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.

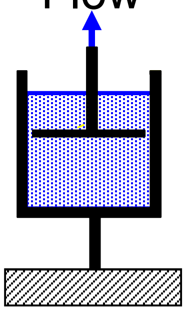




Basic Material Behaviors

Water	Oil	Soap	Egg white	Polymer Melt	Ceramic ?	Metal

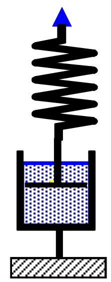
Flow

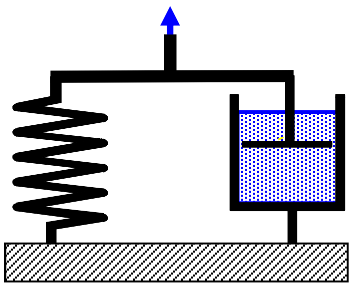


Viscous Liquids

$$\text{Viscosity} = \frac{\text{Stress}}{\text{Strain Rate}}$$

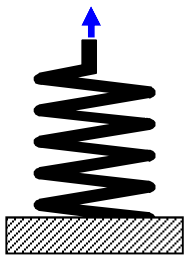
Flow & Deformation





Viscoelastic

Deformation



Elastic Solids

$$\text{Modulus} = \frac{\text{Stress}}{\text{Strain}}$$

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

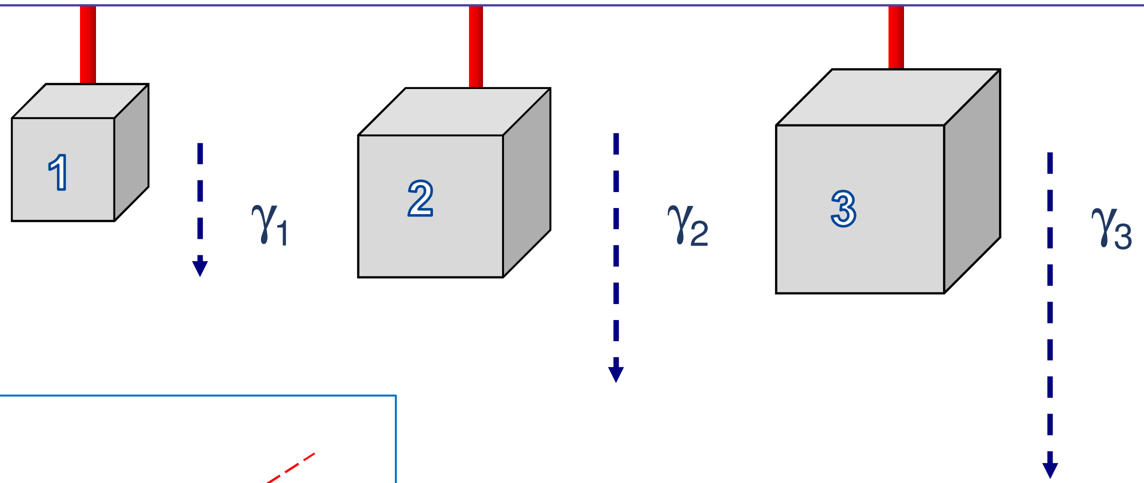
$$\frac{\text{Stress}}{\text{Shear rate}} = \text{Viscosity}$$

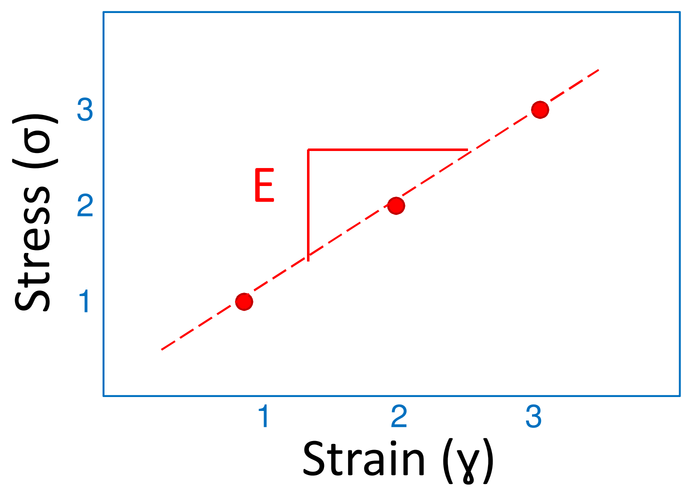
$$\frac{\text{Stress}}{\text{Strain}} = \text{Modulus}$$

Elastic Behavior of an Ideal Solid

Hooke's Law of Elasticity: Stress = Modulus · Strain

$$\sigma = E \cdot \gamma$$

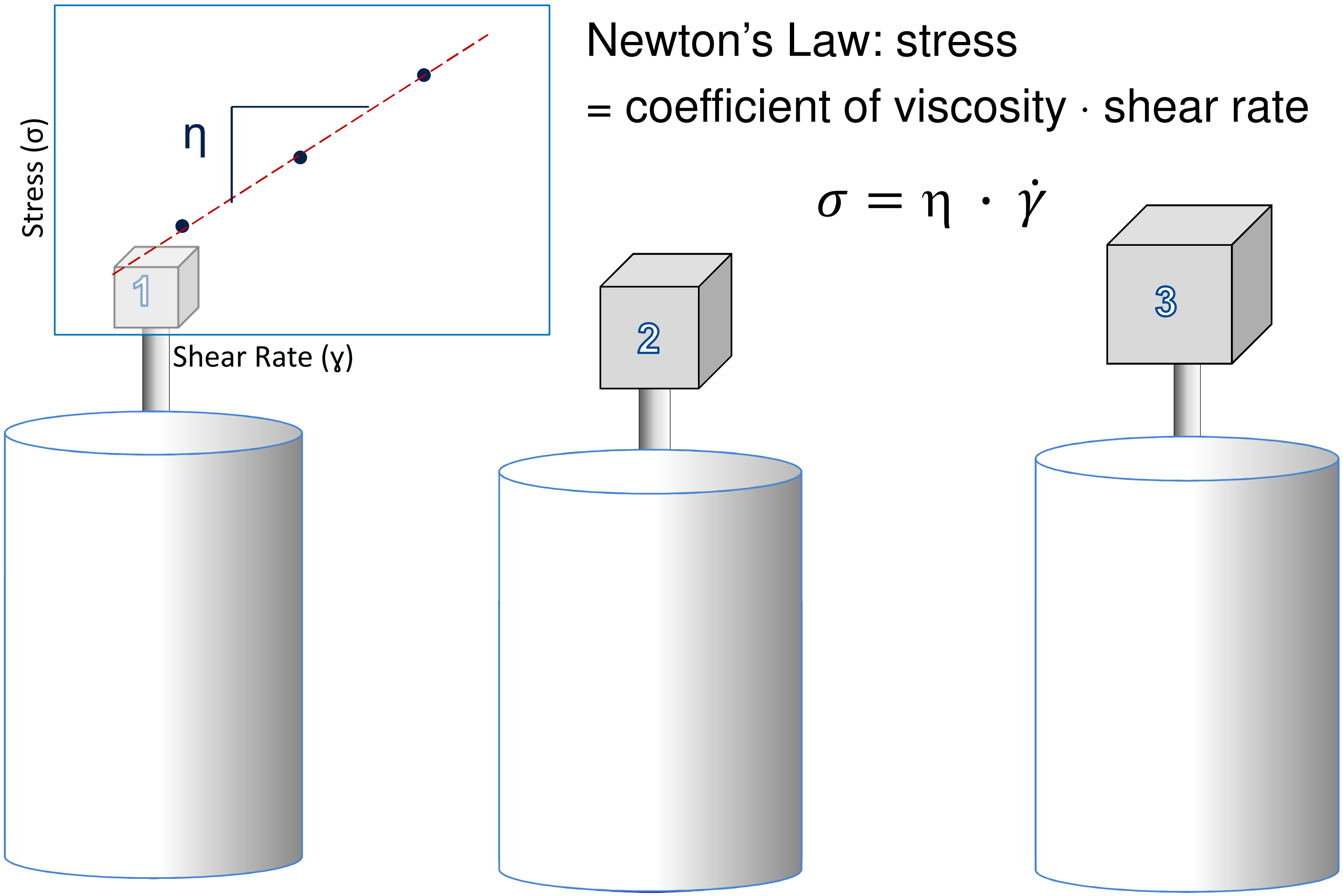




Viscous Behavior of an Ideal Liquid

Newton's Law: stress
= coefficient of viscosity · shear rate

$$\sigma = \eta \cdot \dot{\gamma}$$



Viscoelasticity Defined

Range of Material Behavior

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

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

Purely Viscous ----- *Visco*elastic ----- 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.

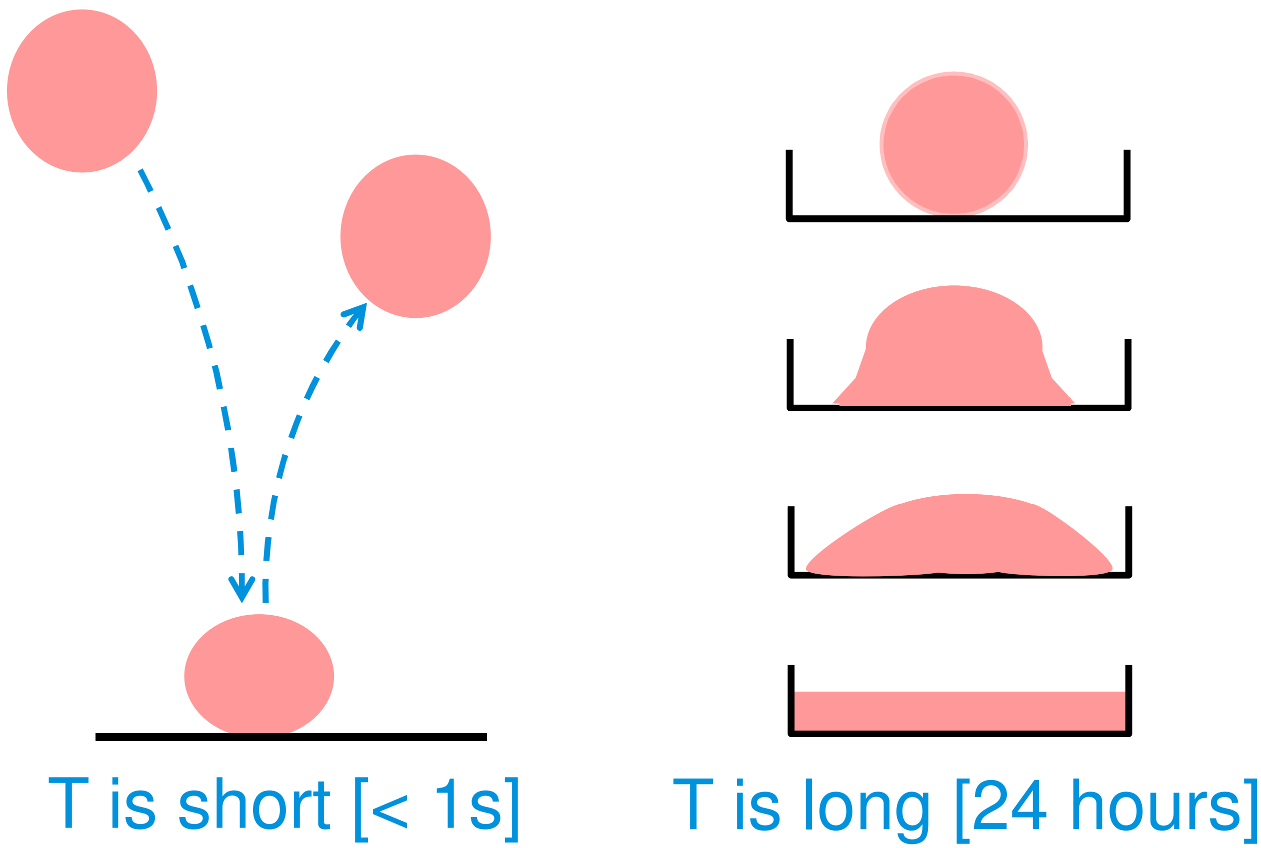
Solid or Liquid?

- 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

http://www.theatlantic.com/technology/archive/2013/07/the-3-most-exciting-words-in-science-right-now-the-pitch-dropped/277919/

Time-Dependent Viscoelastic Behavior

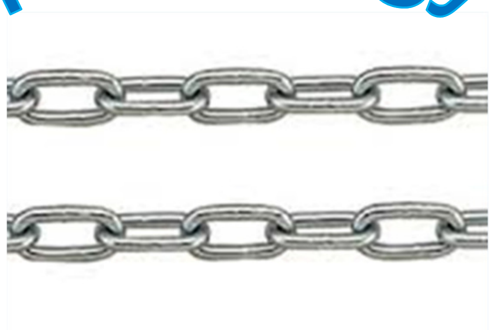


Importance of Rheological Measurements

- Investigating molecular structure
- Guide and troubleshooting processing
- Evaluate product performance

Rheology

Molecular structure



Product performance

viscoelastic properties

Basic Parameters and Units

Stress = Force /Area [Pa, or dyne/cm^2]

σ = shear stress

Strain = Geometric Shape Change [no units]

γ = 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 η

S.I. units x 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

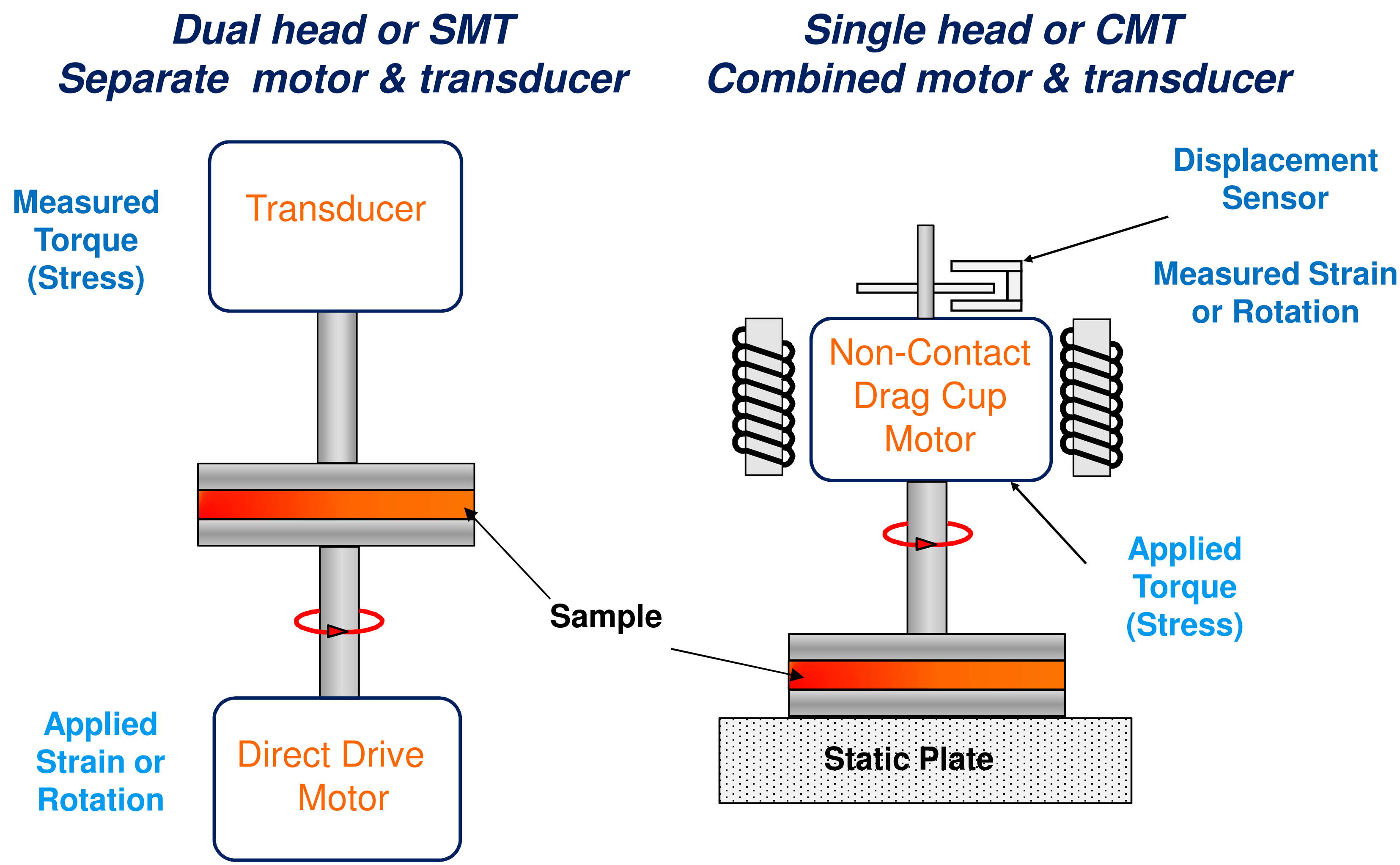
ARES G2

Controlled Strain
Dual Head
SMT

DHR

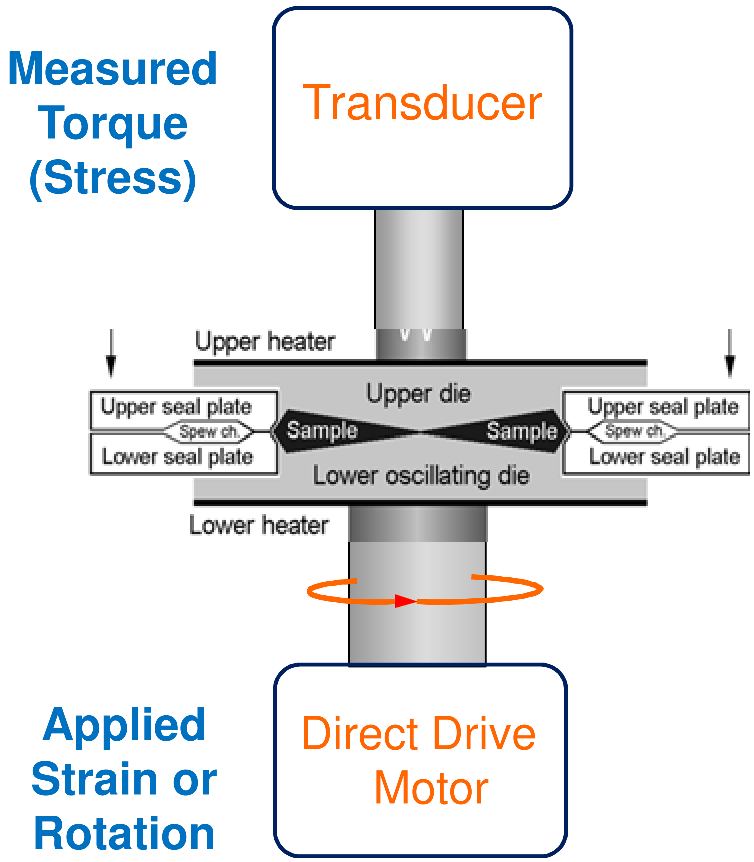
Controlled Stress
Single Head
CMT

Rotational Rheometer Designs



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

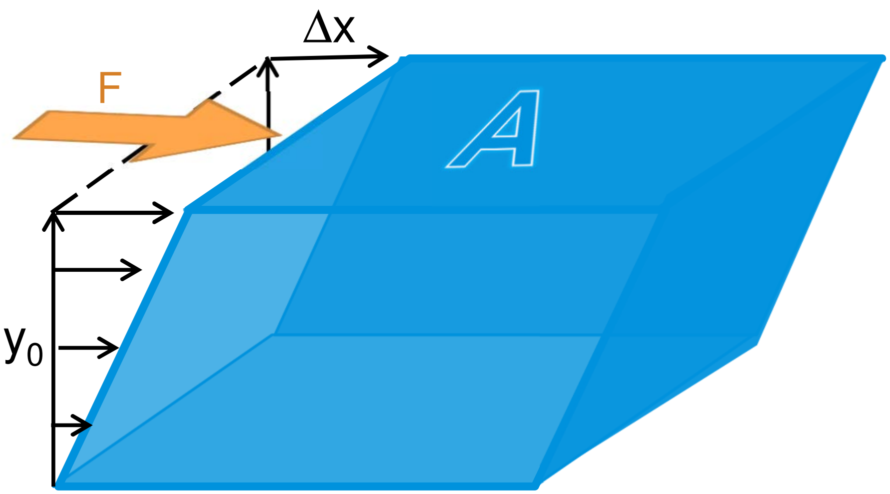


RPA Elite, RPA Flex and MDR

Controlled Strain
SMT or Dual Head

How do Rheometers Work?

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



Shear stress $\sigma = \frac{F}{A}$

Shear strain $\gamma = \frac{\Delta x}{y_0}$

Shear rate $= \dot{\gamma} = \frac{1}{y_0} \cdot \frac{dx(t)}{dt}$

$$\frac{\text{Stress}}{\text{Shear rate}} = \text{Viscosity}$$

$$\frac{\text{Stress}}{\text{Strain}} = \text{Modulus}$$

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:

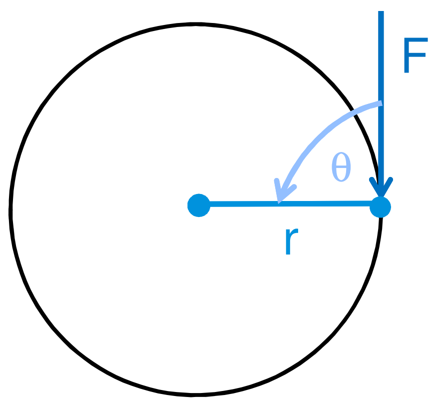
1. Torque (Force)
2. Angular Displacement
3. Angular Velocity

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 $\theta = 90^\circ$ as shown)



Calculated parameter: stress

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

$$\sigma = M \cdot K_\sigma$$

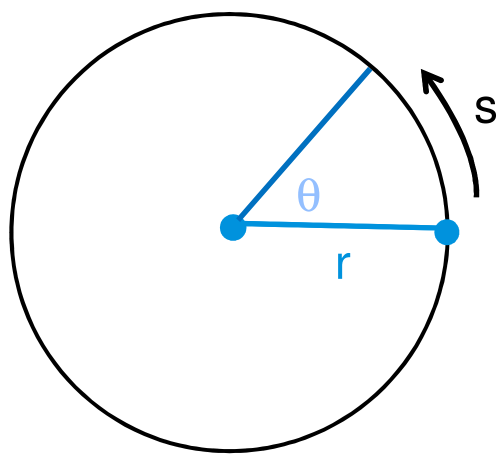
  - σ = shear stress (Pa or Dyne/cm^2)
  - M = torque (N·m or gm·cm)
  - K_σ = stress constant

- The stress constant, K_σ, 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·180/π

$$\theta = s/r$$



Calculated parameter: strain

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

$$\gamma = \theta \cdot K_\gamma$$

  - γ = shear strain (no units)
  - θ = angular displacement (radians)
  - K_γ = strain constant

- The strain constant, K_γ, is dependent on measurement geometry and/or initial sample dimensions
- Calculate percent strain (γ%) 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

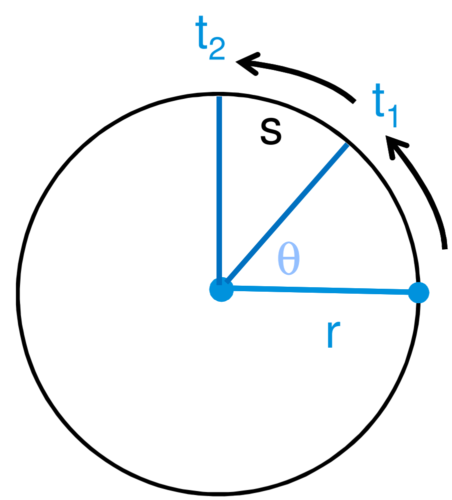
Geometry constants

Measured parameter: angular velocity

- Angular velocity (Ω) is the change in angular displacement (θ) per unit time of measurement

  - Note: linear velocity V = Δs/Δt

$$\Omega = \Delta\theta/\Delta t$$



  - Ω = angular velocity (radians/s)
  - θ = angular displacement (radians)
  - t = time (s)

Calculated parameter: shear rate

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

$$\dot{\gamma} = \Omega \cdot \mathrm{K}_{\gamma}$$

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

- The strain constant, K_{γ}, 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

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

DHR - DMA mode (optional)	
Motor Control	FRT
Minimum Force (N) Oscillation	0.1
Maximum Axial Force (N)	50
Minimum Displacement (µm) Oscillation	1.0
Maximum Displacement (µm) Oscillation	100
Displacement Resolution (nm)	10
Axial Frequency Range (Hz)	1×10^{-5} to 16

ARES-G2 Rheometer Specifications

Force/Torque Rebalance Transducer (Sample Stress)	
Transducer Type	Force/Torque Rebalance
Transducer Torque Motor	Brushless DC
Transducer Normal/Axial Motor	Brushless DC
Minimum Torque (µN.m) Oscillation	0.05
Minimum Torque (µN.m) Steady Shear	0.1
Maximum Torque (mN.m)	200
Torque Resolution (nN.m)	1
Transducer Normal/Axial Force Range (N)	0.001 to 20
Transducer Bearing	Groove Compensated Air

Driver Motor (Sample Deformation)	
Maximum Motor Torque (mN.m)	800
Motor Design	Brushless DC
Motor Bearing	Jeweled Air, Sapphire
Displacement Control/ Sensing	Optical Encoder
Strain Resolution (µrad)	0.04
Minimum Angular Displacement (µrad) Oscillation	1
Maximum Angular Displacement (µrad) Steady Shear	Unlimited
Angular Velocity Range (rad/s)	$1x\ 10^{-6}$ to 300
Angular Frequency Range (rad/s)	$1x\ 10^{-7}$ to 628
Step Change, Velocity (ms)	5
Step Change, Strain (ms)	10

Orthogonal Superposition (OSP) and DMA modes	
Motor Control	FRT
Minimum Transducer Force (N) Oscillation	0.001
Maximum Transducer Force (N)	20
Minimum Displacement (µm) Oscillation	0.5
Maximum Displacement (µm) Oscillation	50
Displacement Resolution (nm)	10
Axial Frequency Range (Hz)	$1\ x\ 10^{-5}$ to 16

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

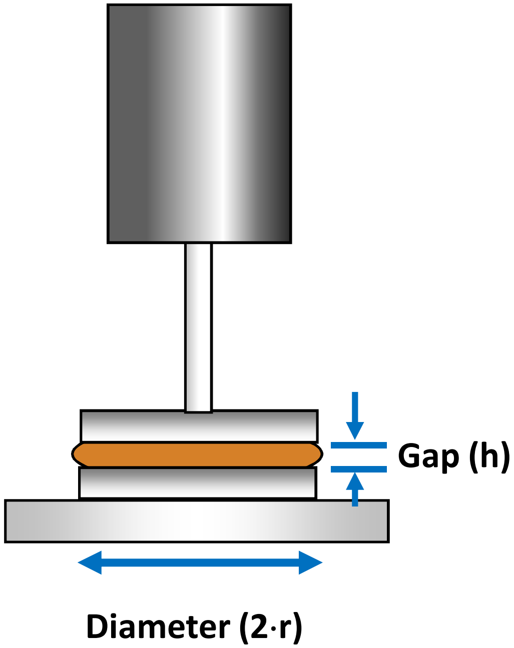
- Geometry - material of construction, size and surface
- In general, lower viscosity use larger diameter or larger contact area and higher viscosity or more solid-like smaller diameter
- Consider:
  - Volume requirements
  - Particle size, settling or mixing necessary
  - Loading procedure for structured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

Cones and Plates

Smooth, Sandblasted, and Cross hatched

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

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·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

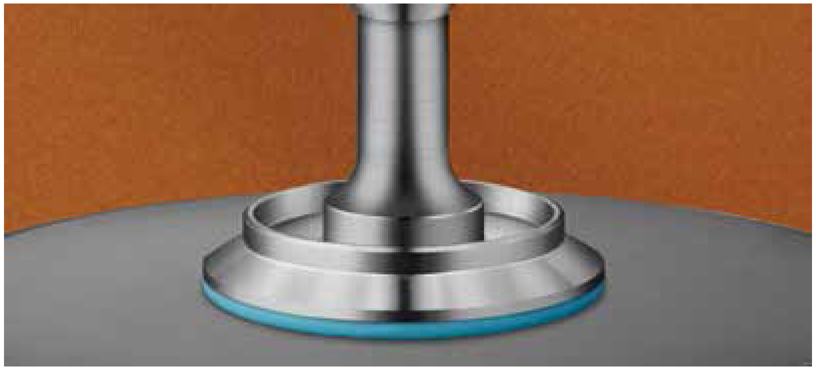
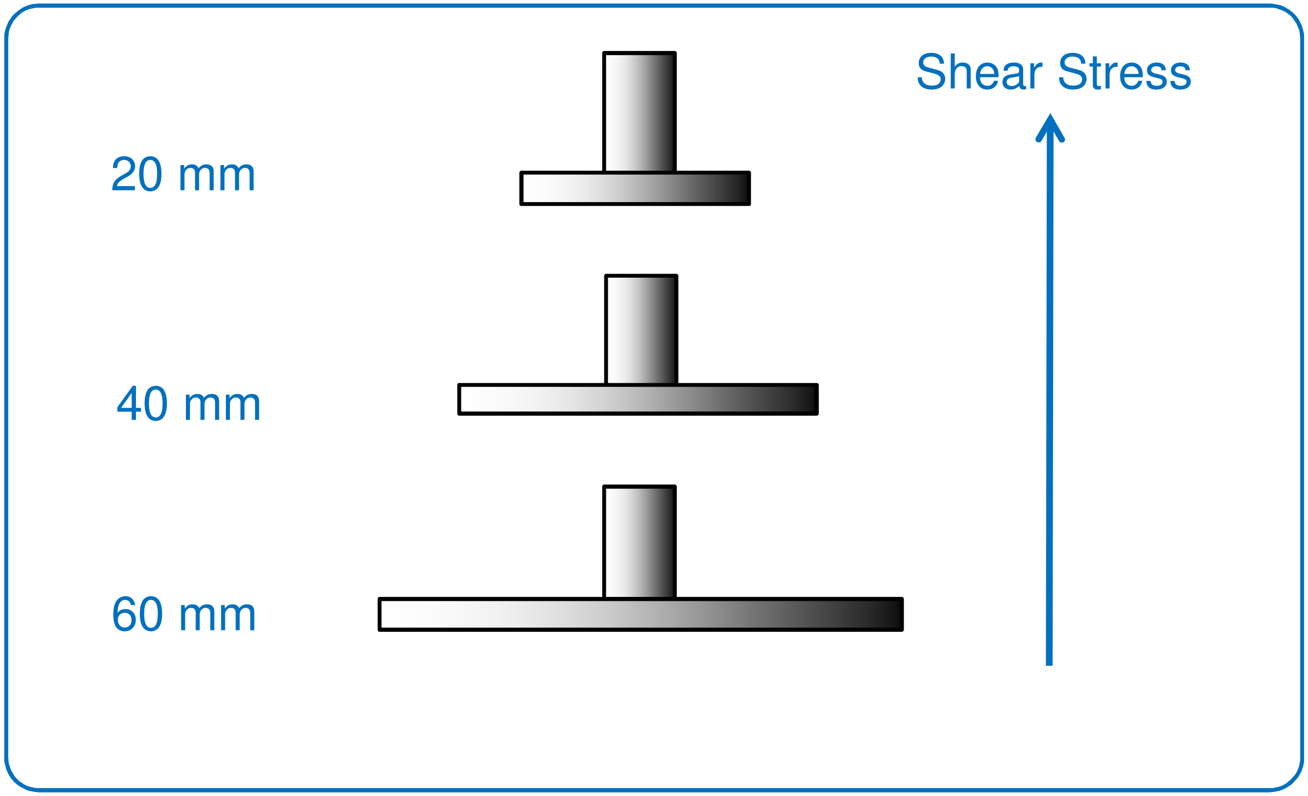


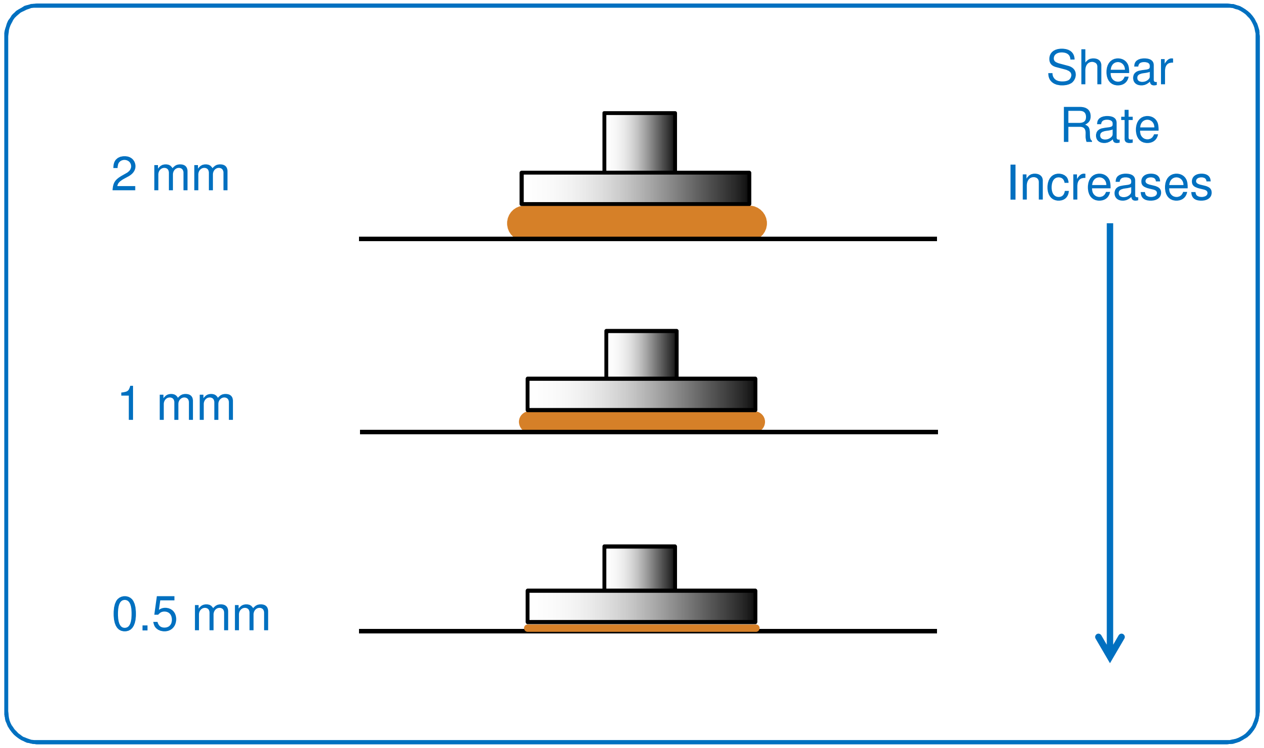
Plate Diameters



As diameter decreases, shear stress increases

$$\sigma = M\frac{2}{\pi r^3}$$

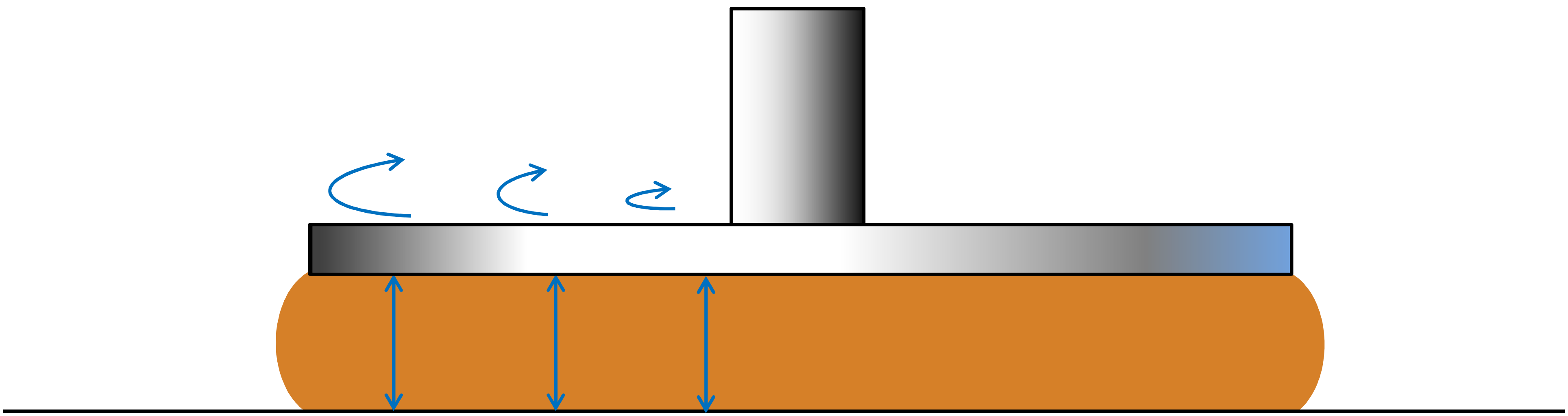
Plate Gaps



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



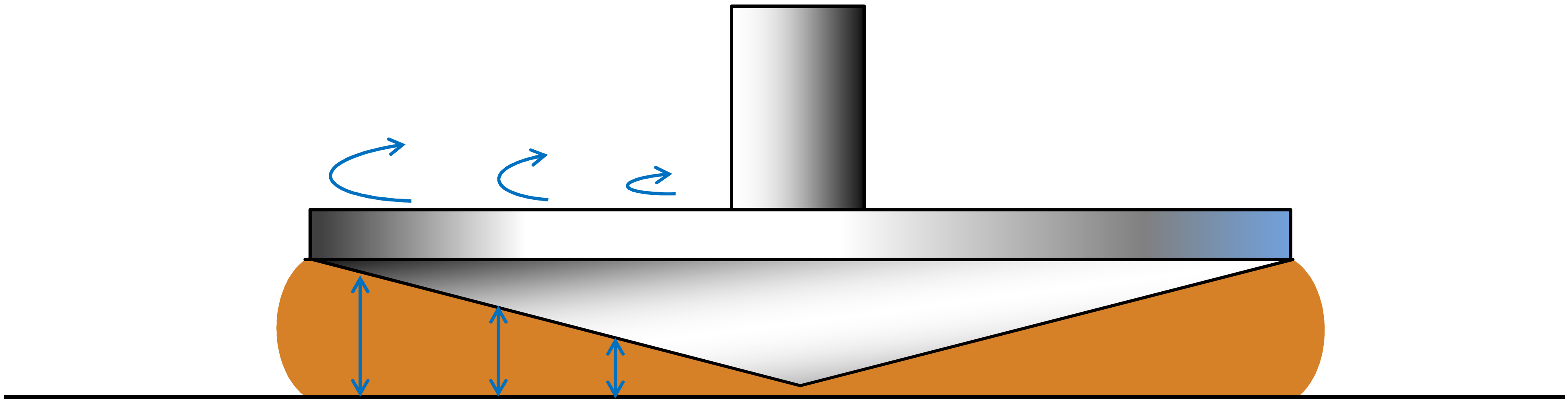
$$\gamma = \frac{dx}{h}$$

dx increases further from the center,
h stays constant

Single-point correction for the parallel plate geometry (0.76 radius)
[M.S. Carvalho, M. Padmanabhan and C.W. Macosko, *J. Rheol.* 38 (1994) 1925-1936]

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

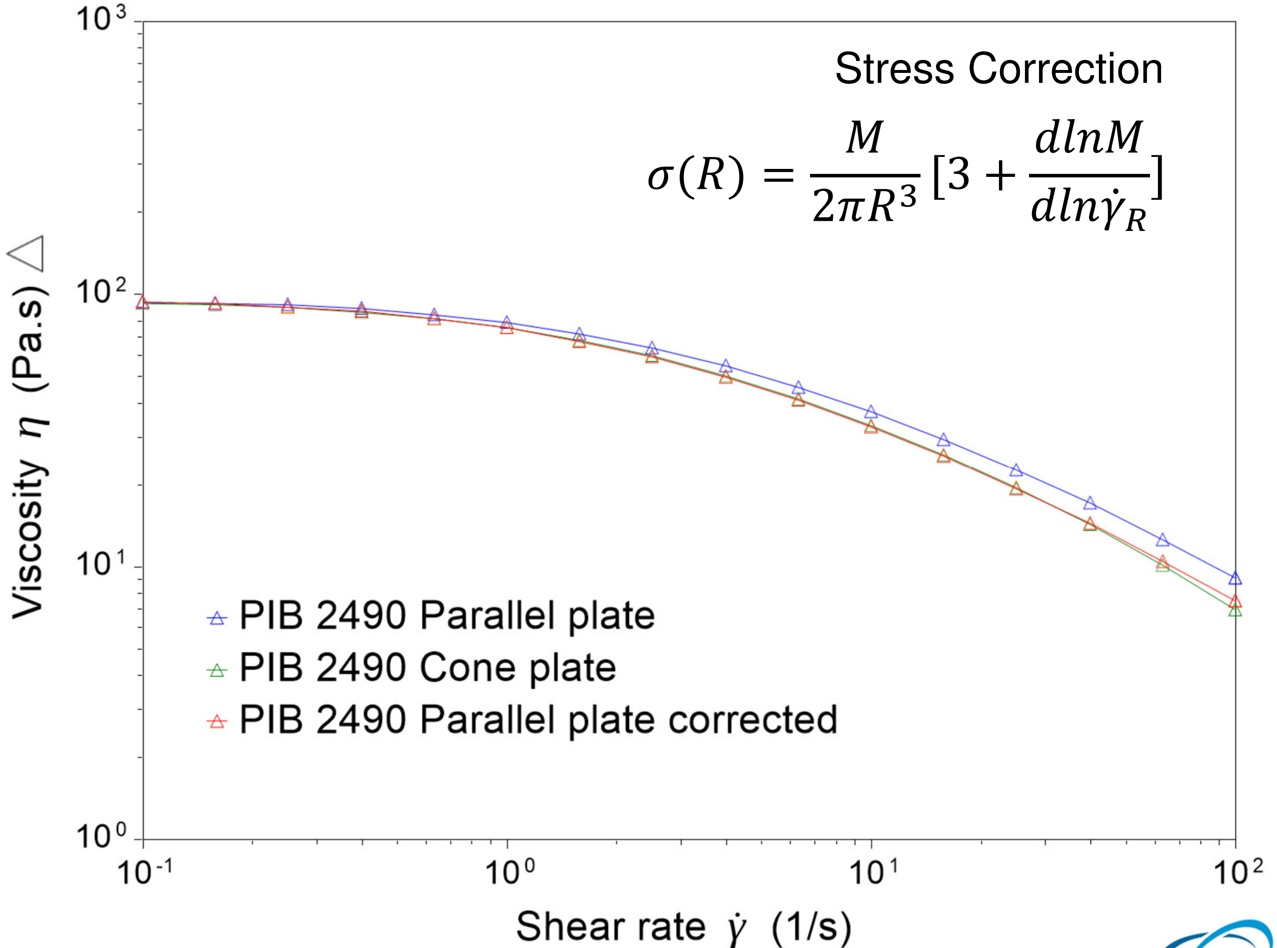


$$\gamma = \frac{dx}{h}$$

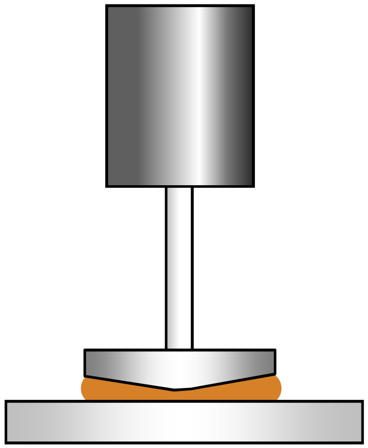
h increases proportionally to *dx*, γ is uniform

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.



Cone and Plate

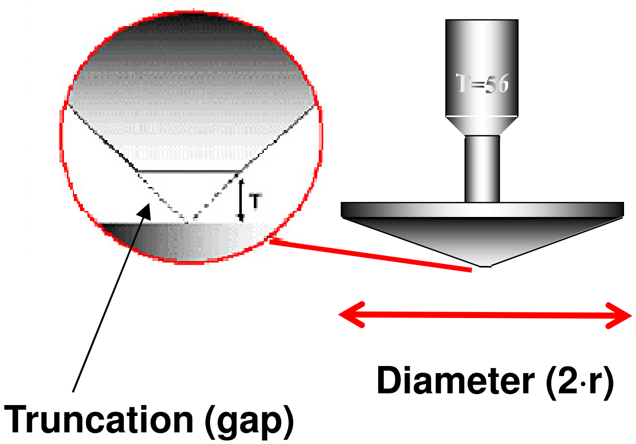


Strain Constant: $K_\gamma = \frac{1}{\beta}$

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

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

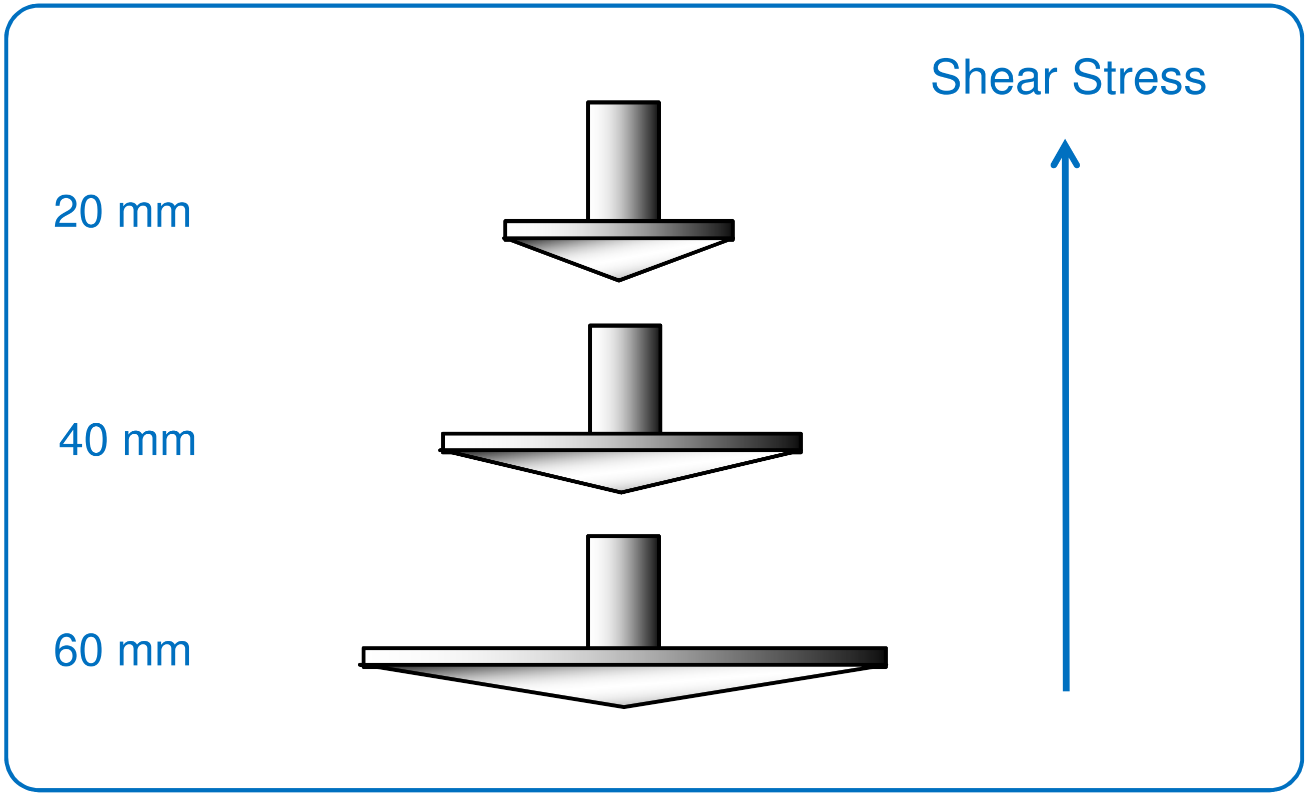
(to convert torque, N·m, to shear stress, Pa. The radius, r, is expressed in meters)



When to use Cone and Plate

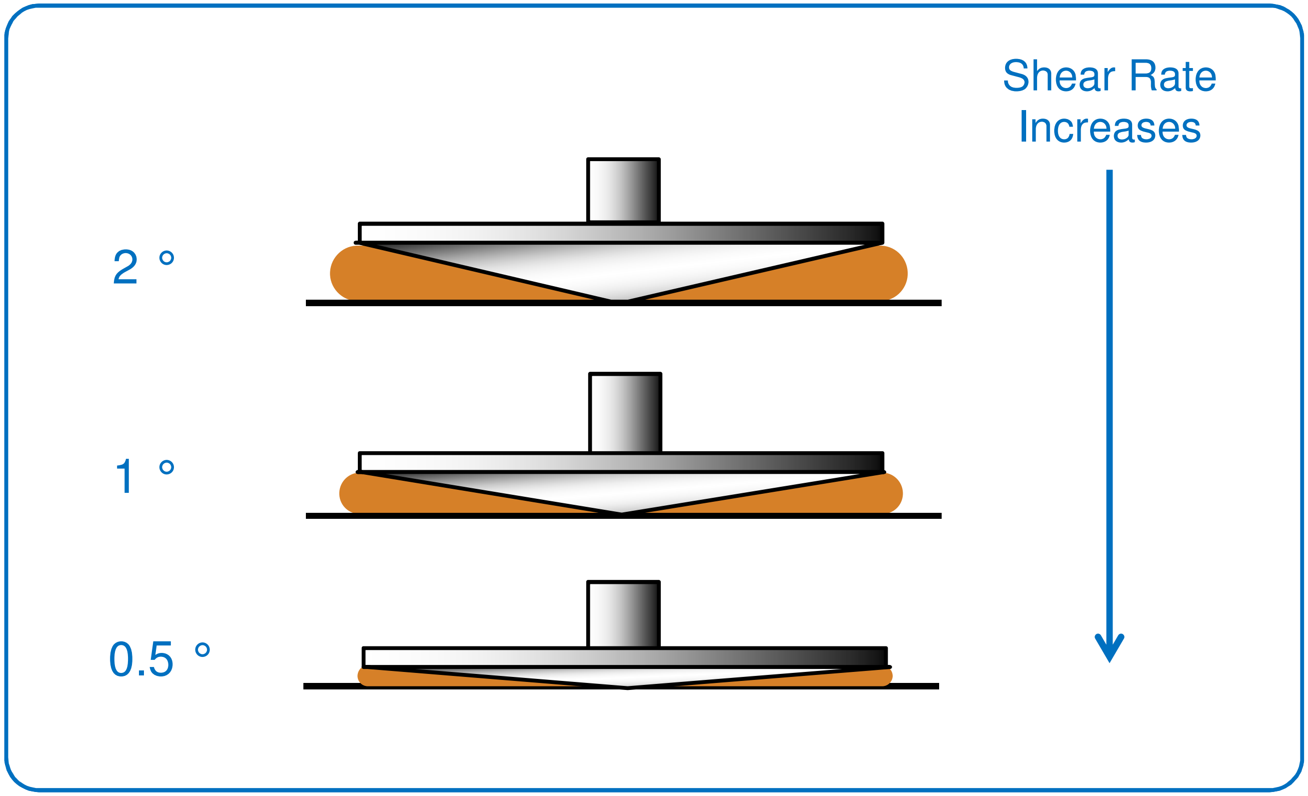
- Very Low to High Viscosity Liquids
- High Shear Rate measurements
- Normal Stress Growth
- Unfilled Samples
- Isothermal Tests
- Small Sample Volume

Cone Diameters



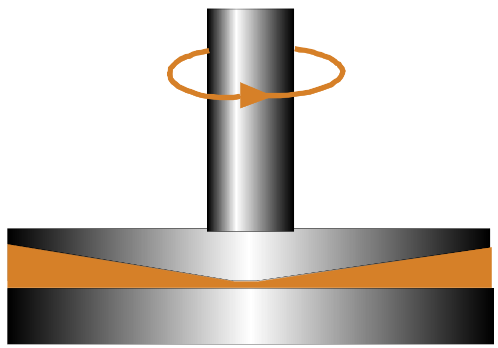
As diameter decreases, shear stress increases $\sigma = M \frac{3}{2\pi r^3}$

Cone Angles



As cone angle decreases, shear rate increases $\dot{\gamma} = \Omega \frac{1}{\beta}$

Limitations of Cone and Plate



Cone & Plate

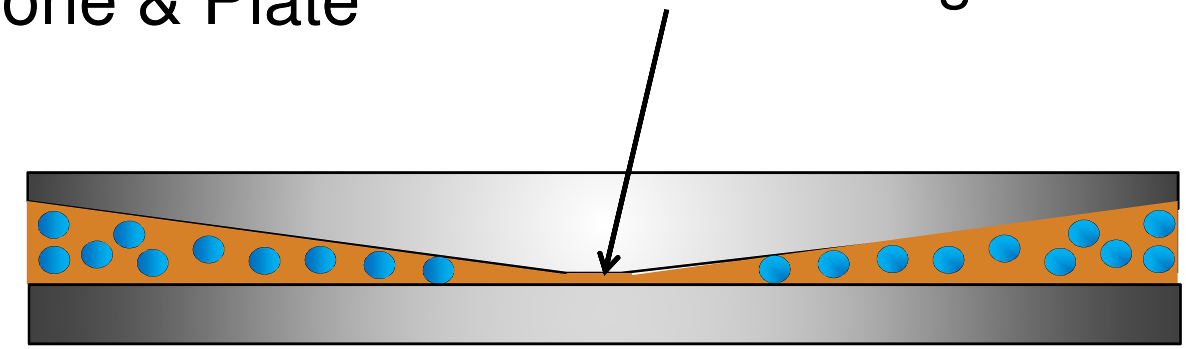
Typical Truncation Heights:

1° degree ~ 20 - 30 microns

2° degrees ~ 60 microns

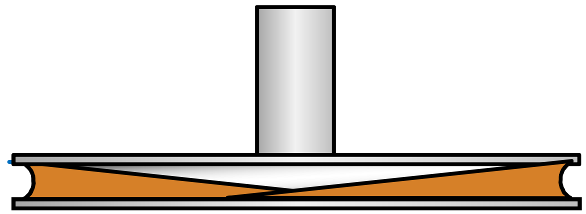
4° degrees ~ 120 microns

Truncation Height = Gap

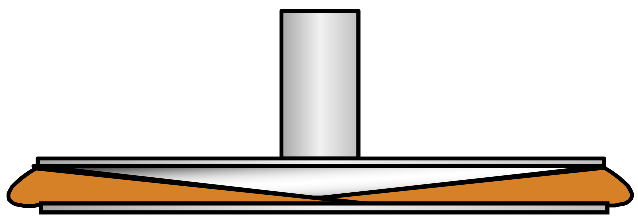


Gap must be > or = 10 [particle size]!!

