimetry
Applications of Rheology
Advanced Accessories
# DHR Humidity Accessory

<table>
<thead>
<tr>
<th>Features</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature Range</td>
<td>5 °C – 120 °C</td>
</tr>
<tr>
<td>Temperature Accuracy</td>
<td>±0.5 °C</td>
</tr>
<tr>
<td>Heating/Cooling Rate</td>
<td>±1 °C/min maximum</td>
</tr>
<tr>
<td>Humidity Range</td>
<td>5-95%</td>
</tr>
<tr>
<td>Humidity Accuracy</td>
<td>5-90%RH: ±3% RH</td>
</tr>
<tr>
<td></td>
<td>&gt;90%RH: ±5% RH</td>
</tr>
<tr>
<td>Humidity Ramp Rate</td>
<td>±2% RH/min increasing or decreasing</td>
</tr>
</tbody>
</table>

- **Surface Diffusion**
- **Bulk Diffusion**
- **Film/fiber Tension**
DHR Humidity Accessory

Elmers Glue Curing Under Humidity Control @ 50°C

- Bulk diffusion geometry at 50°C and constant RH (10%, 30% and 60%)
- The test frequency - 1.0 rad/s and oscillation torque - 5 µN·m

![Diagram showing the curing process of Elmers glue under different humidity conditions.]
Modular Microscope Accessory (DHR)

- Connecting Rheology with structure under flow conditions (counter rotation option also available). Modular video camera, light source, and interchangeable optical objectives.
MagnetoRheology Accessory (DHR)

- The MR Accessory enables characterization of magneto-rheological fluids under the influence of a controlled field.

- Applied fields up to 1 T with temperature range of -10 °C to 170 °C (standard and extended temperature options).

- The system accommodates an optional Hall probe for real-time measurement and closed-loop control of the sample field.
Magneto Rheology Accessory (DHR)

- Lord MR Fluid MRF-140CG (081610) – 300µm gap at 20°C
Small Angle Light Scattering (DHR)

- Simultaneous rheology and structure information
- Laser Light creates interference pattern
- Pattern reflects size, shape, orientation and arrangements of objects that scatter
- Objects scatter due to differences in refractive index
Interfacial Accessories

- Steady Shear Viscosity at air/liquid and liquid/liquid interface.
- Qualitative Viscoelastic measurements at air/liquid and liquid/liquid interface.
- Quantitative Viscoelastic measurements at air/liquid and liquid/liquid interface.
- Interfacial shear rheology of thin layers at liquid-liquid or liquid-gas interfaces
- Effect of particles, surfactants or proteins at the interface
- Applications: food, biomedical, enhanced oil recovery
Surface Concentration Effects on Interfacial Viscosity

Surface viscosity of Span 65 layer deposited on water

Shear Rate $\dot{\gamma}$ [1/s] vs. Viscosity $\eta_s$ [Pa.s.m]

Surface loading: 0.3 - 8 molecules/nm$^2$

Water
Interfacial properties Span65 @ water-dodecane interface

**SPAN 65 @ Water-dodecane interface**

- **Storage Modulus** $G'_s$
- **Loss Modulus** $G''_s$

**Strain** $\gamma$ [ ]

**Raw Phase** $\delta$

**T** = 25 °C

Linear region
SPAN65® Water-Dodecane Interface

**Interfacial properties Span65 @ water-dodecane interface**

**SPAN 65 @ Water-dodecane interface**
- T = 25 °C
- γ = 0.1%

**Storage & Loss Modulus** [N/m]
- G'
- G''

**Frequency** ω [rad/s]

**Raw Phase** [°]
Dielectric Accessory

Agilent E4980A LCR meter

Ground Geometries with Ceramic Insulator (standard or disposable)
Dielectric Accessory

- Stand-alone or combined Dielectric-rheology
- LCR Fully programmable from TRIOS
- Wide temperature range: -160 to 350 °C
- Applications: Characterize polar materials such as PVC, PVDF, PMMA, PVA
Electro-Rheology (ER) Accessory

- Plates and DIN concentric cylinders

Ground Geometries with Ceramic Insulator
Electro-Rheology (ER) Accessory

- Wide range of voltage profiles
  - Constant voltage
  - Step voltage, ramp voltage
  - Sine wave voltage function
  - Triangle wave voltage function
  - Wave functions with DC offsets
- Fully programmable from TRIOS

Applications:
- Hydraulic valves and clutches
- Shock absorbers
- Bulletproof vests
- Polishing slurries
- Flexible electronics
Peltier Plate Tribo-rheometry Geometries

- Ball on three Plates
- Three Balls on Plate
- Ring on Plate
- 4 Balls

Also available for ETC
ARES G2 FCO and APS Tribology Accessory

- High temperature with FCO
  - Applications: Automotive, High temp. greases/oils, Asphalt, Rubber
- Close to Room Temperature - APS and Plate
  - Applications: Personal care products, Lubricants, Foods
Coefficient of Friction Measurement

PVC on Steel with 2.0 Pa.s oil as lubricant
Geometry: 3 Balls on Plate
Temperature: 25°C, Procedure: Flow ramp
Tribo-Rheometry: Exfoliants