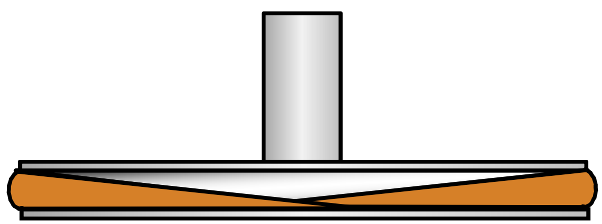
Correct Sample Loading – parallel plate and cone-plate



× <u>Under</u> Filled sample:
Lower torque contribution

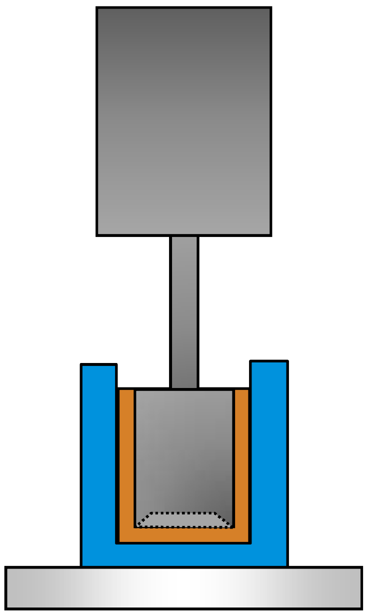


× <u>Over</u> Filled sample:
Additional stress from drag along the edges



✓ **Correct Filling**

Concentric Cylinder



Strain Constant:

$$K_\gamma = \frac{1 + \left(\frac{r_2}{r_1}\right)^2}{\left(\frac{r_2}{r_1}\right)^2 - 1}$$

(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)

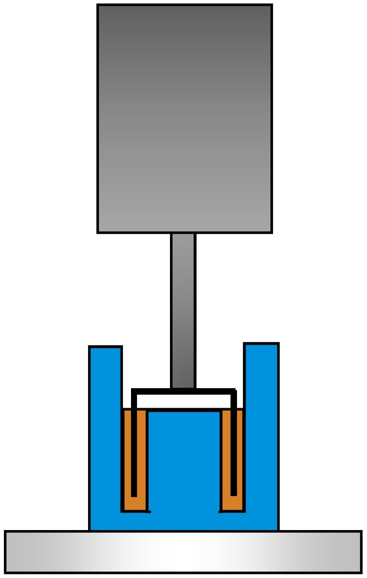
Stress Constant:

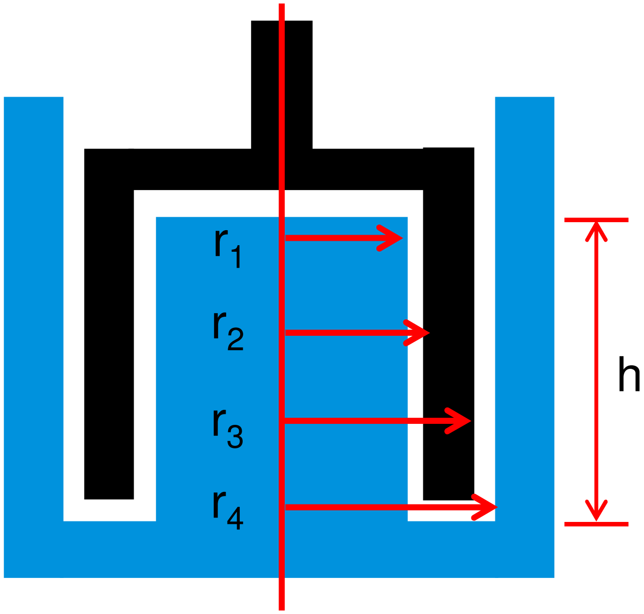
$$K_\sigma = \frac{1}{4\pi l}\left[\frac{1 + \left(\frac{r_2}{r_1}\right)^2}{c_l {r_2}^2}\right]^*$$

(to convert torque, N·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: $$K_\sigma = \frac{(r_1^2 + r_2^2)}{4\pi h \cdot r_2^2 (r_1^2 + r_3^2)}$$

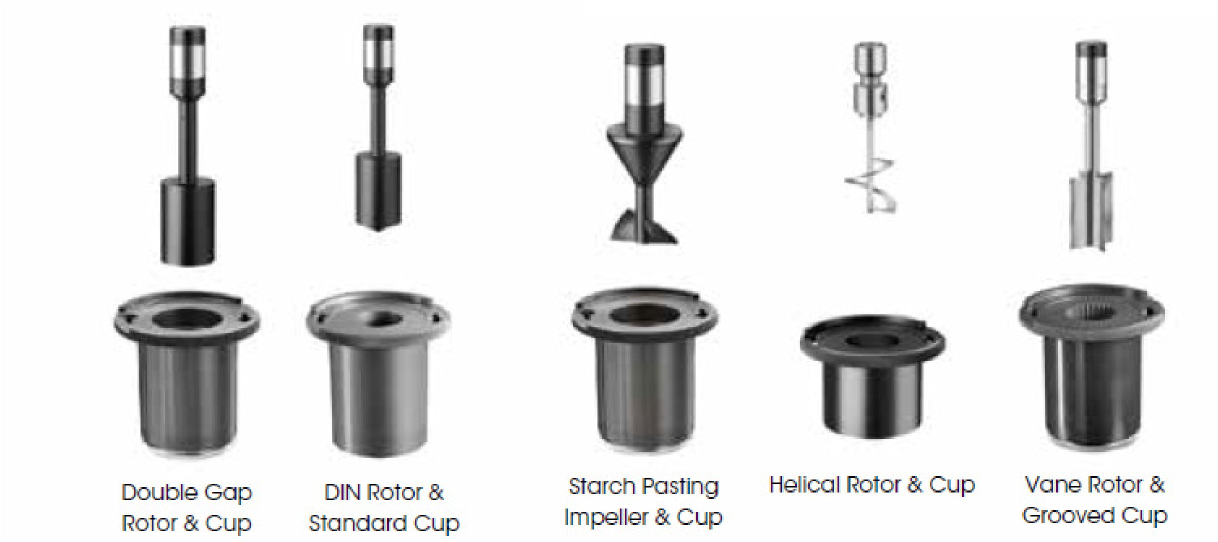
When to Use Concentric Cylinders

Peltier Concentric Cylinder

Electrically Heated Cylinder (EHC)

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

Peltier Concentric Cylinders

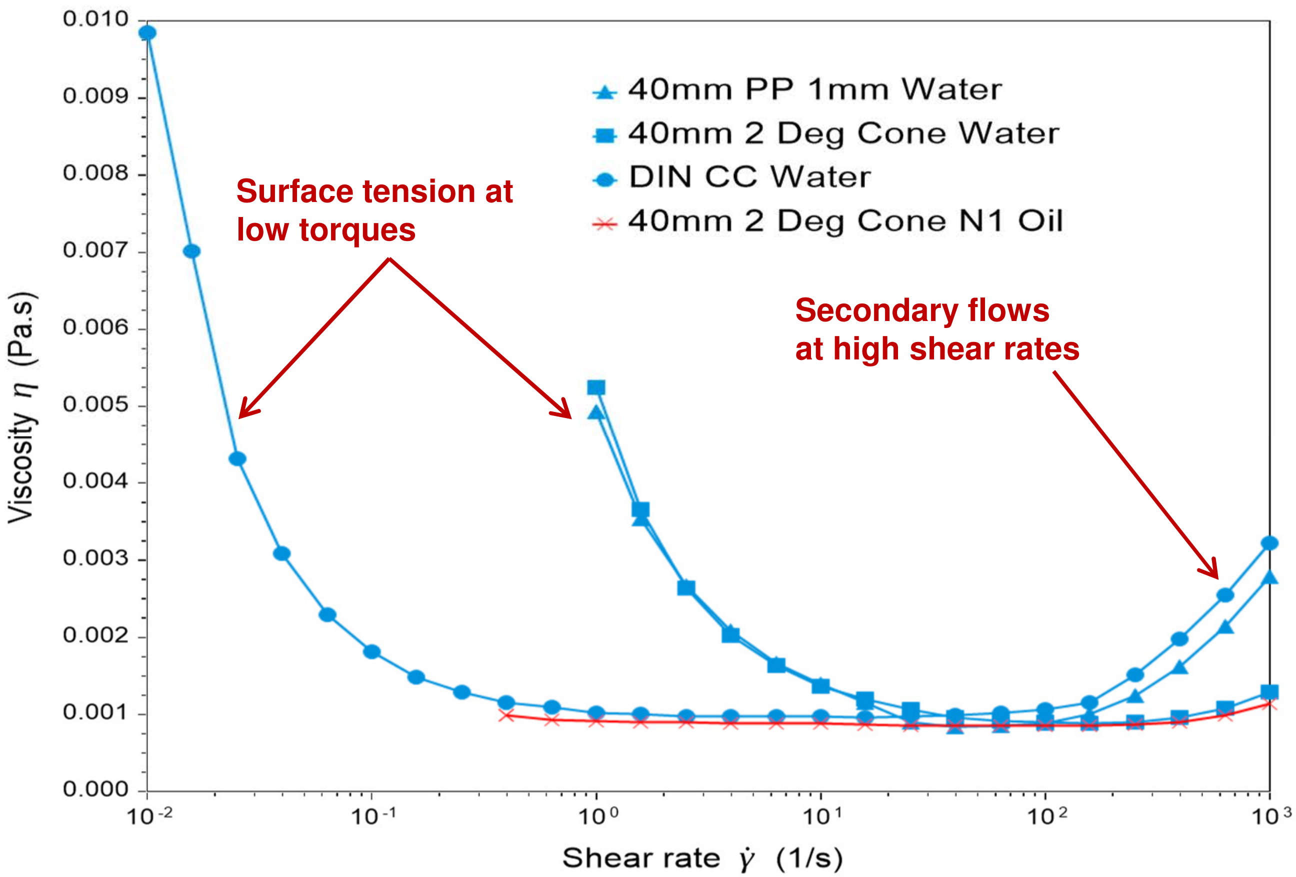


Concentric Cylinder Cup and Rotor Compatibility Chart

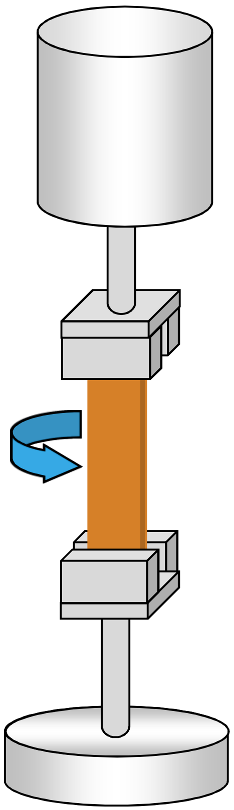
Cup/Rotor	DIN	Recessed End	Starch Impeller	Vane	Wide Gap Vane	Double Gap	Helical Rotor
Standard (rad= 15 mm)	●	●		●	●		
Large Diameter (rad= 22 mm)	●	●	●	●	●		●
Starch (rad= 18.5 mm)	●	●	●	●	●		●
Grooved				●	●		
Double Gap						●	
Helical (rad= 17 mm)							●

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



Torsion Rectangular



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

$$K_\tau = \frac{\left(3 + \frac{1.8}{w}\right)}{(w \cdot t^2)}$$

w = Width

l = Length

t = Thickness

Advantages:

- High modulus samples
- Small temperature gradient
- Simple to prepare

Disadvantages:

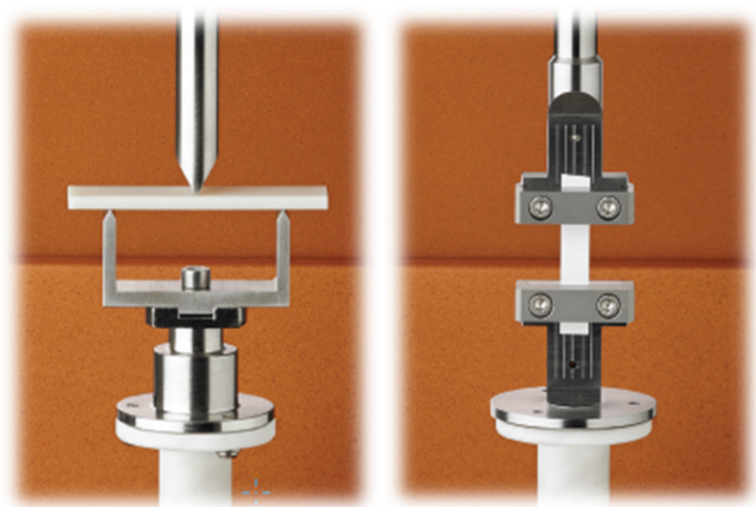
- No pure Torsion mode for high strains

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 δ
  - DMA measures E', E", and Tan δ
    - 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

Geometry	Application	Advantage	Disadvantage
Cone/plate	fluids, melts viscosity > 10mPas	true viscosities	temperature ramp difficult
Parallel Plate	fluids, melts viscosity > 10mPas	easy handling, temperature ramp	shear gradient across sample
Couette	low viscosity samples < 10 mPas	high shear rate	large sample volume
Double Wall Couette	very low viscosity samples < 1mPas	high shear rate	cleaning difficult
Torsion Rectangular	solid polymers, composites	glassy to rubbery state	Limited by sample stiffness
DMA	Solid polymers, films, Composites	Glassy to rubbery state	Limited by sample stiffness (Oscillation and stress/strain)

Setting up Rheological Experiments

Flow Tests

Newtonian & Non-Newtonian Behavior

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

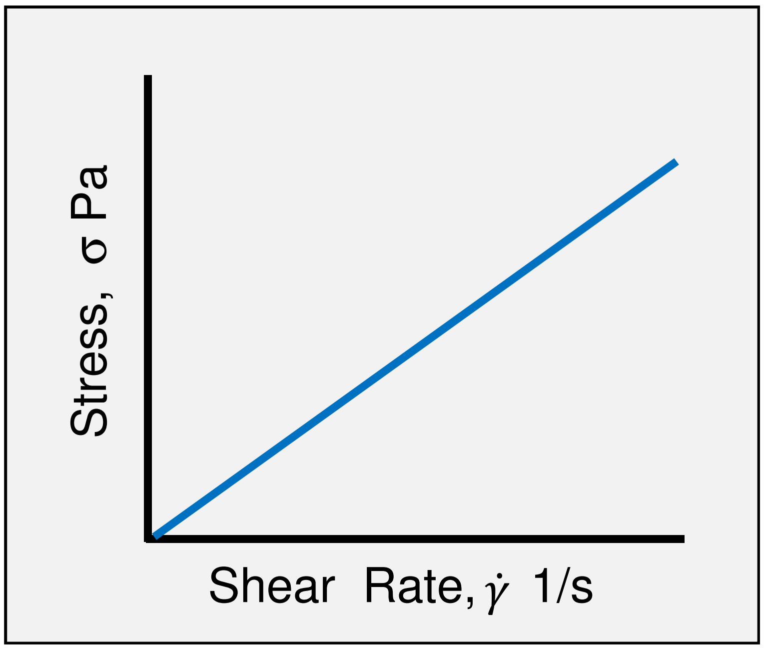
- **Non- Newtonian**
  - **Viscosity is shear dependent**
    - ✓ Decrease with shear – shear thinning
    - ✓ Increase with shear – shear thickening
  - **Viscosity is time dependent**
    - ✓ Decrease with time – Thixotropic
    - ✓ Increase with time – Rheopectic

Viscosity Values

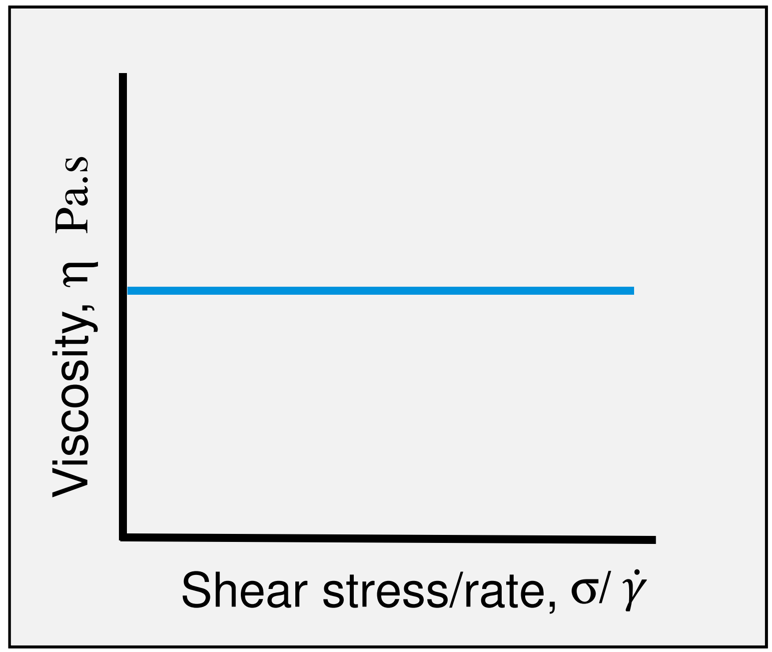
Materials	Viscosity η (Pa.s)
Air /Gas	0.00001
Water	0.001
Milk/ Coffee	0.01
Olive oil	0.1
Glycerol	1
Liquid Honey	10
Molasses	100
Polymer Melt	1000
Asphalt Binder	100,000

Newtonian Fluids

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



$$Viscosity = \frac{\sigma}{\dot{\gamma}}$$

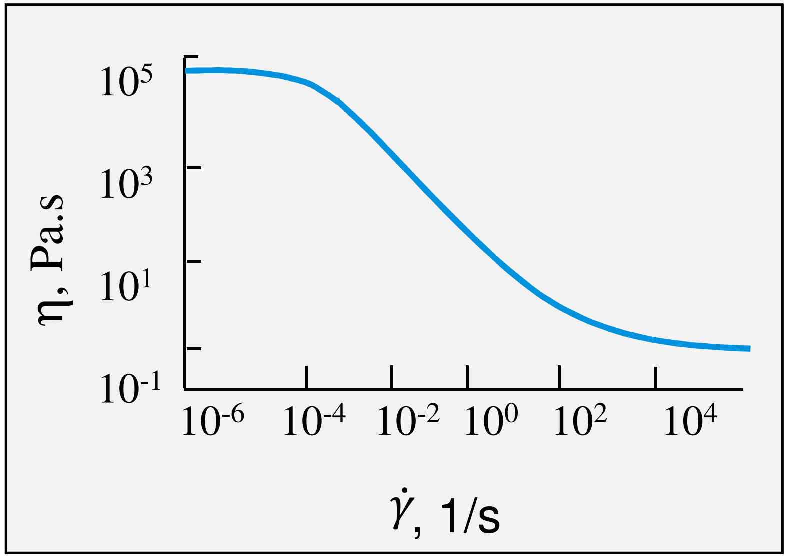


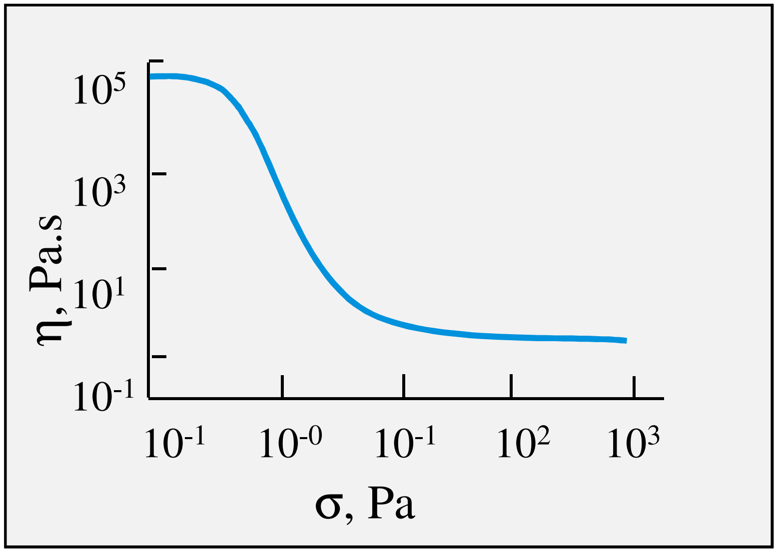
Viscosity constant

Shear Thinning Fluids

- Viscosity decrease with shear rate and shear stress
- Examples:

    hand wash, paint, coating, shampoo….

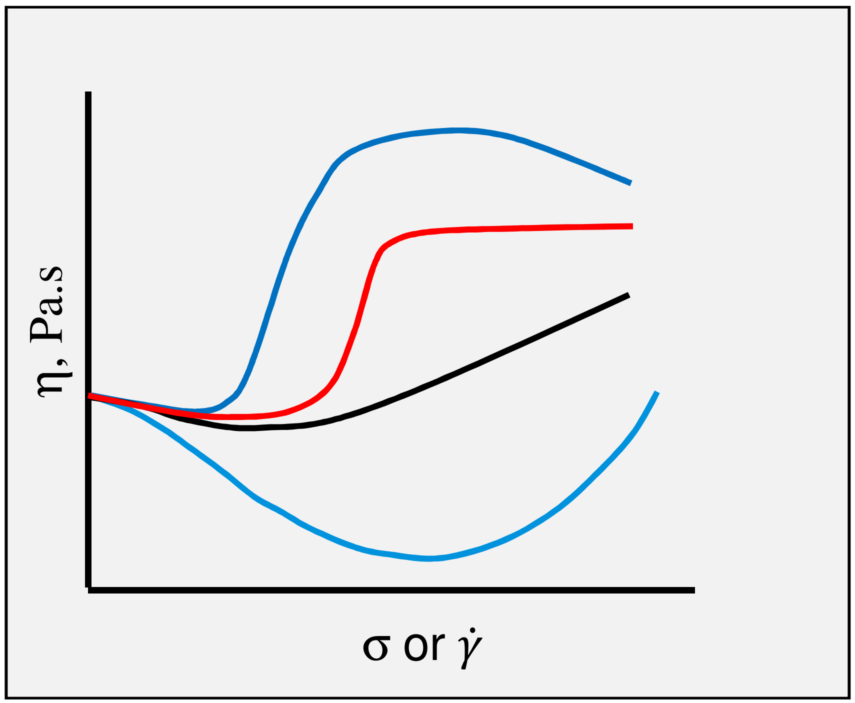




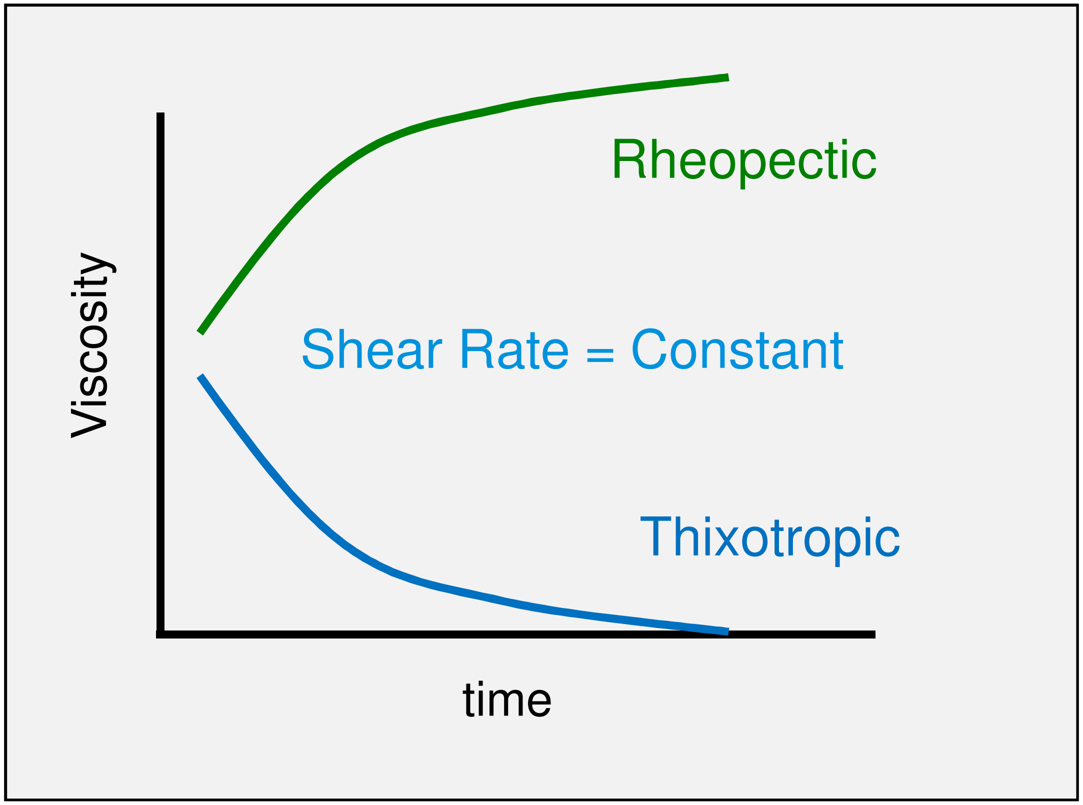
Shear Thickening Fluids

- Viscosity increase with shear rate and shear stress
- Examples:

  highly concentrated cornstarch slurry; mud slurry



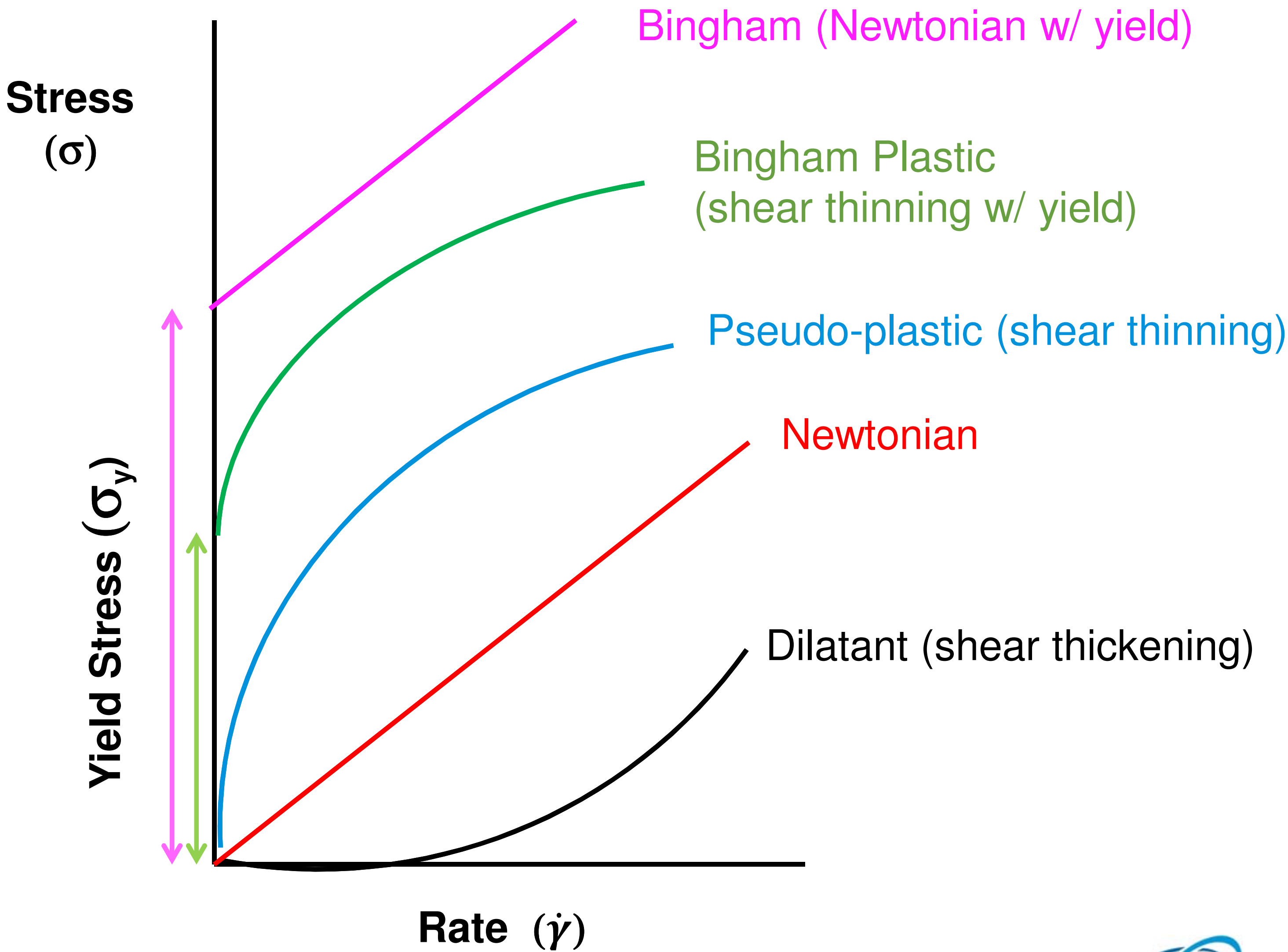
Time Dependent Fluids



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

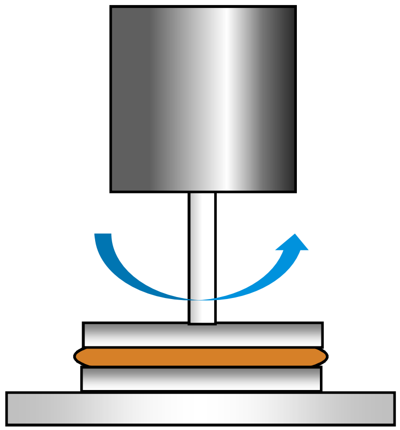
A thixotropic material becomes more fluid with increasing time of applied force

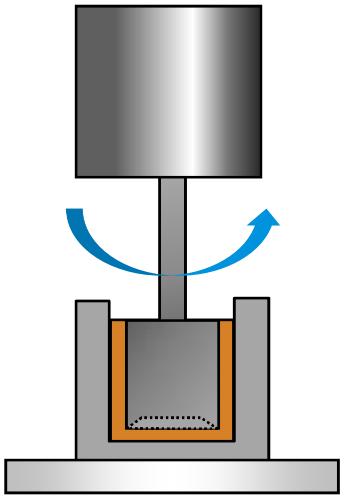
Summary of Flow Diagrams



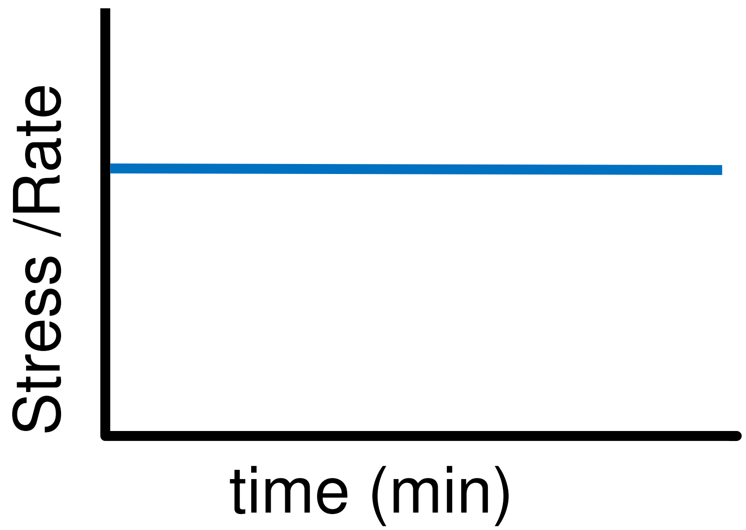
Rheological Methods

- Common rheological methods for measuring viscosity of liquids
  - Single rate/stress flow
  - Continuous rate/stress ramp
  - Stepped or steady state flow
  - Flow temperature ramp





Single Rate/Stress Test

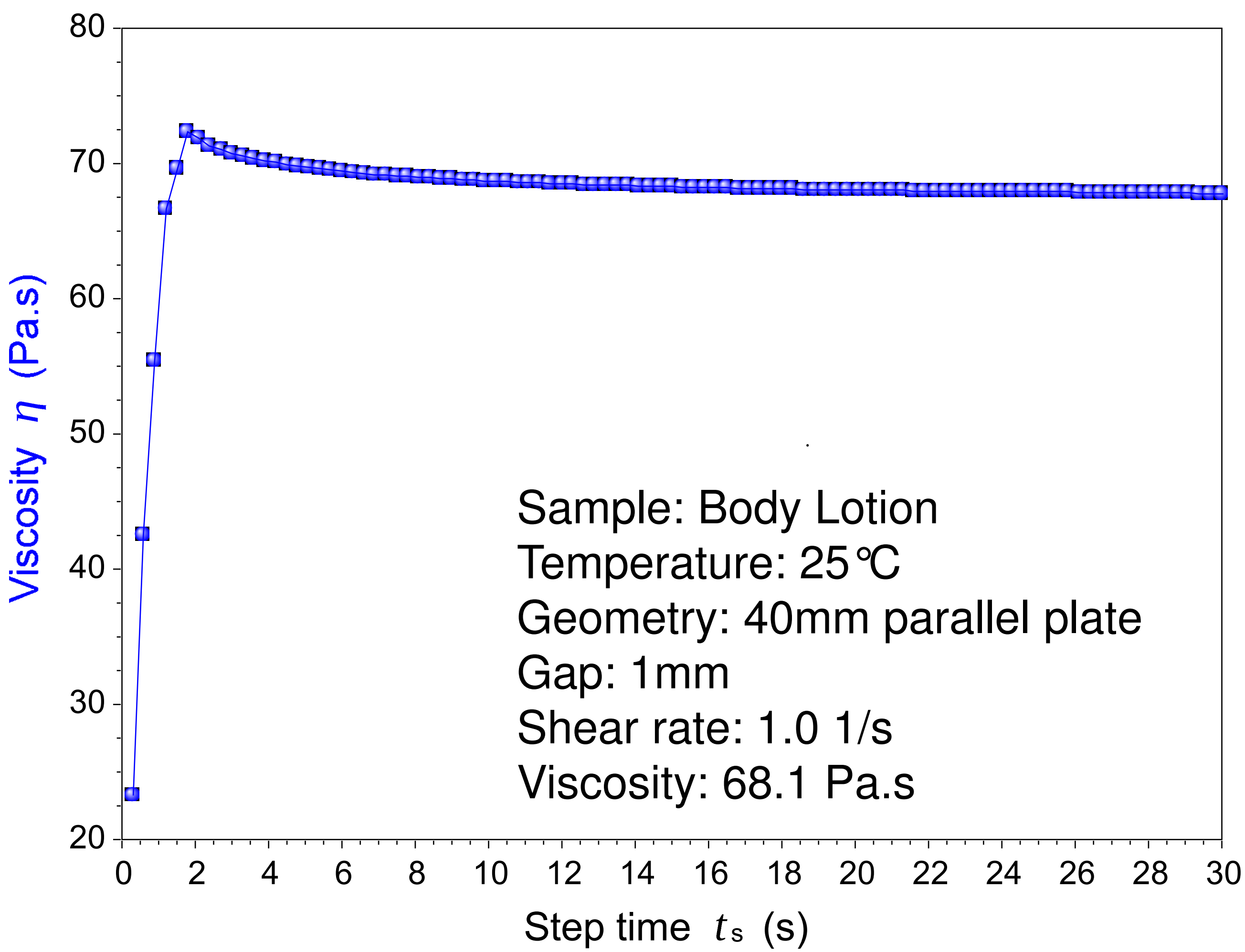


- Isothermal temperature
- Constant rate vs. time
- Constant stress vs. time

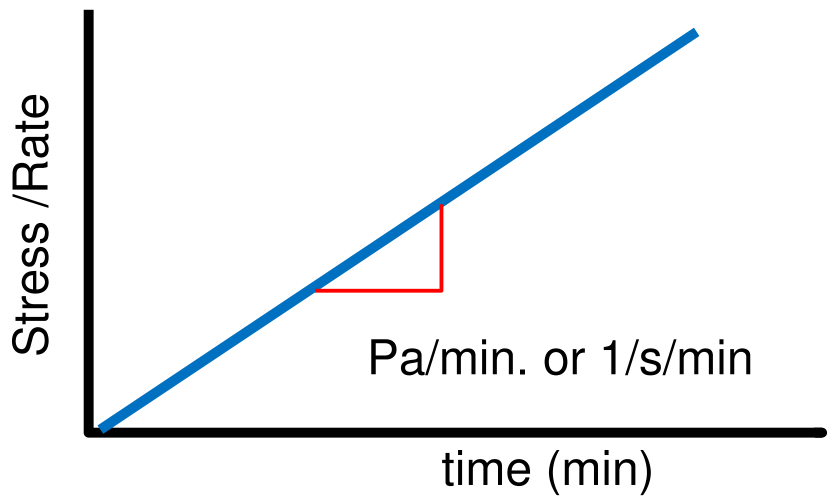
USES

- Single point testing
- Scope the time for steady state under certain rate

Body Lotion: Single Rate Test



Continuous Ramp



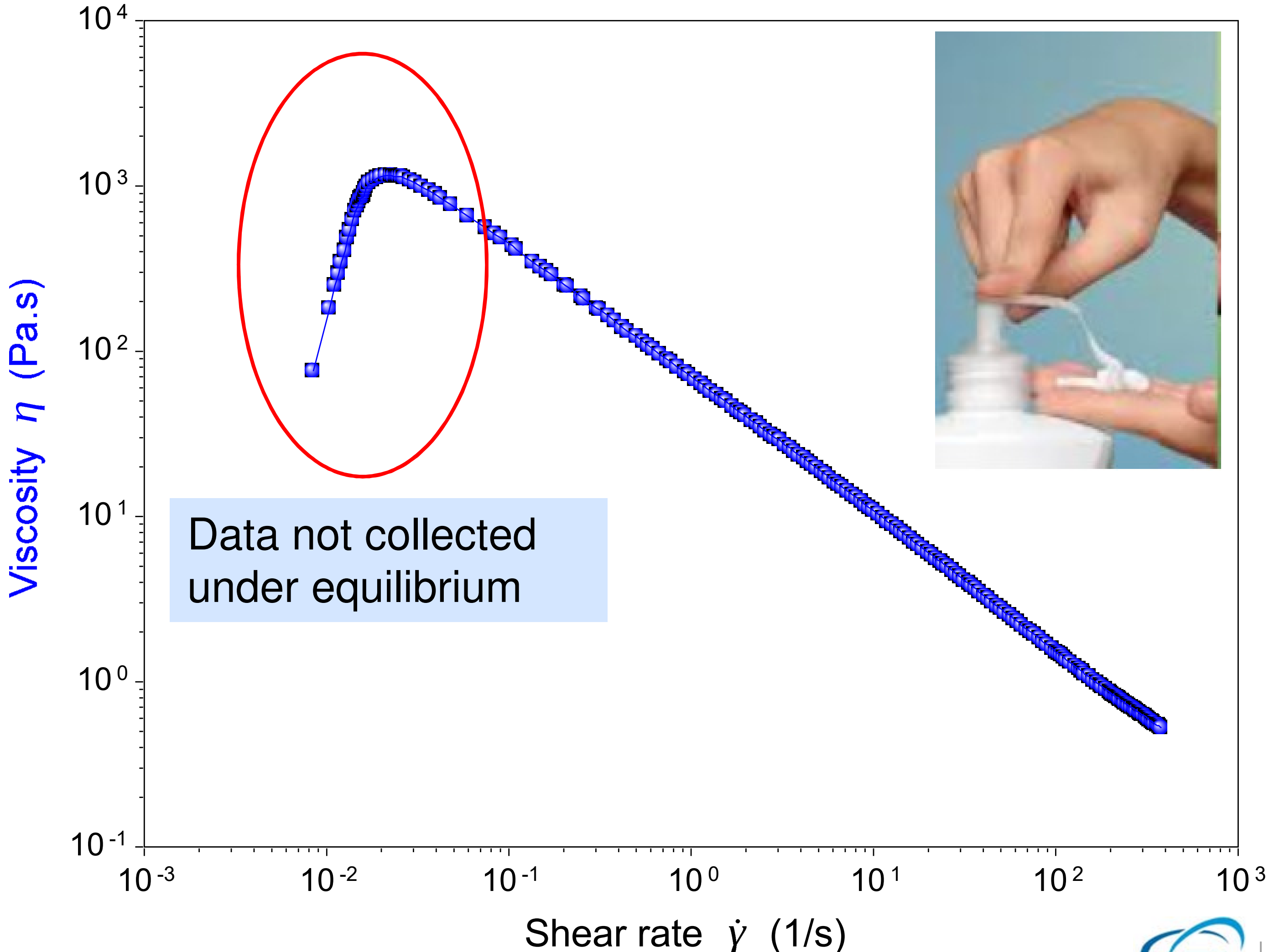
- Isothermal temperature
- Ramp stress or shear rate at a constant speed

USES

- Scouting viscosity over wide range of shear
- Measure yield stress

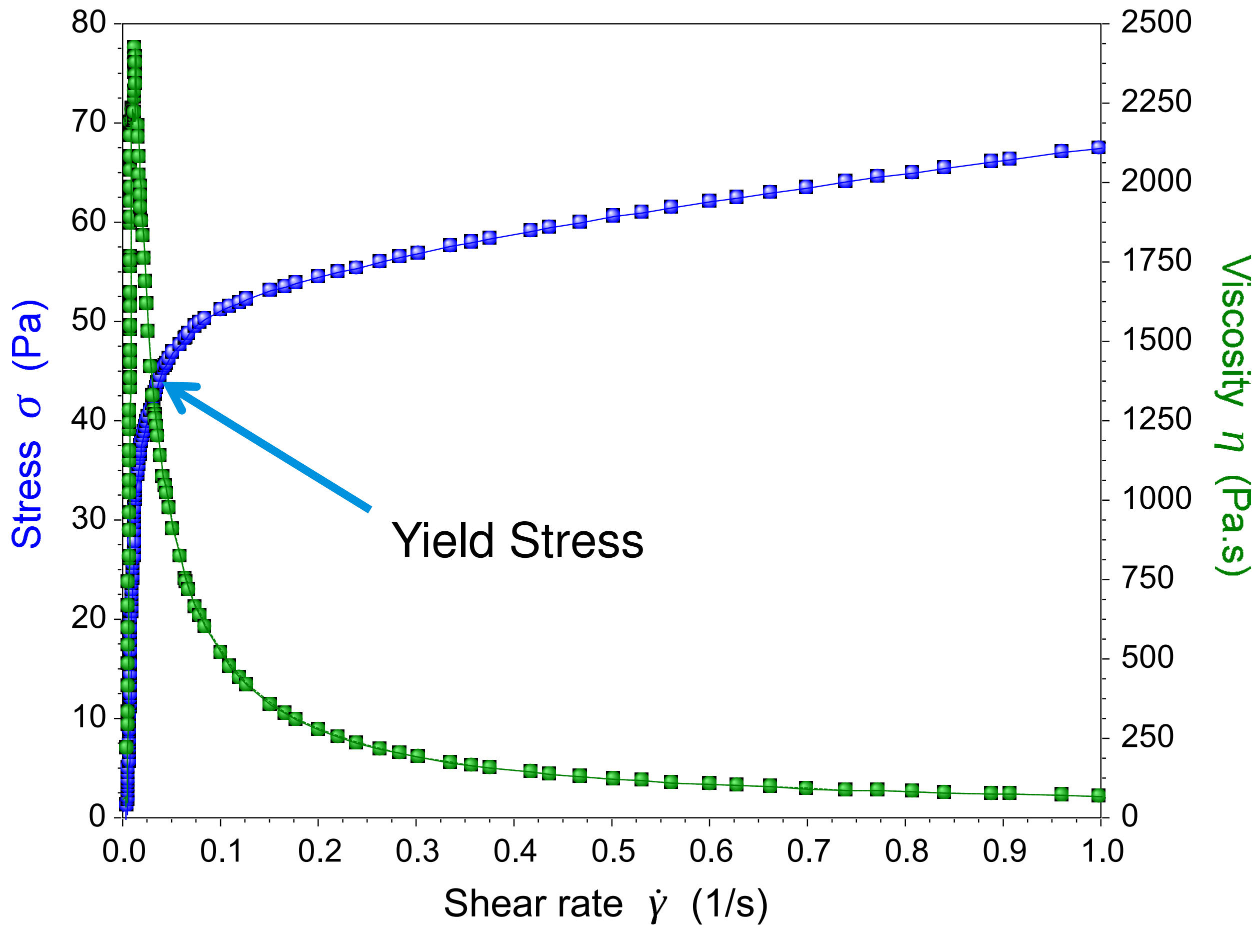
Viscosity of a Body Lotion

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

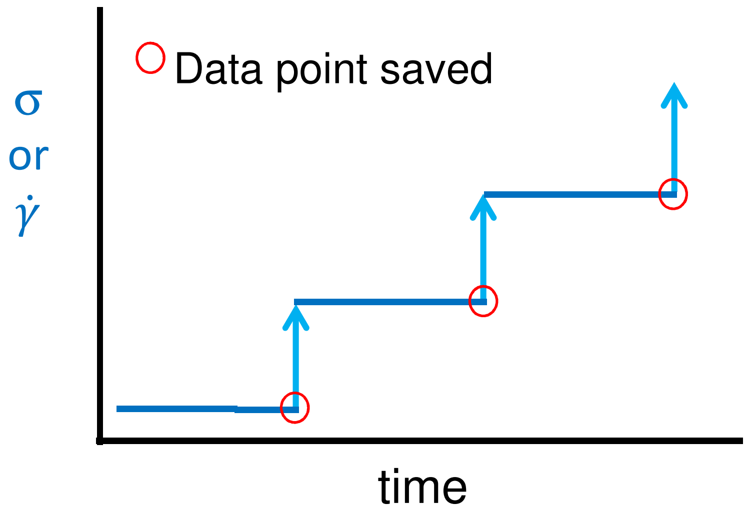


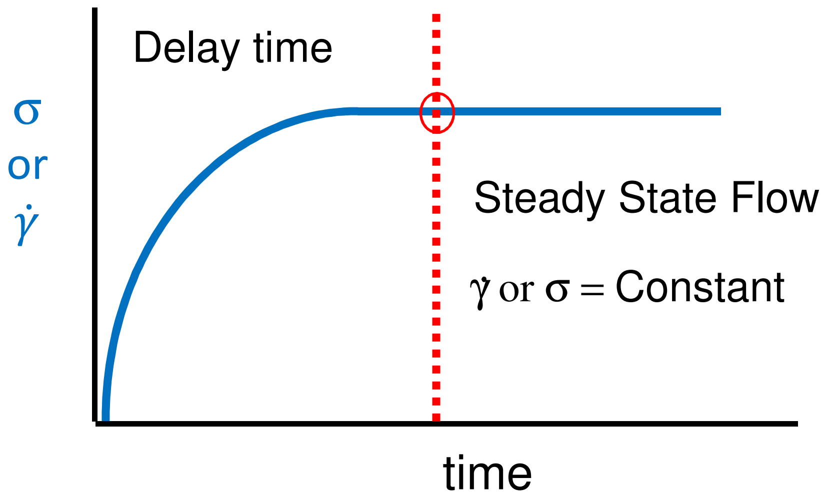
Measure Yield Stress of a Body Lotion

- Body lotion does not flow unless the applied stress exceeds a certain value – the yield point.



Stepped or Steady-State Flow





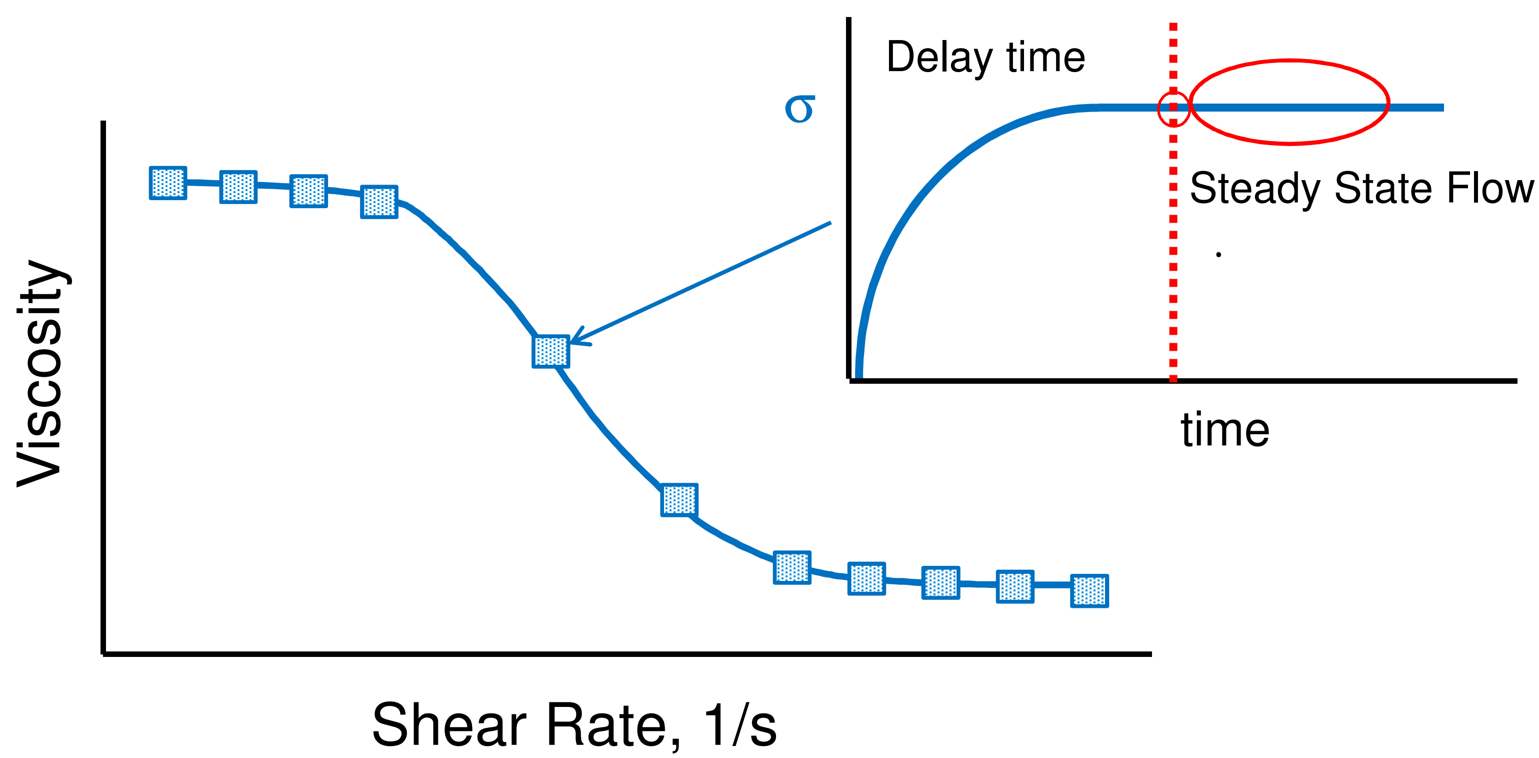
- Step stress or shear rate from low to high on a logarithmic scale
- At each step, viscosity is measured when steady state has been reached

<u>USES</u>

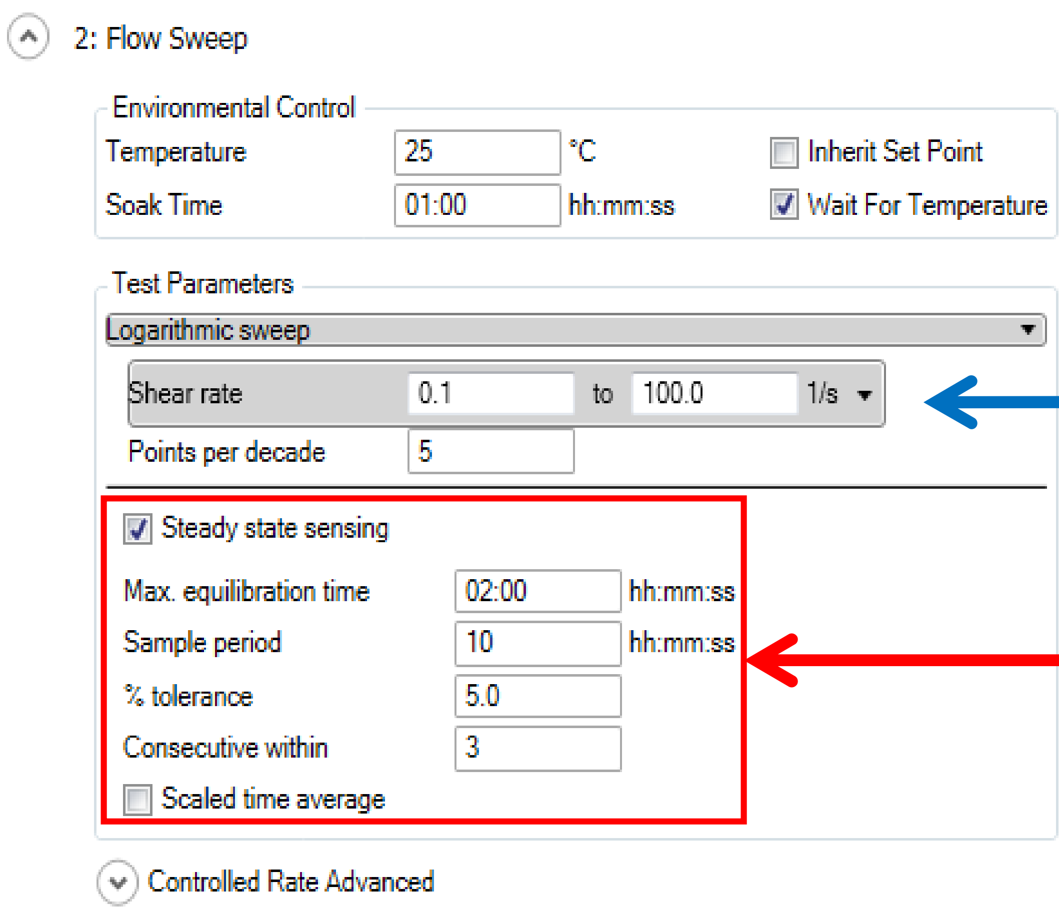
- Viscosity Flow Curves
- Yield Stress Measurements

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

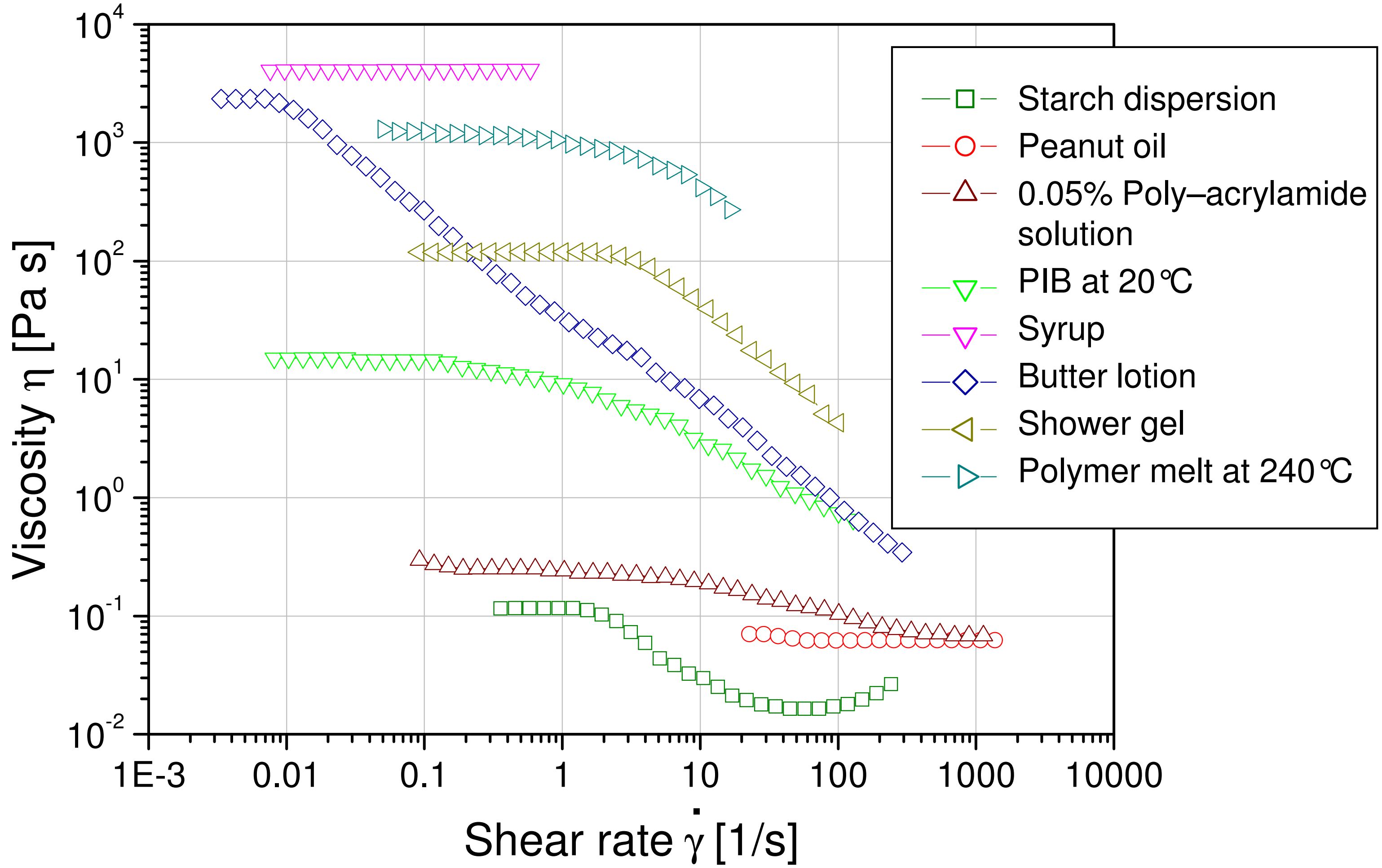


Control variables:

- Shear rate
- Velocity
- Torque
- Shear stress

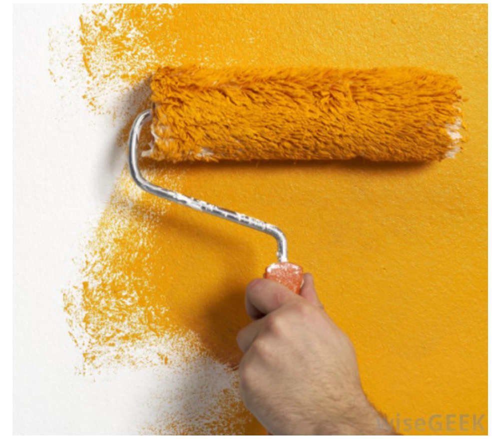
Steady state algorithm

Viscosity Curves of Various Fluids

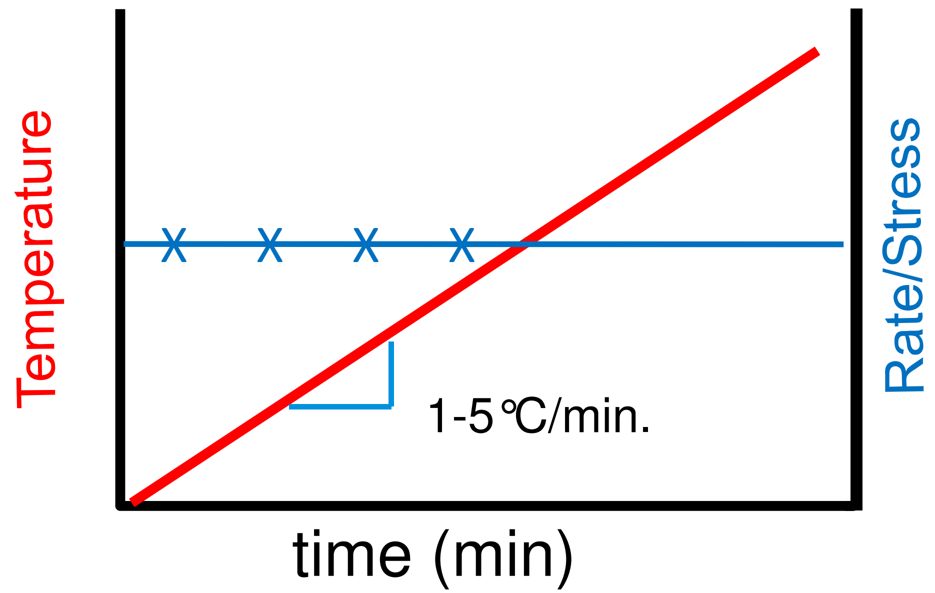


Typical Applications Shear Rates

Process	Shear Rate (1/s)
sedimentation	$10^{-5} – 10^{-2}$
leveling and sagging	$10^{-2} – 1$
chewing, swallowing, dipping coating,	$1 – 10^{2}$
pipe flow, pumping, mixing, stirring	$1 – 10^{3}$
brushing, painting, extruding	$10^{2} – 10^{4}$
milling, spraying, rubbing	$10^{3} – 10^{5}$
high speed coating	$>10^{5}$



Flow Temperature Ramp

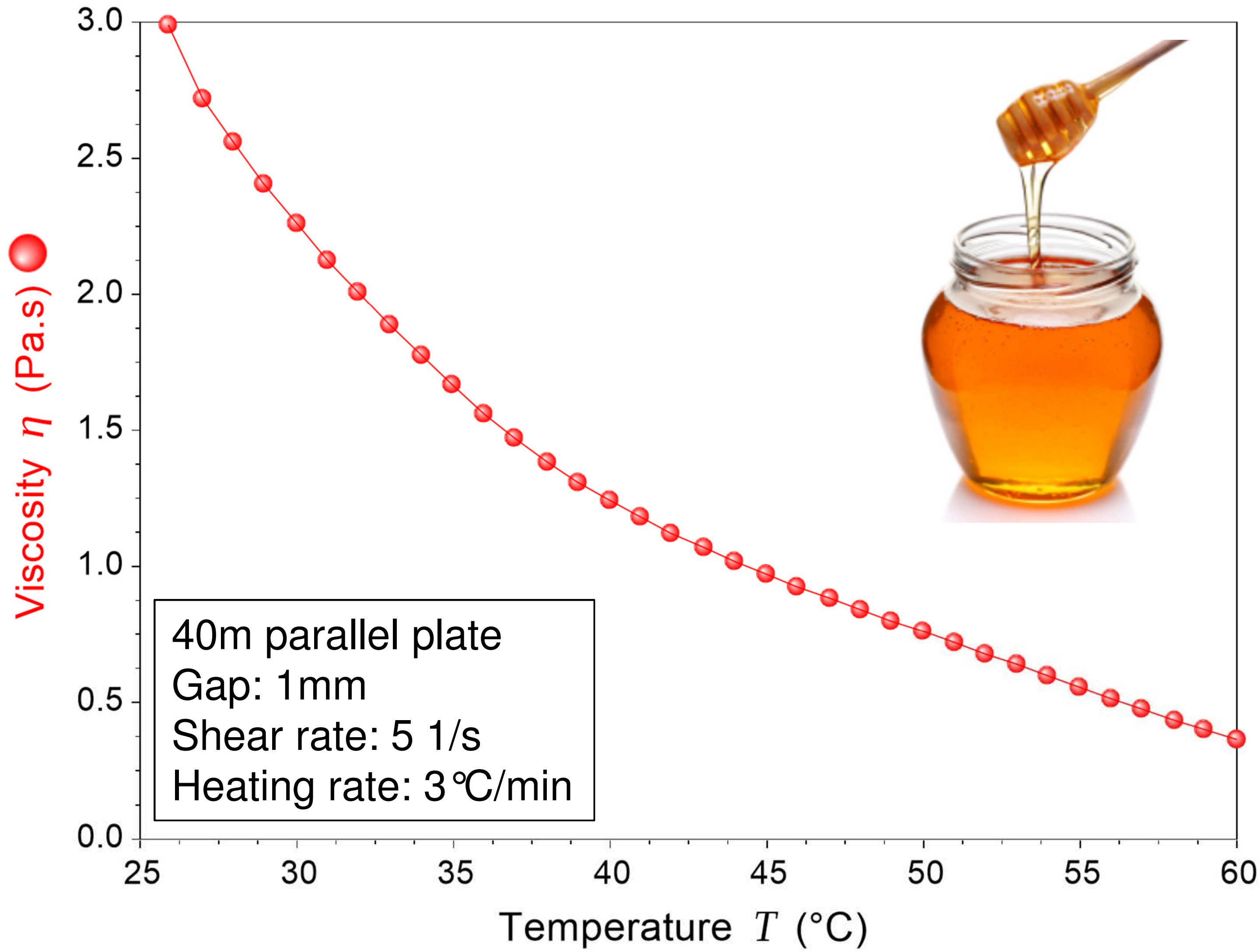


- Constant shear stress or shear rate
- Ramp temperature

USES

- Measure the viscosity change vs. temperature

Viscosity of Honey: Temperature Dependence



Setting up Rheological Experiments

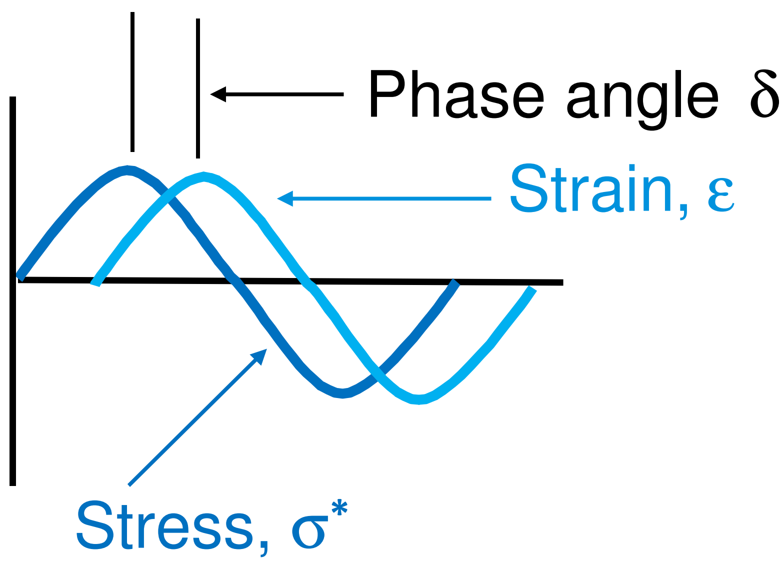
Oscillatory Tests

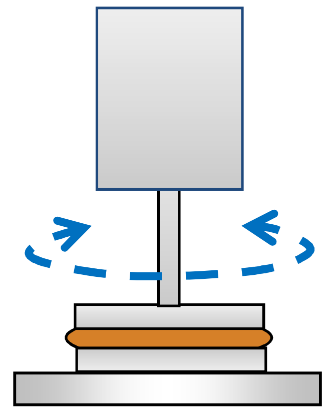
Outline

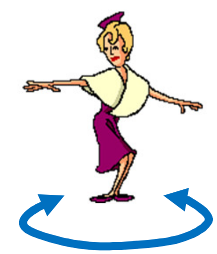
- Understanding Oscillation
- Approach to Oscillation Experimentation
  - Stress and Strain Sweep
  - Time Sweep
  - Frequency Sweep
  - Temperature Ramp
  - Temperature Sweep (TTS)

Dynamic Oscillatory Tests

- Most commonly used tests in adhesive evaluations





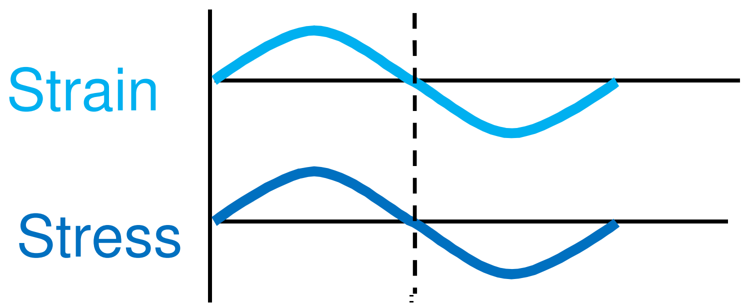


- Apply a sinusoidal stress to the sample at a certain frequency
- Monitor sample response in strain deformation
- The shift between the input stress and output strain is the phase angle

Dynamic Testing: Response for Classical Extremes

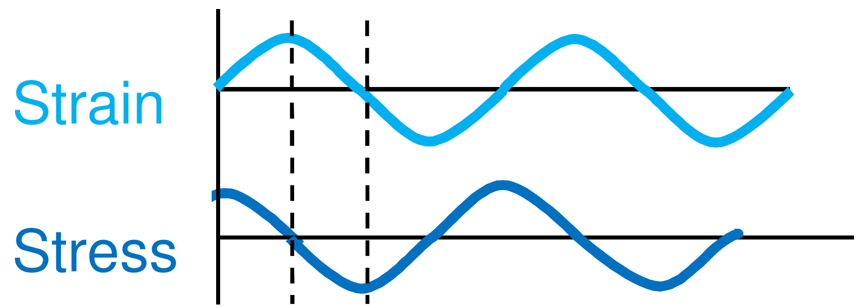
Purely Elastic Response
(Hookean Solid)

$\delta = 0°$

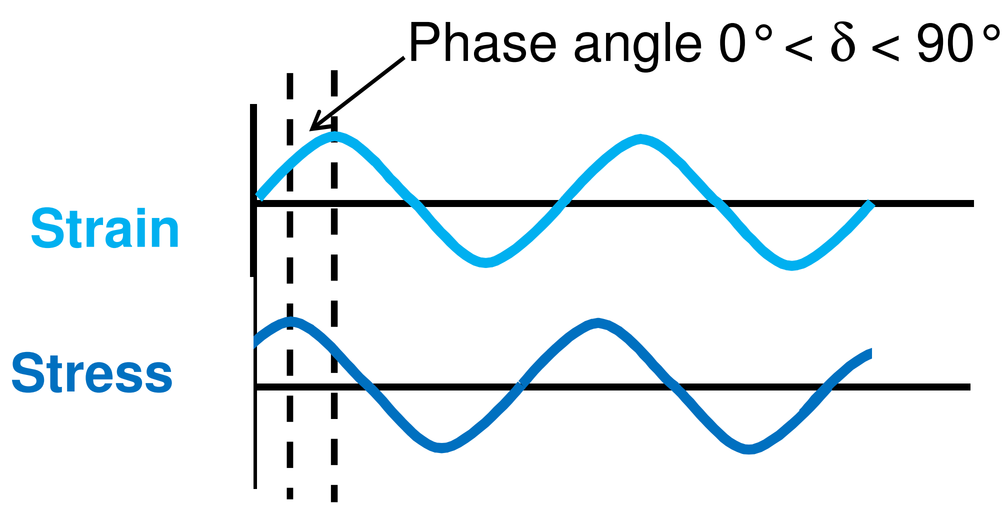


Purely Viscous Response
(Newtonian Liquid)

$\delta = 90°$



Viscoelastic Response



Viscoelastic Parameters

The Modulus: Measure of materials overall resistance to deformation.

$$G^* = \left(\frac{Stress^*}{Strain}\right)$$

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

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

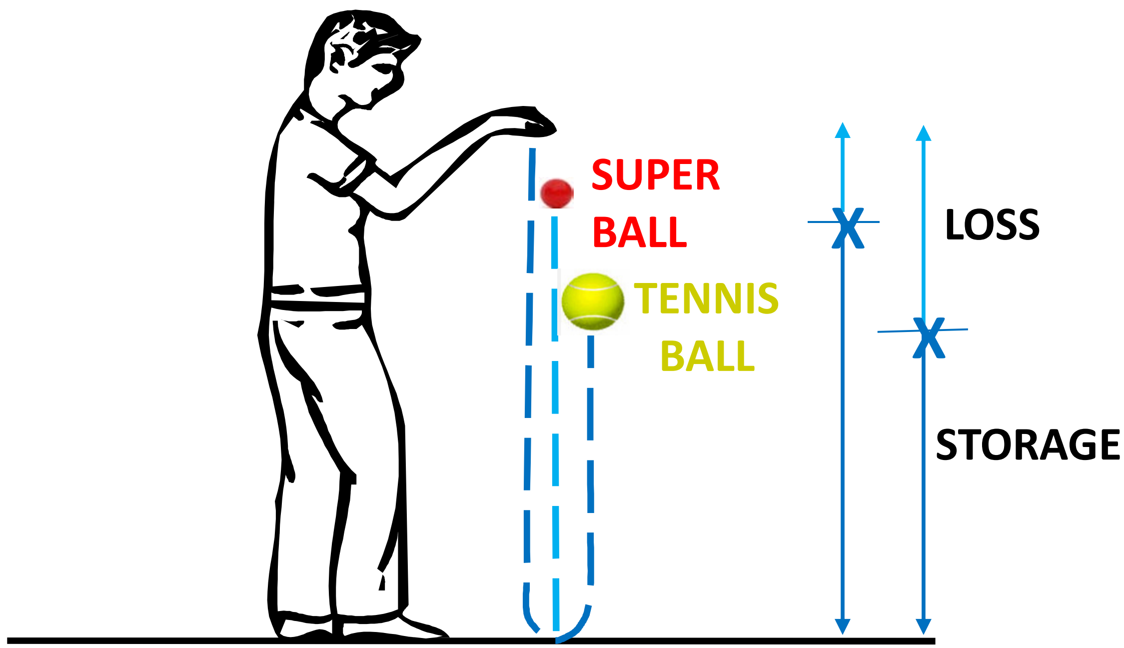
The Viscous (loss) Modulus: The ability of the material to dissipate energy. Energy lost as heat.

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

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

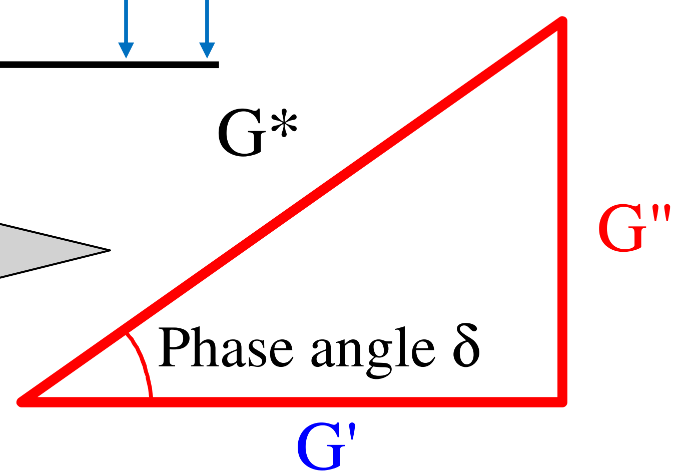
$$\tan\delta = \left(\frac{G''}{G'}\right)$$

Storage and Loss of a Viscoelastic Material



Dynamic measurement represented as a vector

$$G^* = (G'^2 + G''^2)^{1/2}$$



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:

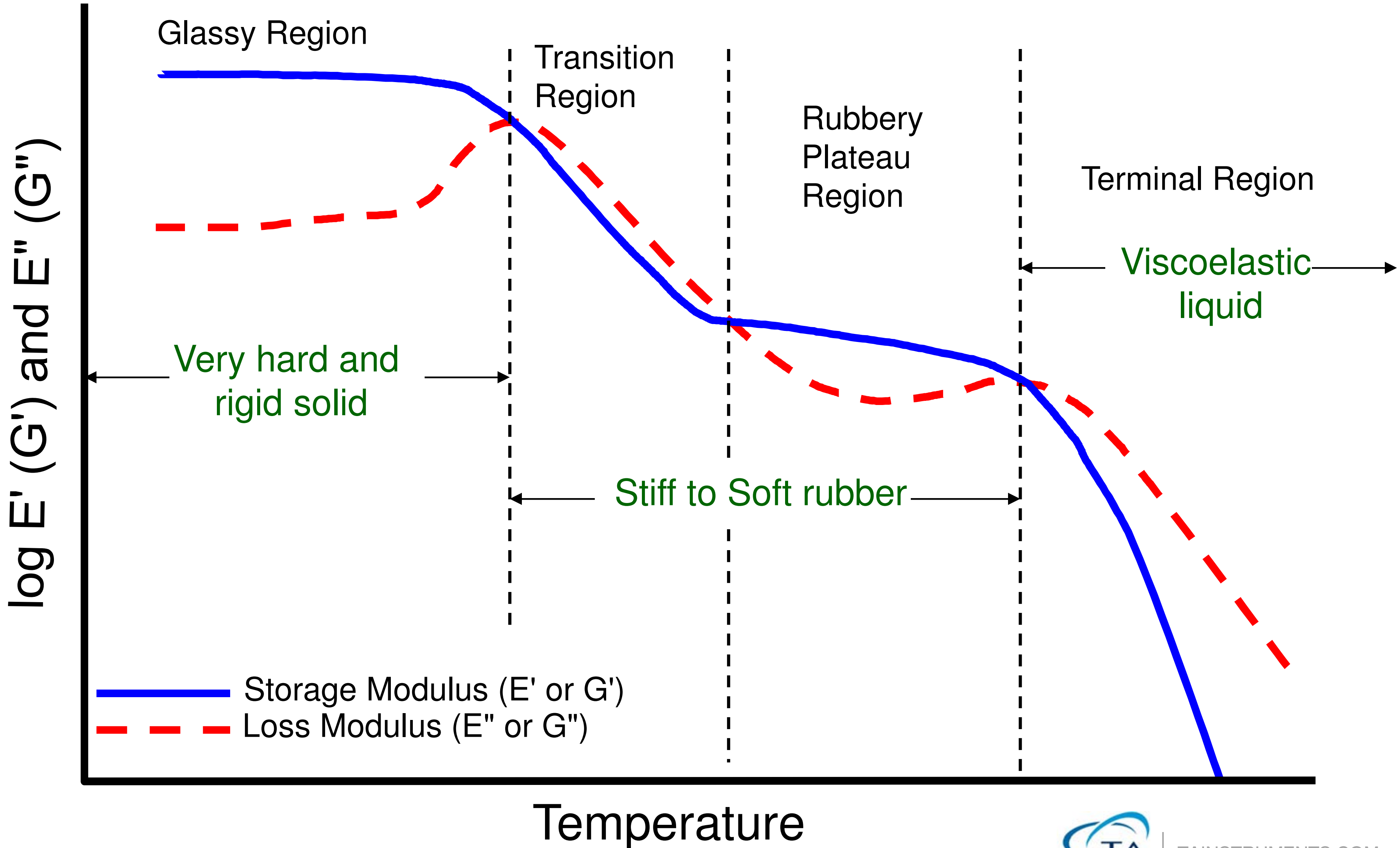
$$\eta^* = \eta' - i\,\eta''$$

or

$$\eta^* = G^*/\omega$$

Note: frequency must be in rad/sec!

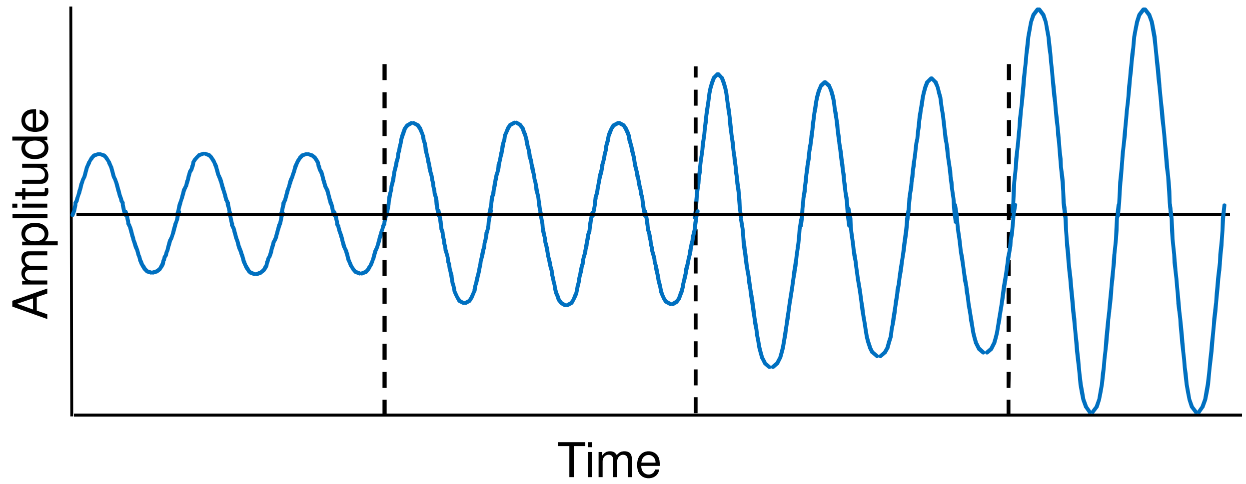
Viscoelastic Spectrum for a Typical Amorphous Polymer



Dynamic oscillation methods

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

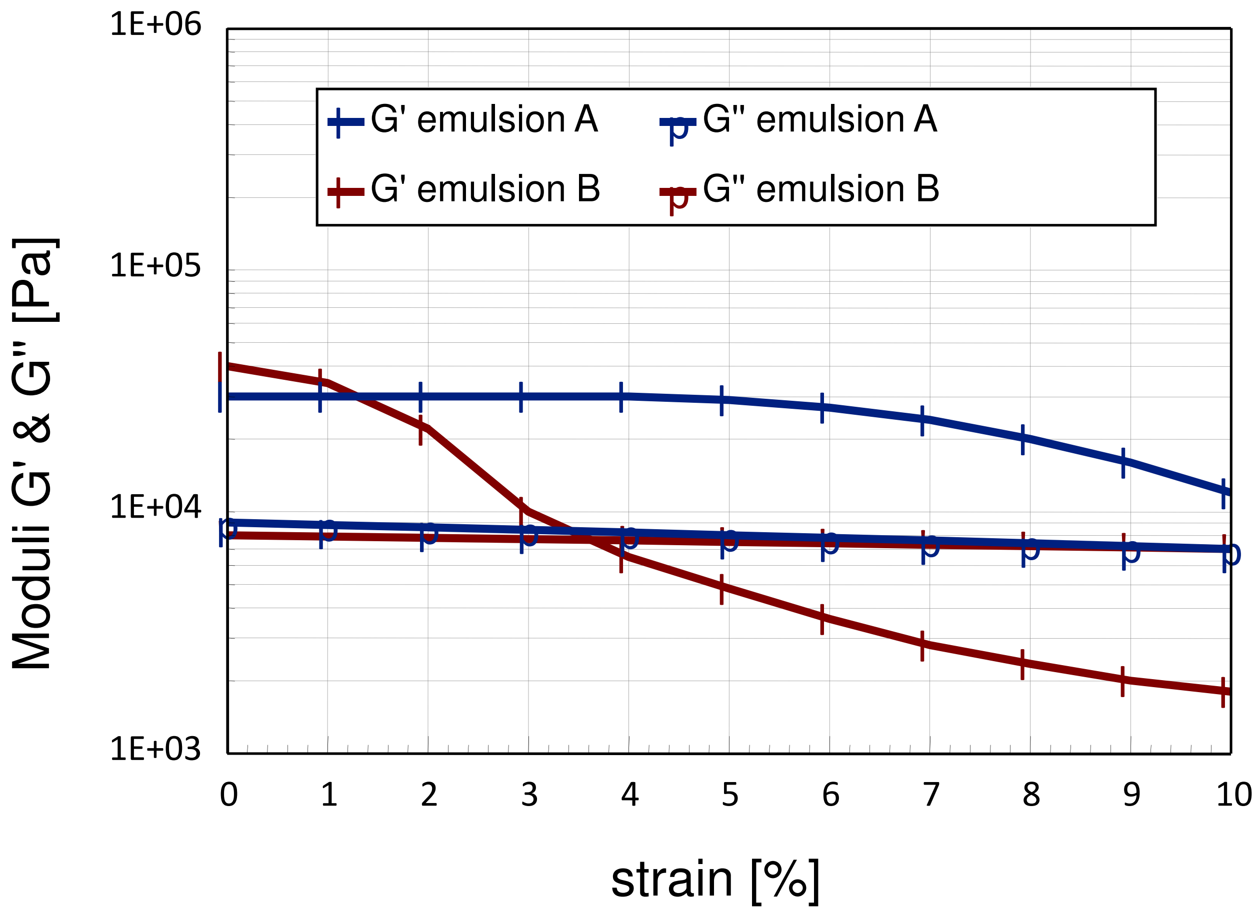
Strain, stress, or amplitude sweep



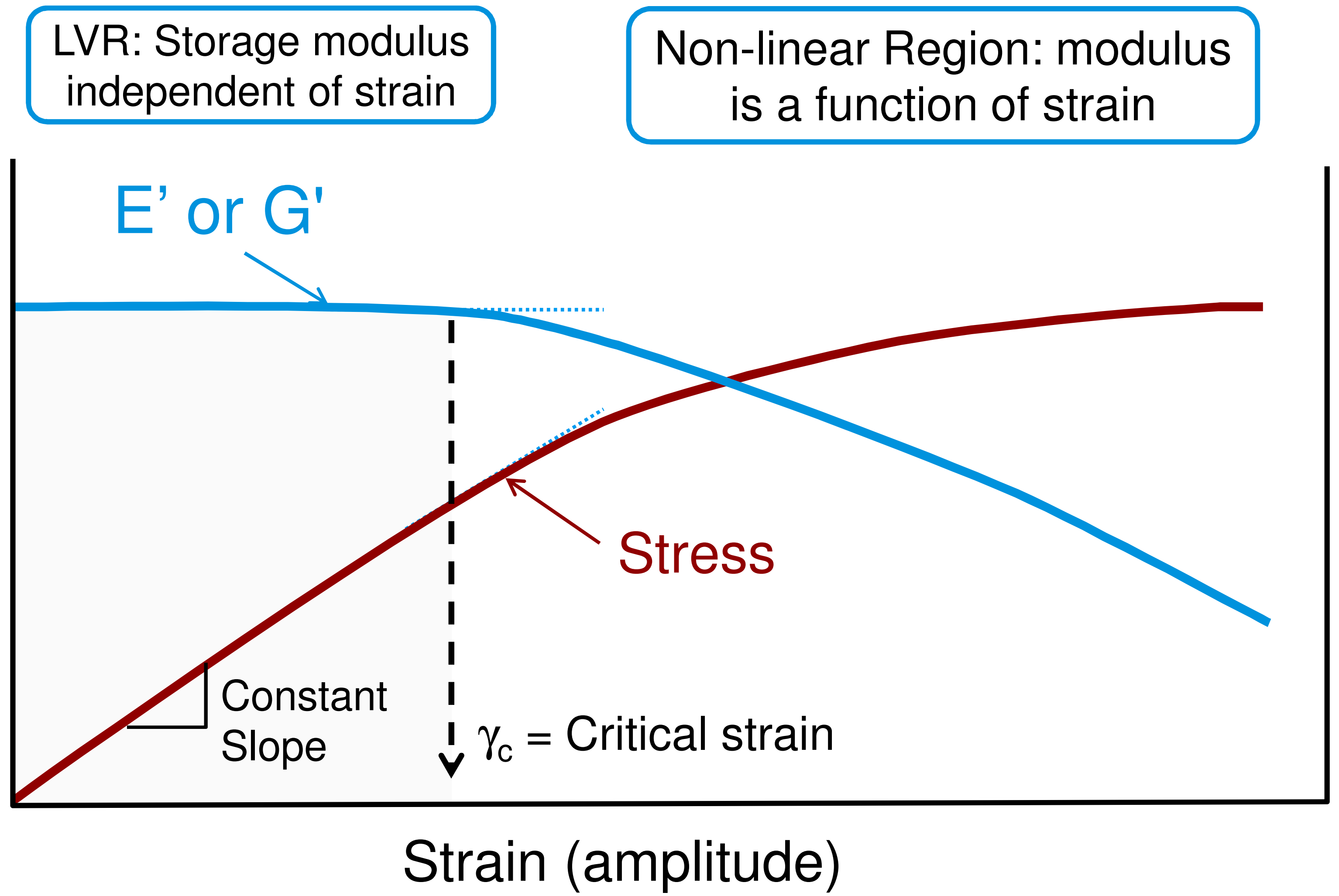
- The material response to increasing deformation amplitude is monitored at a constant frequency and temperature
- Determine LVR or yield stress
  - Tests assumes sample is stable

Creams/Lotions: Predict Stability

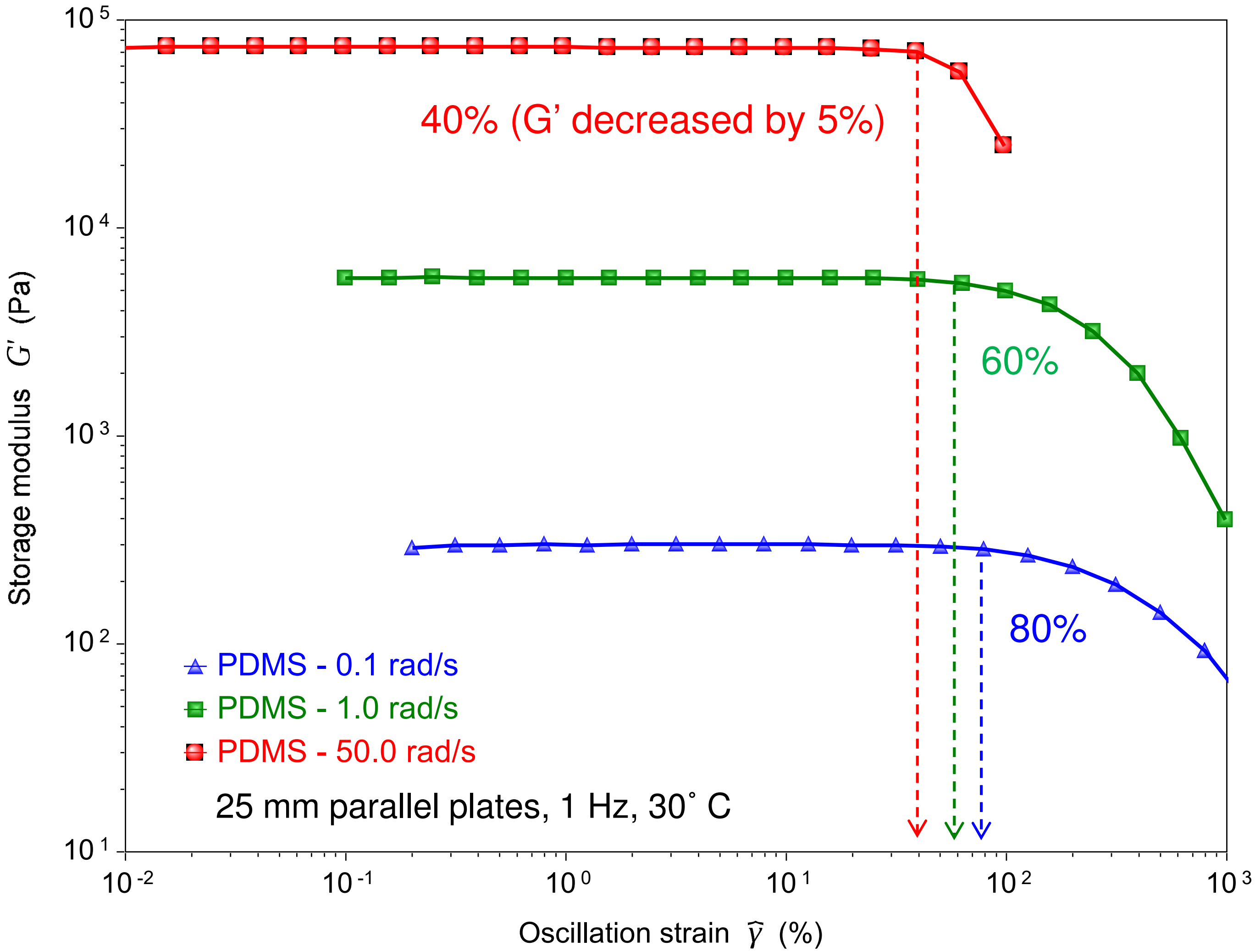
Stability, phase separation of a cosmetic cream



Dynamic Strain Sweep: Material Response



Frequency dependence of LVR



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

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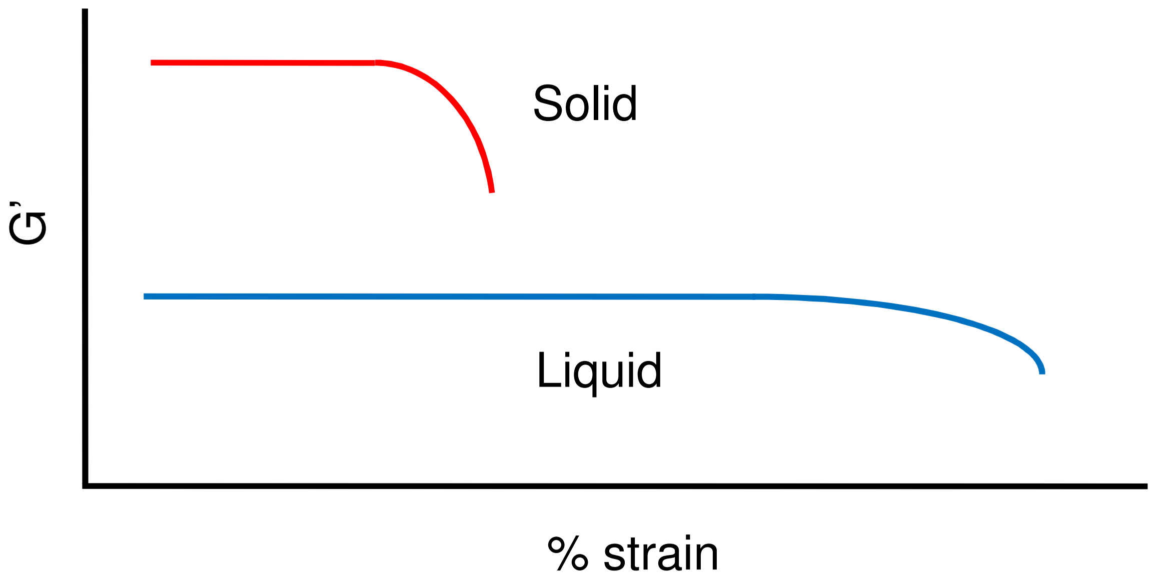
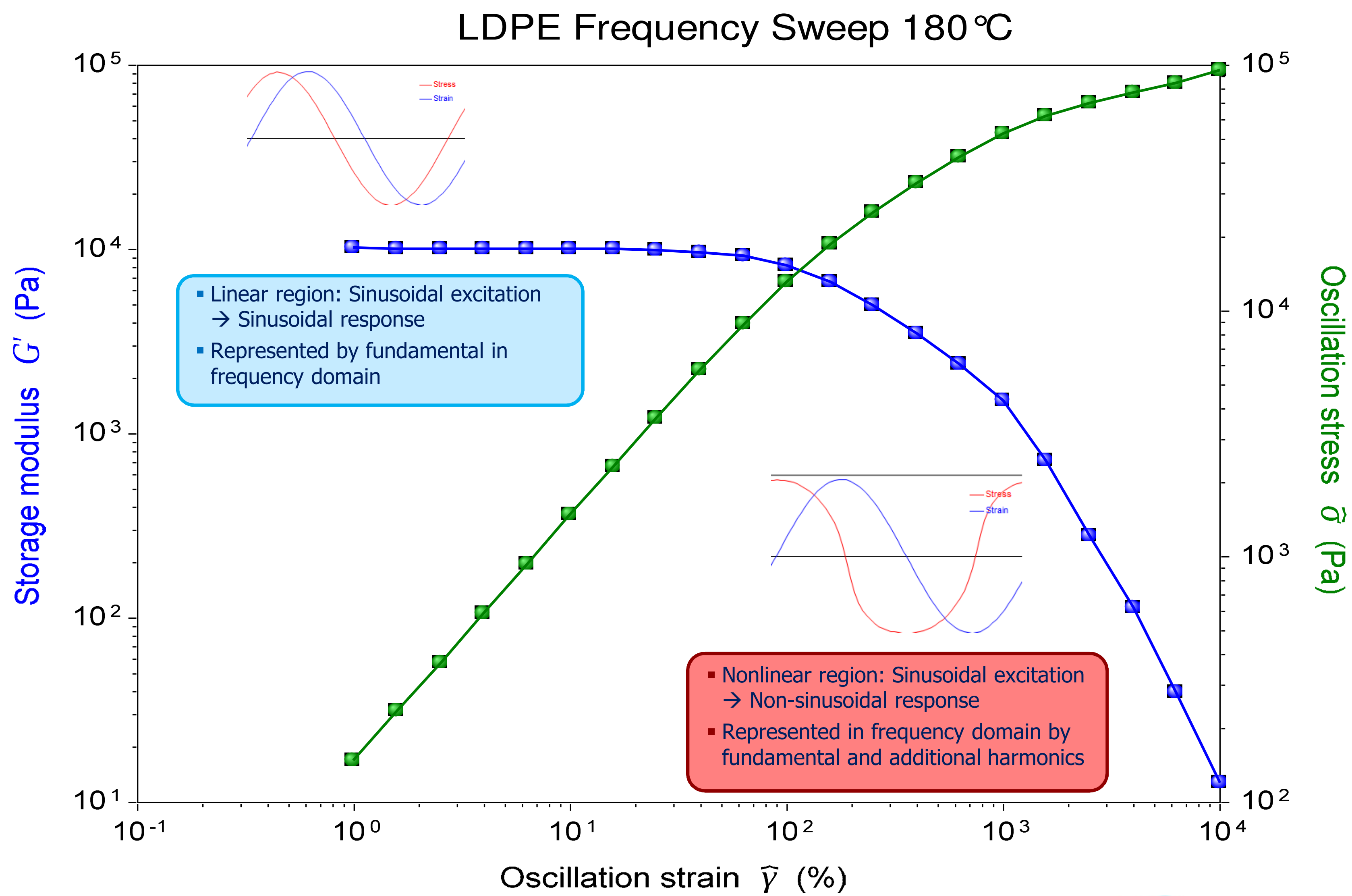
Temperature Dependence of LVR

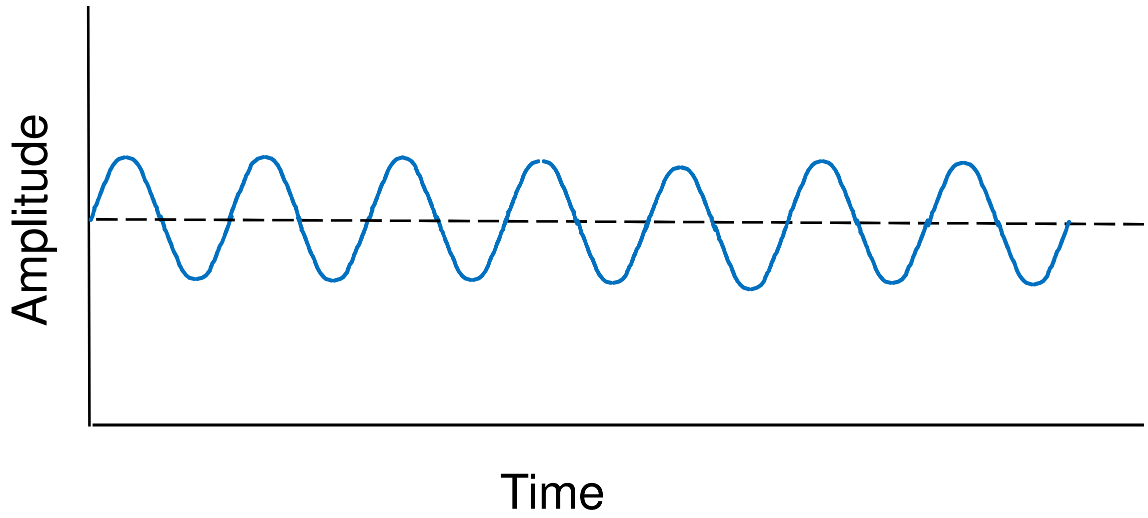
- In general, the LVR is shortest when the sample is in its most solid form.