![Graph showing the coefficient of friction (μ) as a function of sliding speed (v_s) for different exfoliants at various normal forces.](#)
Orthogonal Superposition Features on ARES G2

- OSP on steady shear to monitor structural changes in materials (alternative to LAOS measurements)
- 2D-SAOS measurements to quantify anisotropy in materials
- Mentioned DMA capabilities previously in the polymer analysis section
- Simultaneous multiaxial testing of soft solids such as gels, foams, rubbers,...
Structure breakdown monitored by OSP

Steady shear breaks down gel structure and moves flow region to shorter times scales (high frequencies)
Appendix 1: Time Temperature Superposition (TTS)
Time and Temperature Relationship

- Linear viscoelastic properties are both time-dependent and temperature-dependent.
- Some materials show a time dependence that is proportional to the temperature dependence.
  - Decreasing temperature has the same effect on viscoelastic properties as increasing the frequency.
- For such materials, changes in temperature can be used to “re-scale” time, and predict behavior over time scales not easily measured.
Time Temperature Superpositioning Benefits

- TTS can be used to extend the frequency beyond the instrument’s range
- Creep TTS or Stress Relaxation TTS can predict behavior over longer times than can be practically measured
- Can be applied to amorphous, non modified polymers
- Material must be thermo-rheological simple
  - One in which all relaxations times shift with the same shift factor $a_T$
When Not to Use TTS

- If crystallinity is present, especially if any melting occurs in the temperature range of interest
- The structure changes with temperature
  - Cross linking, decomposition, etc.
  - Material is a block copolymer (TTS may work within a limited temperature range)
  - Material is a composite of different polymers
  - Viscoelastic mechanisms other than configuration changes of the polymer backbone
    - e.g. side-group motions, especially near the Tg
    - Dilute polymer solutions
    - Dispersions (wide frequency range)
    - Sol-gel transition
Guidelines for TTS

- Decide first on the Reference Temperature: $T_0$. What is the use temperature?

- If you want to obtain information at higher frequencies or shorter times, you will need to conduct frequency (stress relaxation or creep) scans at temperatures lower than $T_0$.

- If you want to obtain information at lower frequencies or longer times, you will need to test at temperatures higher than $T_0$.

- Good idea to scan material over temperature range at single frequency to get an idea of modulus-temperature and transition behavior.
TTS Shifting

![Graph showing the relationship between Storage modulus $G'$ (P) and Frequency $f$ (Hz) for different temperatures. The graph includes lines for temperatures 140, 150, 160, 170, 180, 190, and 200.0 degrees Celsius.](image)
TTS Shifting
TTS Shifting

![Graph showing storage modulus $G'$ versus frequency $f$ for different temperatures.]
TTS Shifting

![Graph showing storage modulus (G') vs frequency (f) for different temperatures: 140, 150, 160, 170, 180, 190, *** 200.0. The graph includes a log-log scale for both axes, with frequencies ranging from $10^{-2}$ to $10^5$ Hz and storage moduli ranging from $10^{2}$ to $10^6$ Pa.](image-url)
TTS Shifting

Storage modulus $G'$ (P)

Frequency $f$ (Hz)

- 140
- 150
- 160
- 170
- 180
- 190
- *** 200.0
TTS Shifting

![Graph showing storage modulus G' as a function of frequency f (Hz) for different temperatures.]

- Temperature values: T=140, T=150, T=160, and a~200.0

- The graph demonstrates the shift in storage modulus with varying temperatures and frequencies.
Shift Factors $a_T$ vs Temperature
Master Curves can be generated using shift factors derived from the Williams, Landel, Ferry (WLF) equation

\[ \log a_T = -c_1(T - T_0)/c_2 + (T - T_0) \]
- \( a_T \) = temperature shift factor
- \( T_0 \) = reference temperature
- \( c_1 \) and \( c_2 \) = constants from curve fitting
  - Generally, \( c_1 = 17.44 \) & \( c_2 = 51.6 \) when \( T_0 = T_g \)
When not to use the WLF Equation

- Sometimes you shouldn’t use the WLF equation (even if it appears to work)
- If $T > T_g + 100 \, ^\circ C$
- If $T < T_g$ and polymer is not elastomeric
- If temperature range is small, then $c_1$ & $c_2$ cannot be calculated precisely

- In these cases, the Arrhenius form is usually better
  \[ \ln a_T = \left( \frac{E_a}{R} \right) \left( \frac{1}{T} - \frac{1}{T_0} \right) \]
  
  - $a_T$ = temperature shift factor
  - $E_a$ = Apparent activation energy
  - $T_0$ = reference temperature
  - $T$ = absolute temperature
  - $R$ = gas constant
  - $E_a$ = activation energy
Verify Data for TTS

Polystryene
Verify Data for TTS

Polystryene
References for TTS


Appendix 2: Rheometer Calibrations
DHR and AR
DHR – Calibration Options

- Instrument Calibrations
  - Inertia (Service)
  - Rotational Mapping
  - Oscillation Mapping (recommended for interfacial measurements)
DHR – Inertia Calibration