Linear and Non-linear Viscoelasticity



Time sweep

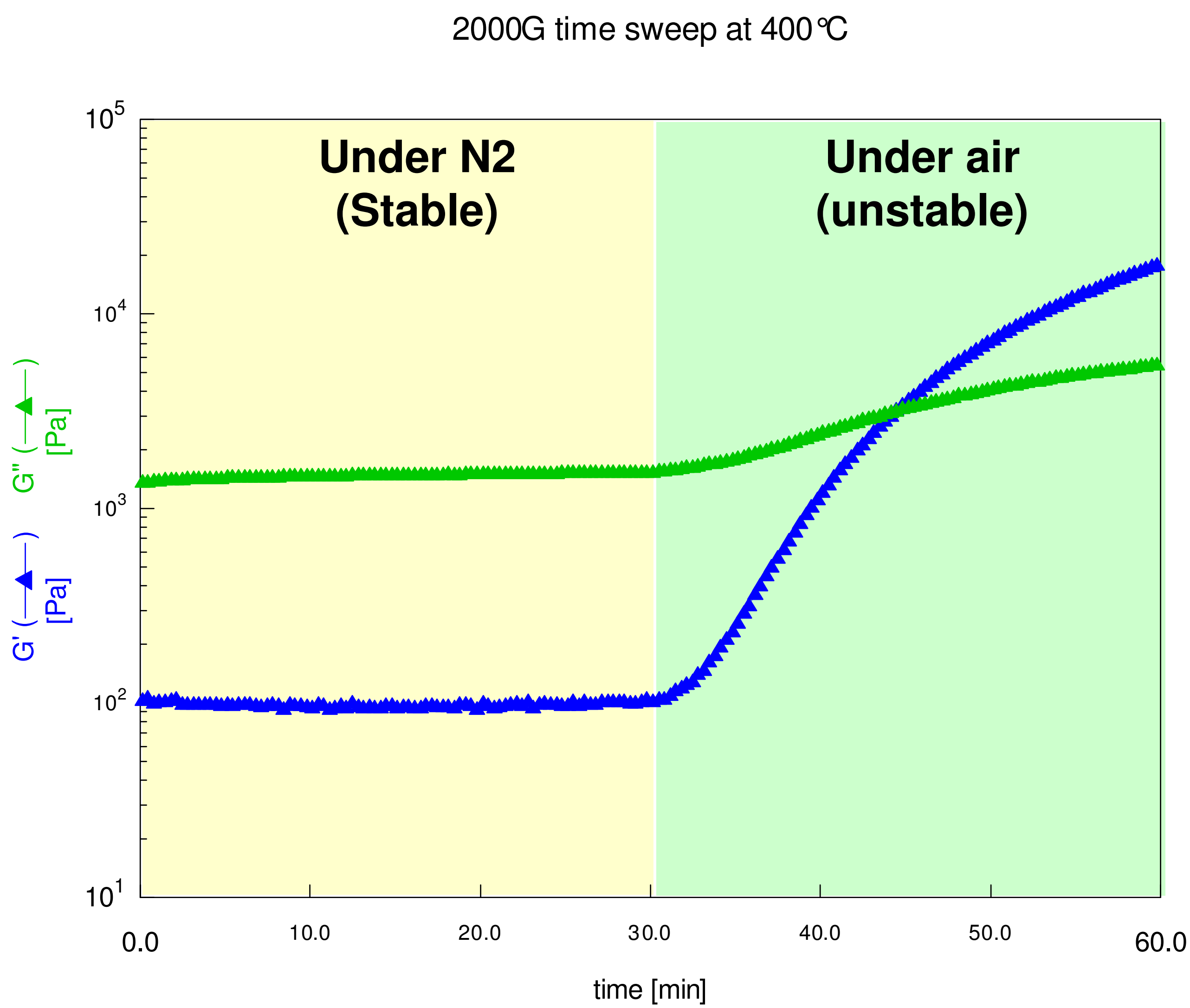


- The material response is monitored at a constant frequency, amplitude, and temperature
- Determine stability (e.g. evaporation, degradation), thixotropy, and curing studies
  - Amplitude within LVR

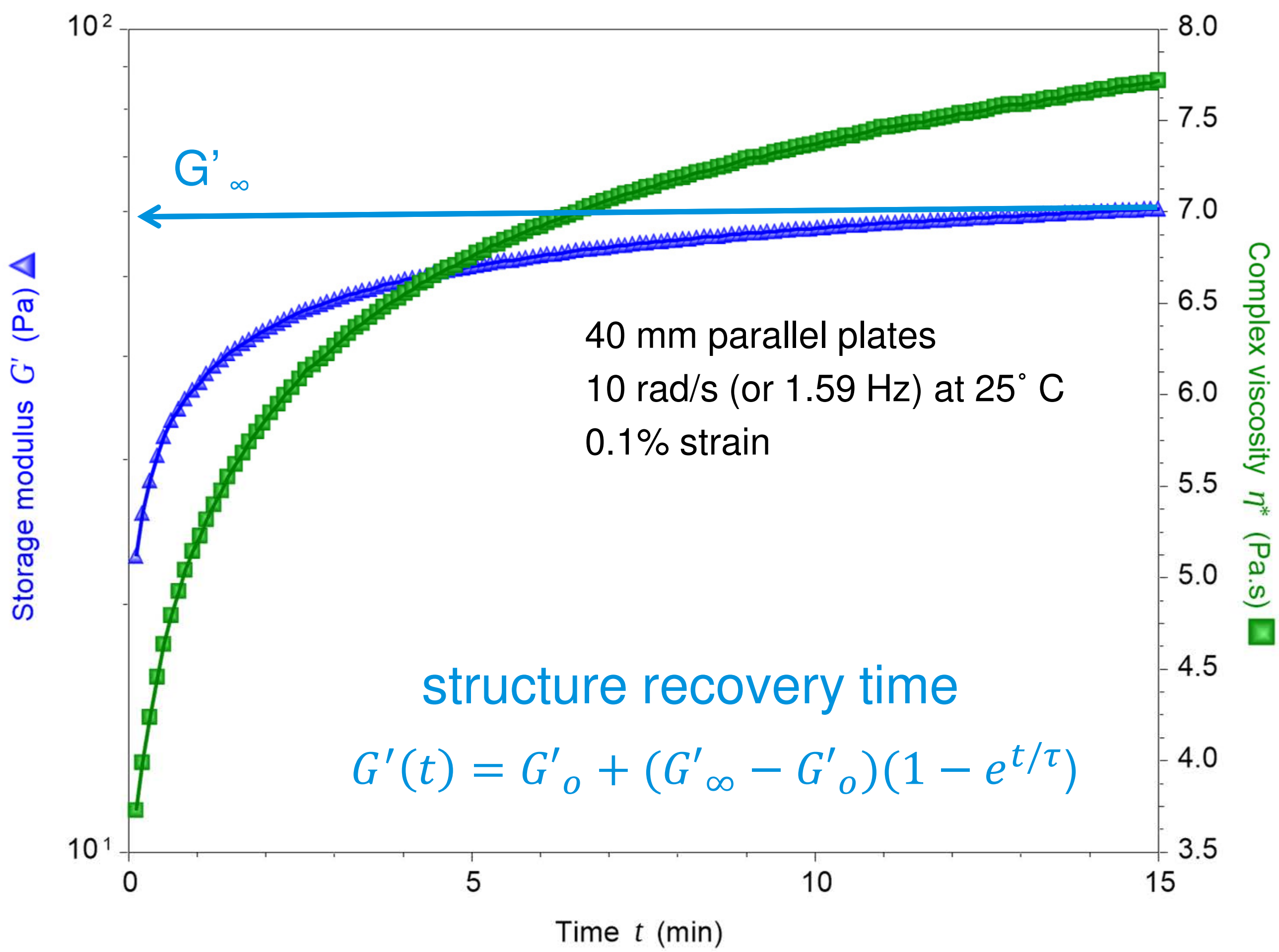
Importance of Time Sweep

- 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

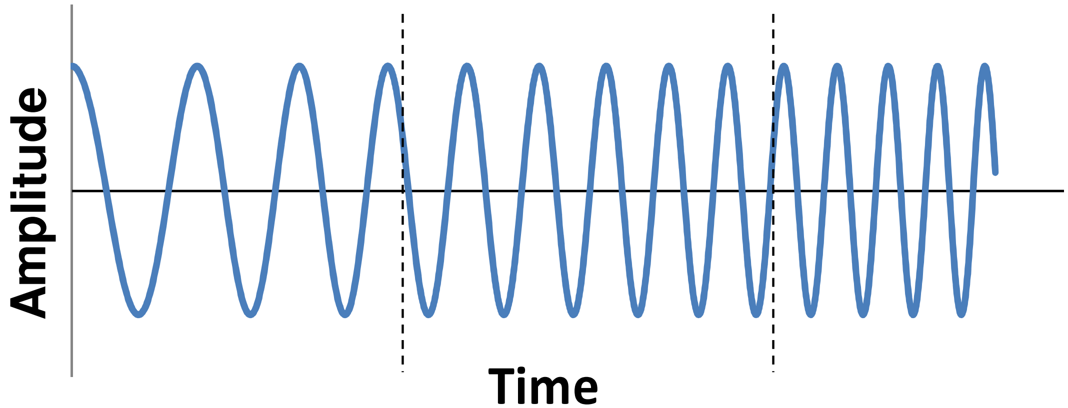


Structure Recovery of a Paint



- Monitor the increase of the G‘ or complex viscosity as function of time
- Thixotropic recovery can be described by the recovery time (τ)
  - Rule out evaporation

Frequency sweep

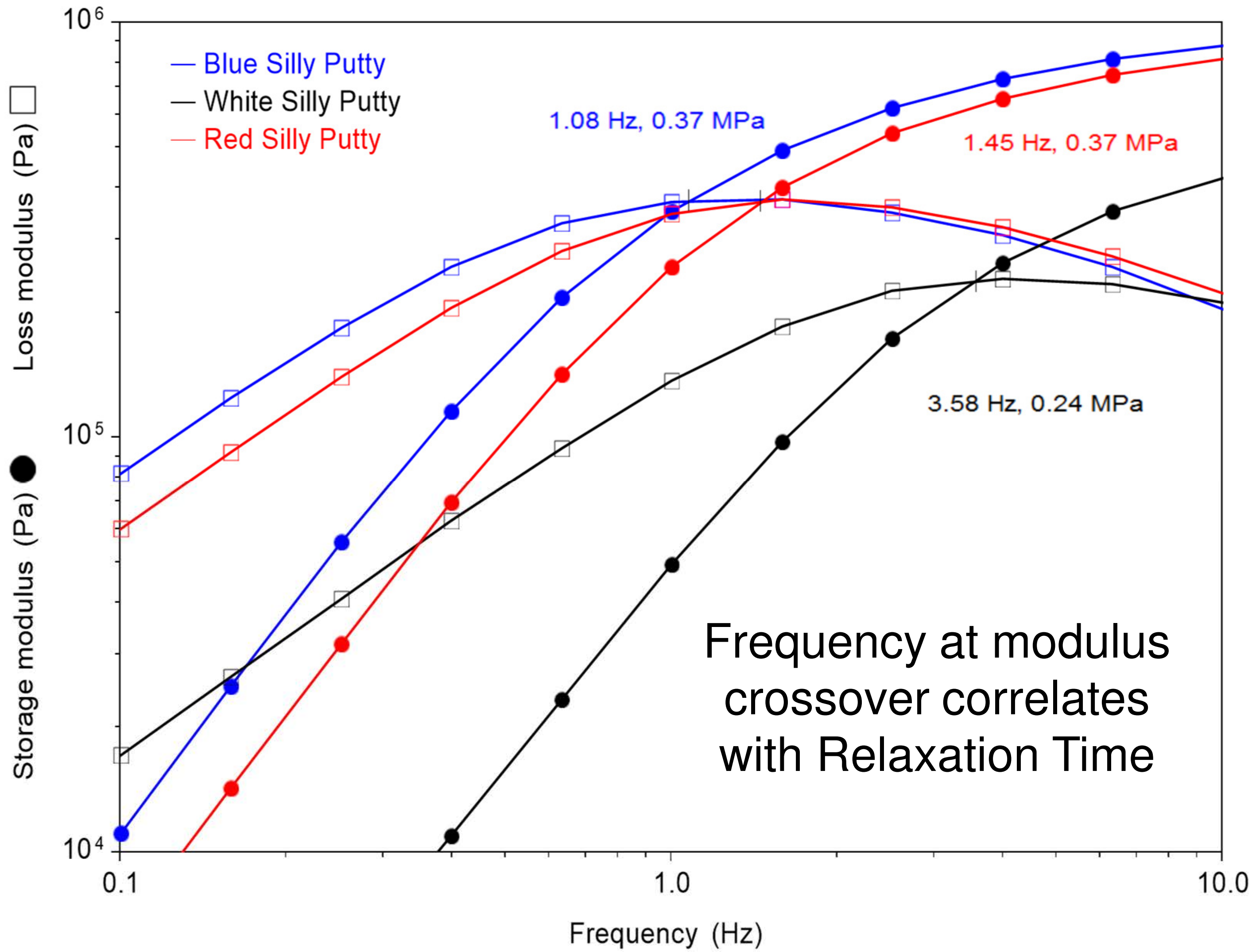


- The material response to increasing frequency (rate of deformation) is monitored at a constant amplitude and temperature
- Determine stability over the expected duration of test
  - Low frequencies = longer times
  - Amplitude within LVR

Time-Dependent Viscoelastic Behavior

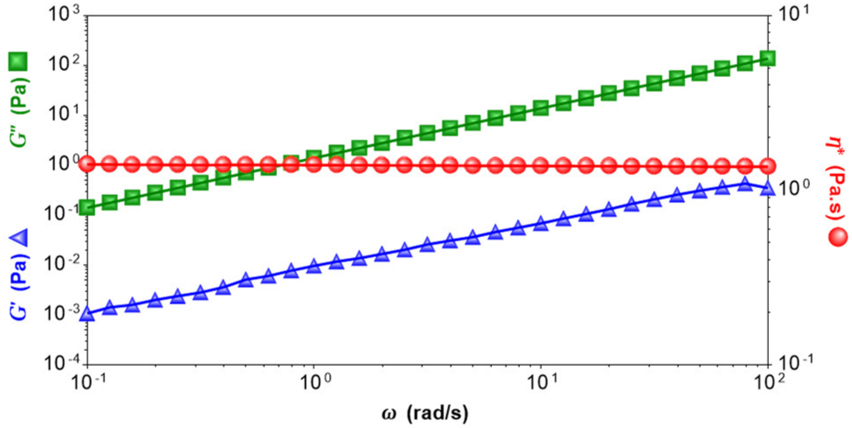
- Silly Putties have different characteristic relaxation times
- Dynamic (oscillatory) testing can measure time-dependent viscoelastic properties more efficiently by varying frequency (deformation time)

Frequency Sweep- Time Dependent Viscoelastic Properties

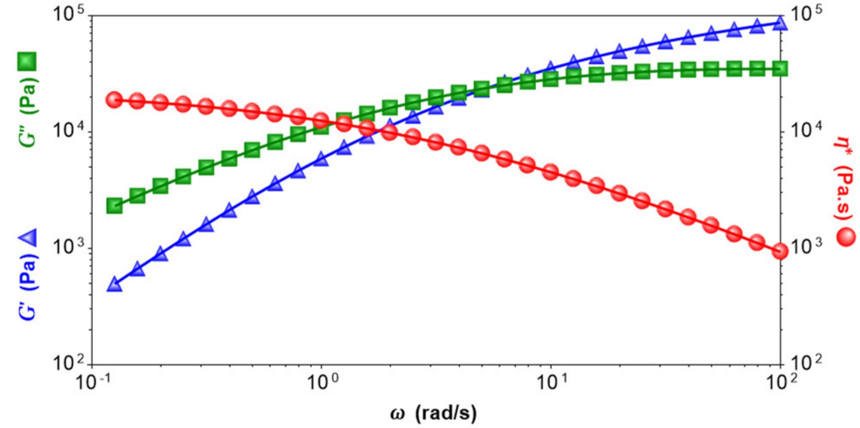


Differences in elasticity using frequency sweep

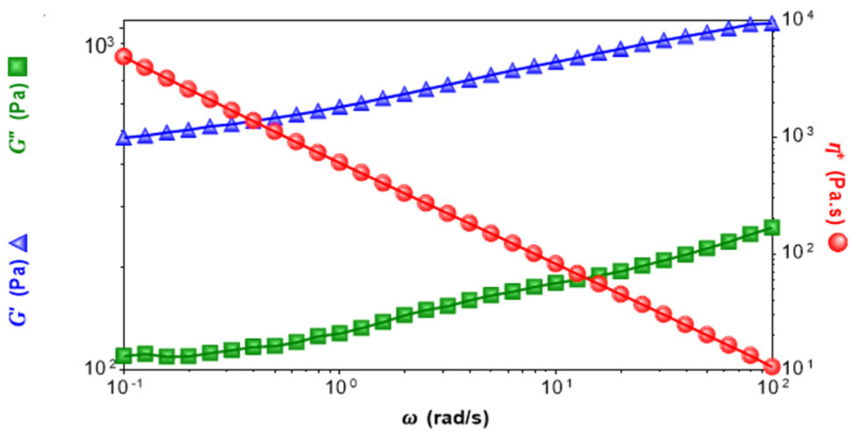
Mineral oil



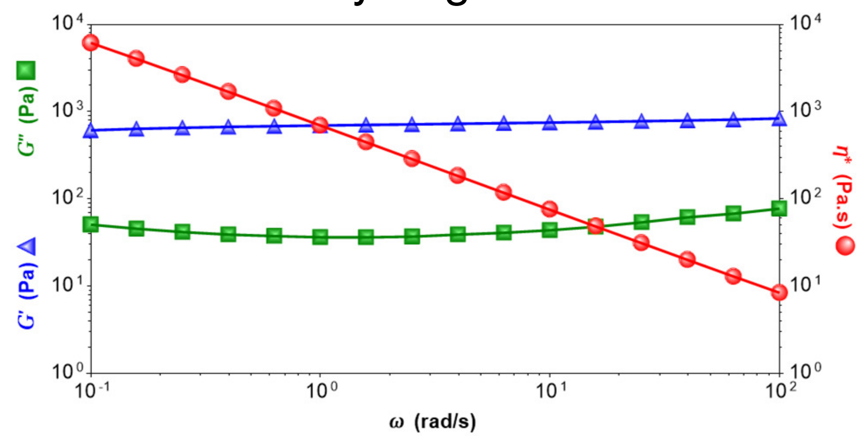
PDMS



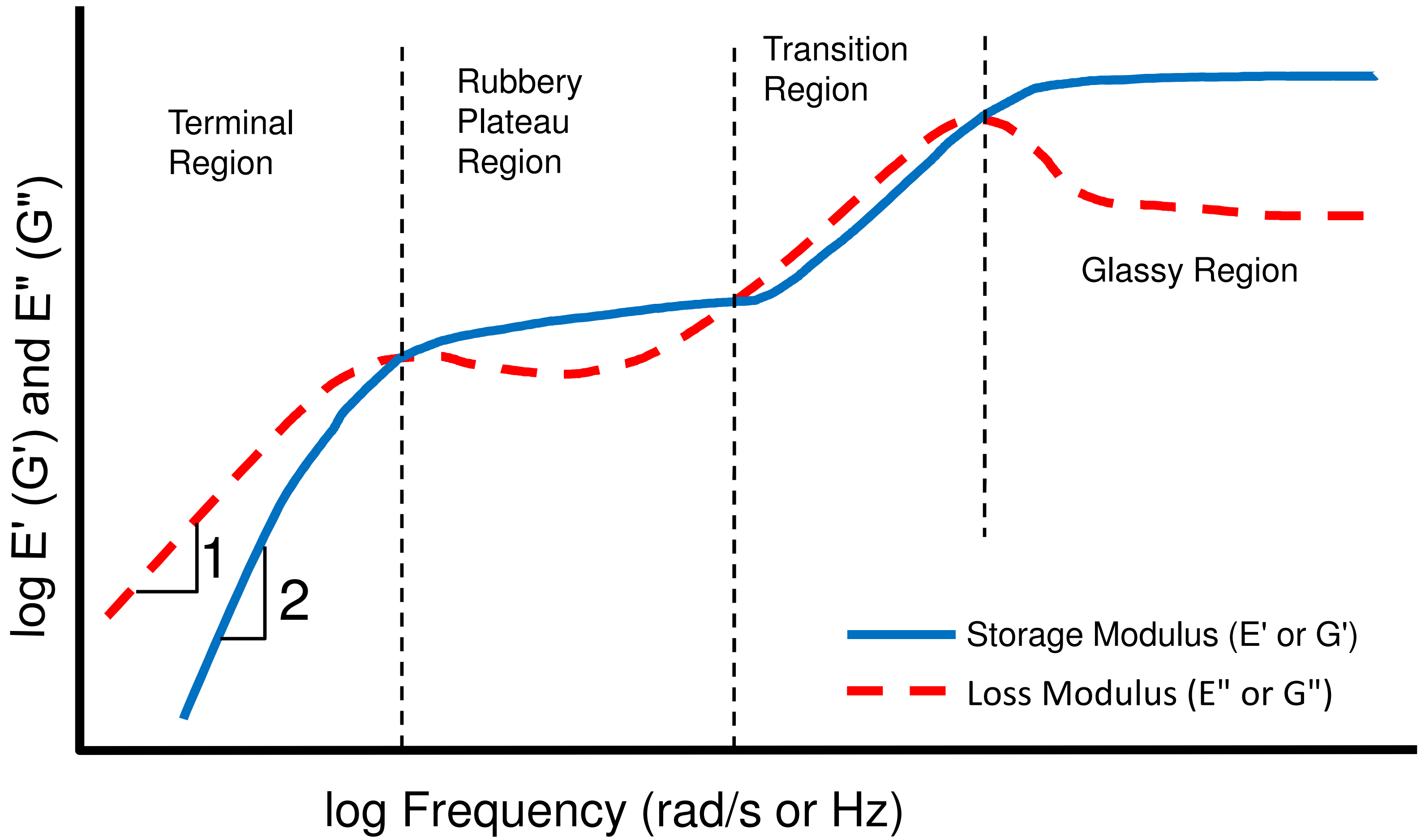
Skin cream



Hydrogel

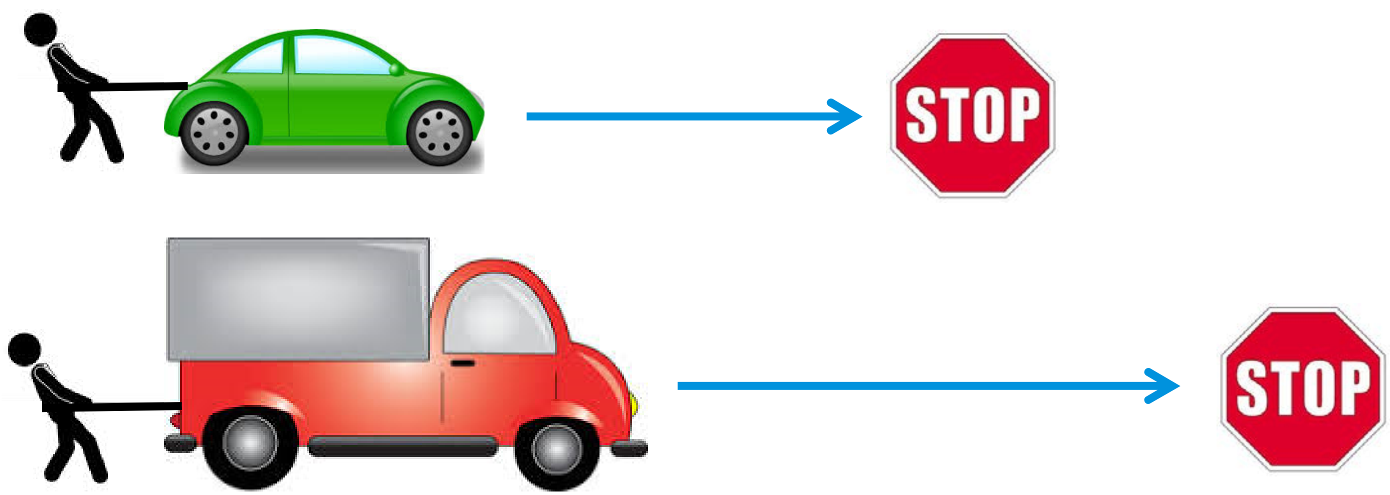


Frequency Sweep: Material Response



Inertial Effects

- What is Inertia?
  - <u>Definition</u>: That property of matter which manifests itself as a resistance to any change in momentum of a body
  - Instrument has inertia
  - Sample has inertia

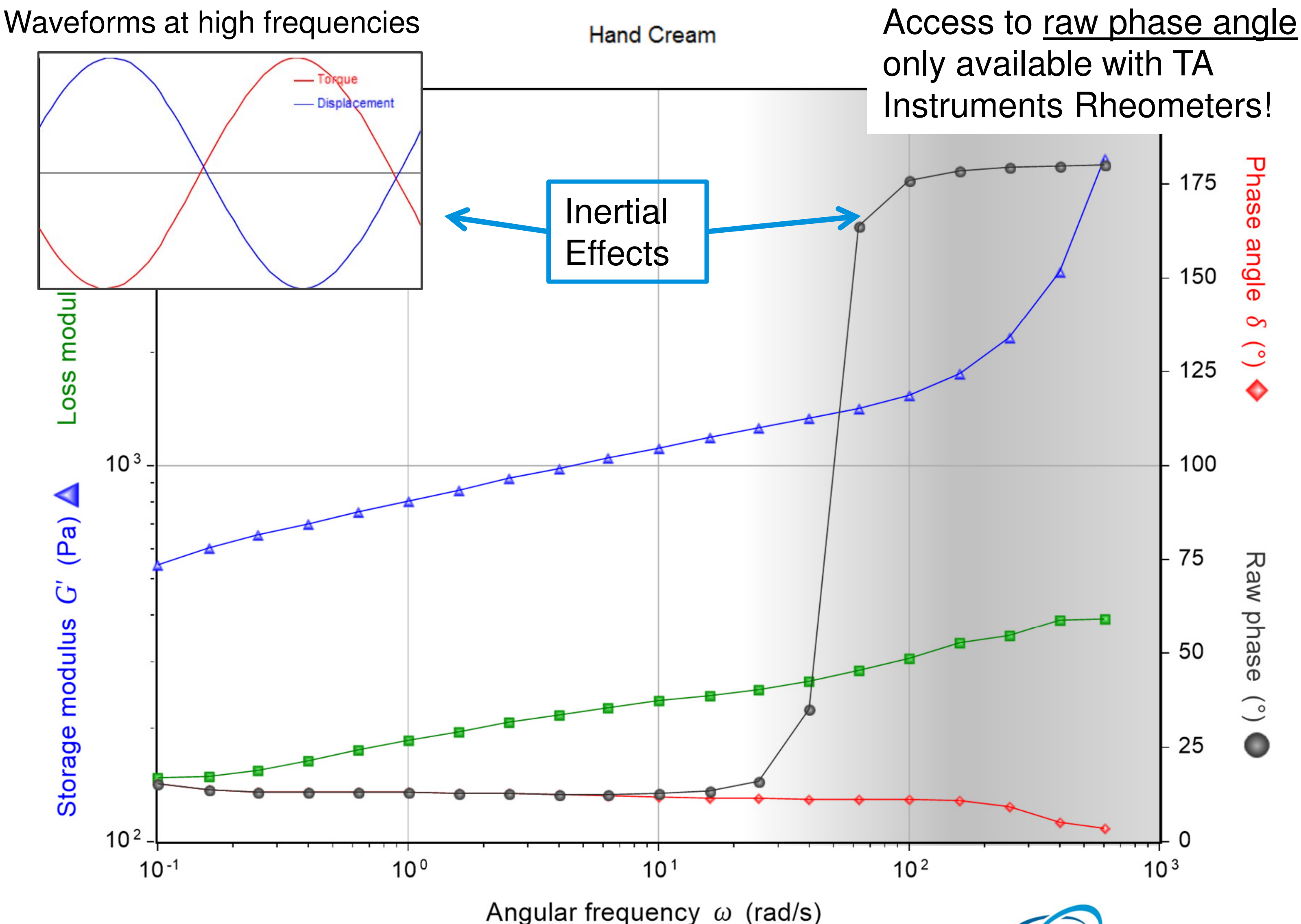


Inertial Effects in Oscillation for DHR

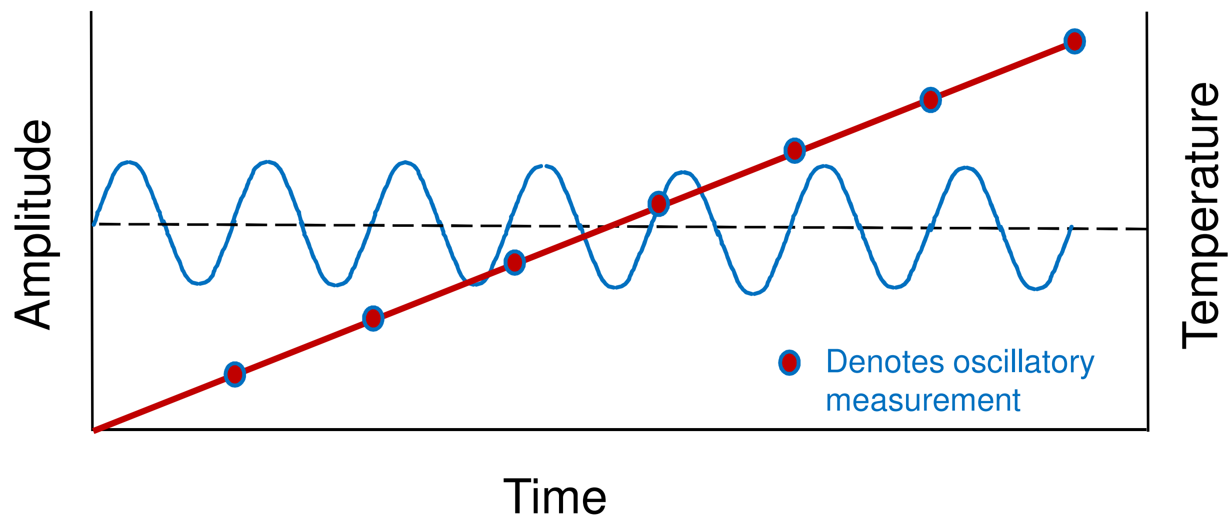
- Inertia consideration
  - Viscosity limitations with frequency
  - Minimize inertia by using low mass geometries
  - Monitor inertia using Raw Phase in degree
  - When Raw Phase is greater than:
    - **150° degrees for AR series**
    - **175° degrees for DHR series**
    - This indicates that the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

Raw Phase × Inertia Correction = delta

DHR Correction for Inertia

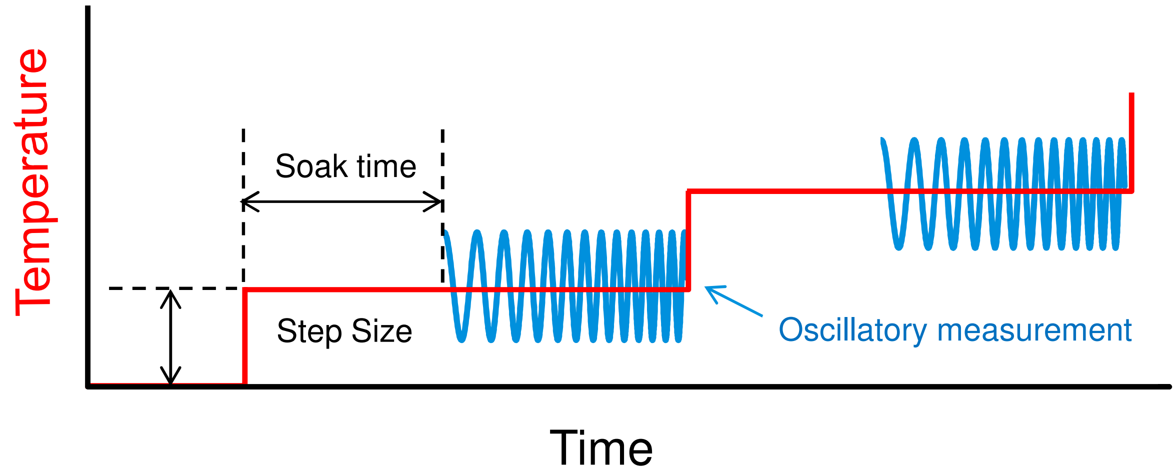


Dynamic temperature ramp



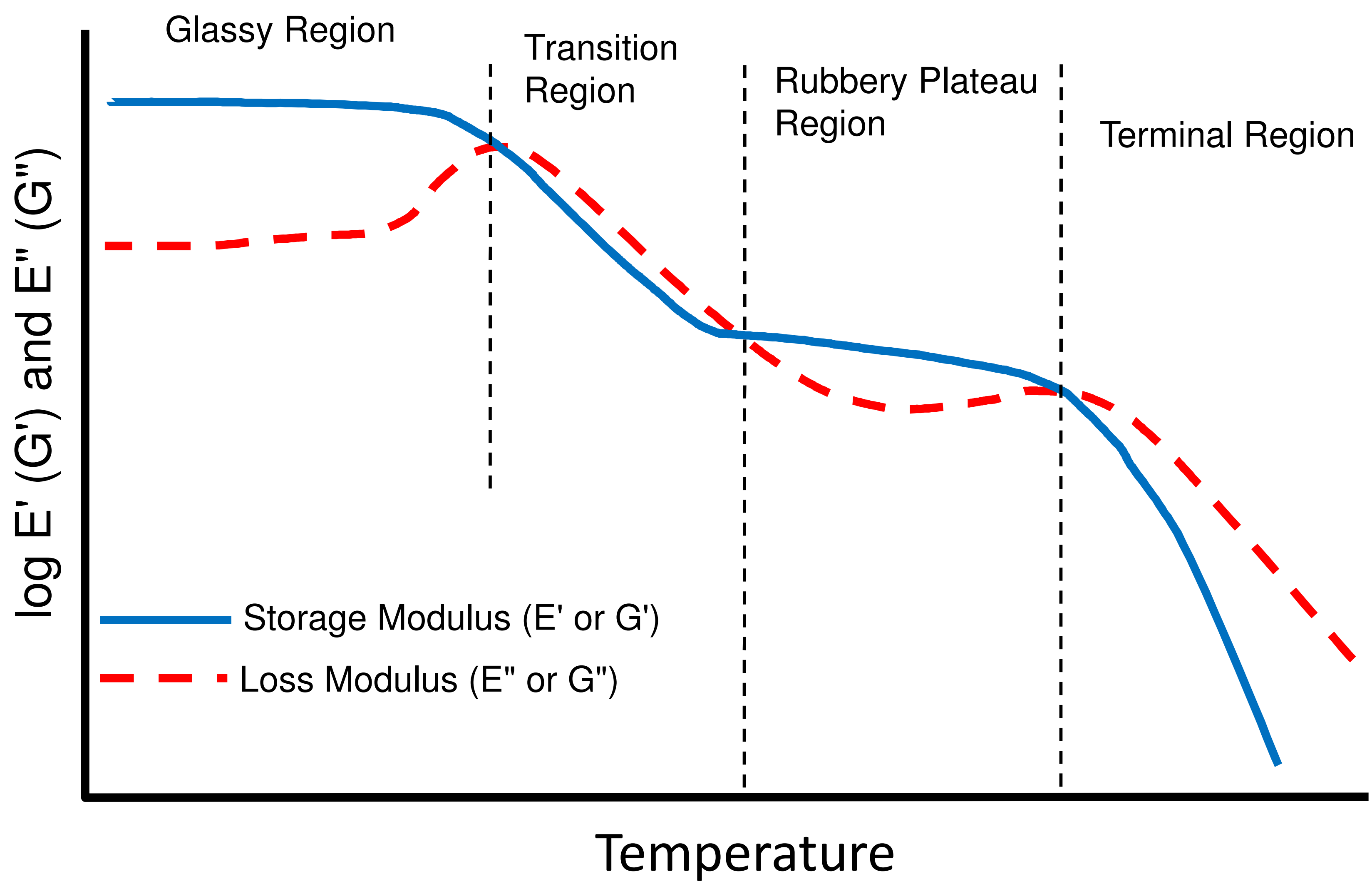
- Linear heating rate is applied and the material response is monitored at a constant frequency and constant amplitude
- Common heating/cooling rate: 2-5 ℃/min
- Amplitude within LVR

Temperature sweep (or step) - Single /Multi-Frequency

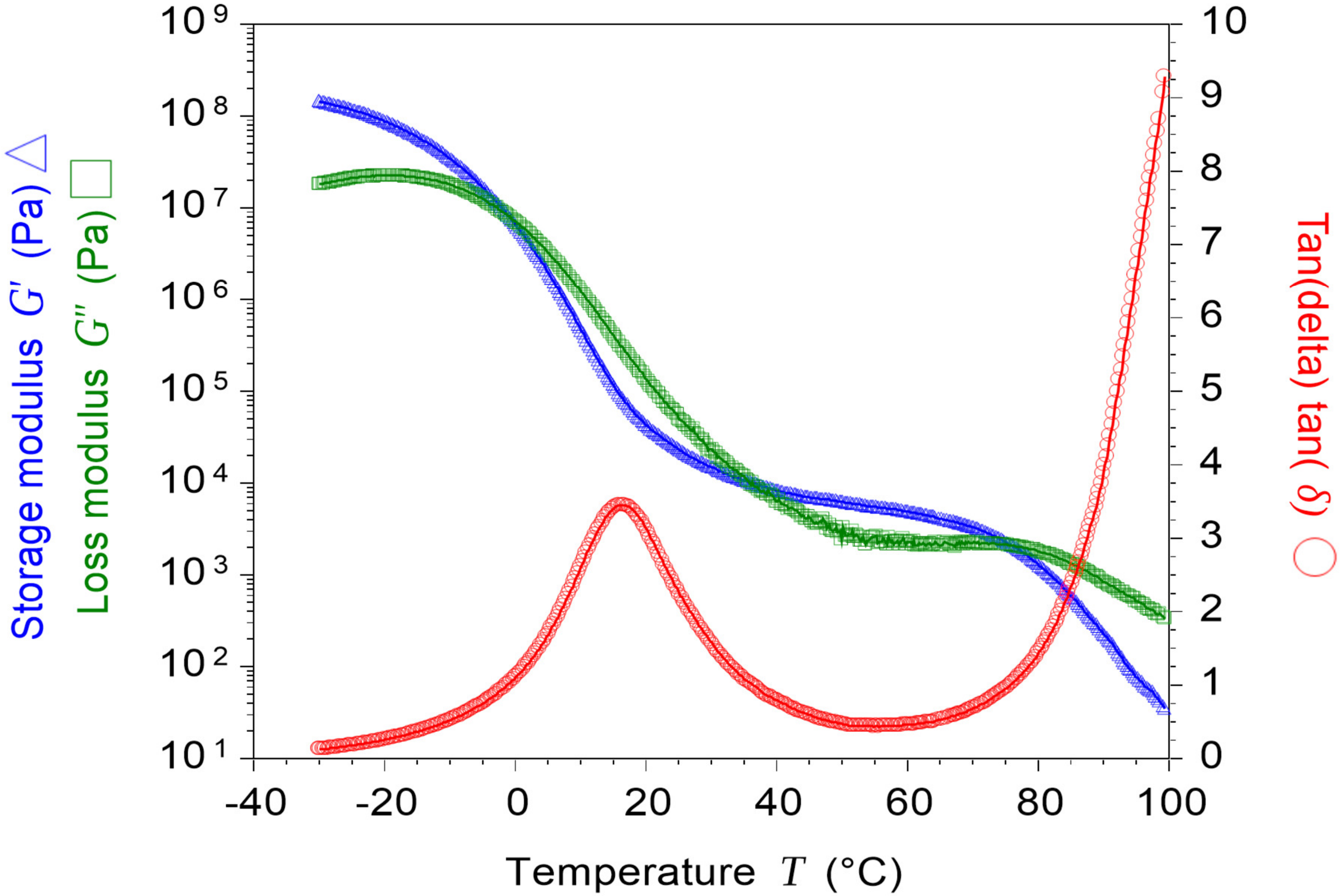


- Step and hold temperature then monitor material response
  - No thermal lag
- Common step: 5-10 degrees per step
- Amplitude within LVR

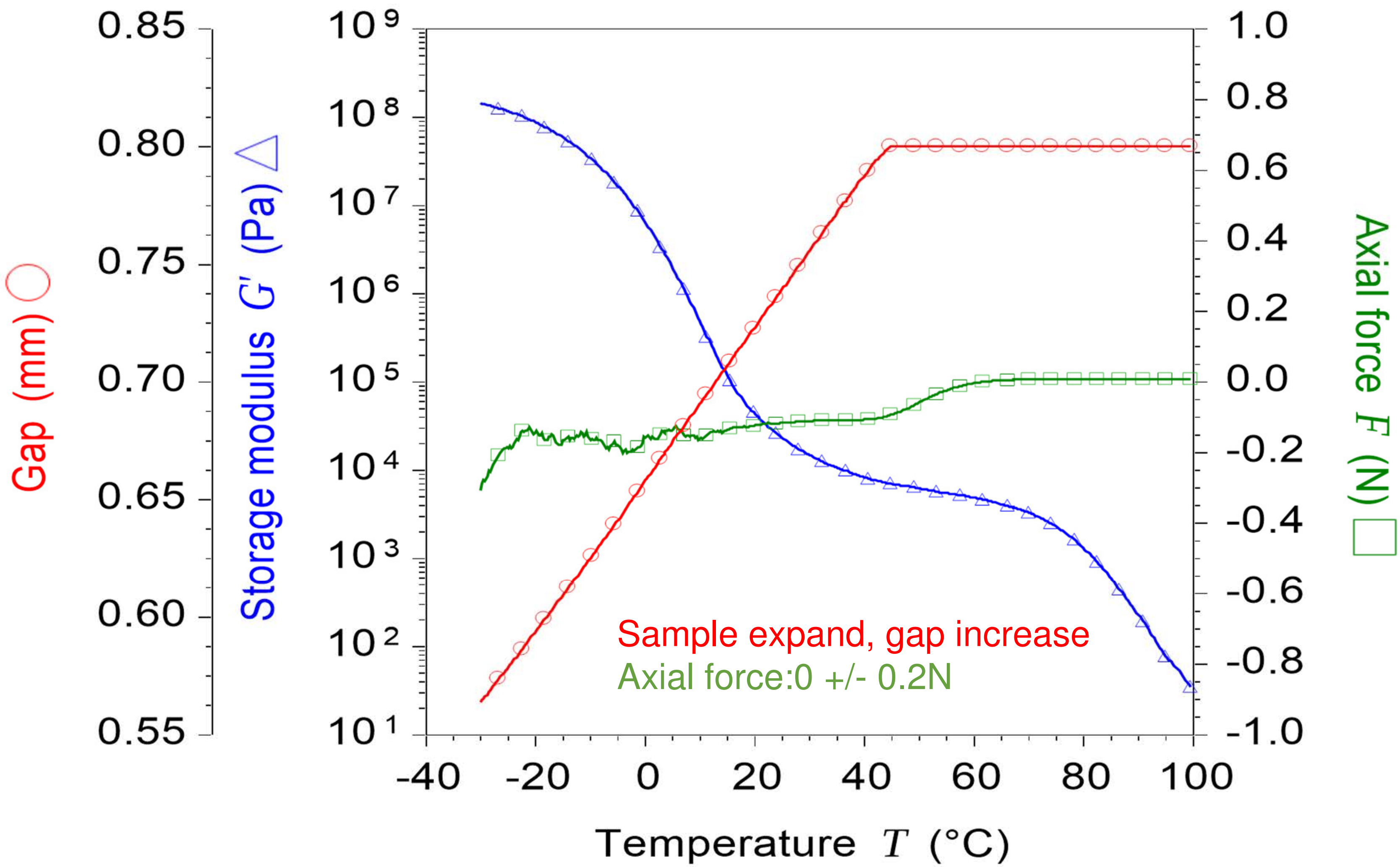
Dynamic Temperature Ramp or Sweep: Material Response



Temperature Ramp of an Adhesive



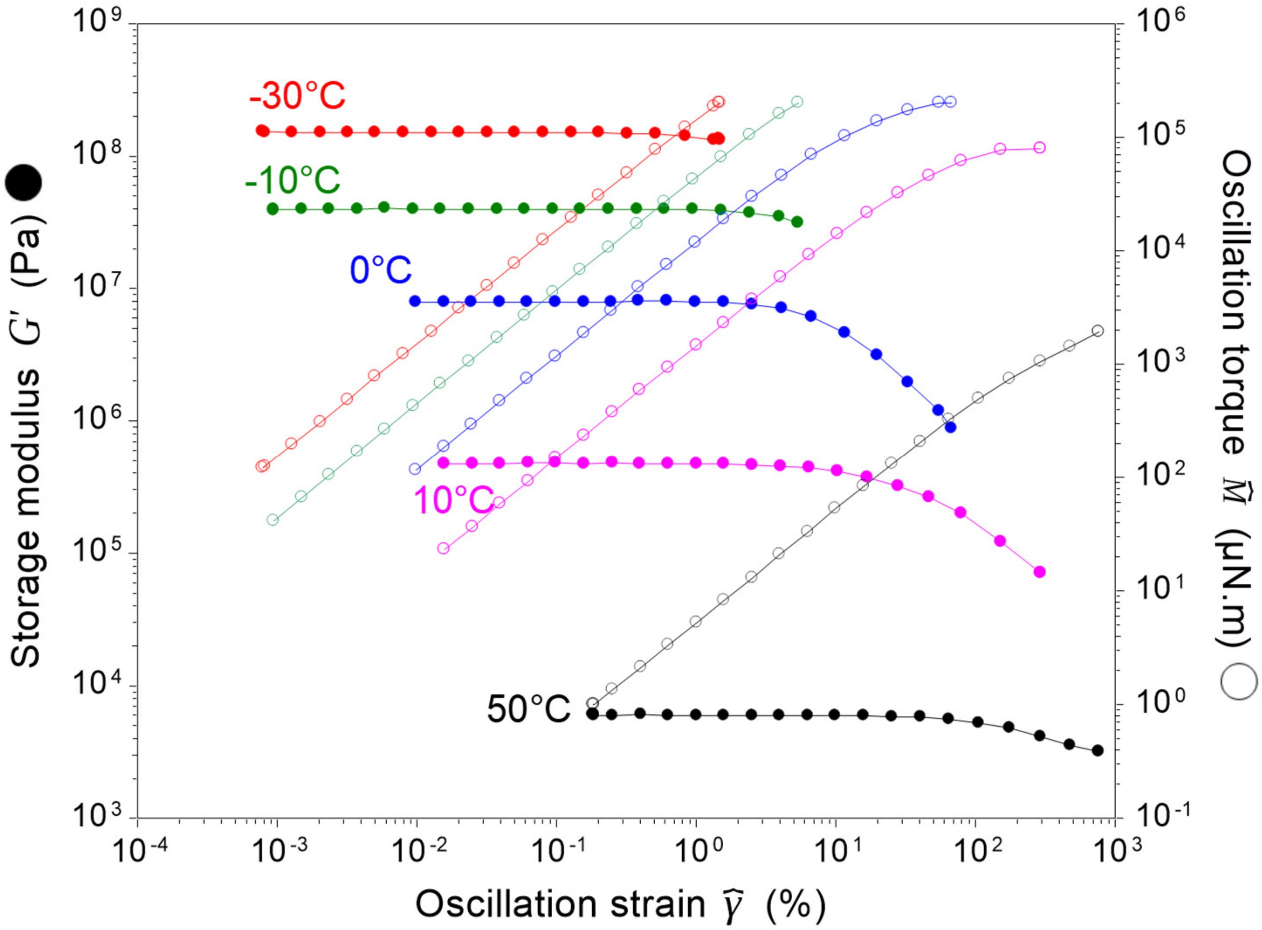
Using Axial Force Control in a Temp Ramp Test



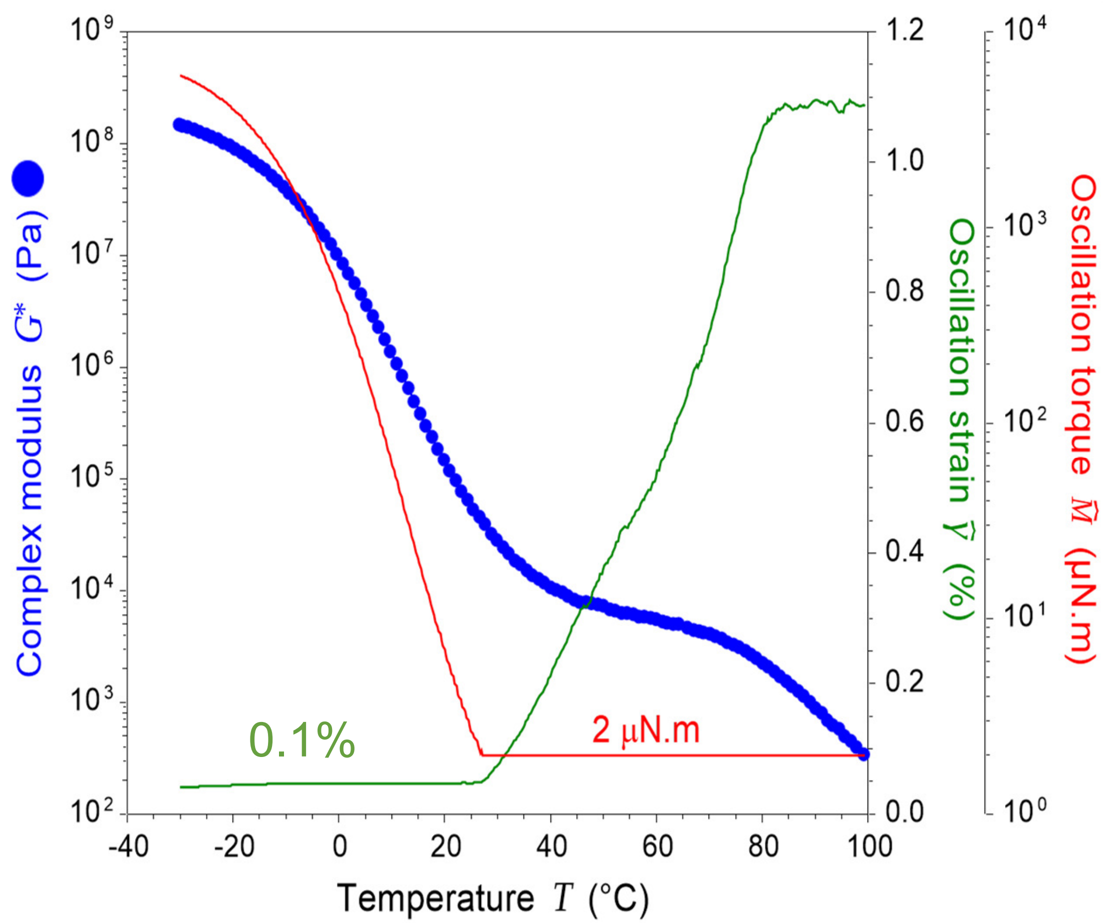
Adjusting strain and torque in temperature ramp

@ Low temperature:
A small strain is preferred.

@ High temperature:
A large strain is preferred.