- Go to the Calibration tab and select Instrument
  - Make sure there is no geometry installed and then click calibrate
DHR – Geometry Calibration

- Geometry Calibrations:
  - Inertia
  - Friction
  - Gap Temperature Compensation
  - Rotational Mapping
TA Tech Tip – Geometry Calibrations

- Videos available at www.tainstruments.com under the Videos tab or on the TA tech tip channel of YouTube™ (http://www.youtube.com/user/TATechTips)
Appendix 2: Rheometer Calibrations
ARES-G2
ARES-G2 – Calibration Options

- Instrument Calibrations
  - Temperature Offsets
  - Phase Angle (Service)
  - Measure Gap Temperature Compensation
  - Transducer

- Geometry Calibrations:
  - Compliance and Inertia (from table)
  - Gap Temperature Compensation
ARES-G2 – Transducer Calibration

Transducer Calibration Procedure
- Torque
- Normal Force

Torque Calibration
1. Install the calibration fixture and pulley (without weight)
2. Zero Torque Transducer
3. Hang weight from the pulley
   - Calibration mass: 500.000 g
   - Moment arm length: 2.50000 cm
   - Applied Torque: 1250.00 g cm
4. Measure resulting torque
   - New calibration factor: 0.00000 g cm

Transducer
- Torque: 0.720 g cm
- Normal Force: 53.202 g
- Status: Initializing Transducer

Torque Calibration Factor: 2106.05 g cm
Normal Force Calibration Factor: 2090.05 g
ARES-G2 – Geometry Calibration

- Gap Temperature Compensation
  - Enter manually or run calibration

- Compliance and Inertia
  - (from table in Help menu)

- Geometry Constants
  - Calculated based on dimensions
What if the online table does not list a compliance value for my specific geometry? Use the compliance value for a geometry of the same/similar dimension, type, and material.
ARES-G2 - Gap Temperature Compensation

Gap Temperature Compensation Calibration:

Geometry Name: 40mm parallel plate, Stainless steel

Notes:

Current Expansion Coefficient: 0.00000 µm/°C
New Expansion Coefficient:

Temperature / Time Profile:

- Run at Gap
- Maintain Zero Gap

Maintain Force: 5.0 N
Starting Temperature: -60 °C
Start Temperature Equilibration Time: 300 s
Ramp Temperature

Temperature Ramp Rate: 1.0 °C/min
Final Temperature: 65 °C
Final Temperature Equilibration Time: 300 s

Commit

Run
General Rheometer Maintenance

- **Air Supply**
  - Dry particulate-free air (dew point -40 °C)
  - Check filters/regulators on a periodic basis to ensure proper pressure, free of moisture/oil/dirt buildup.
  - If air must be turned off, then make sure that the bearing lock is fastened
    - NOTE: Do not rotate drive-shaft if air supply is OFF!

- **Location**
  - Isolate the instrument from vibrations with a marble table or Sorbathane pads.
  - Drafts from fume hoods or HVAC systems and vibrations from adjacent equipment can contribute noise to measurements, particularly in the low torque regime. Use a Draft Shield to isolate instrument from drafts.
General Rheometer Maintenance - Peltier

- **Circulator Maintenance**
  - Proper operation of a fluid circulator is vital for correct and efficient operation of Peltier-based temperature control devices.
  - Check fluid levels and add anti-fungal additive regularly.
    - Note: if operating circulator below 5°C then it is recommended to fill the circulator with a mixture or material with a lower freezing point than water to prevent permanent circulator damage.
      - Example: add ~20% v/v ethanol to water
  - Keep it clean!
    - Flush and clean circulator, Peltier system, and tubing at first sight of contamination.
    - When not in use, it is strongly recommended to deactivate the Peltier device and turn off the circulator.
Verify Rheometer Performance

- Rheometers are calibrated from the factory and again at installation.
- TA recommends routine validation or confidence checks using standard oils or Polydimethylsiloxane (PDMS).

- PDMS is verified using a 25 mm parallel plate.
  - Oscillation - Frequency Sweep: 1 to 100 rad/s with 5% strain at 30°C
  - Verify modulus and frequency values at crossover

- Standard silicone oils can be verified using cone, plate or concentric cylinder configurations.
  - Flow – Ramp: 0 to 88 Pa at 25°C using a 60 mm 2° cone
    - Service performs this test at installation
PDMS Frequency Sweep Results

PDMS #1

Crossover modulus: 271160 dyne/cm²
Crossover x value: 5.38927 rad/s

Storage modulus $G'$ (dyne/cm²)
Loss modulus $G''$ (dyne/cm²)
Complex viscosity $\eta^*$ (poise)

Angular frequency $\omega$ (rad/s)
Load Standard Oil

- Set Peltier temperature to 25°C and equilibrate.
  - Zero the geometry gap

- Load sample
  - Be careful not to introduce air bubbles!

- Set the gap to the trim gap

- Lock the head and trim with non-absorbent tool
  - Important to allow time for temperature equilibration.

- Go to geometry gap and initiate the experiment.
Flow Ramp – Standard Oil (Service Test)