DHR and AR: Non-iterative Sampling



Controlled Strain Advanced

Controlled strain type: Non-iterative sampling

Initial stress: Torque 10.0 µN.m

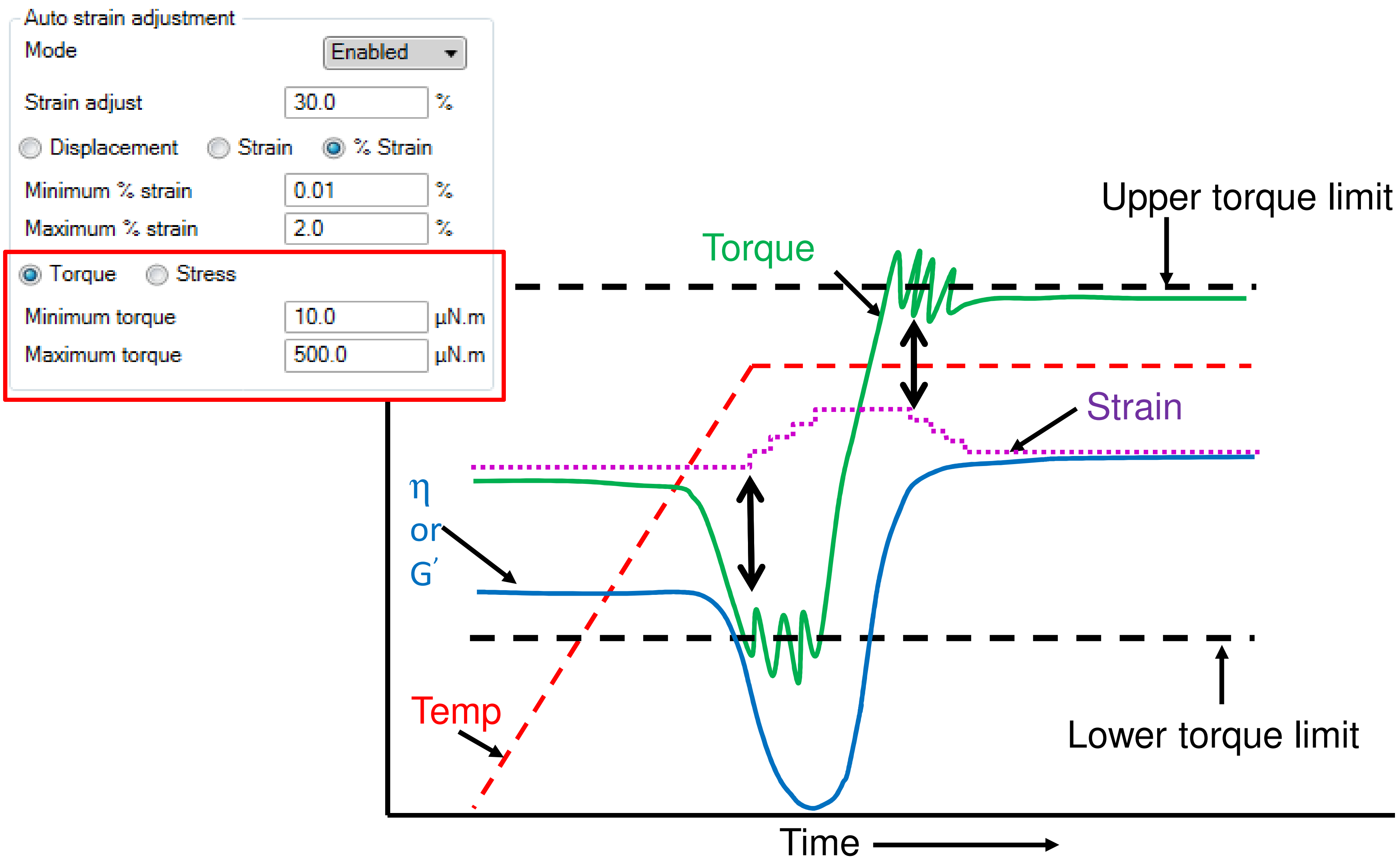
Lower torque limit 2.0 µN.m

Number of tries 4

Initial tolerance 0.5 %

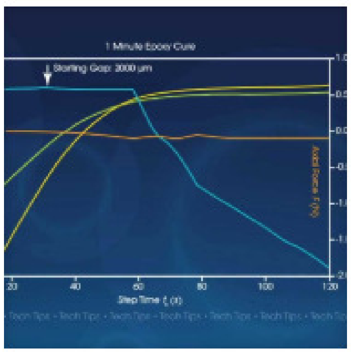
Store all tries as data points

ARES-G2 and DHR: Auto-Strain



TA Tech tips

axial force control



Using Axial Force Control

non-iterative sampling

Non-Iterative Sampling For Thermoset Rheology

auto strain using dhr w/ trios v3.2 or hi

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

Auto-Strain Functionality when using the ARES-G2

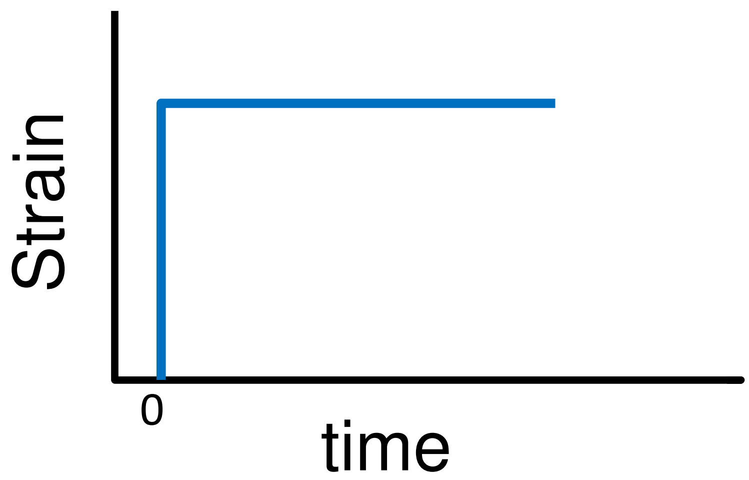
- Videos available at www.tainstruments.com under the Videos tab or on the TA tech tip channel of YouTube™ (https://www.youtube.com/user/TATechTips)

Setting up Rheological Experiments

Transient Tests

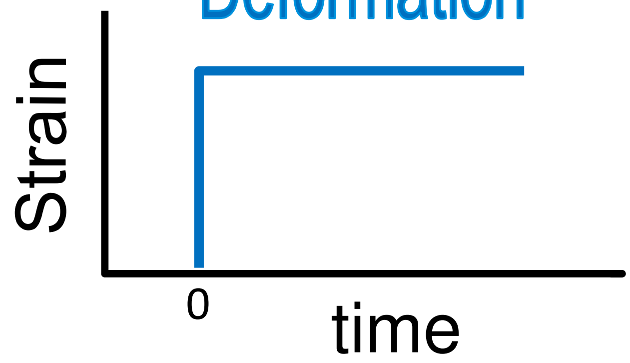
Stress Relaxation Experiment

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



Stress Relaxation Experiment

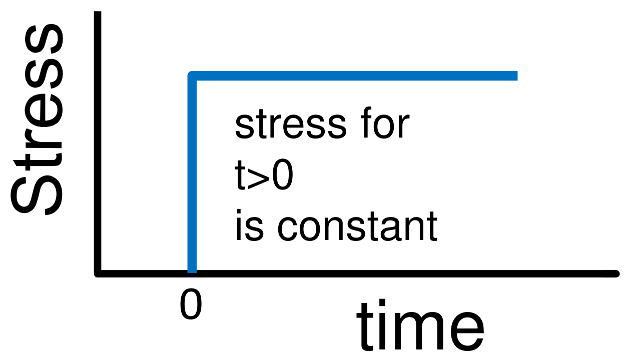
Deformation



Response of Classical Extremes

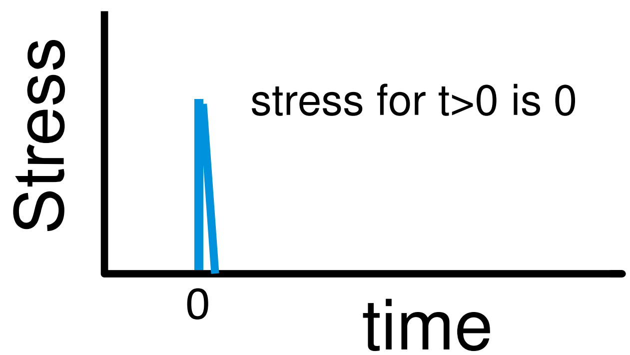
Elastic

Hookean Solid



Viscous

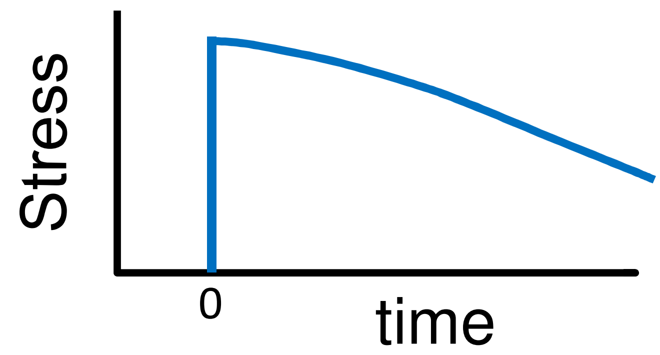
Newtonian Fluid



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)

$$G(t) = \sigma(t)/\gamma$$

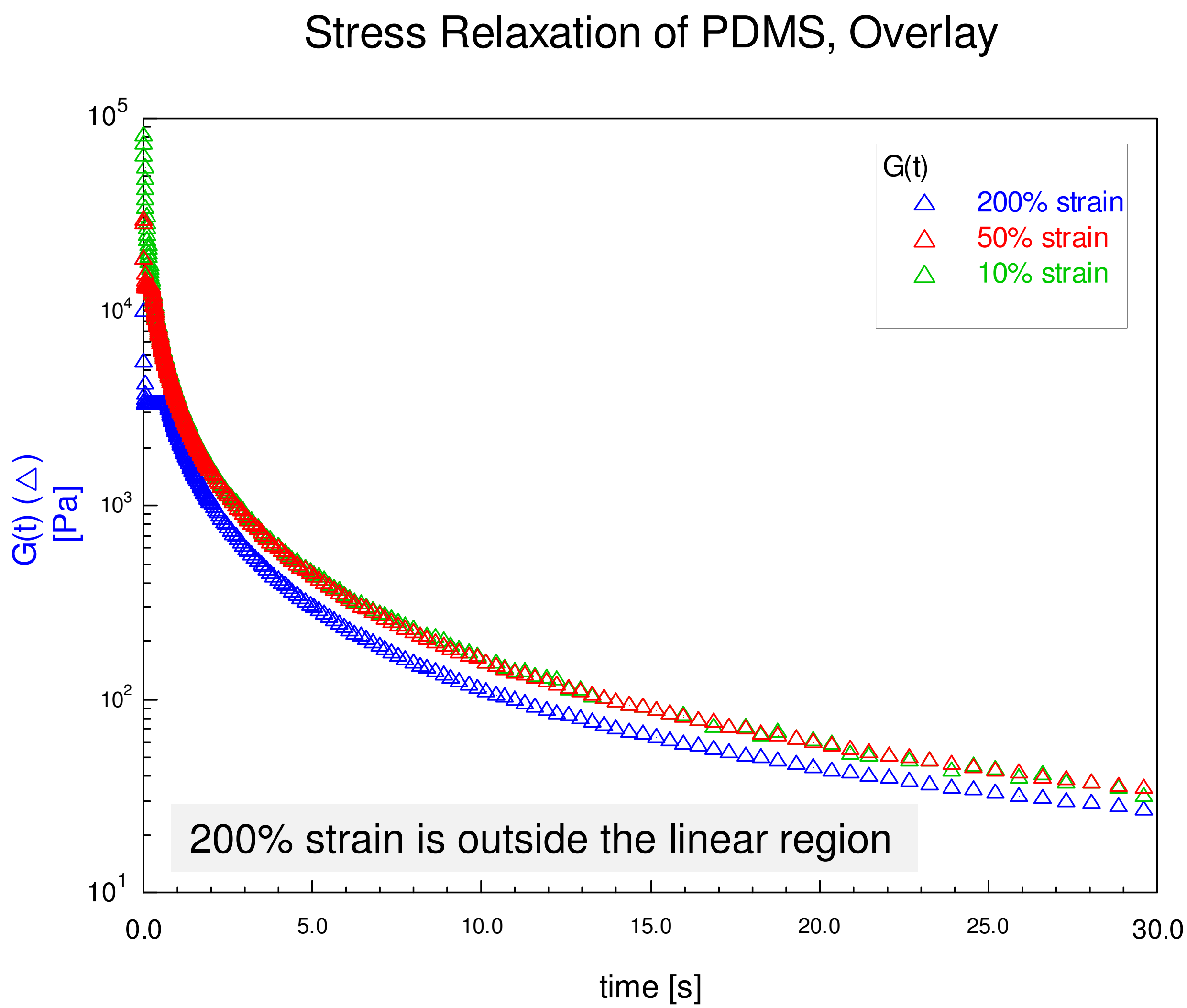
Determining Strain For Stress Relaxation

- **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.

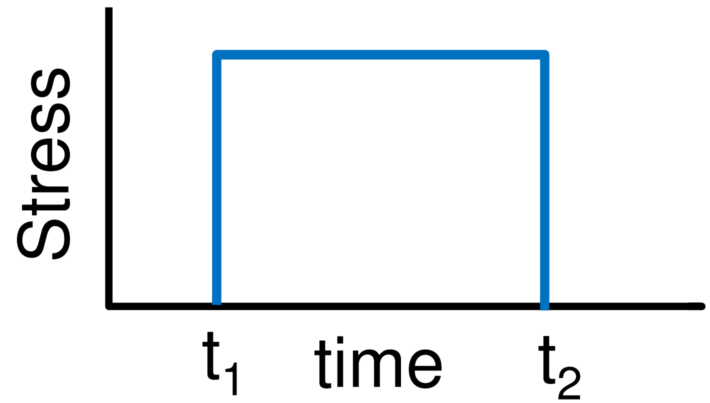
$$\gamma = K_\gamma \times \theta \quad (\%\gamma = \gamma \times 100)$$

Stress Relaxation and Linear Region



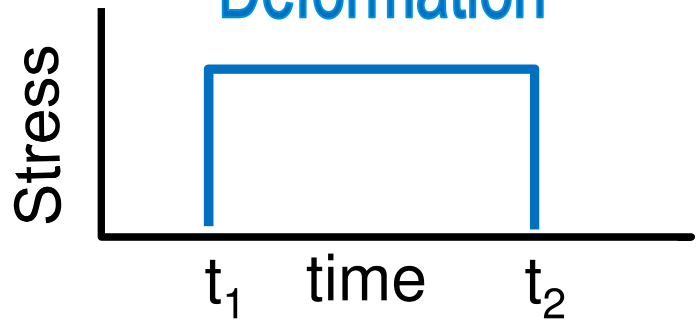
Creep Recovery Experiment

- 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

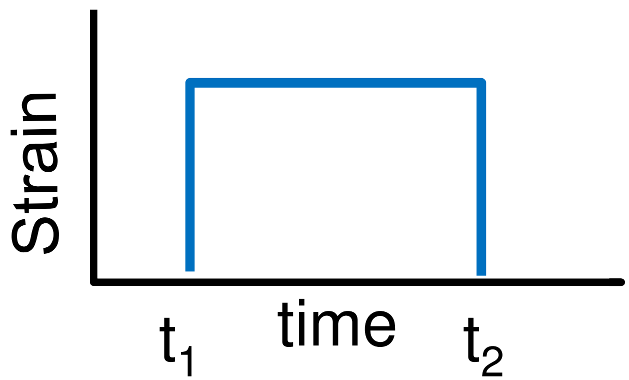
Deformation



Response of Classical Extremes

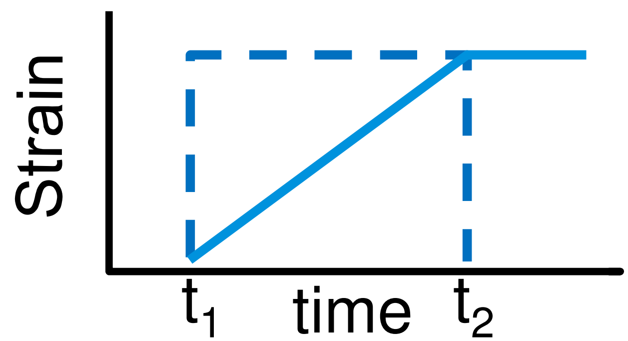
Elastic

- Stain for t>t1 is constant
- Strain for t >t2 is 0

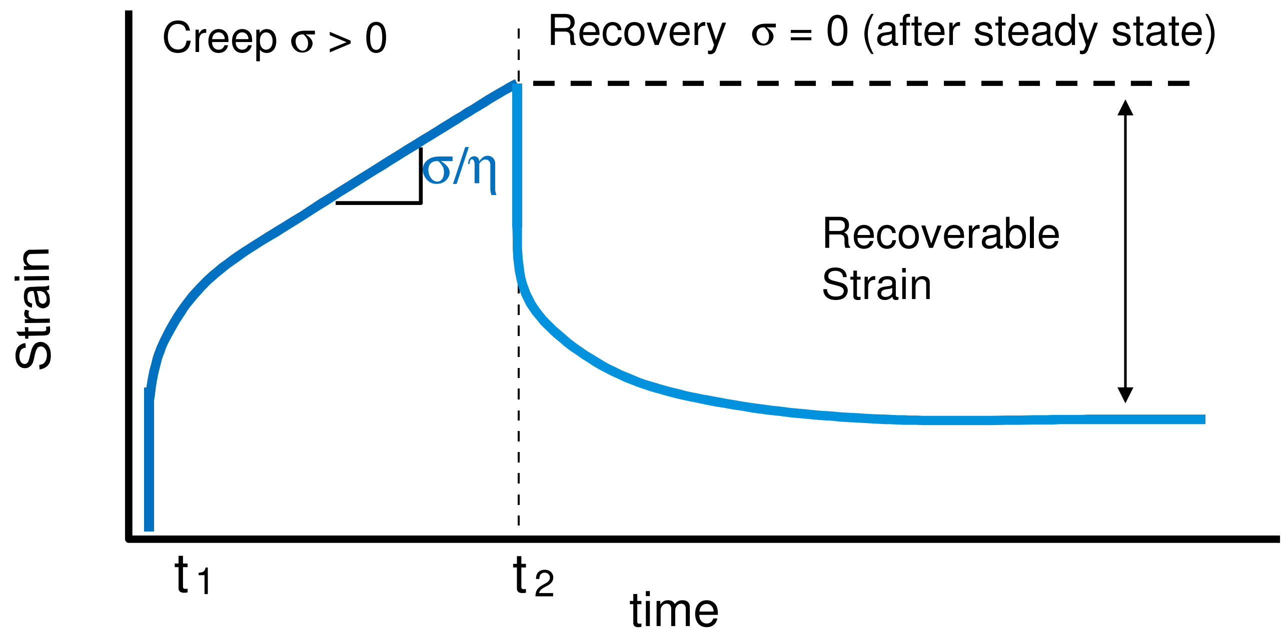


Viscous

- Stain rate for t>t1 is constant
- Strain for t>t1 increase with time
- Strain rate for t >t2 is 0



Creep Recovery: Response of Viscoelastic Material

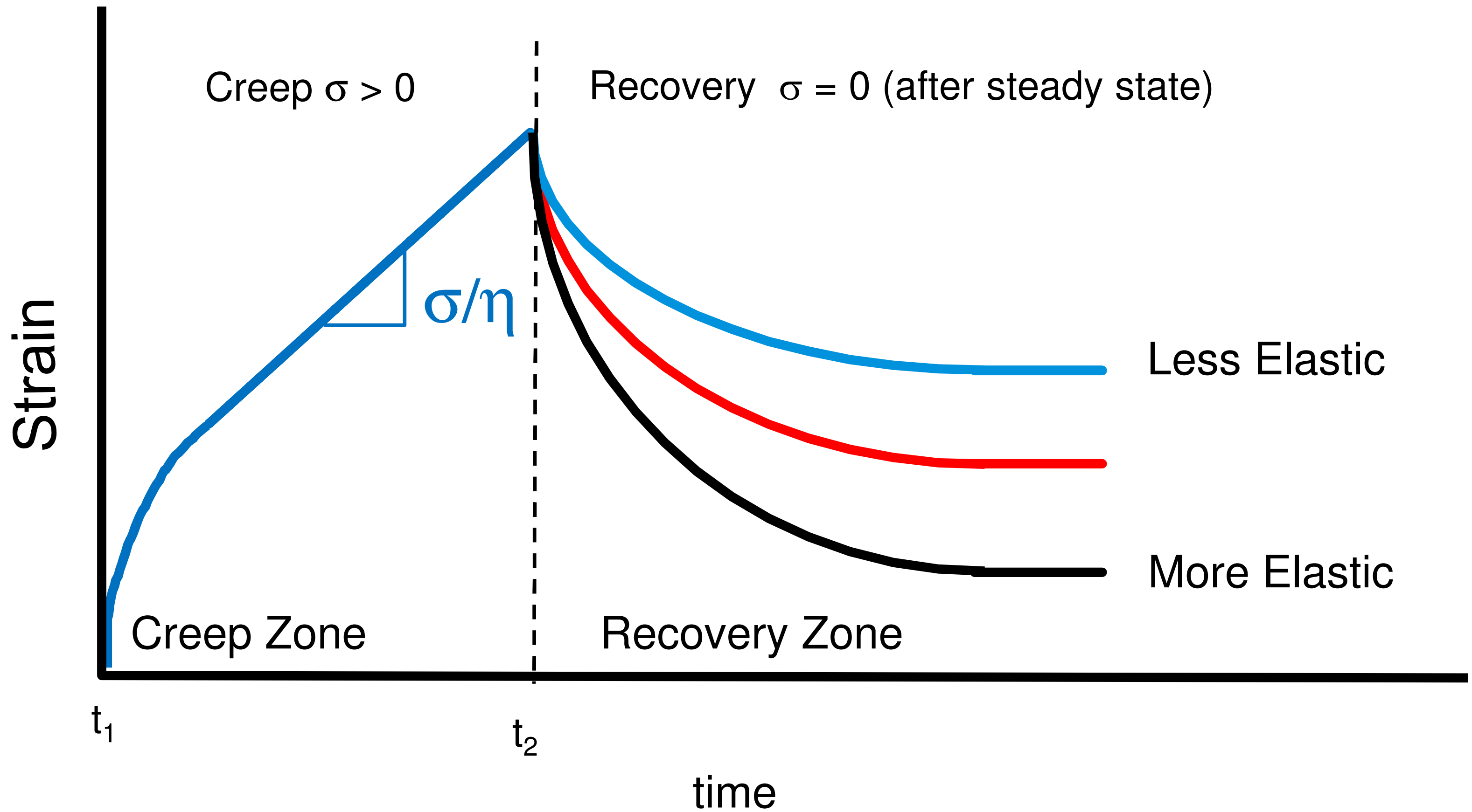


Strain rate decreases with time in the creep zone, until finally reaching a steady state.

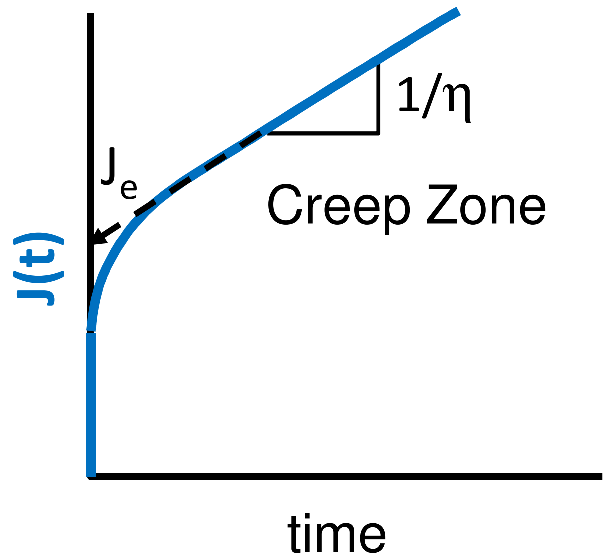
In the recovery zone, the viscoelastic fluid recoils, eventually reaching a equilibrium at some small total strain relative to the strain at unloading.

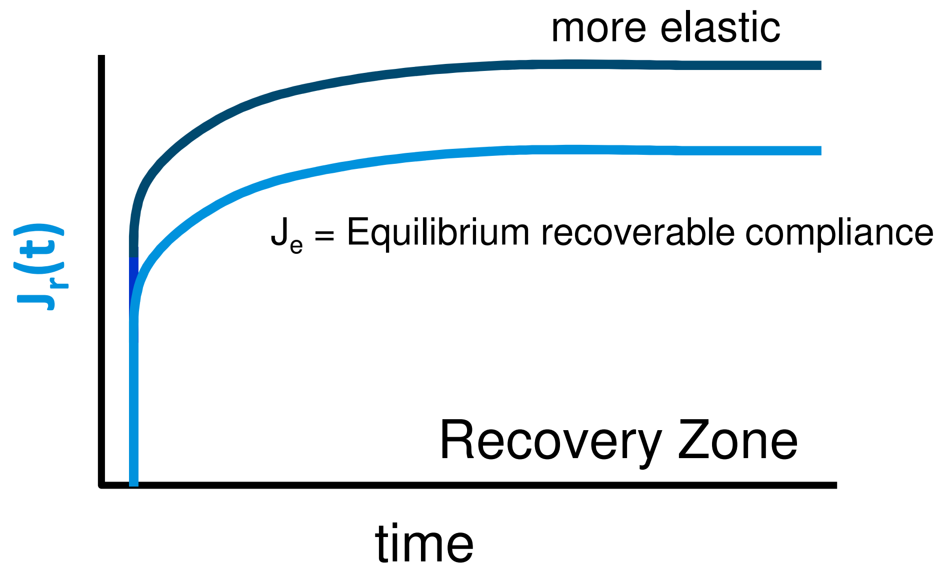
Mark, J., et. al., Physical Properties of Polymers, American Chemical Society, 1984, p. 102.

Creep Recovery Experiment



Creep Recovery : Creep and Recoverable Compliance





<u>Creep Compliance</u>

$$J(t) = \frac{\gamma(t)}{\sigma}$$

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

<u>Recoverable Compliance</u>

$$J_r(t) = \frac{[\gamma_u - \gamma(t)]}{\sigma}$$

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

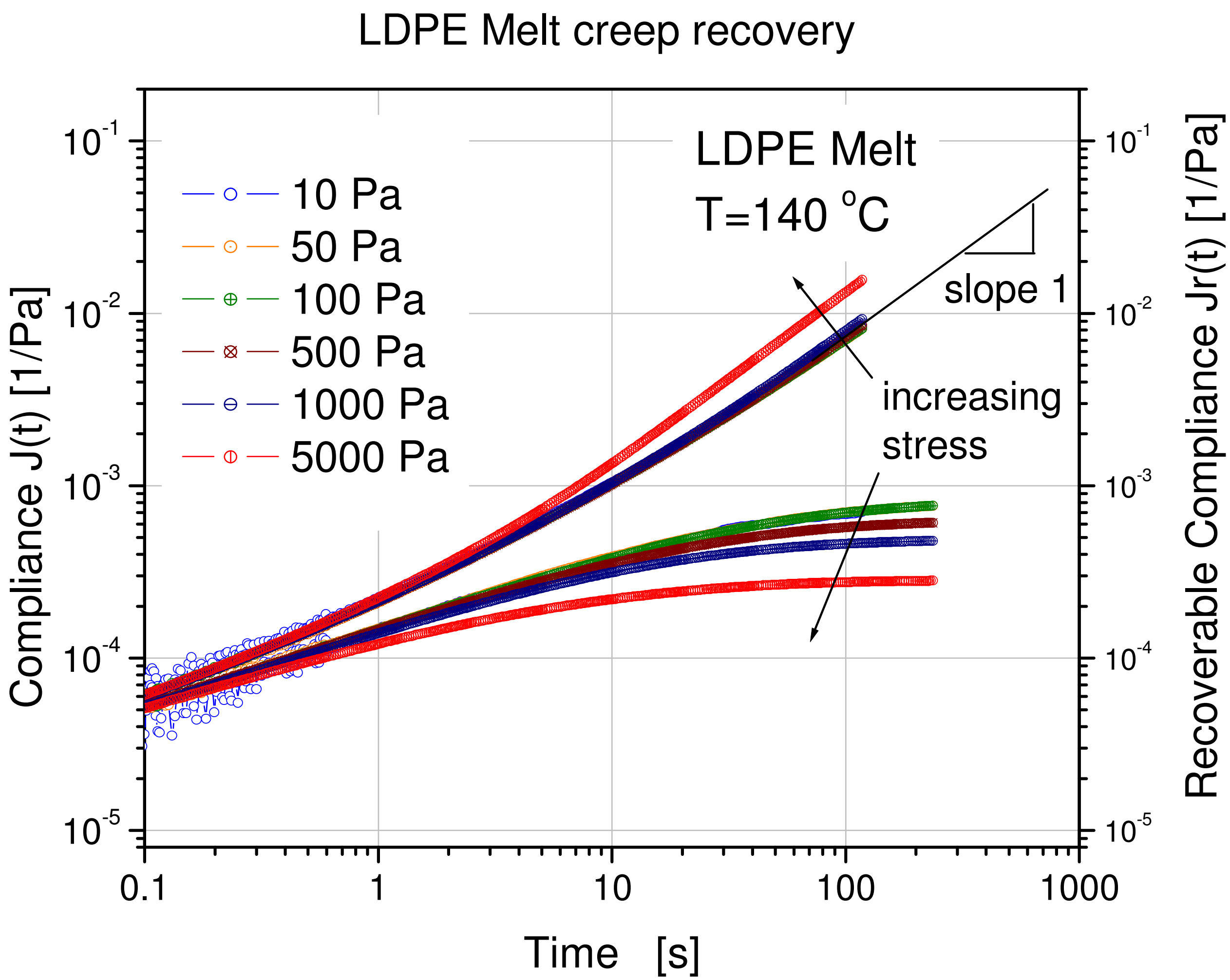
Mark, J., et. al., <u>Physical Properties of Polymers</u>, American Chemical Society, 1984, p. 102.

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 questions 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 calculated this for you.

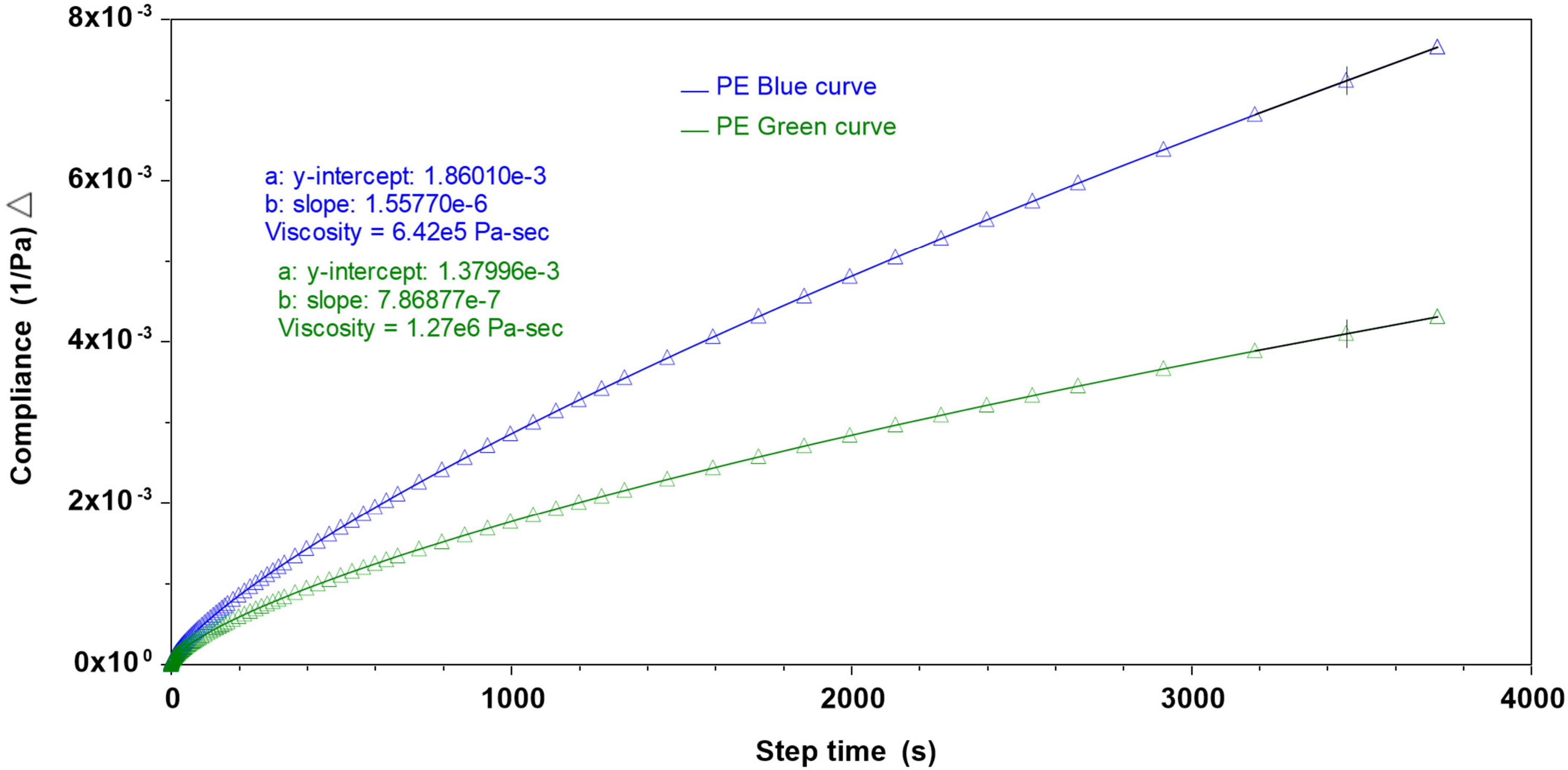
$$\sigma = K_{\sigma} \text{ x } M$$

Creep and Recovery with Increasing Stress



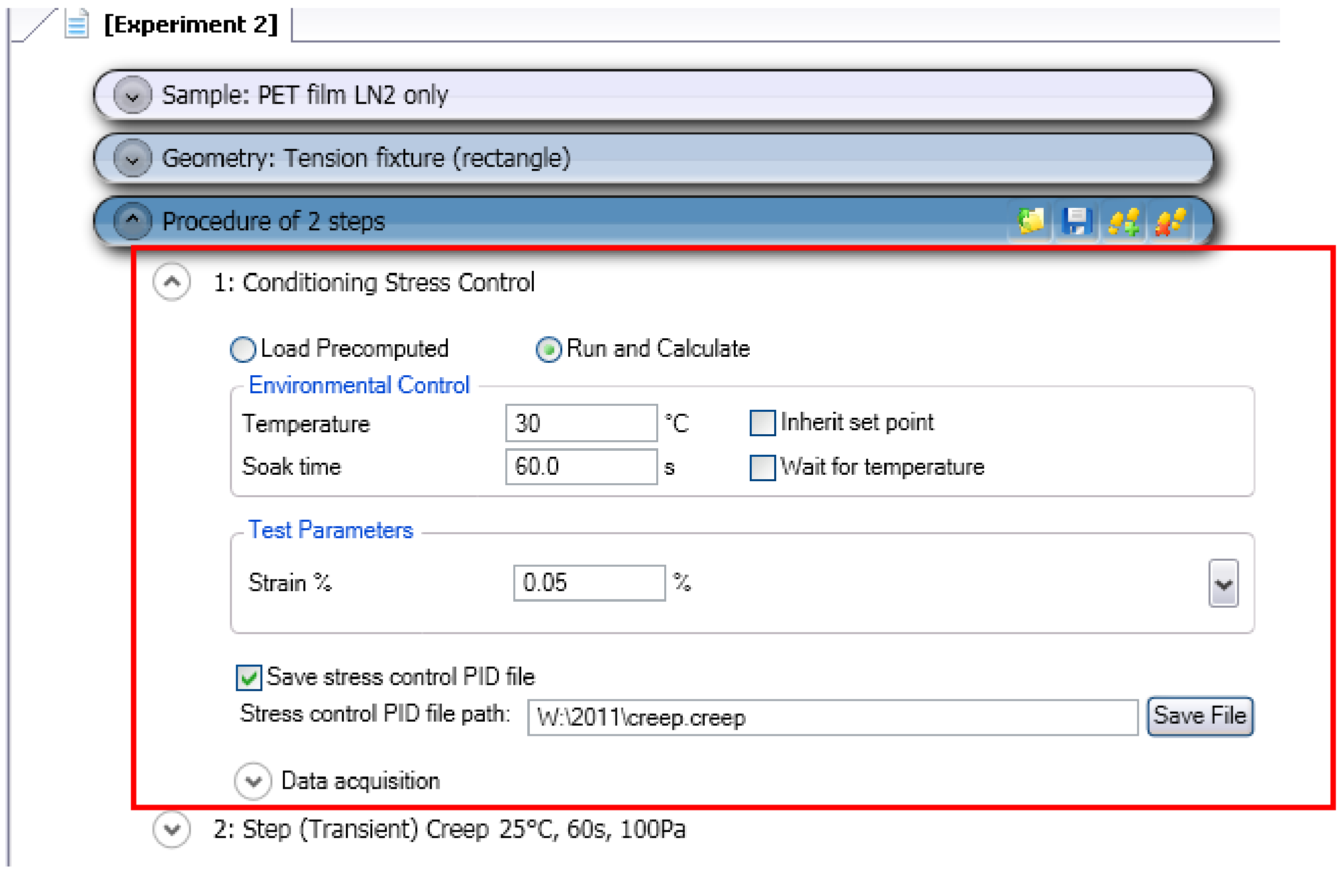
Non linear effects can be detected in recovery before they are seen in the creep (viscosity dominates)

Creep Testing for Zero Shear Viscosity



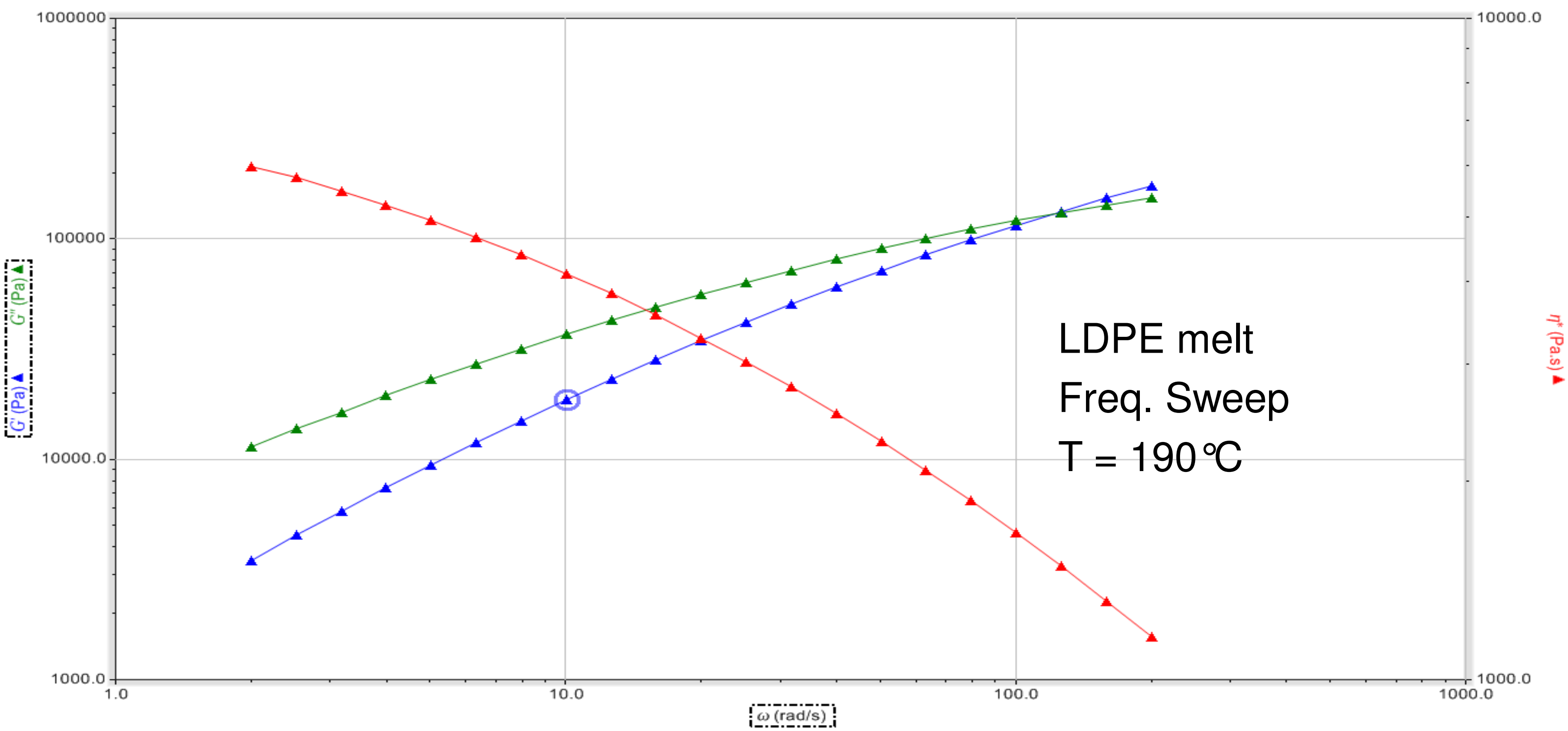
Programming Creep on an ARES-G2

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



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



Applications of Rheology

Polymers

Purpose of a Rheological Measurement

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", η^*
    - 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
  - Controling the environment

Loading Polymer Pellet Samples

Set Environmental System to test temperature

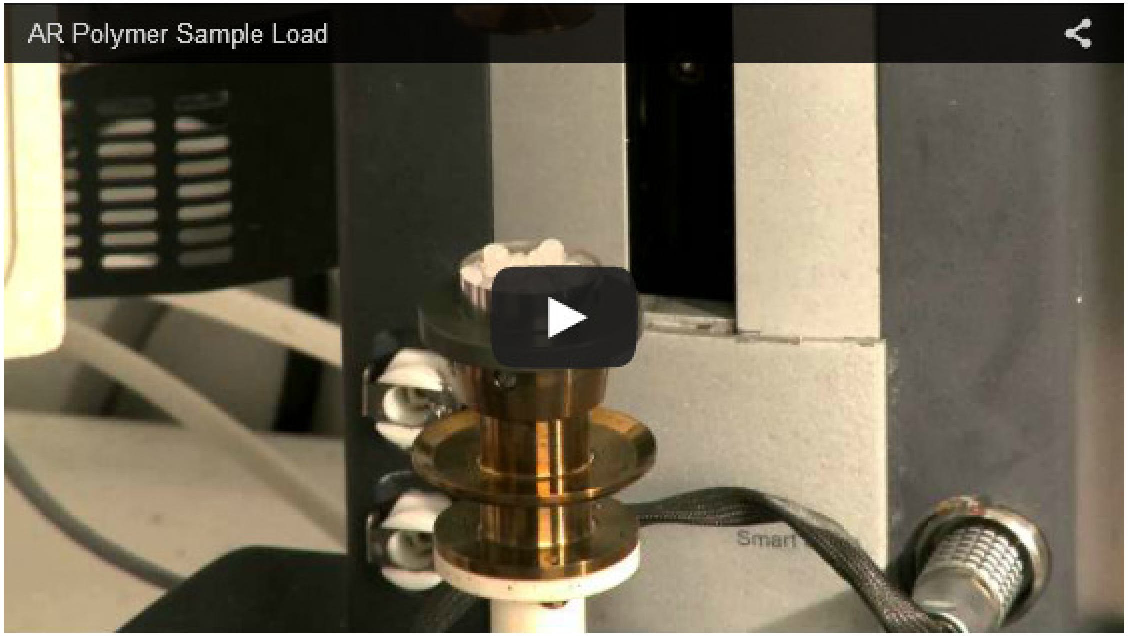
Mount melt ring onto the lower plate and load pellets

Bring the upper plate close to top of melt ring and close the oven

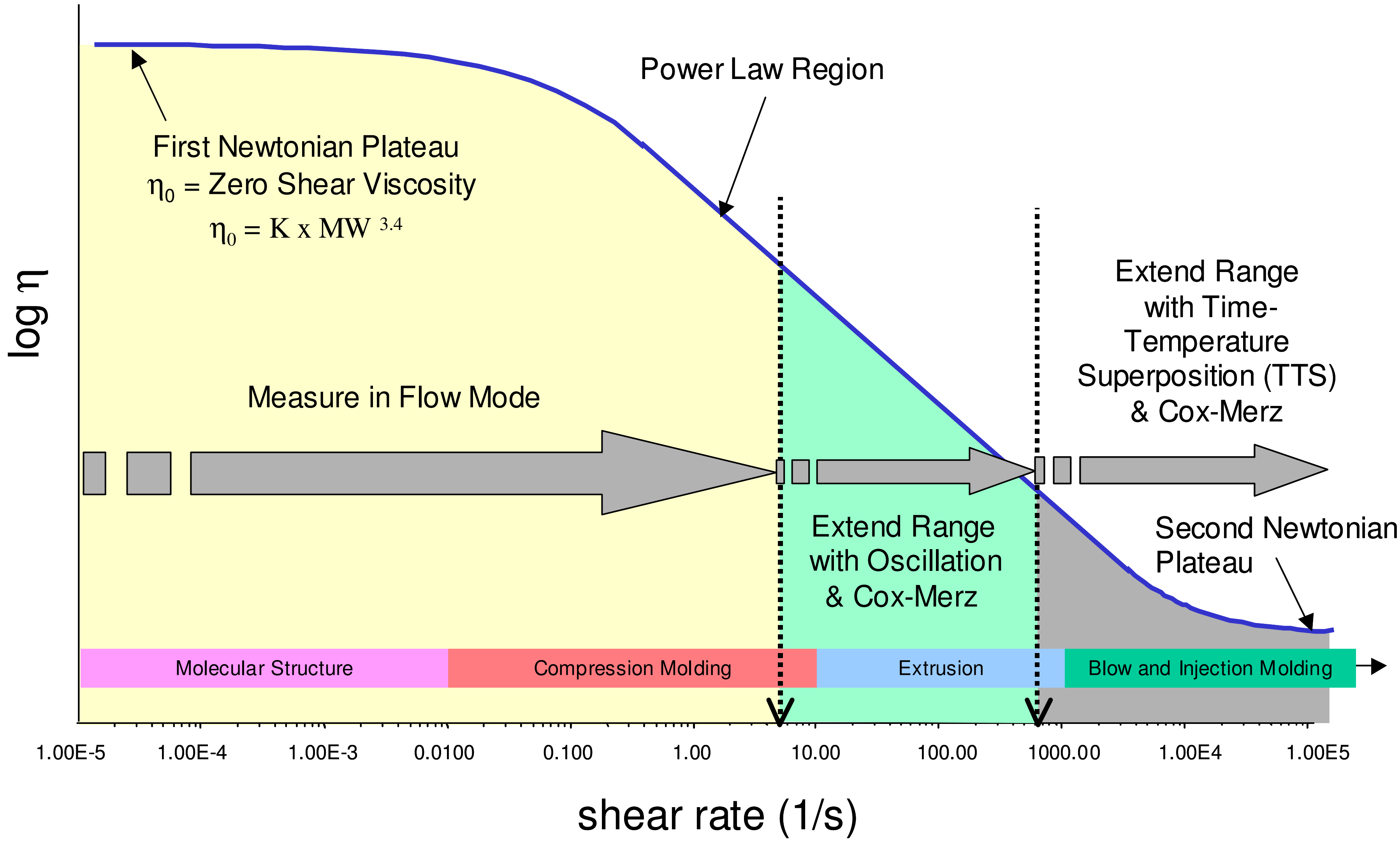
After few minutes, open the oven, remove melt ring and go to trim gap

After sample relaxes, open the oven and trim excess sample

Close the oven and adjust gap to geometry/test gap

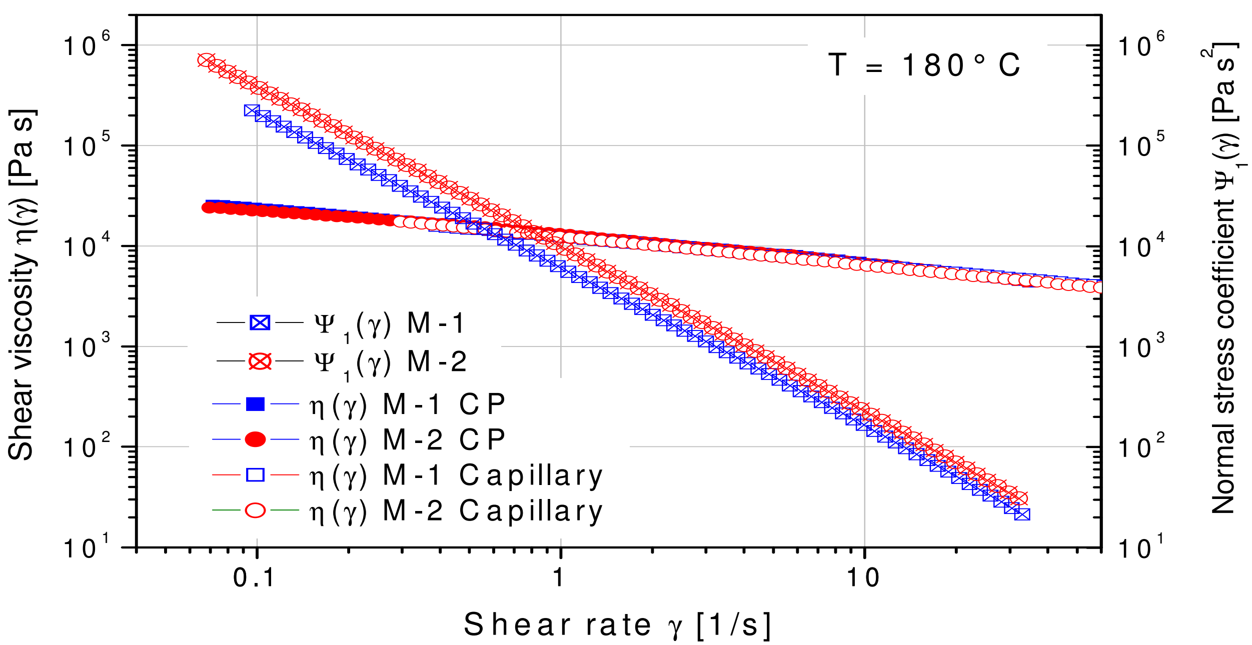


Idealized Flow Curve – Polymer Melts



Effect of HDPE Variations in Blow Molding

Blow Molding Polyethylene



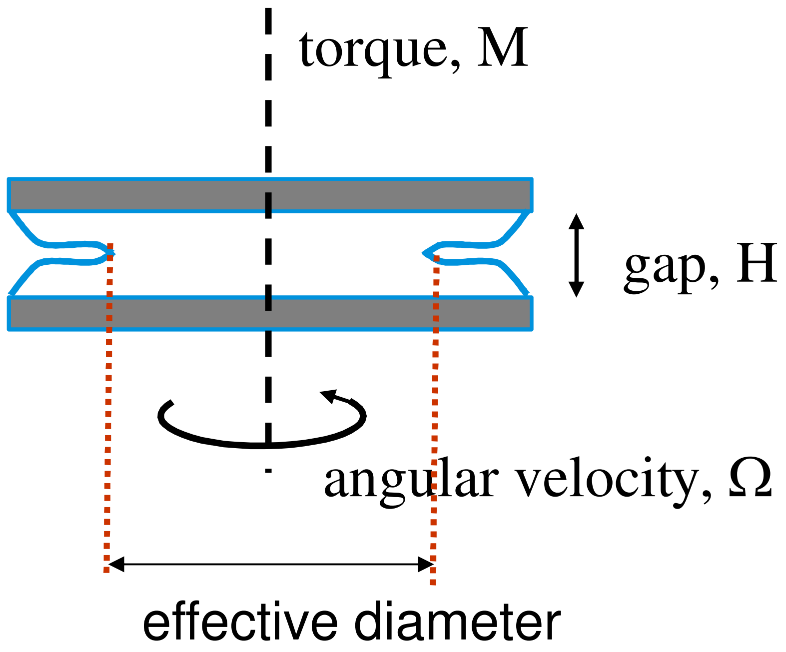
Parameter	Sample	
	M-1	M-2
MFI	0.6	0.5
GPC-M_W	131K	133K
Viscosity at 1 sec^{-1}	8.4K	8.3K
Die Swell	28	42

No differences in MFI, Viscosity, or GPC!

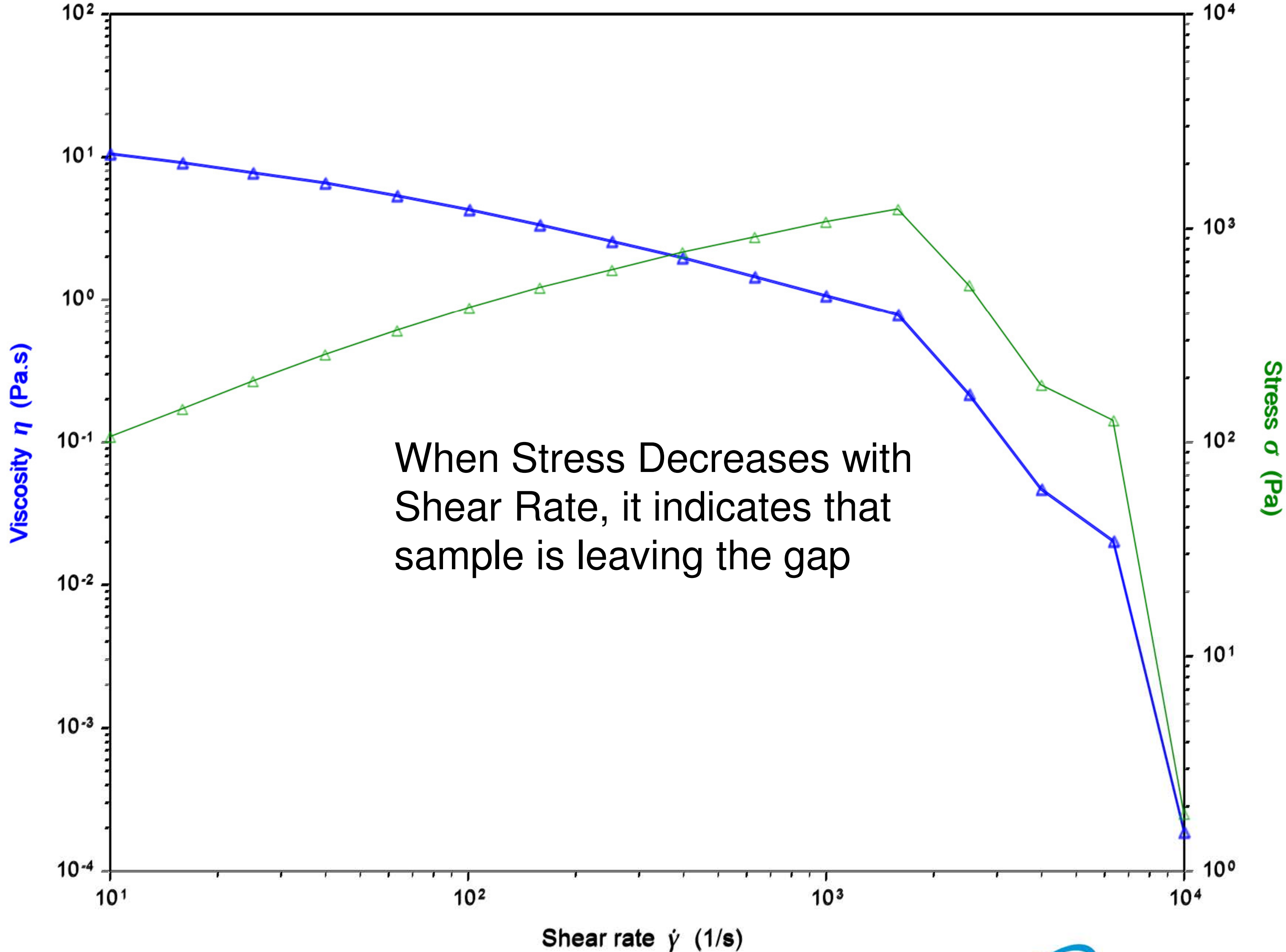
M-2 produces heavier bottles in blow molding due to increased parison swell

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



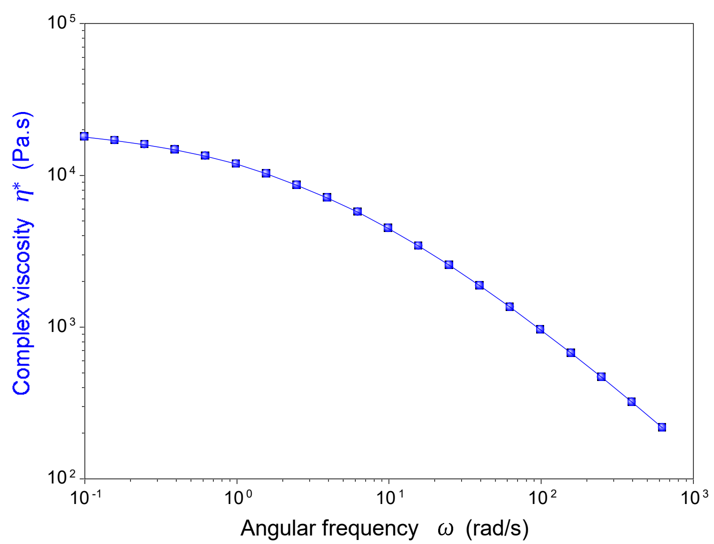
Shear Thinning or Sample Instability?



The Cox-Merz Rule

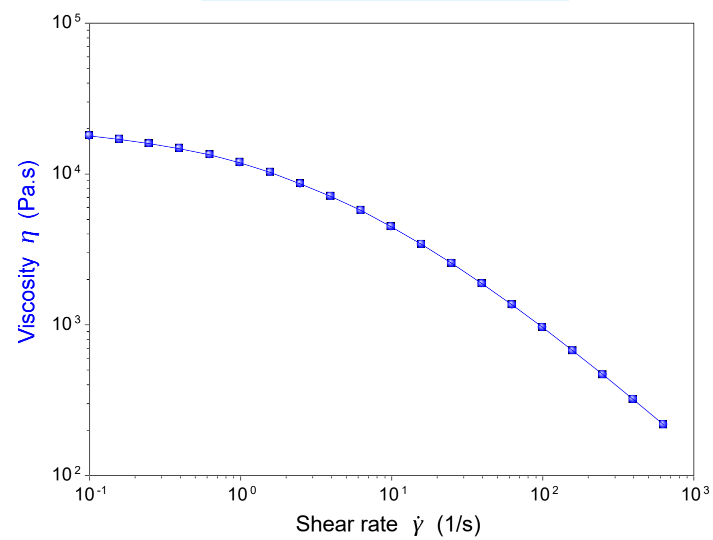
- For materials that exhibit wall slip or edge fracture, one alternative way to obtain viscosity information over shear is to use the Cox-Merz rule
- Cox-Merz “rule” is an empirical relationship. It was observed that in many polymeric systems, the steady shear viscosity plotted against shear rate is correlated with the complex viscosity plotted against frequency

Dynamic frequency sweep



η^* (Pa.s)~ ω (rad/s)

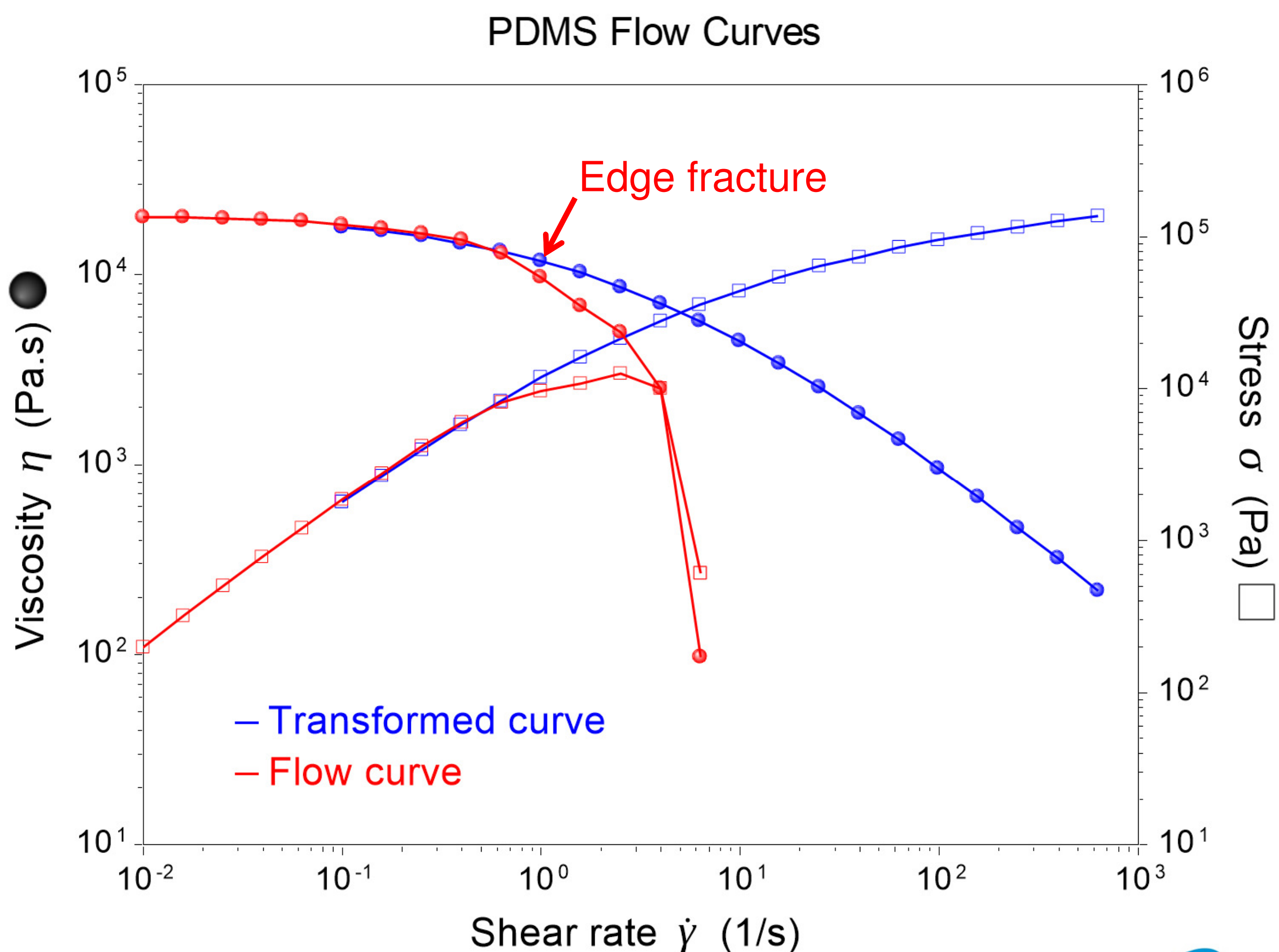
Steady state flow



η (Pa.s)~ $\dot{\gamma}$ (1/s)

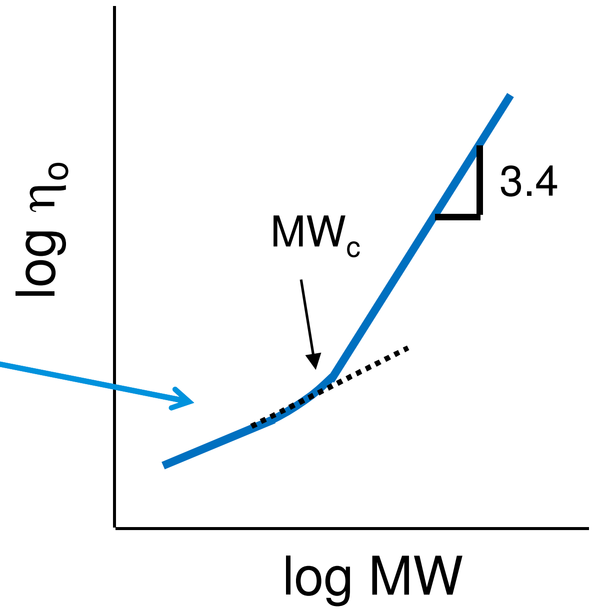
Cox-Merz Transformation Benefit

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



Melt Rheology: MW Effect on Zero Shear Viscosity

- Sensitive to Molecular Weight, MW
- For Low MW (no Entanglements) η_0 is proportional to MW
- For MW > Critical MW_c, η_0 is proportional to $MW^{3.4}$



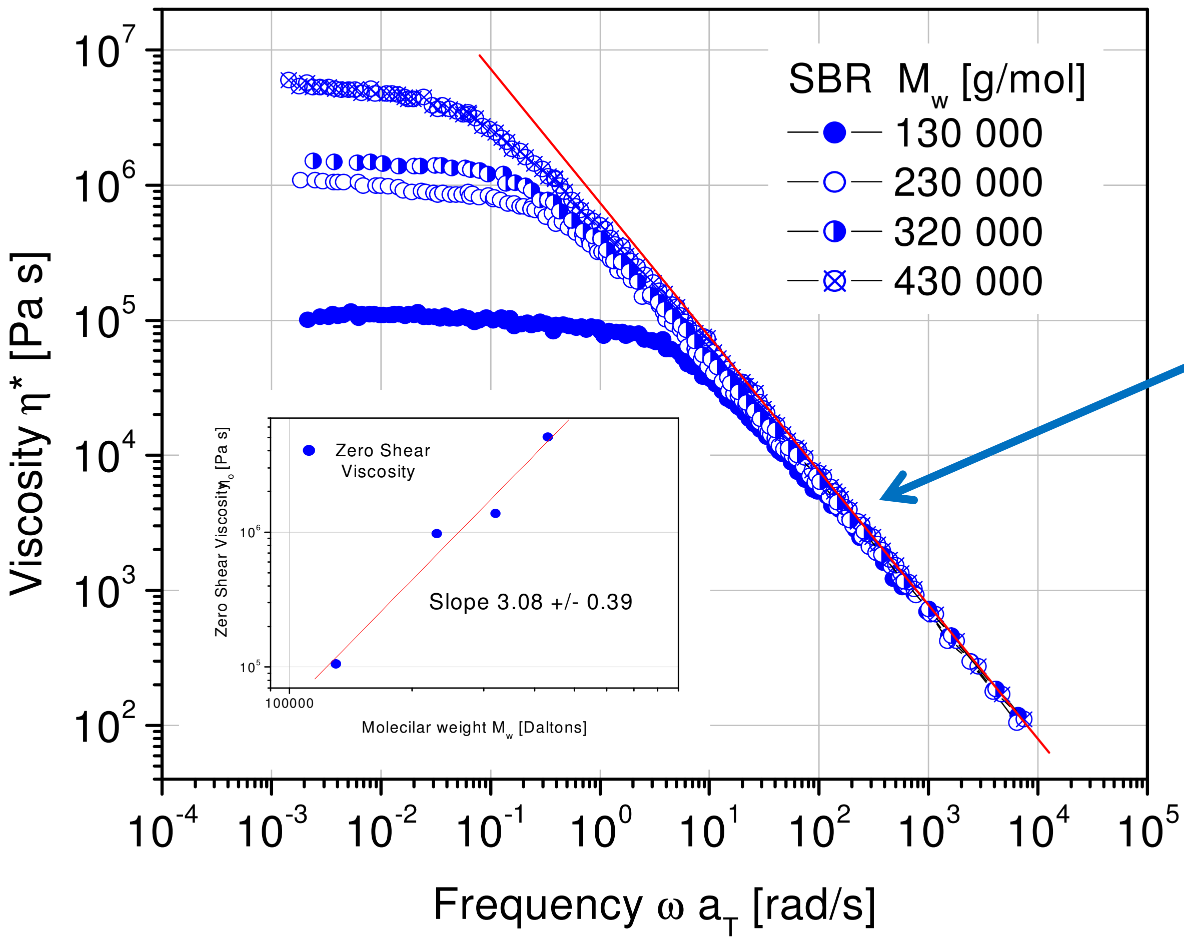
$\eta_0 = K{\cdot}Mw$

$\eta_0 = K{\cdot}Mw^{3.4}$

Ref. Graessley, Physical Properties of Polymers, ACS, c 1984.

Influence of MW on Viscosity

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



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

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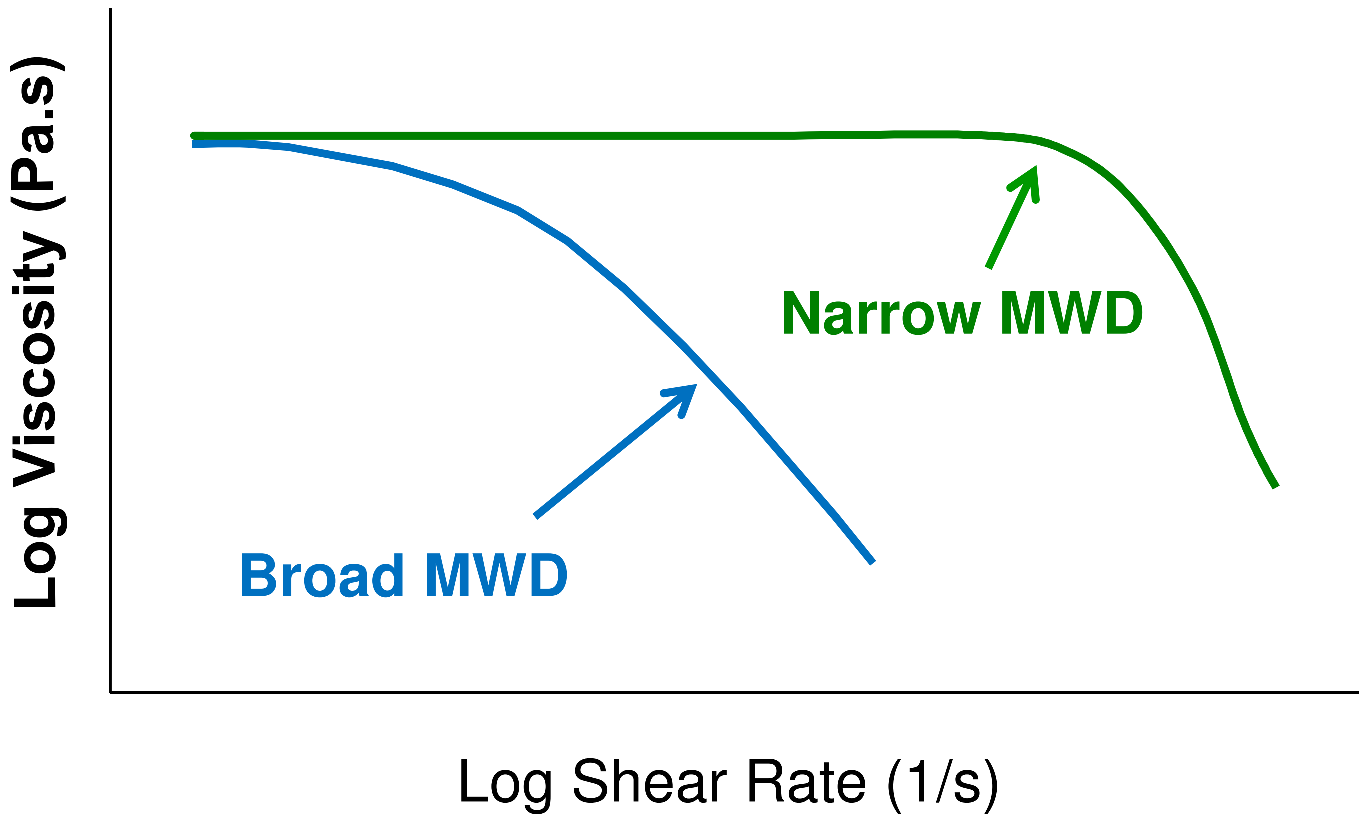
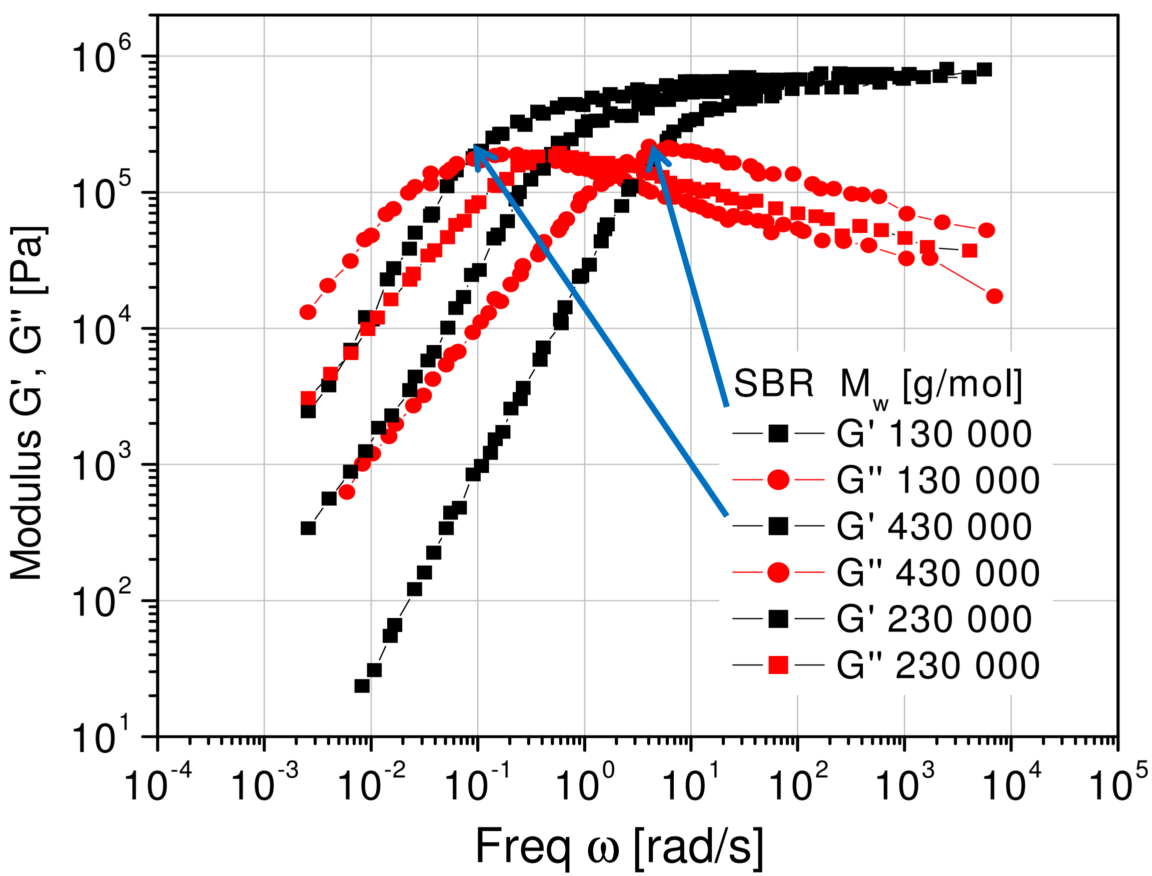
Influence of MWD on Viscosity

- A Polymer with a broad MWD exhibits non-Newtonian flow at a lower rate of shear than a polymer with the same η_0, but has a narrow MWD.

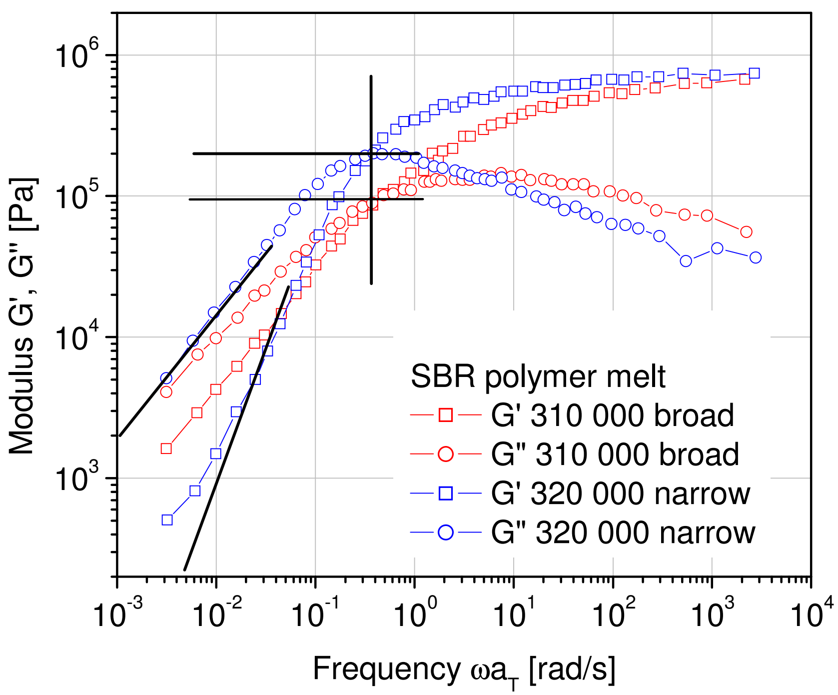


Influence of MW on G‘ and G“

The G‘ and G“ curves are shifted to lower frequency with increasing molecular weight.



Influence of MWD on G‘ and G“

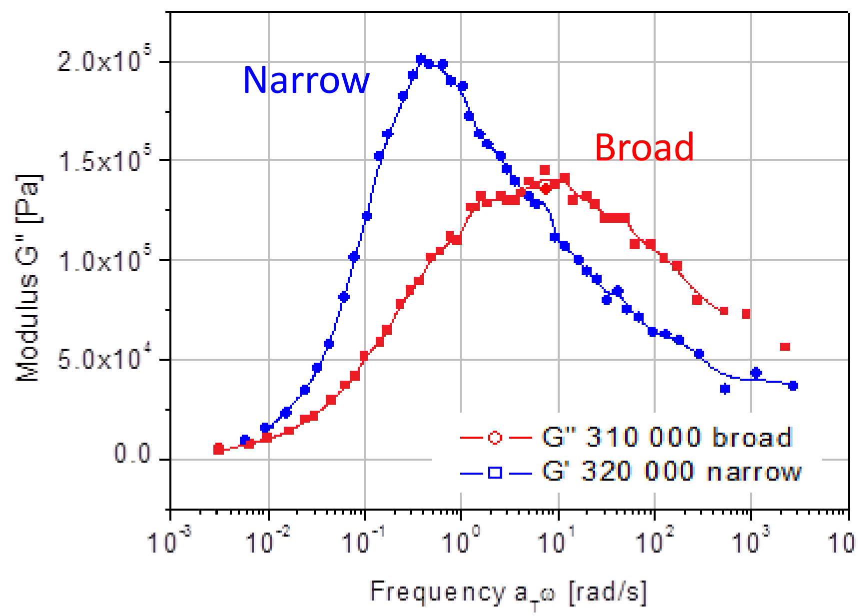


- The maximum in G“ is a good indicator of the broadness of the distribution

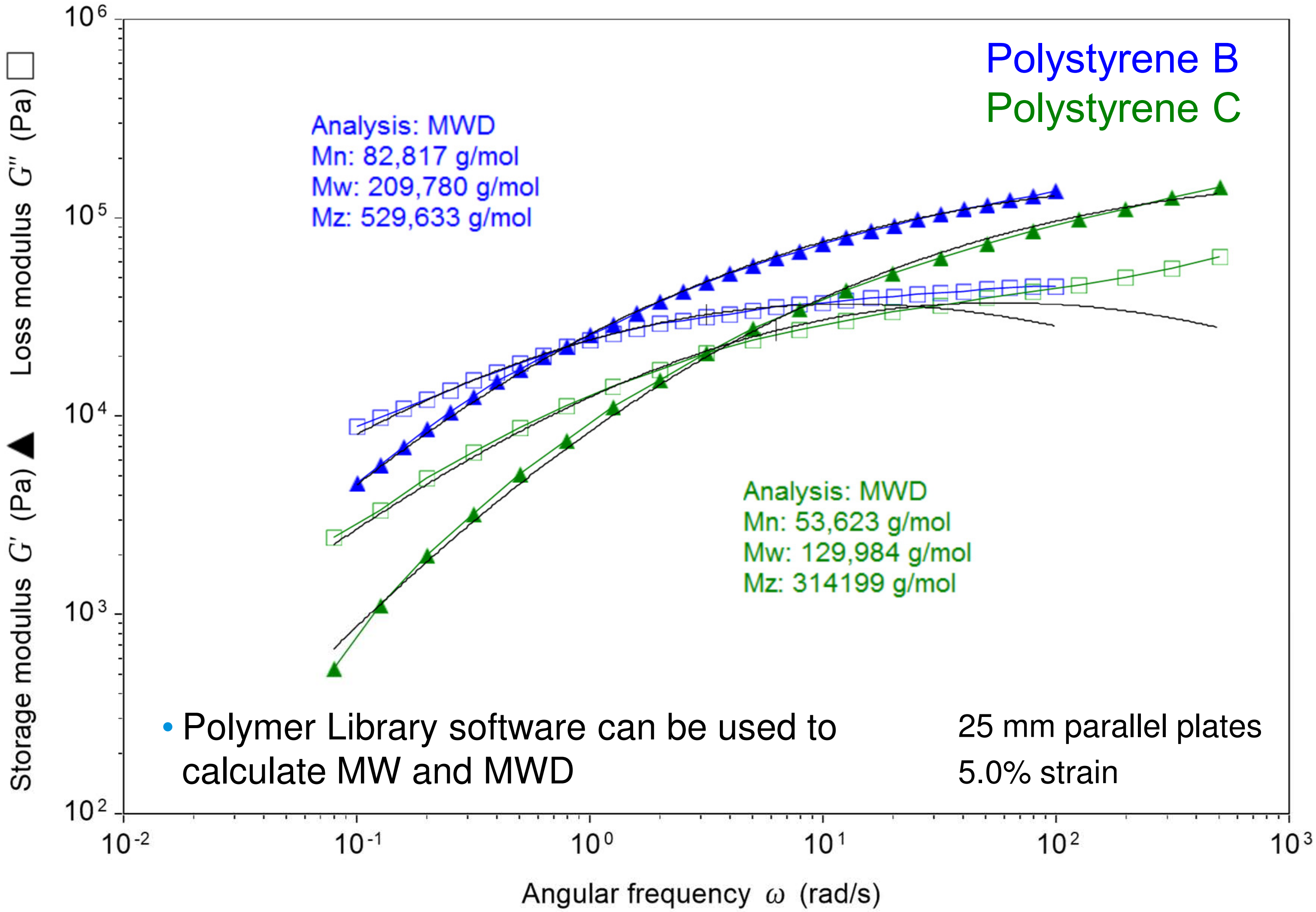
Higher crossover frequency : lower M_w

Higher crossover Modulus: narrower MWD

(note also the slope of G” at low frequencies – narrow MWD steeper slope)



Frequency sweep – polymer melt (ASTM D4440)

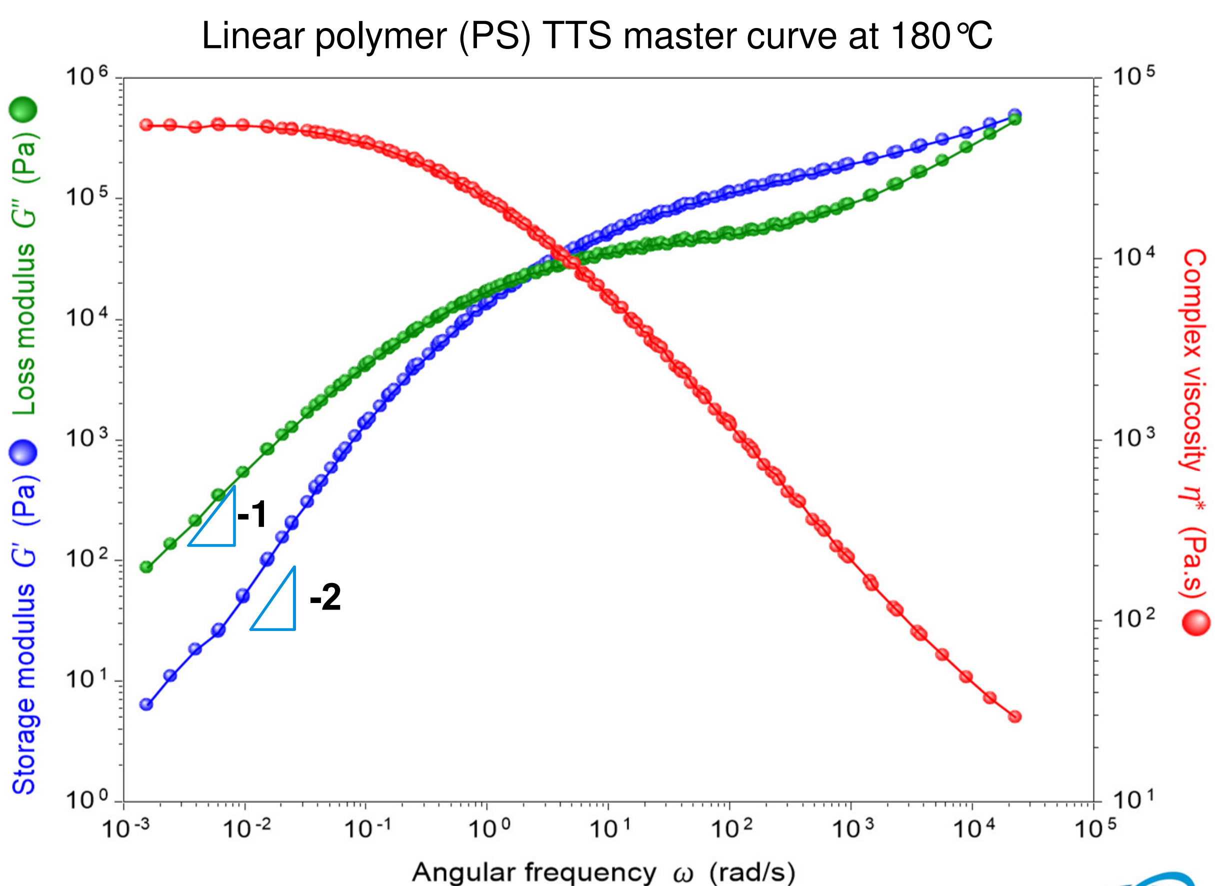


- Polymer Library software can be used to calculate MW and MWD

[João Maia: The Role of Interfacial Elasticity on the Rheological Behavior of Polymer Blends]
[Chris Macosko: Analyzing Molecular Weight Distribution w/ Rheology]

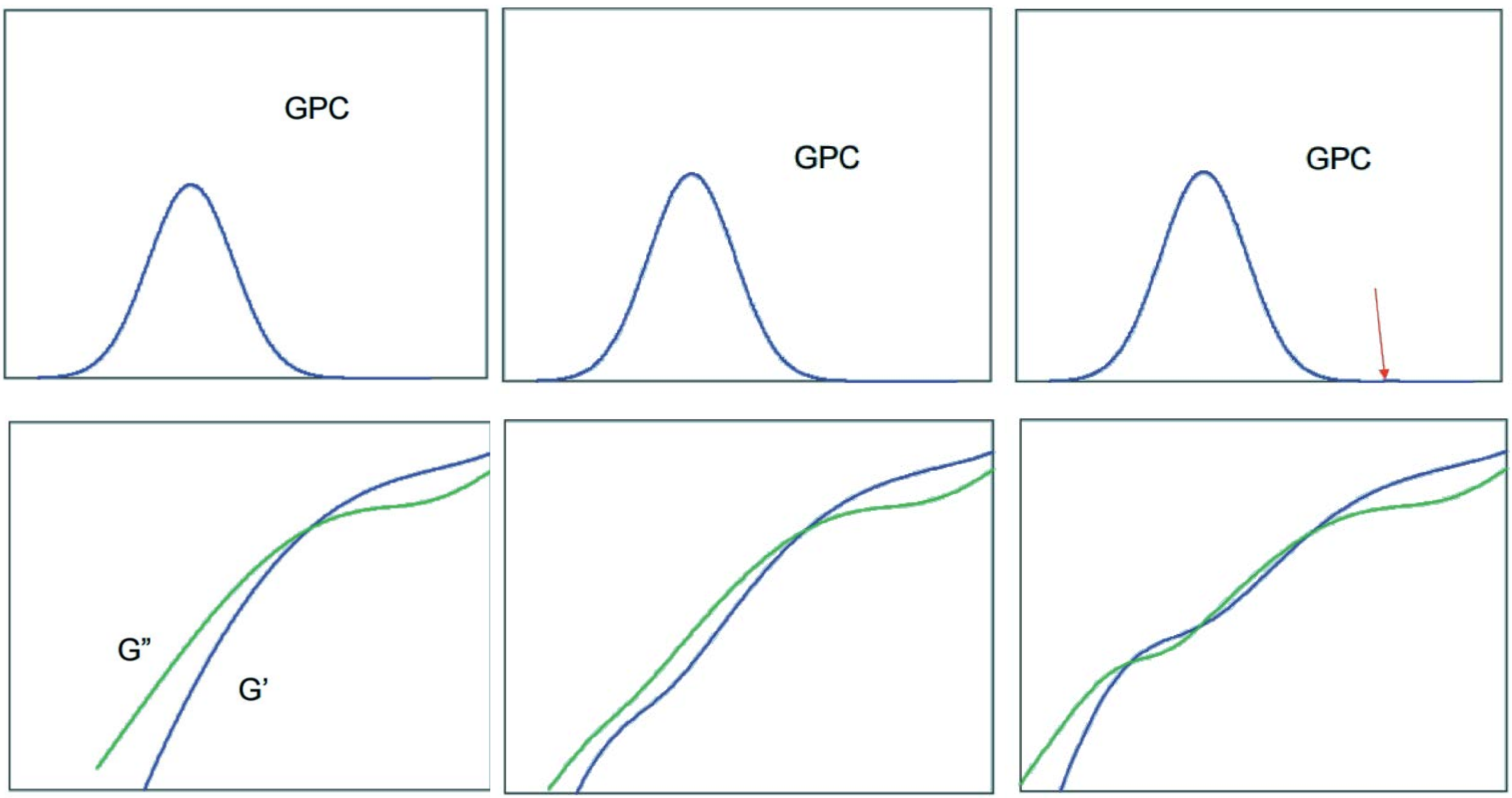
Frequency Sweep-Terminal Regime

- 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



High MW Contributions

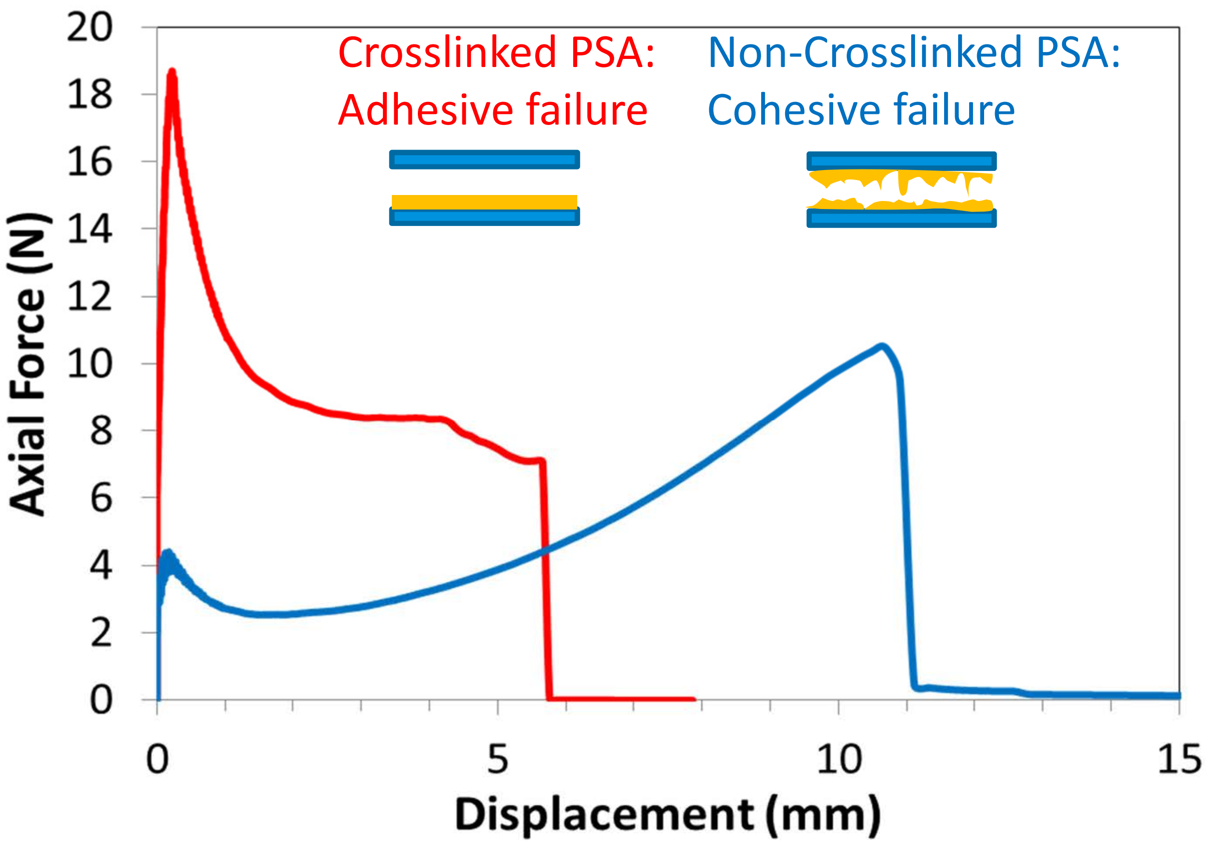
400,000 g/mol PS	400,000 g/mol PS + 1% 12,000,000 g/mol	400,000 g/mol PS + 4% 12,000,000 g/mol

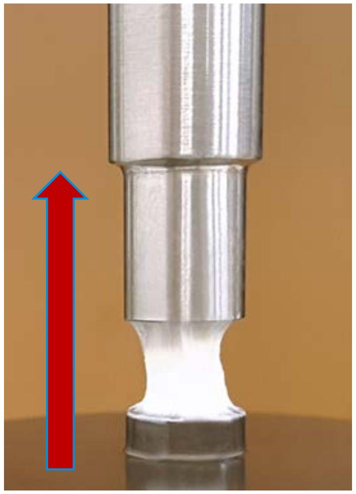


Macosko, TA Instruments Users' Meeting, 2015

Adhesive Tack Testing

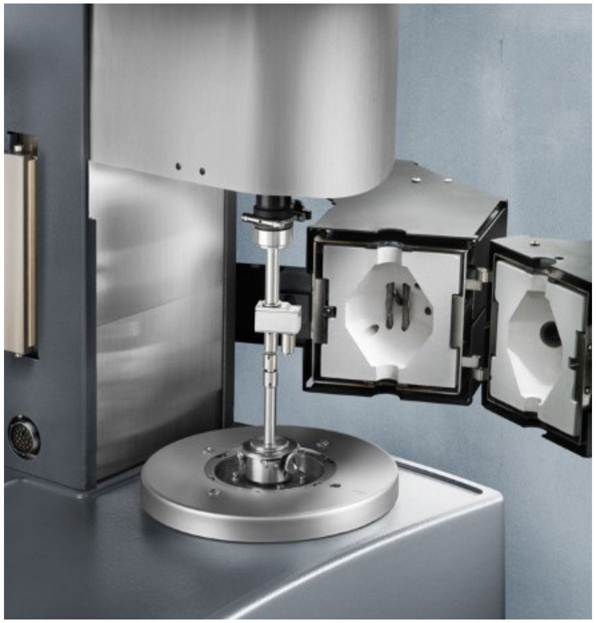
- Tack testing method: ASTM D2979
- Use 8mm parallel plate, axial tensile at 0.1mm/sec
- The maximum force required to pull the plate away is defined as the sample's tackiness.

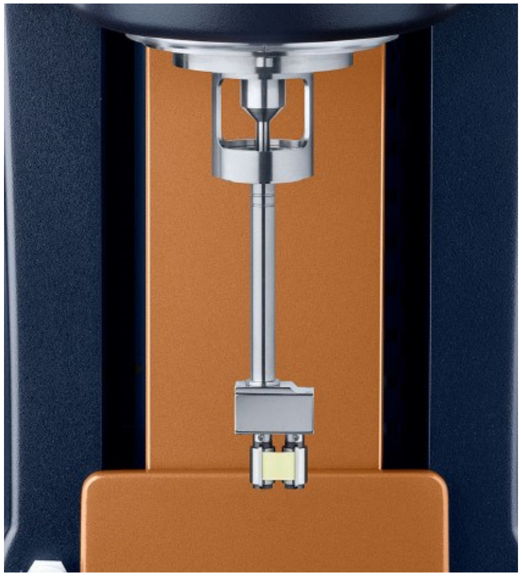




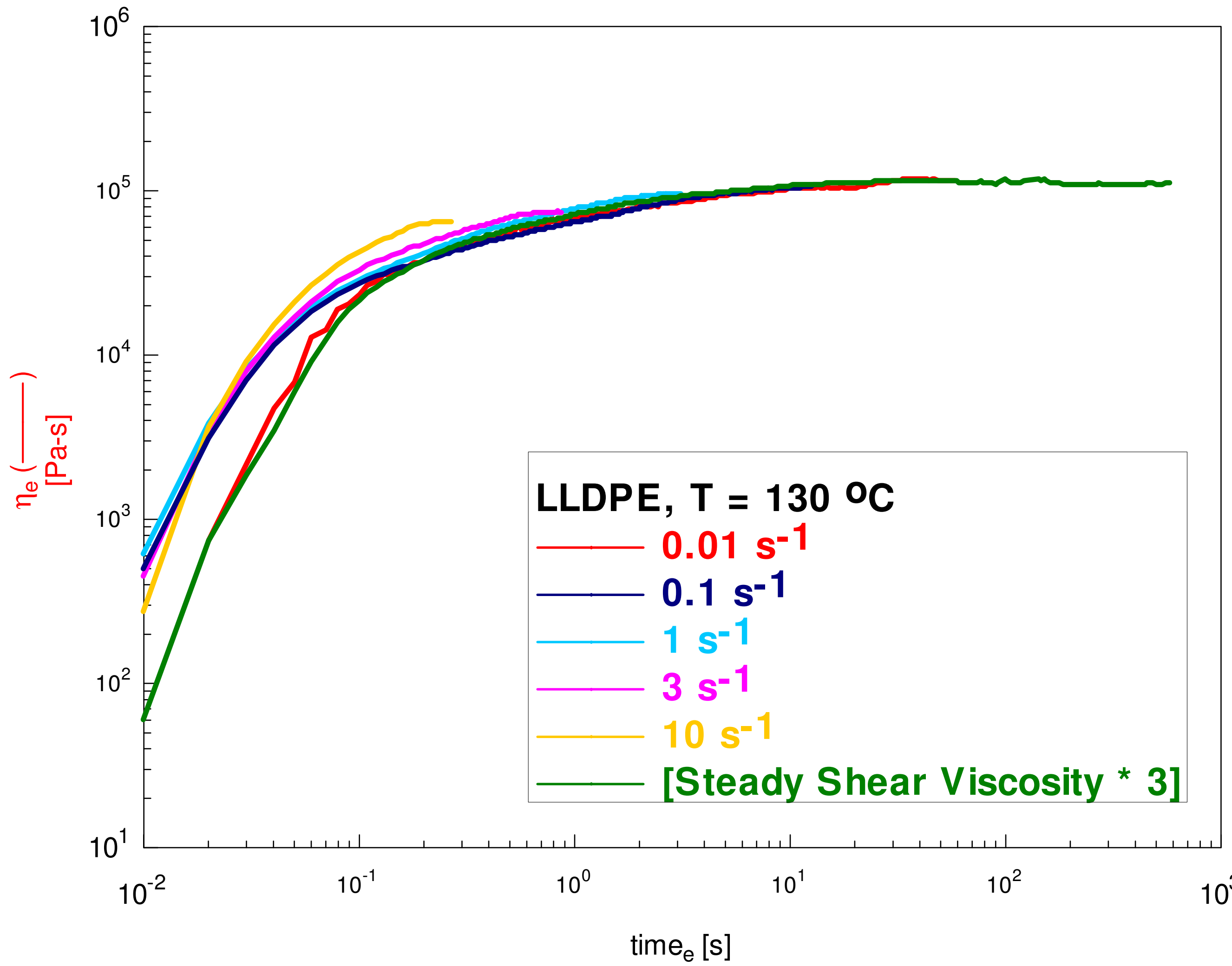
Extensional Viscosity Measurements

- 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

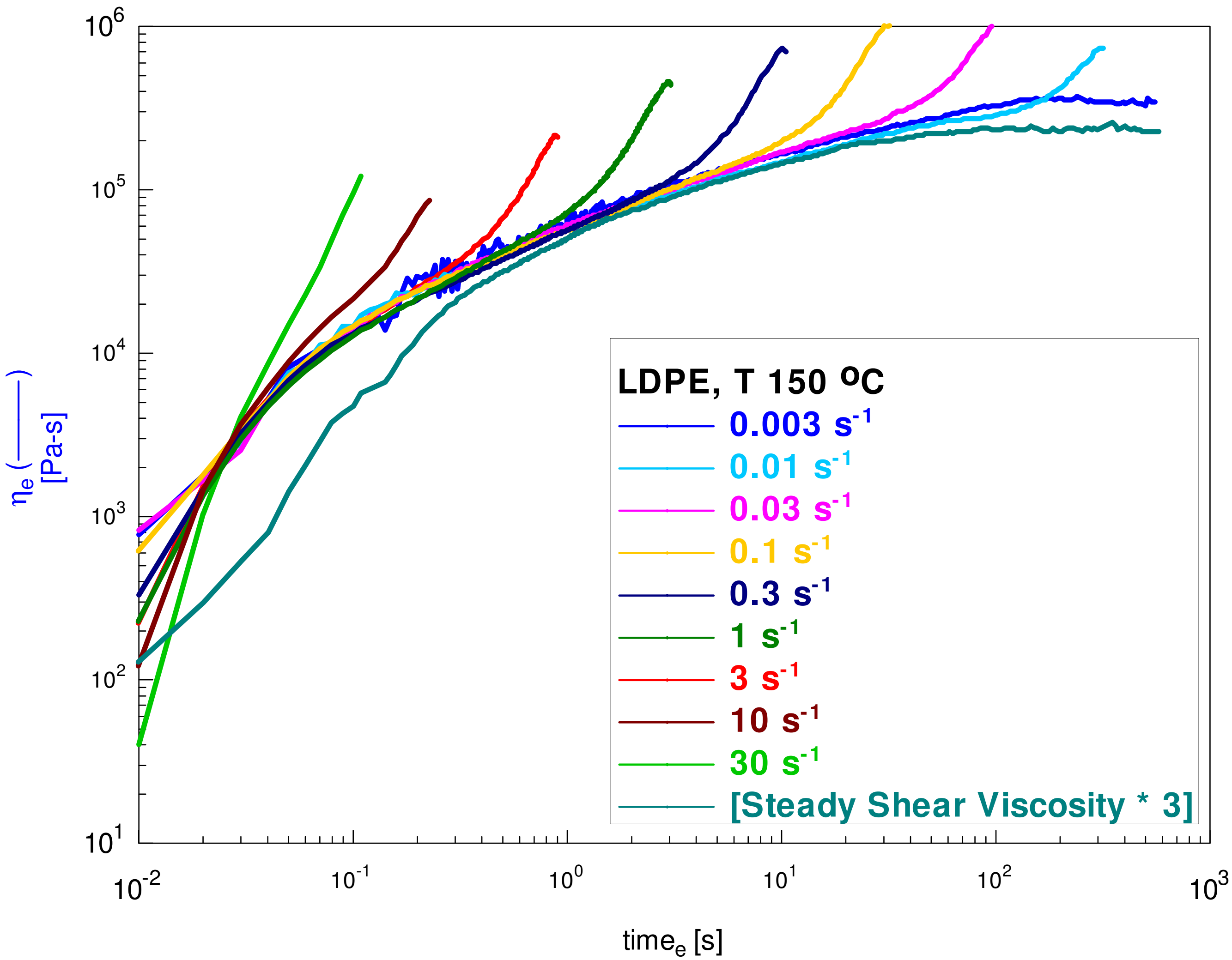




LLDPE (Low branching)



LDPE (High branching)



Thermosetting Polymers

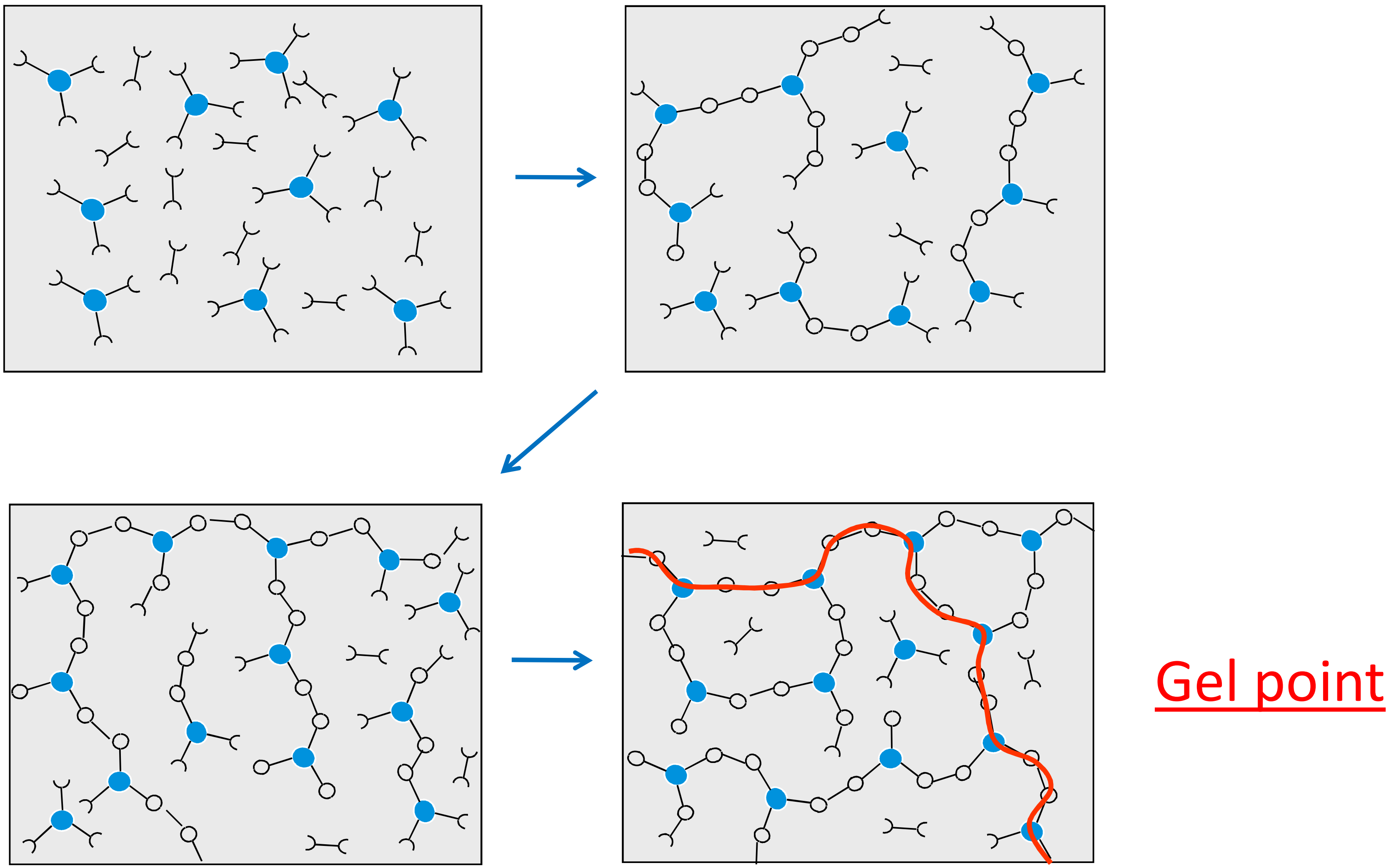
- Thermosetting polymers are perhaps the most challenging samples to analyze on rheometers as they challenge all instrument specifications both high and low.

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

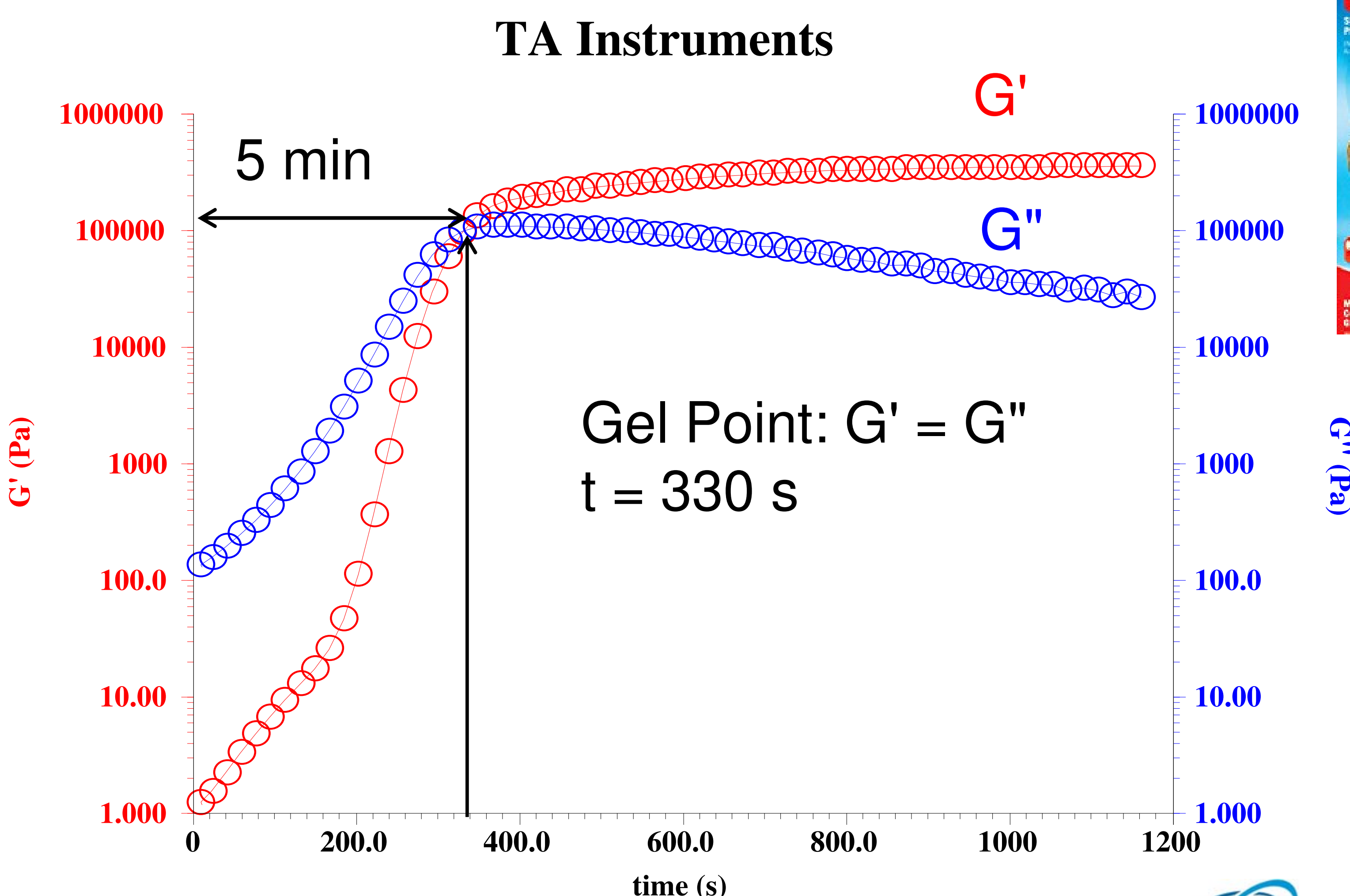
Thermosets Analysis

- 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.)

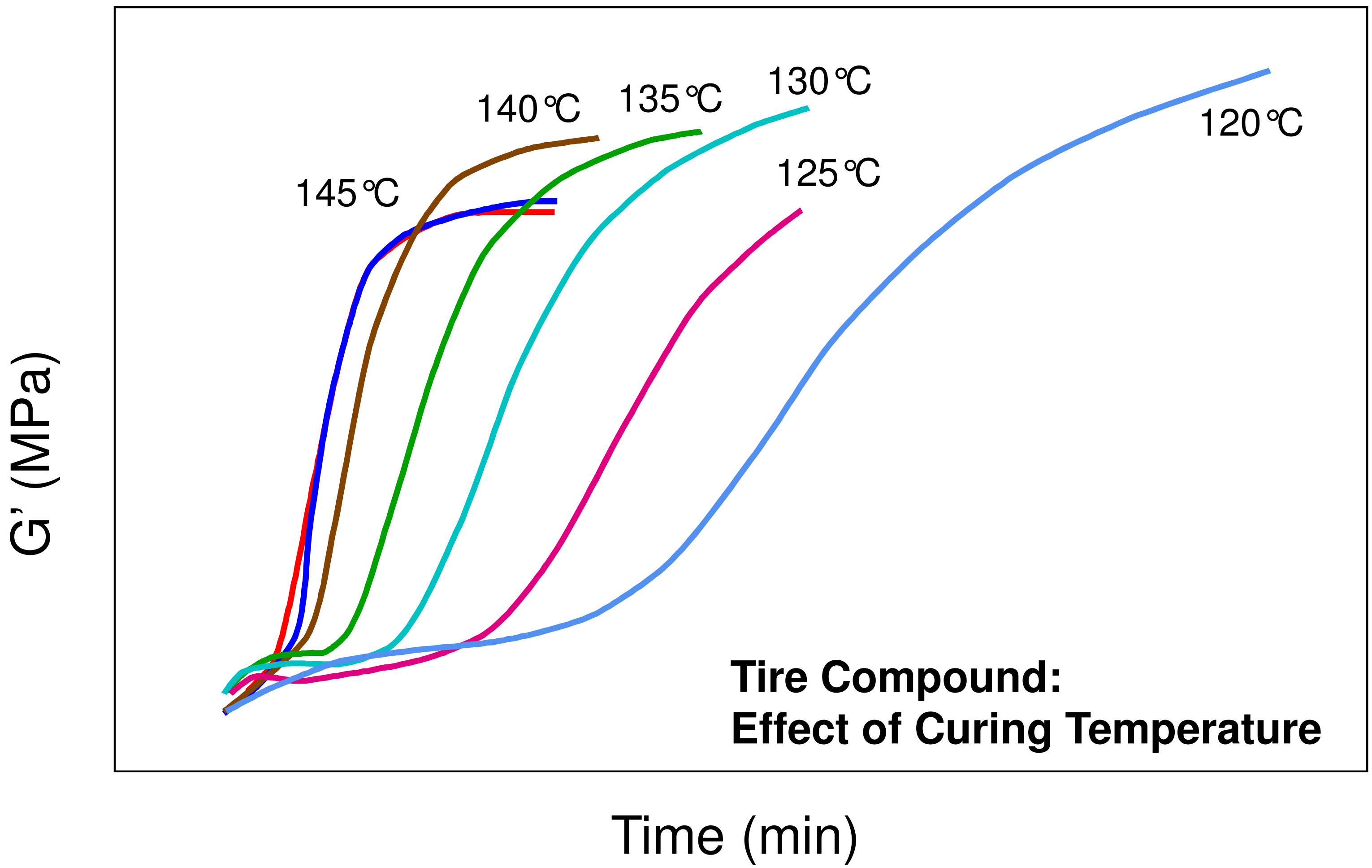
Structural Development During Curing



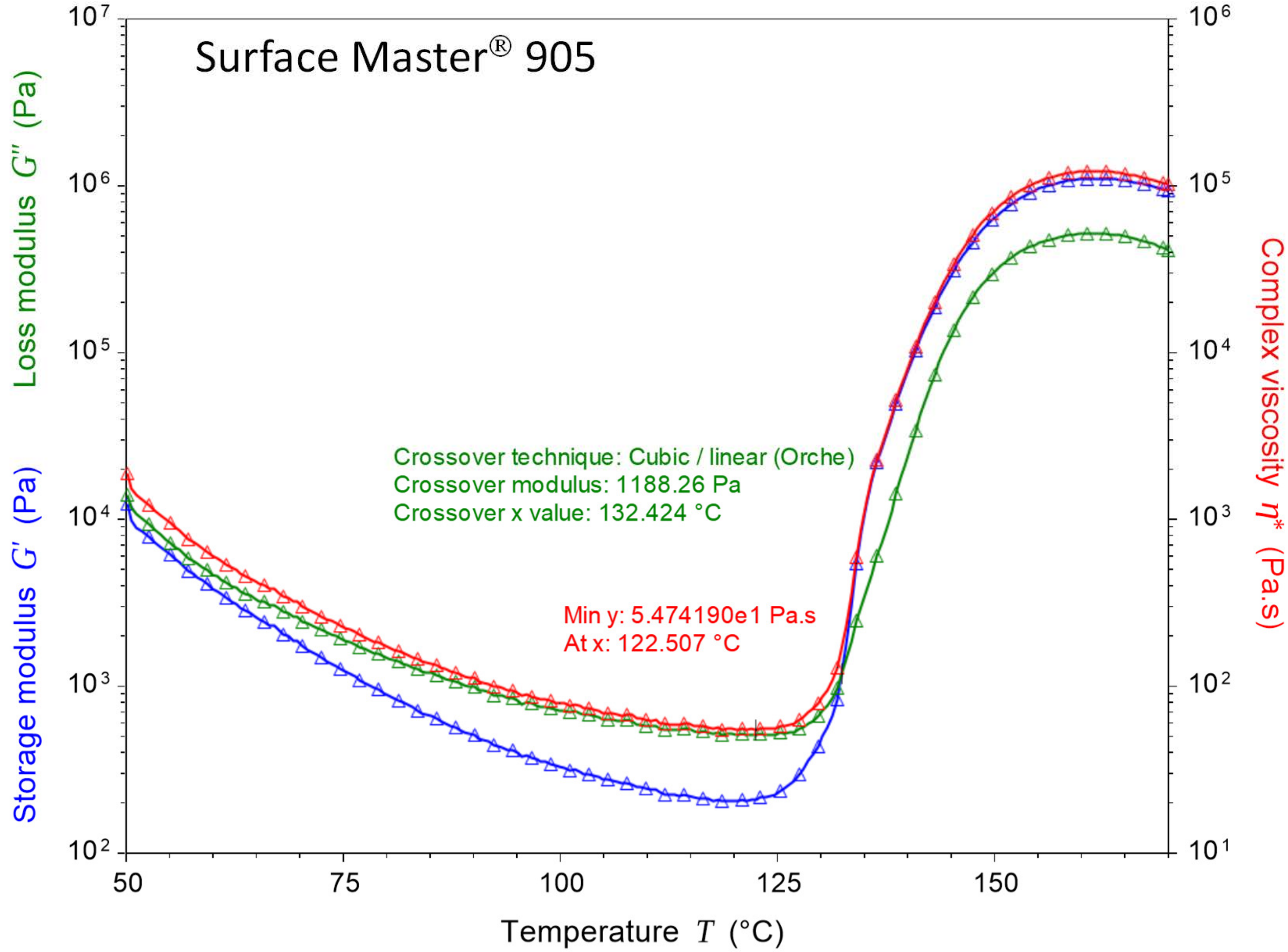
Curing Analysis: Isothermal Curing



Isothermal Curing

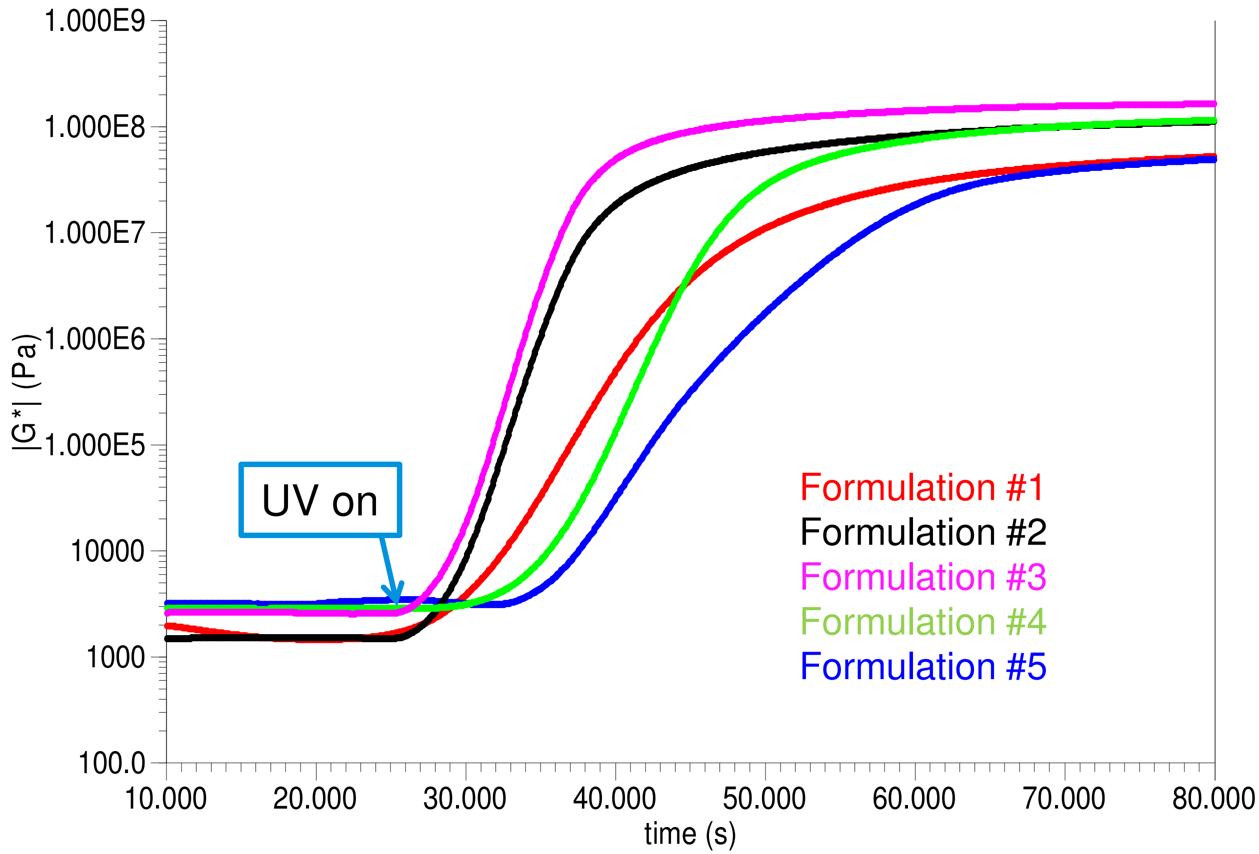


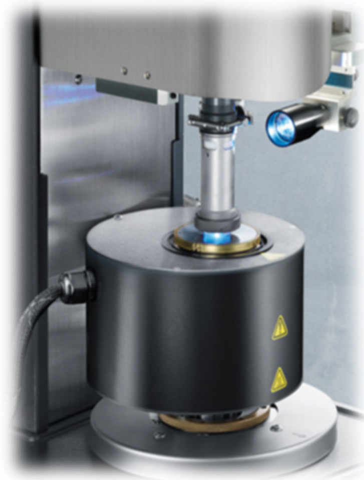
Temperature Ramp Curing



UV Curing

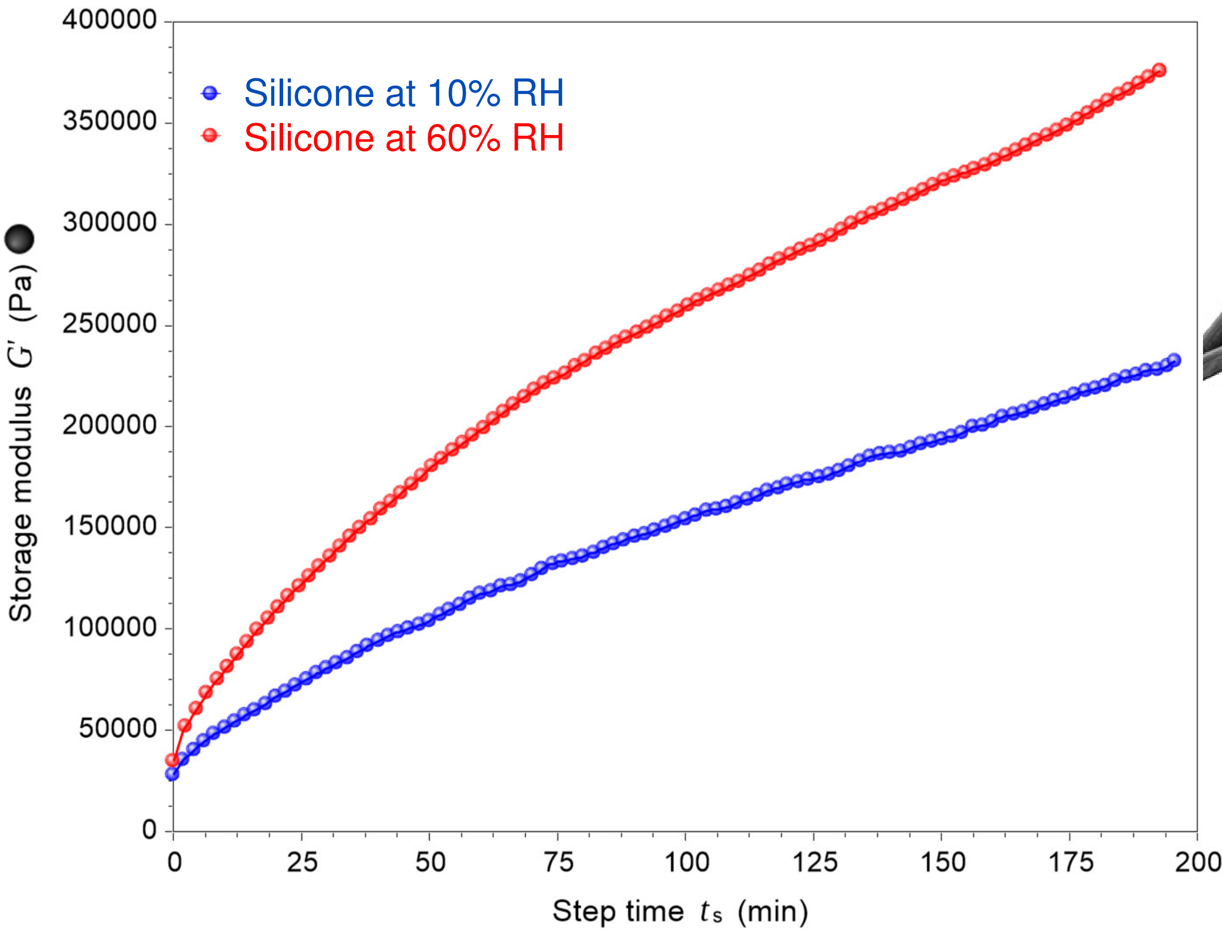
- Monitor UV curing: Dynamic time sweep
- Measure curing time with different formulations, UV intensity and temperature
- Measure cured adhesive modulus





Curing with Controlled Humidity

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



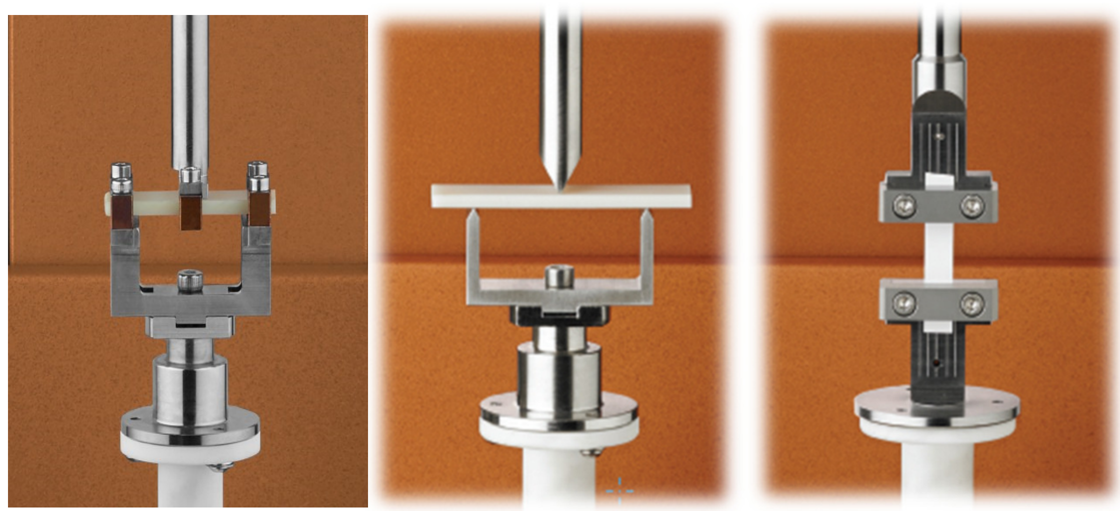
Testing Solids: Torsion and DMA

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

$$E = 2G(1 + \nu)$$

ν : Poisson's ratio

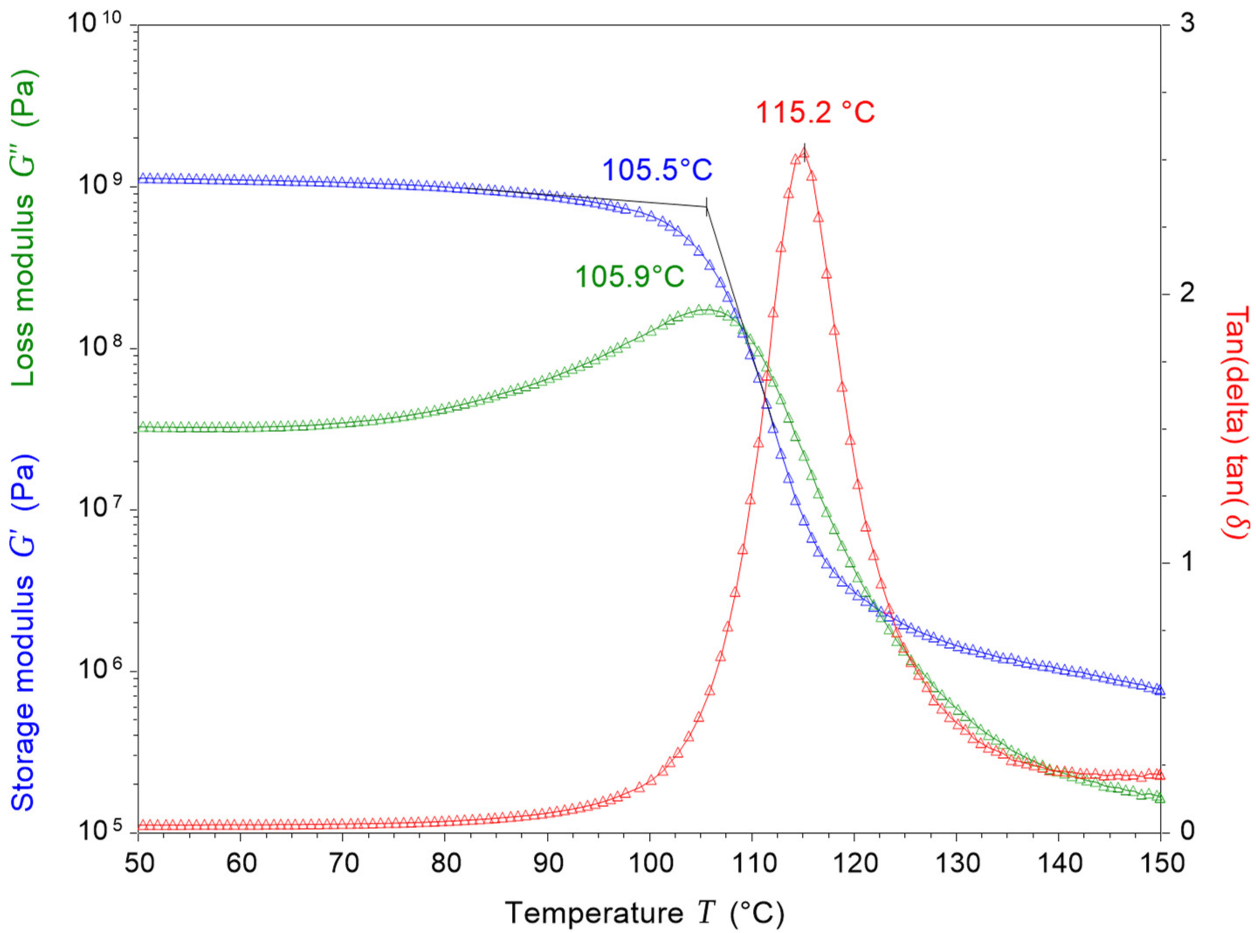
Torsion rectangular and cylindrical clamps



DMA cantilever, 3-point bending and tension clamps

Dynamic Temp Ramp Test

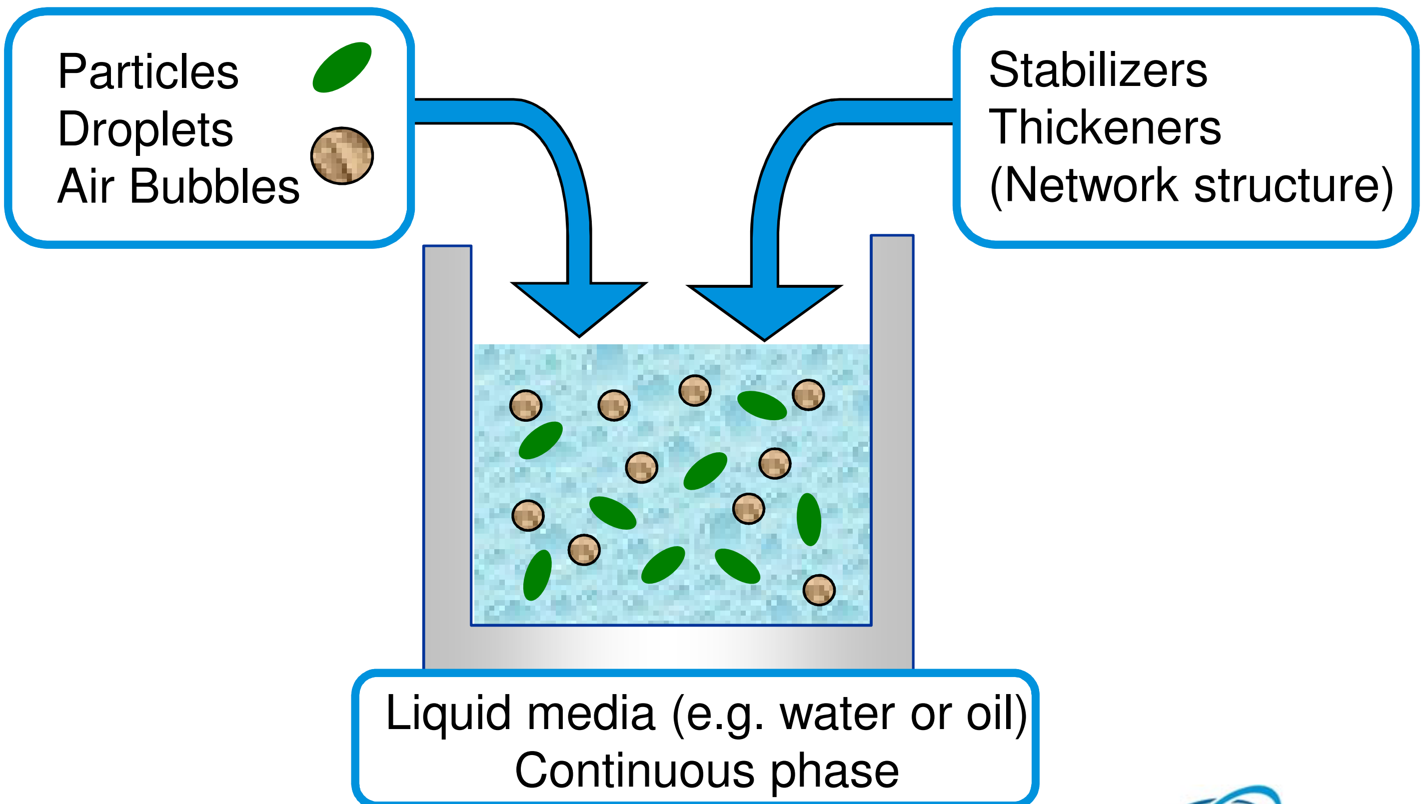
- Measure moduli, tan δ and transitions



Applications of Rheology
Yield stress and thixotropy of structured Fluids

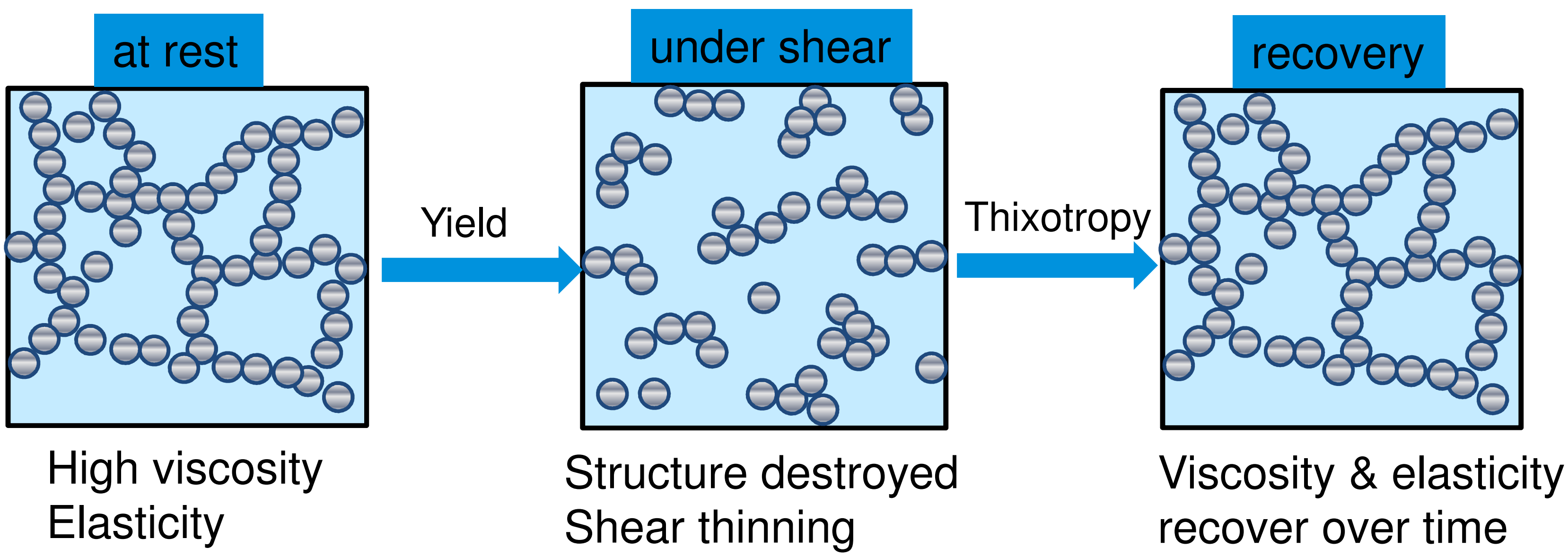
Structured Fluids

- 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**



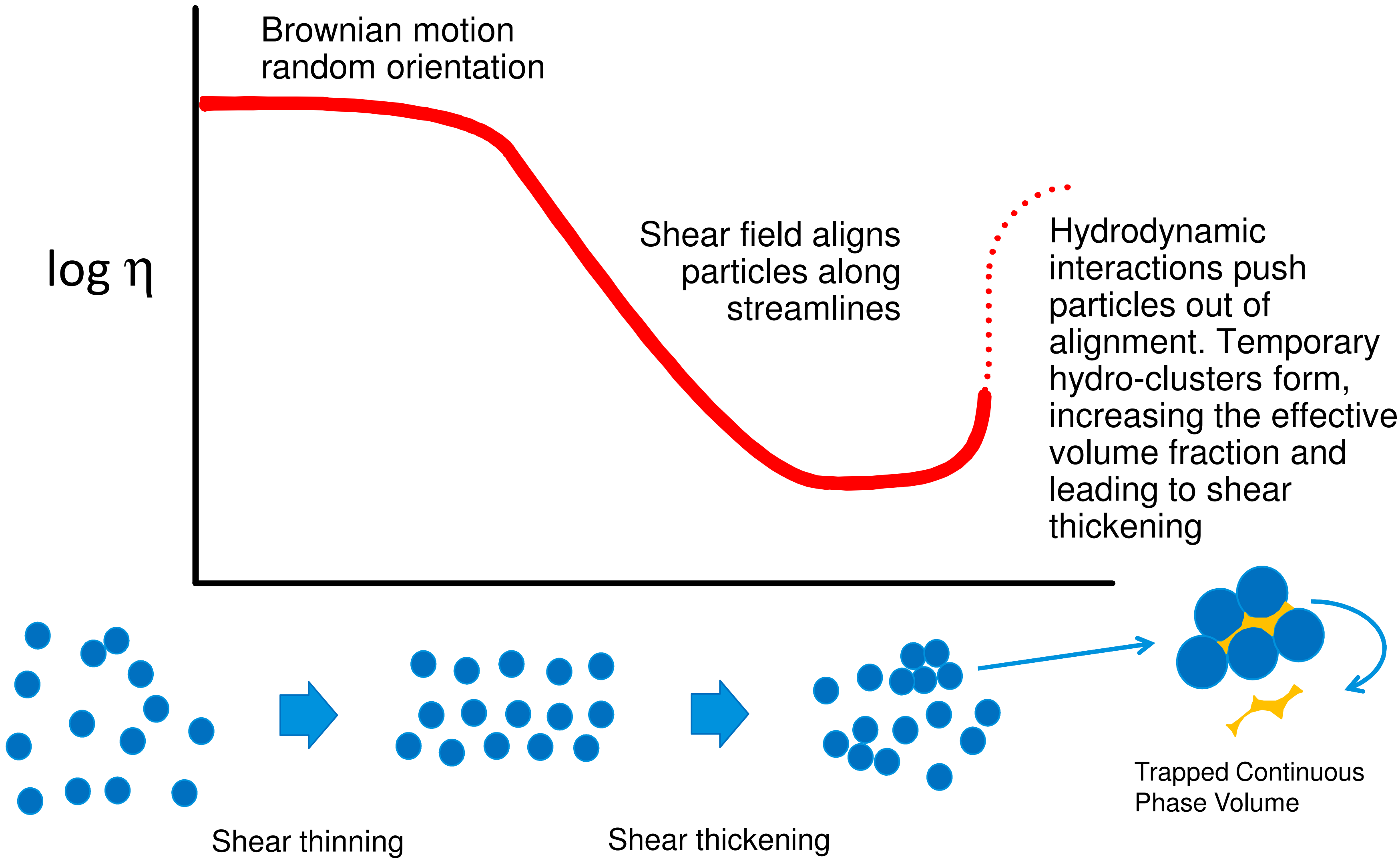
Types of Structured Fluids

- Three categories
  - Suspension — Solid particles in a Newtonian fluid
  - Emulsion — Fluid in a fluid
  - Foam — Gas in a fluid (or solid)

- Examples are:
  - Paints
  - Coatings
  - Inks
  - Adhesives
  - Personal Care Products
  - Cosmetics
  - Foods




Generalized Flow Curve for structured fluids



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

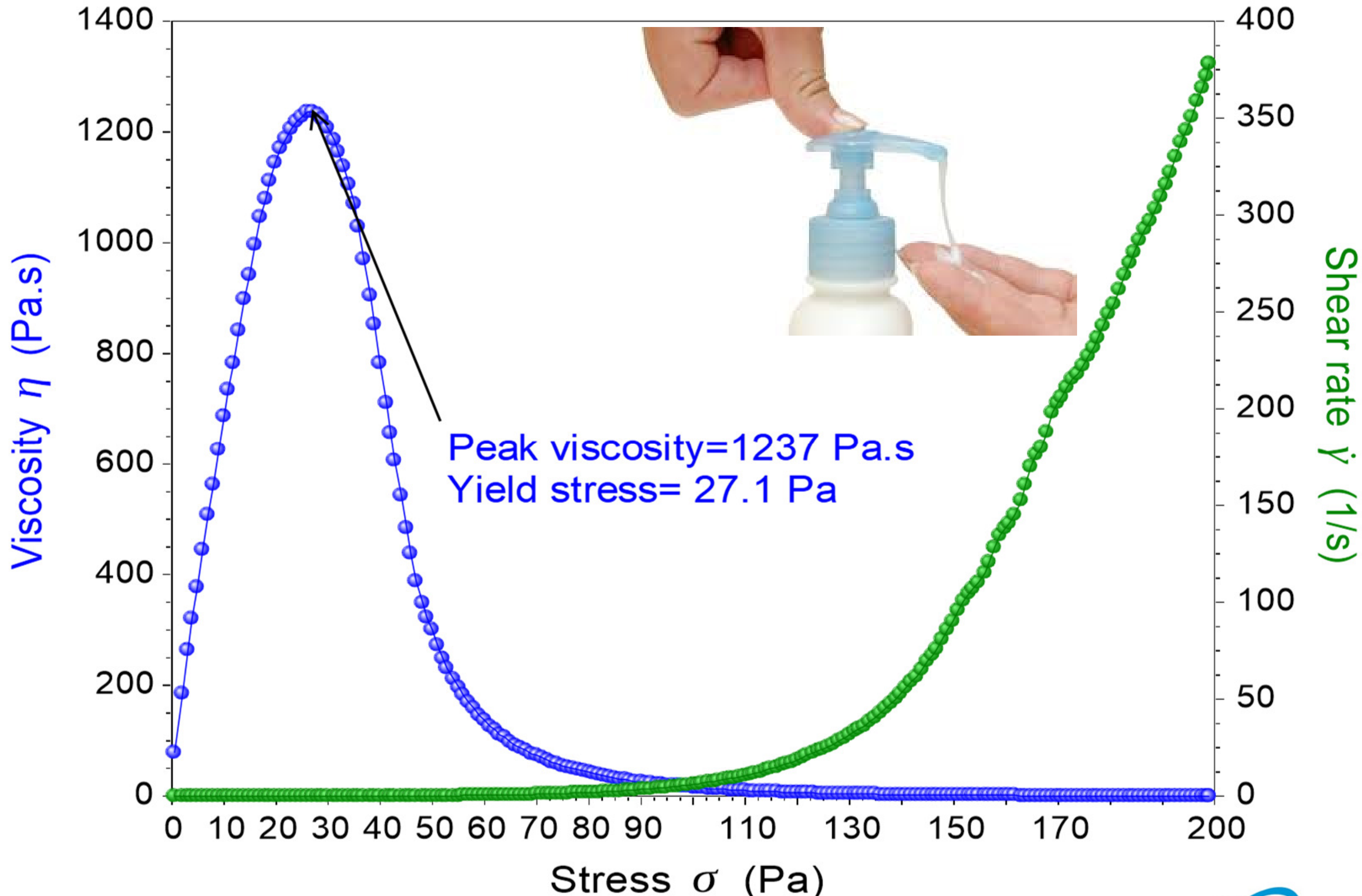
- Yield can be quantitatively measured on a rotational rheometer

- Common methods
  - Stress ramp
  - Stress sweep
  - Shear rate ramp
  - 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

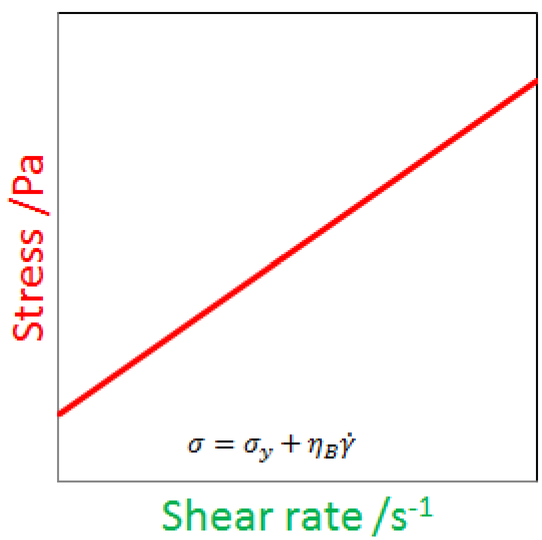
- Stress ramp from 0 to 200 Pa in 60 seconds
- Yield is determined at the point where viscosity shows a peak



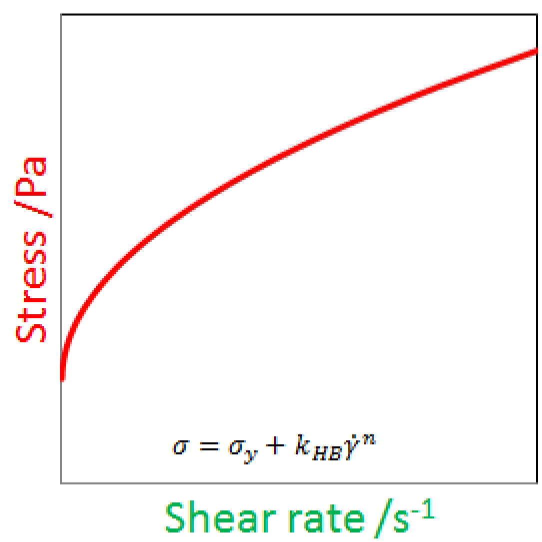
Fit Results with a Flow Models

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

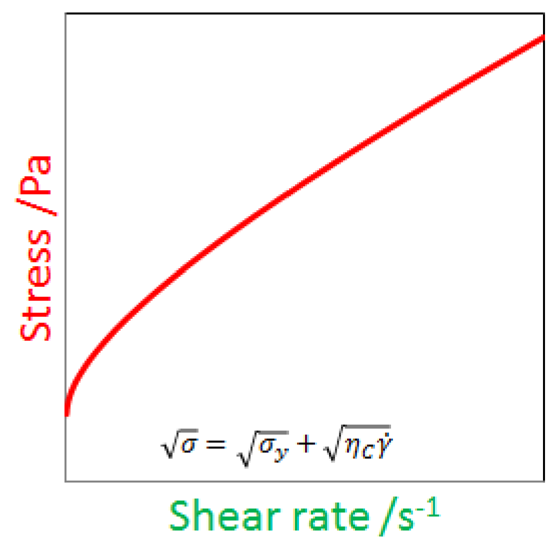
Bingham



Herschel-Bulkley

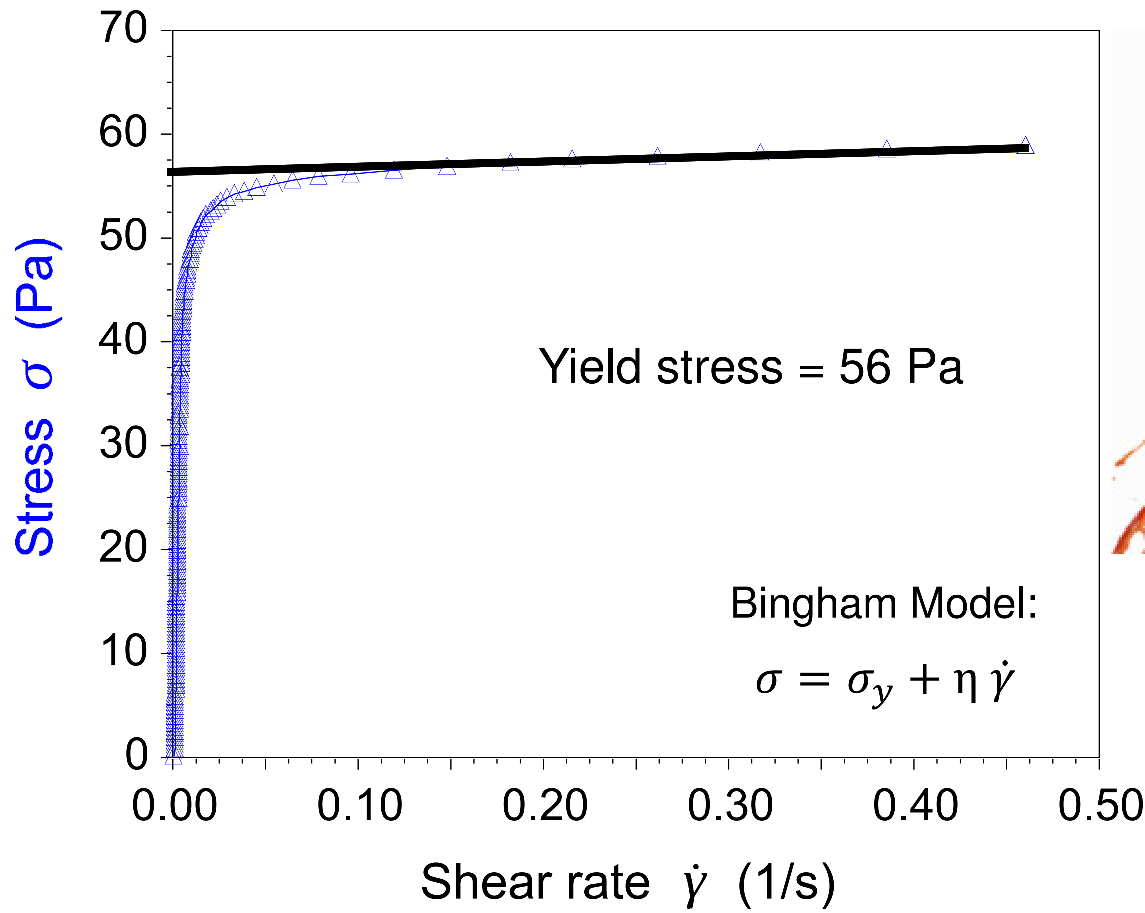


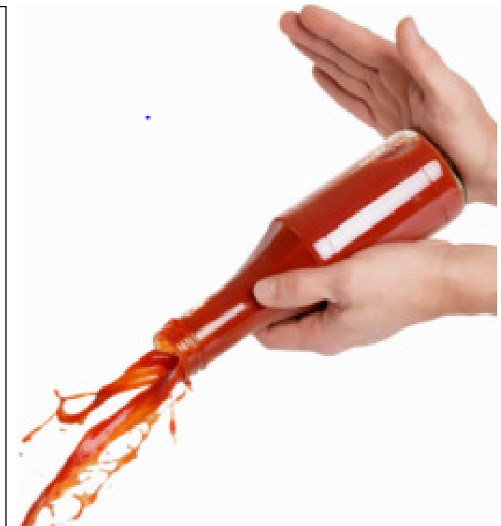
Casson



Yield Stress of Ketchup

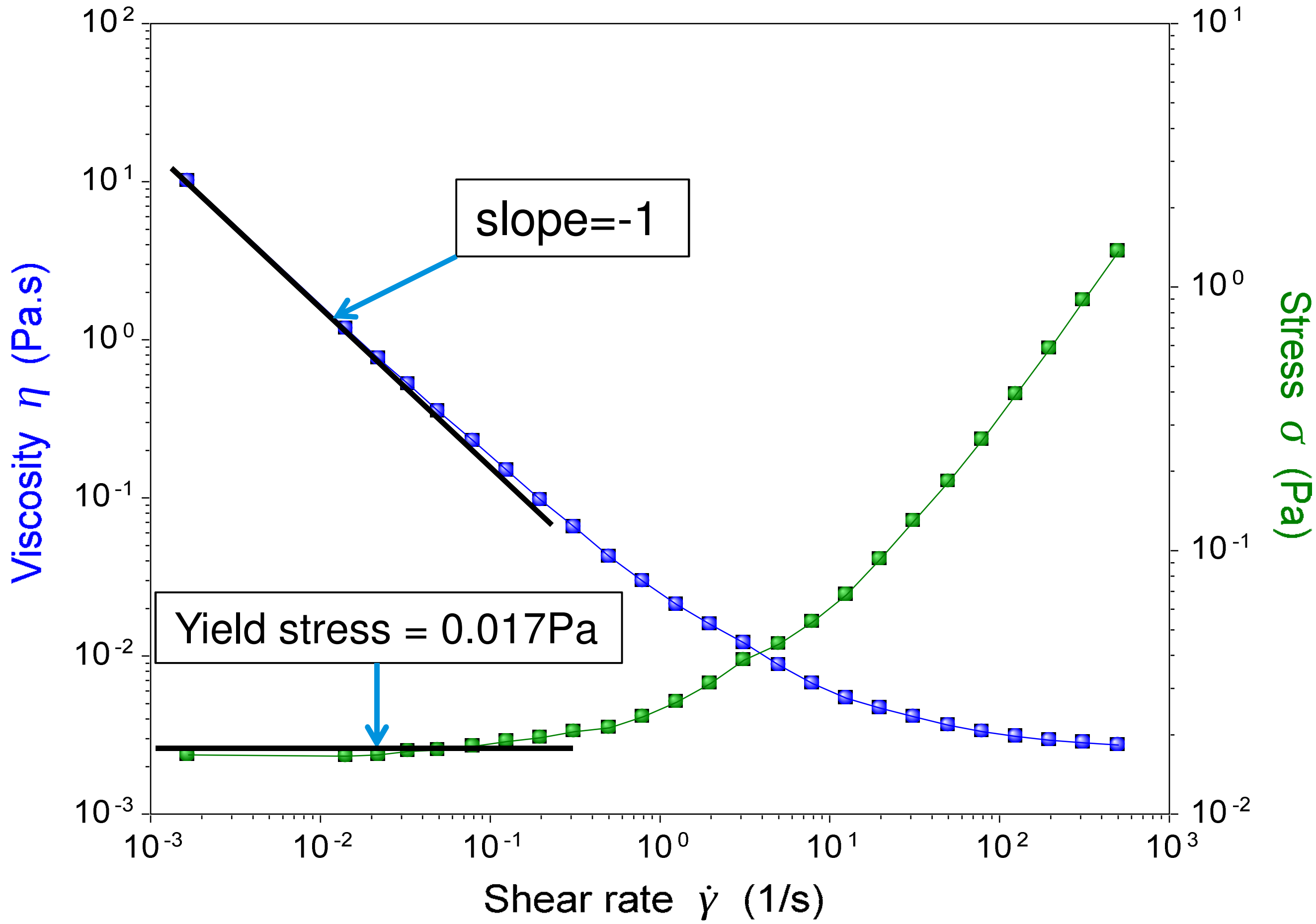
- Stress ramp test on Katchup
- Yield is computed by fitting the flow curve with a mathematical model





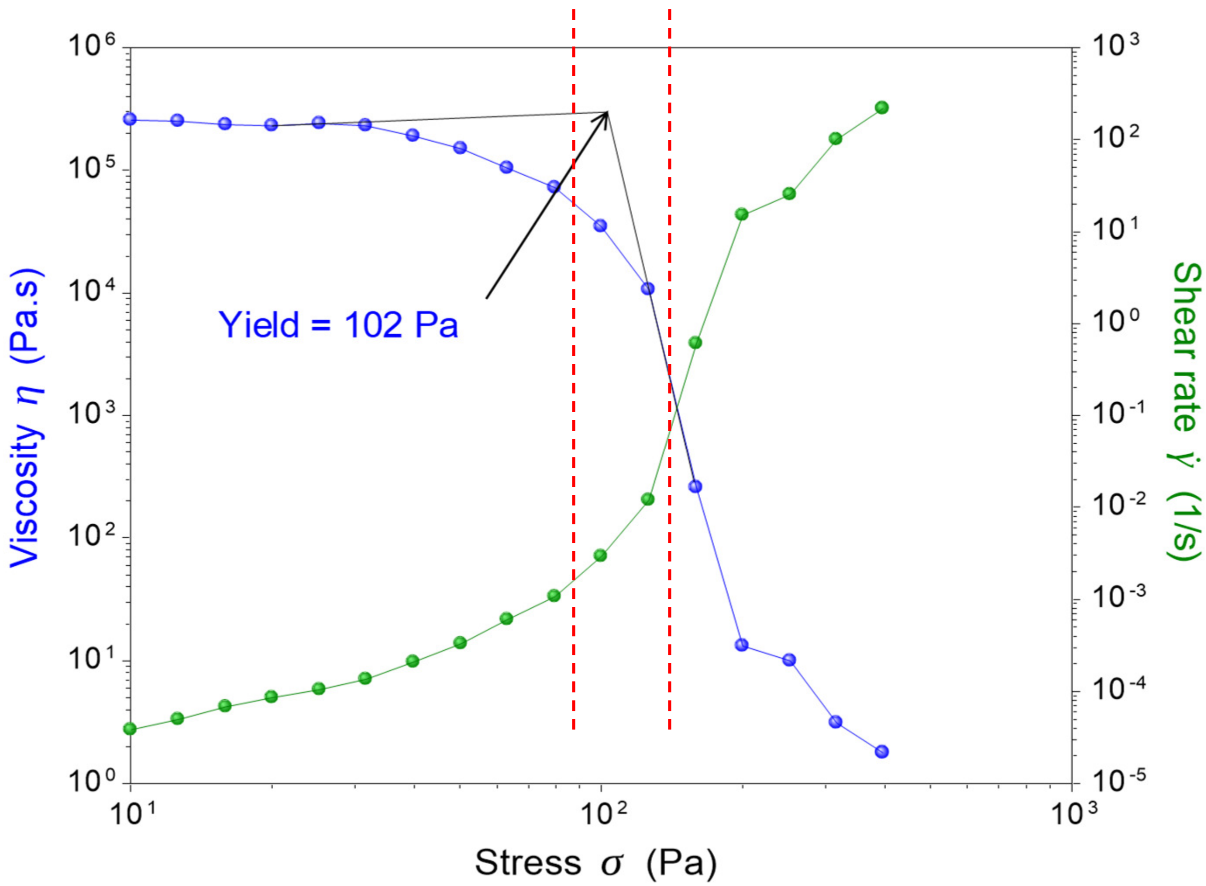
Yield Stress of Orange Juice

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



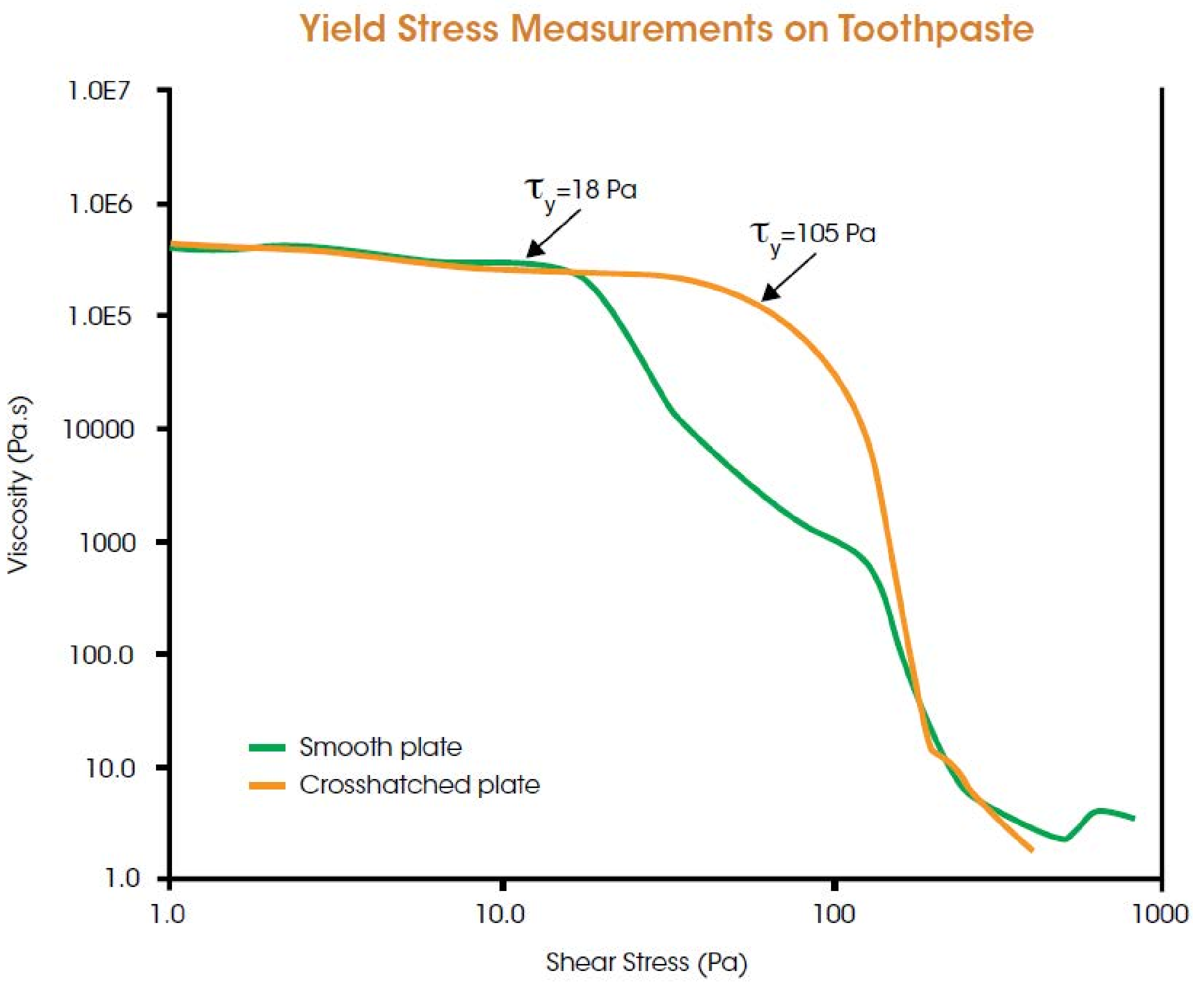
Yield Stress of a Toothpaste

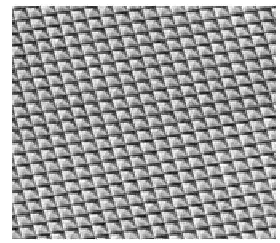
- Steady state stress sweep from 10 Pa to 500 Pa
- Yield stress is determined by a sharp decrease in viscosity over a narrow range of applied shear stress
- Take the onset of viscosity vs. stress curve



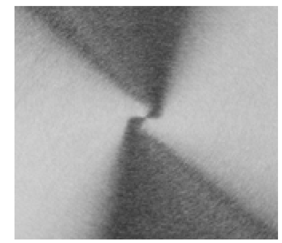
Wall Slip – Artifact Yield

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





crosshatched plate

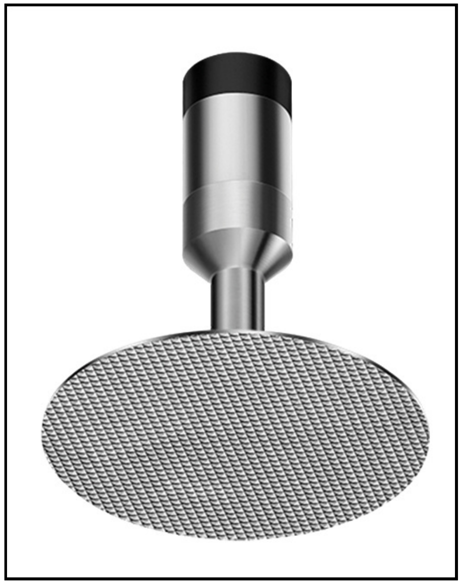


smooth plate

Solutions To Minimize Wall Slip

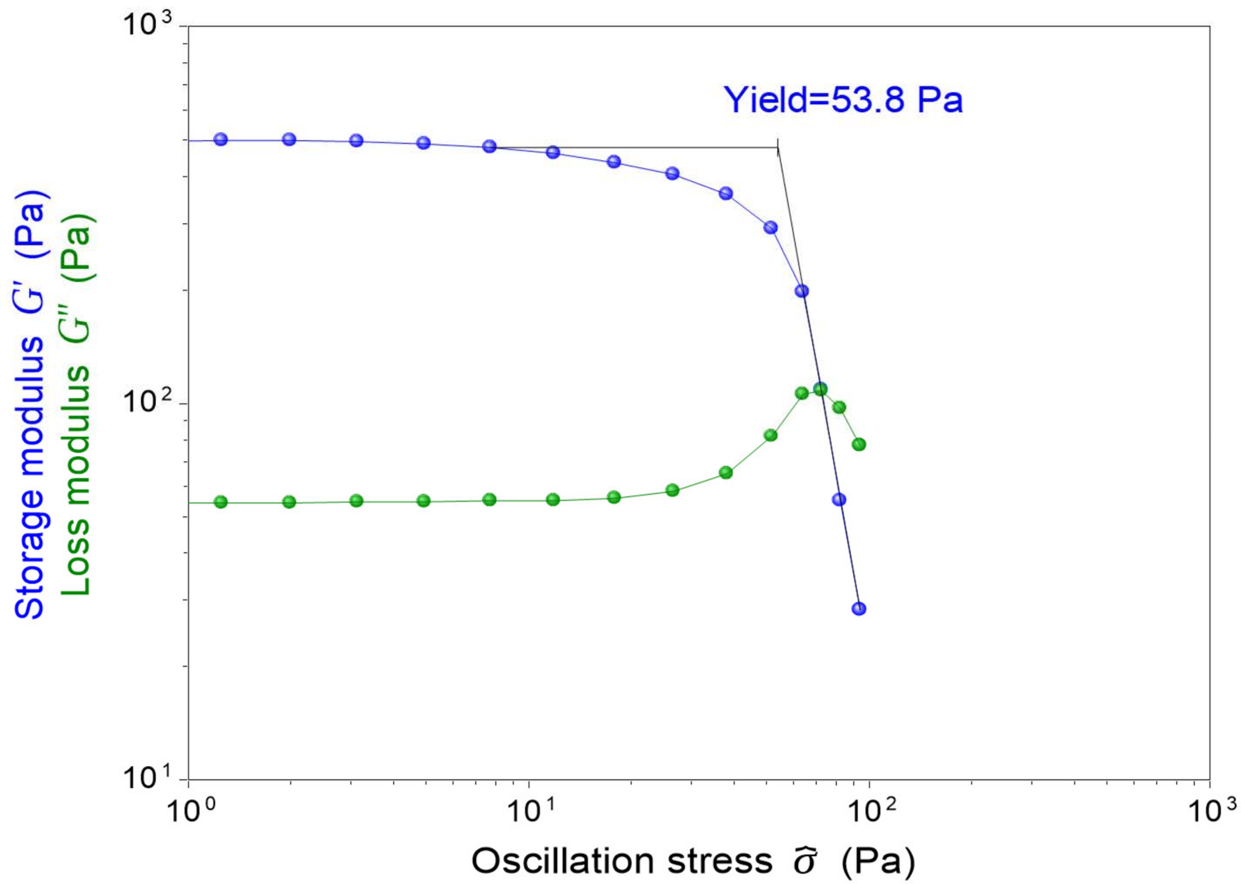
- Diagnosis method
  - Running the same experiment at different gaps. For samples that don’t slip, the results will be independent of the gap
- Solutions
  - Use a grooved cup with vane or helical shape rotor geometry
  - Use a roughened surface geometry



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



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:
  - Control sagging and levelling of paints
  - Start up of pipleline flow after rest

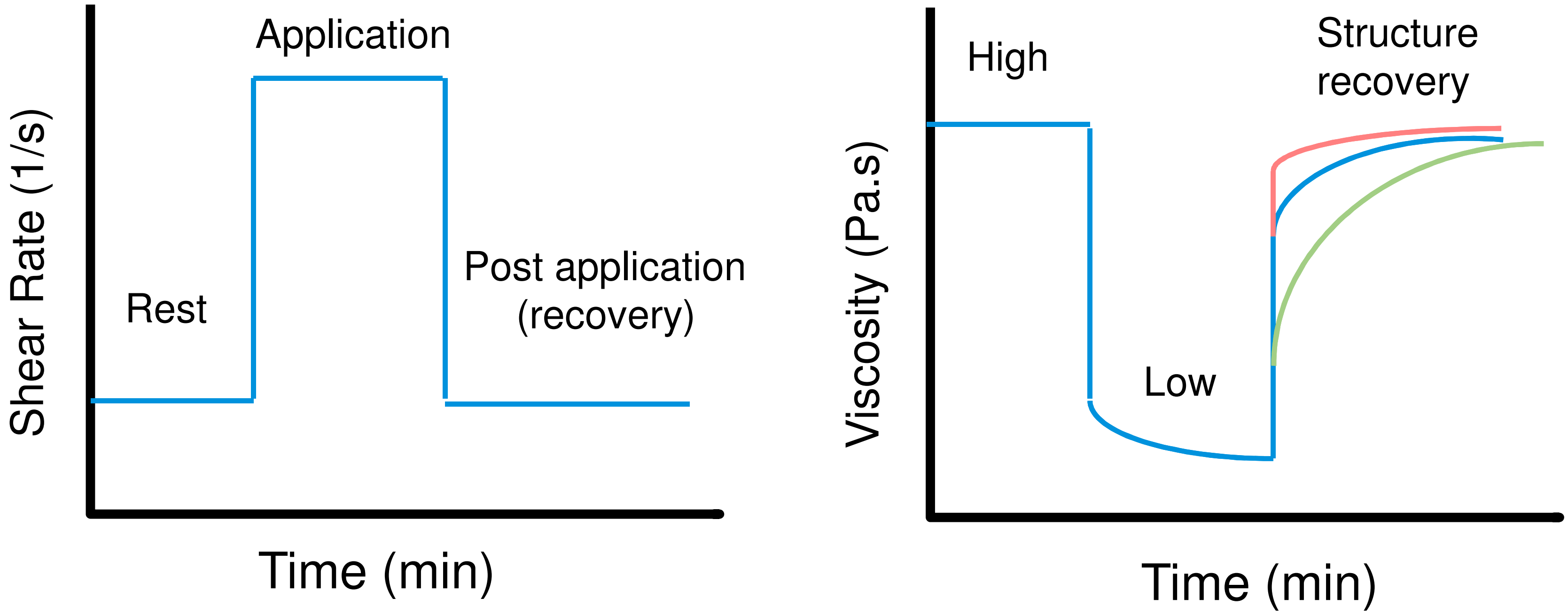
How to Measure Thixotropy

- 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



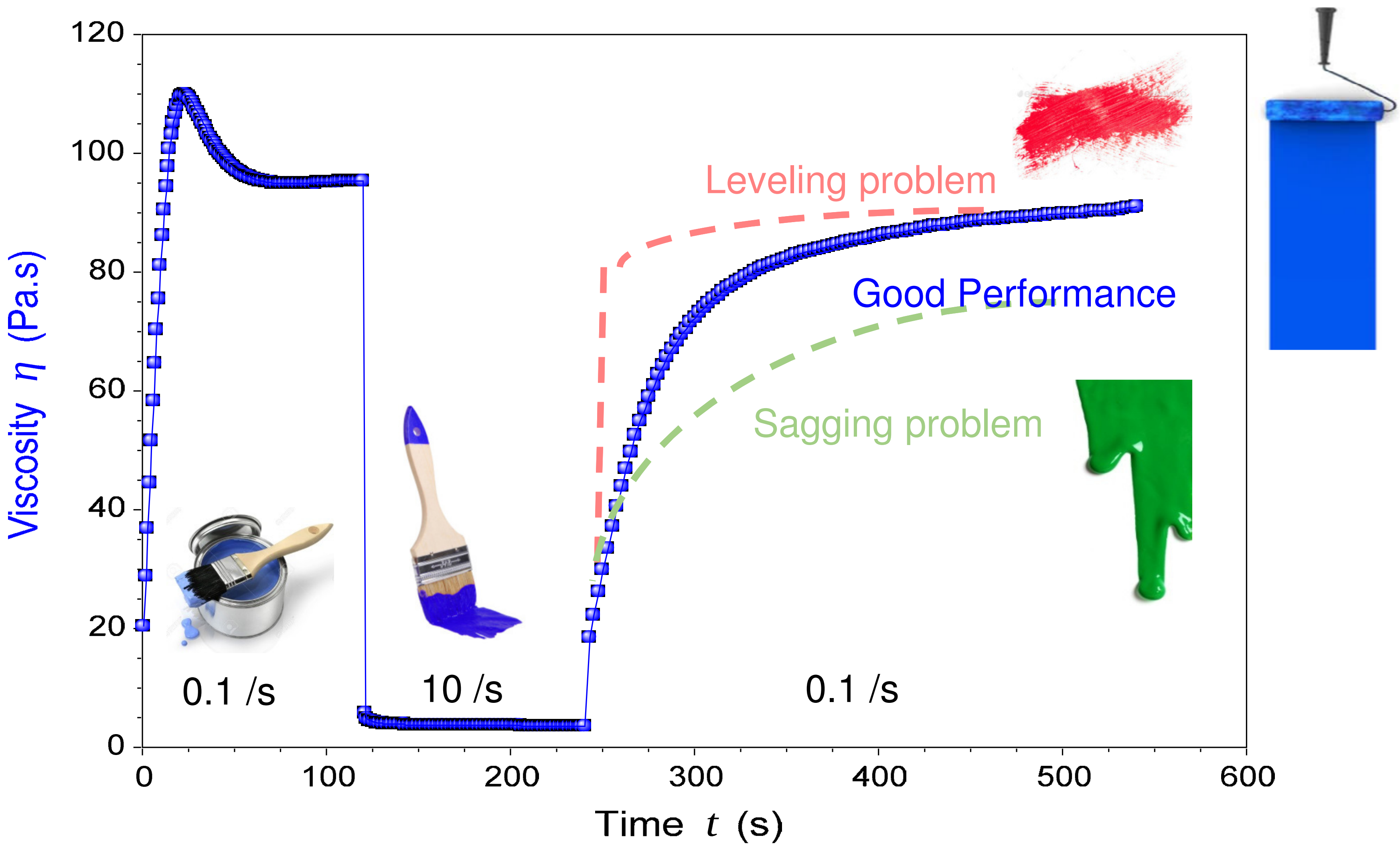
Experimental:

Step 1: Low Shear (e.g. 0.1 1/s), state of rest

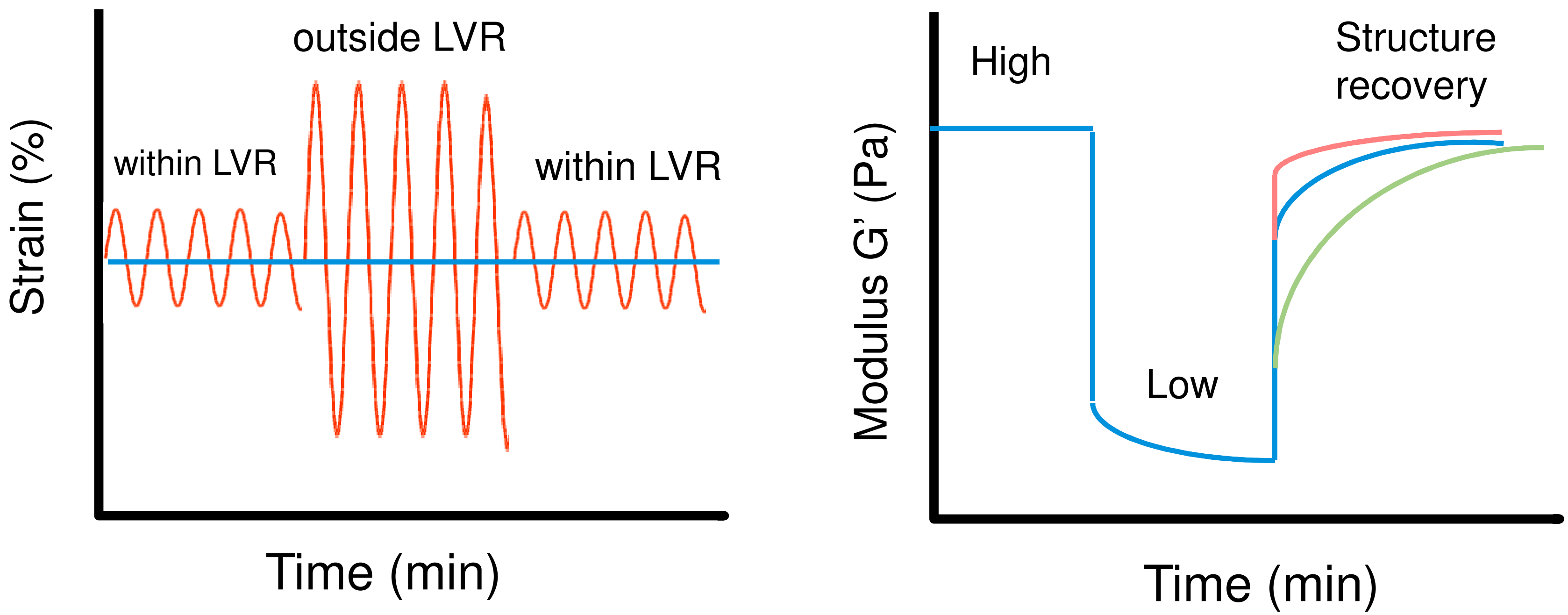
Step 2: High Shear (e.g. 10 1/s), structural destruction

Step 3: Low Shear (e.g. 0.1 1/s), structural regeneration

Thixotropic Analysis of a Blue Paint



Stepped Dynamic Method



Experimental:

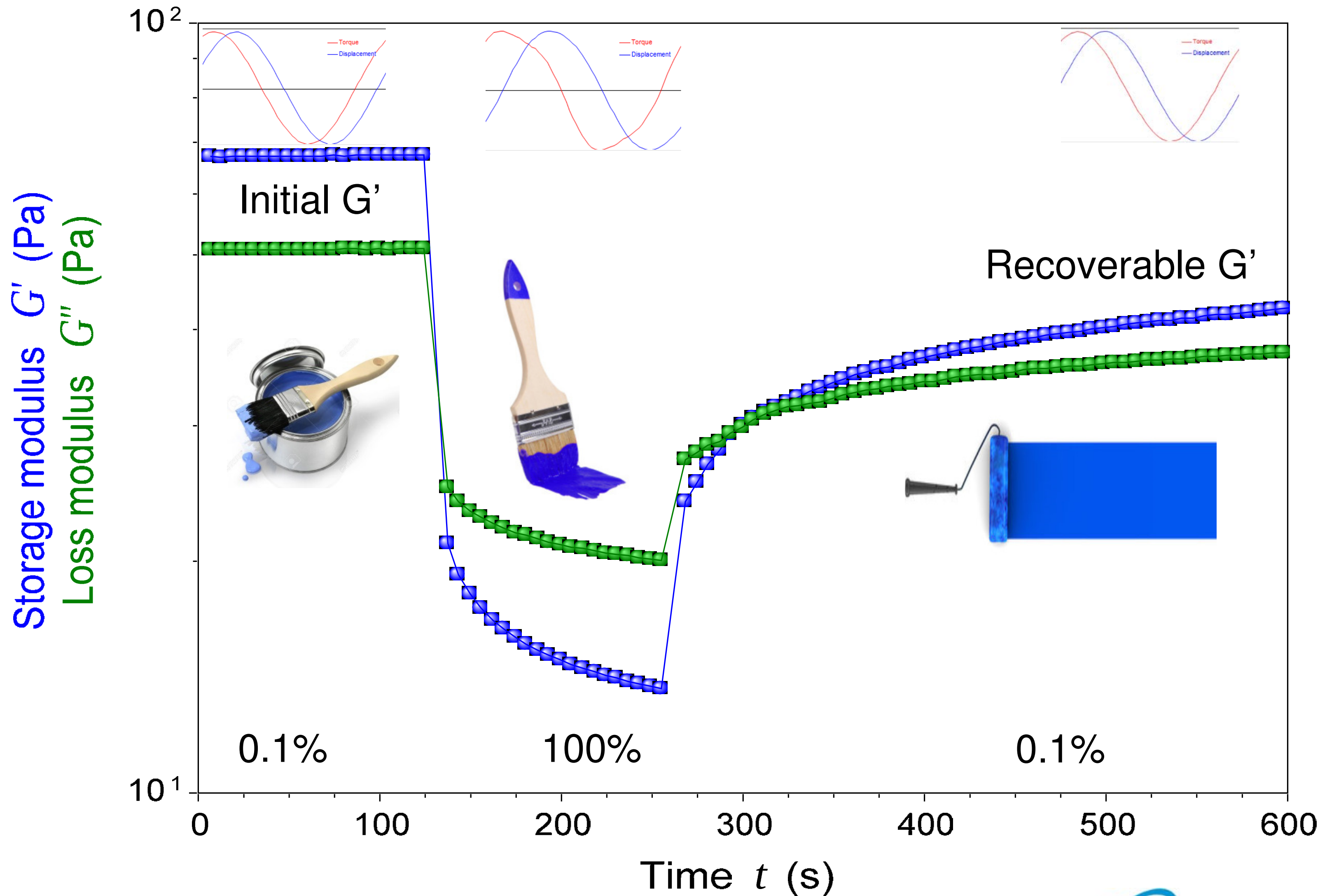
Step 1: Dynamic time sweep within LVR, structure at rest

Step 2: Dynamic time sweep outside LVR, structural destruction

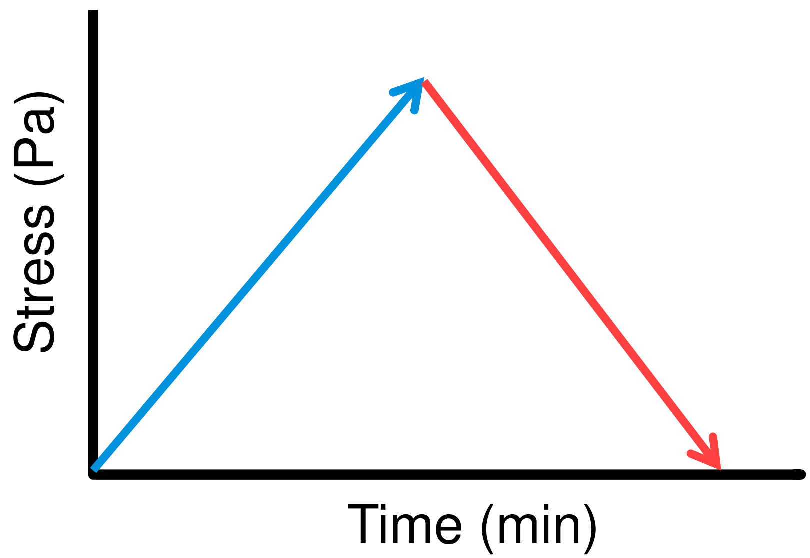
Step 3: Dynamic time sweep within LVR, structural regeneration

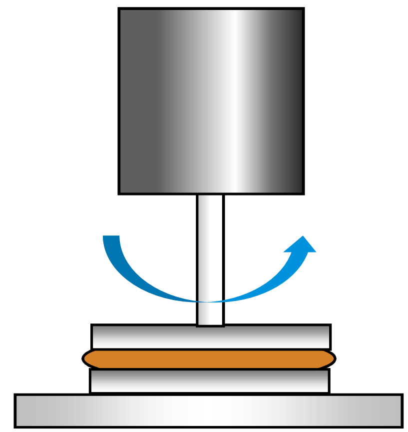
Good for measuring high viscosity samples

Blue Paint: Stepped Time Sweep



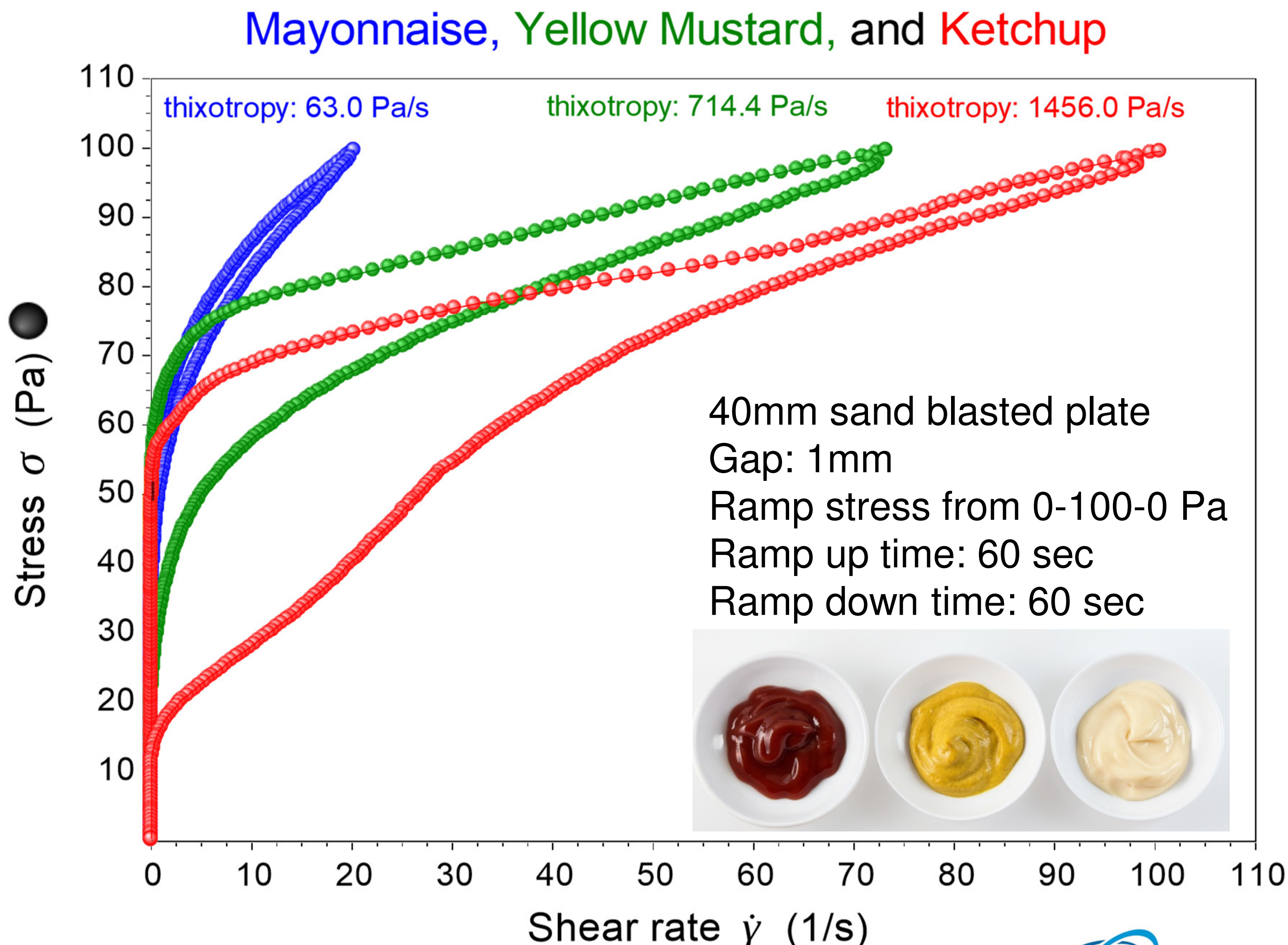
Stress Ramp Up and Down Method



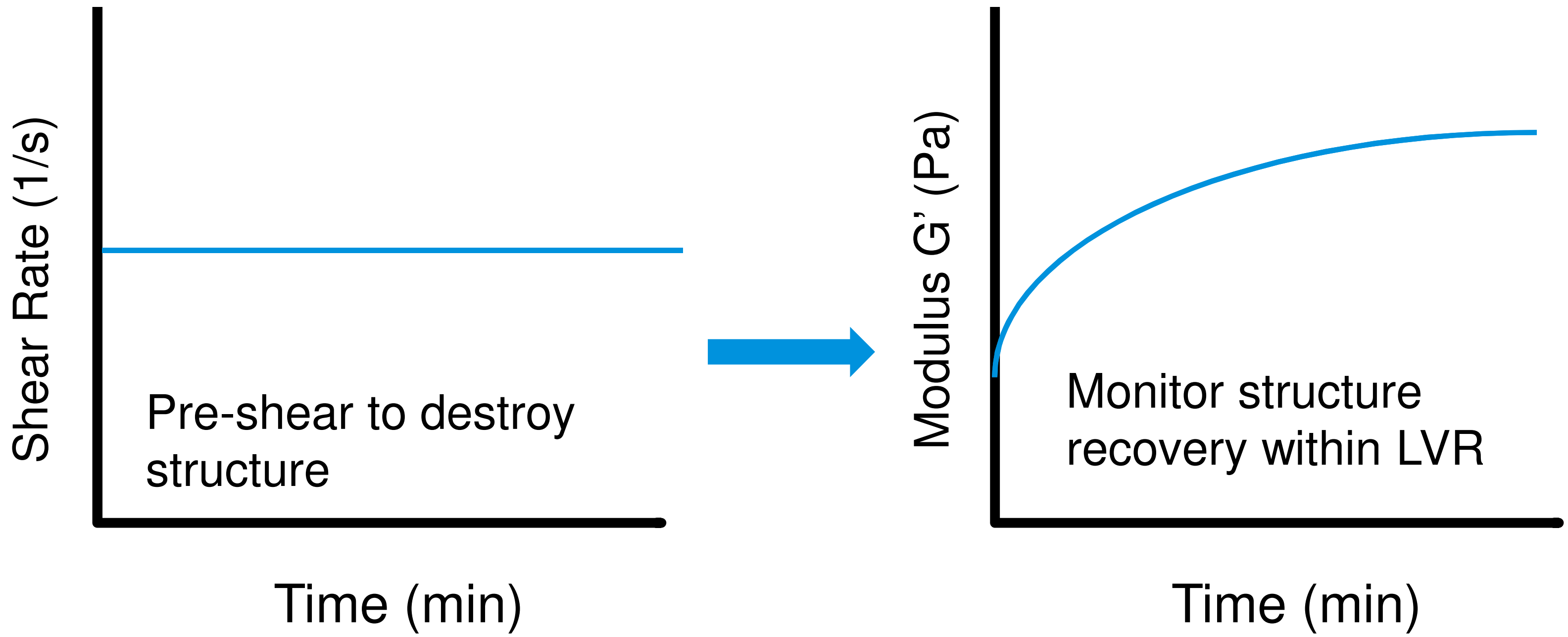


- Ramp shear stress linearly from zero up until sample flows, then ramp stress back down to zero
- Thixotropic index is measured by taking the area between the up and down stress curves
- TA Tech Tip: https://www.youtube.com/watch?v=8lZangOp1SY

Thixotropic Loop Testing on Foods



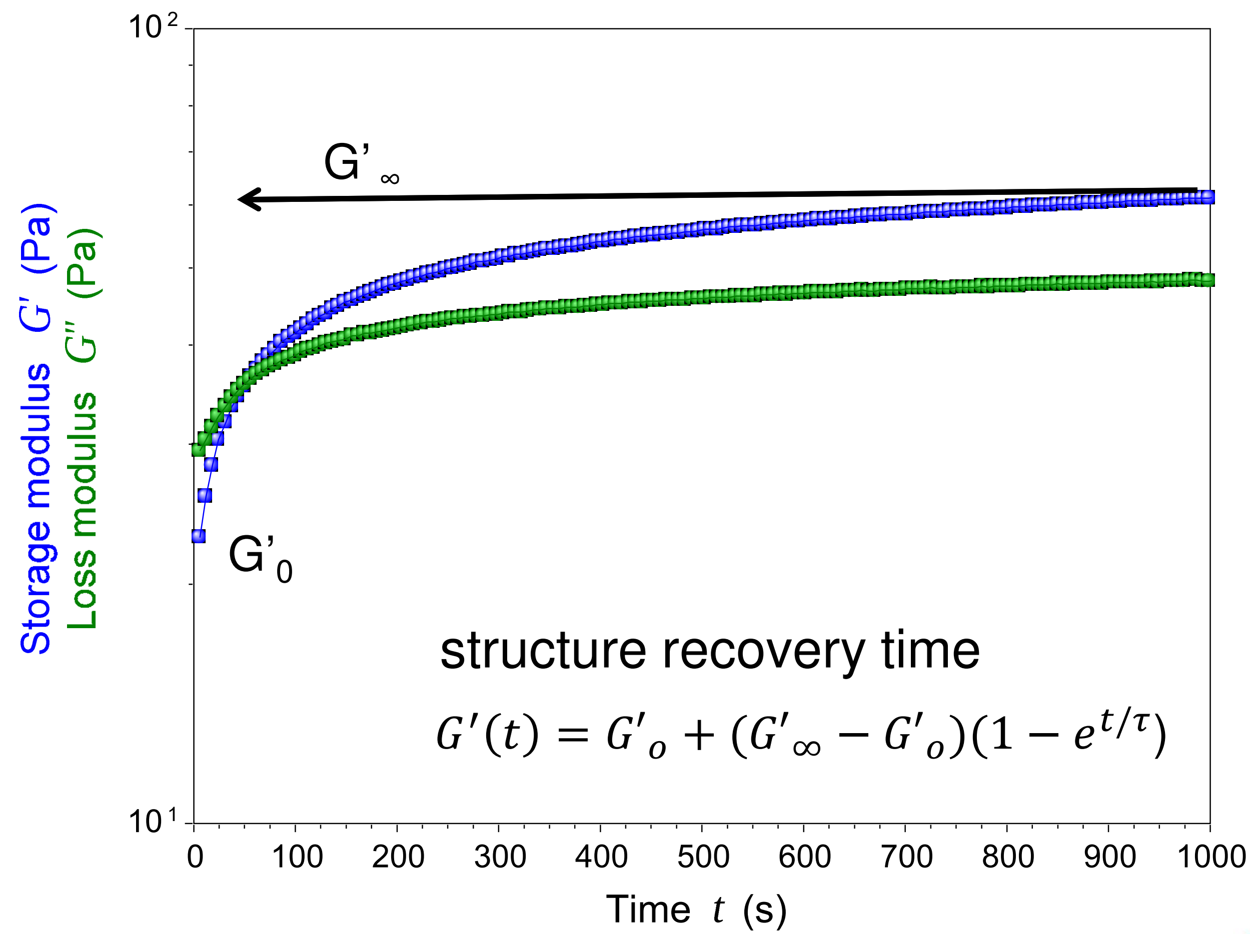
Time Sweep After Pre-shear Method



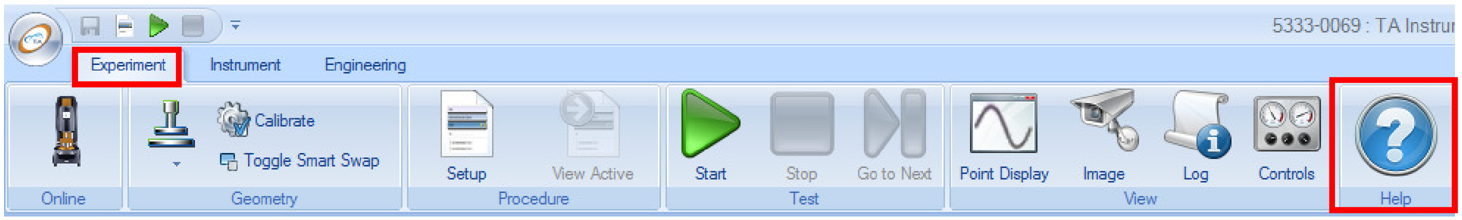
- Apply a constant shear (e.g. 10 or 100 1/s) for a certain time (e.g. 1 min.) to break down structure
- Immediately start a time sweep within the linear region of the material to monitor structure recovery

Blue Paint: Time Sweep After Pre-shear

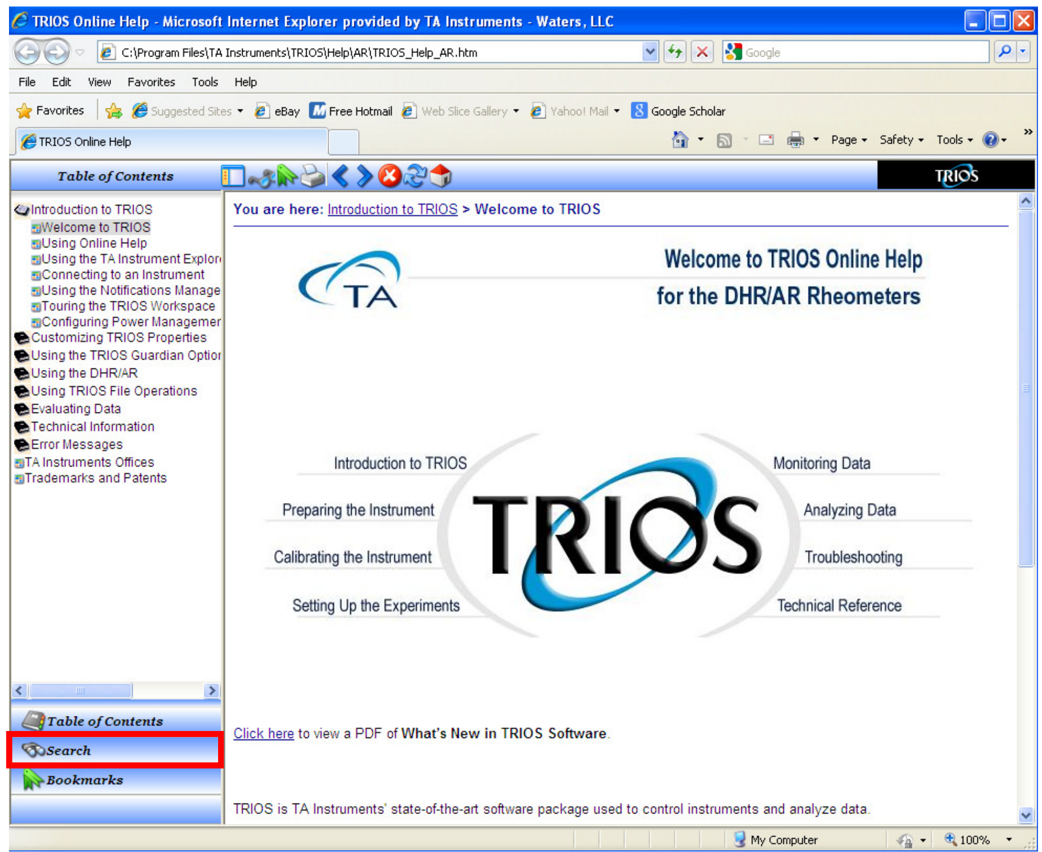
- Monitor the increase of the G‘ as a function of time.
- Thixotropic recovery is described by meausring the recovery time (τ)



TRIOS Help Menu

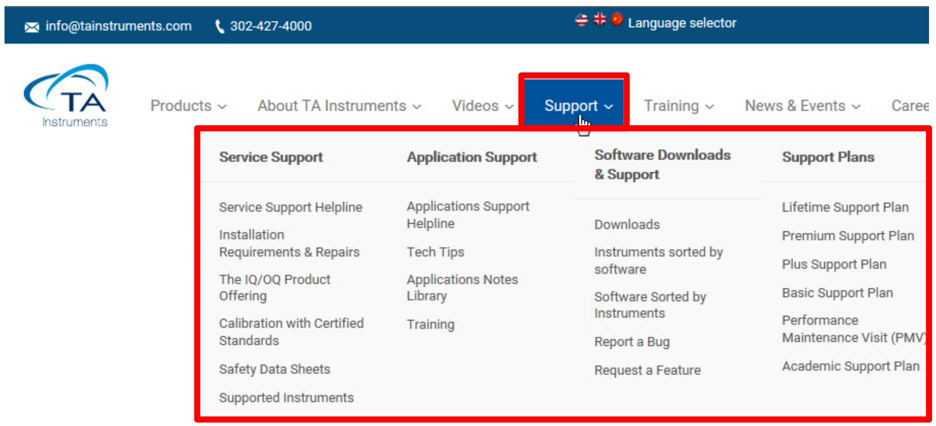


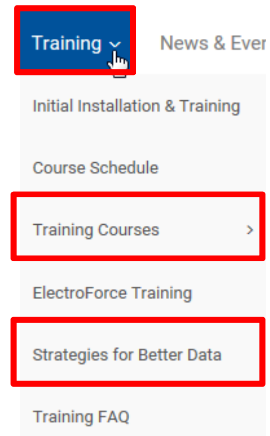
- Browse the contents list or search using the search tab.
- Access to Getting Started Guides also found through the help menu.



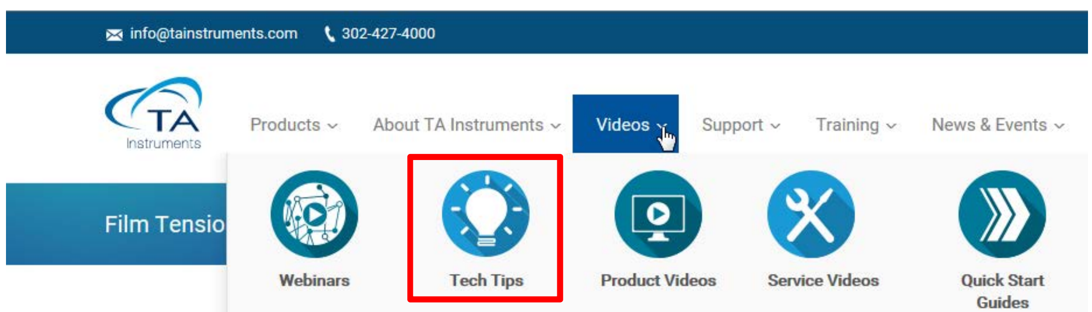
Instructional Videos

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





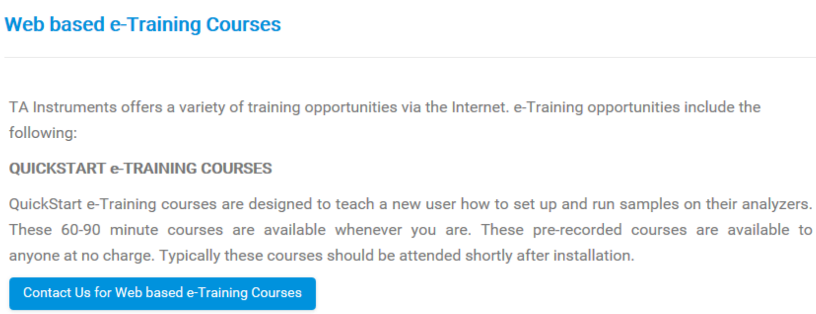
- Select Videos for TA Tech Tips, Webinars and Quick Start Courses

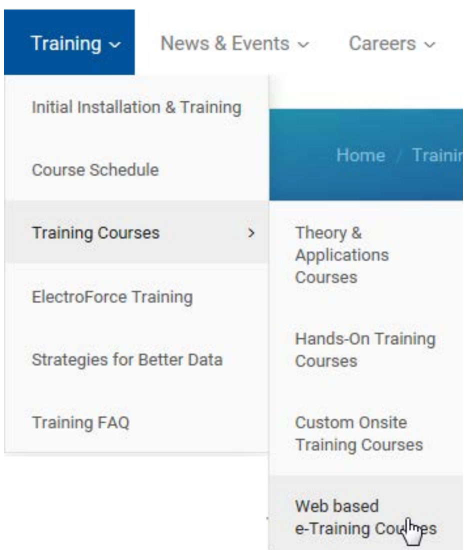


See also: https://www.youtube.com/user/TATechTips

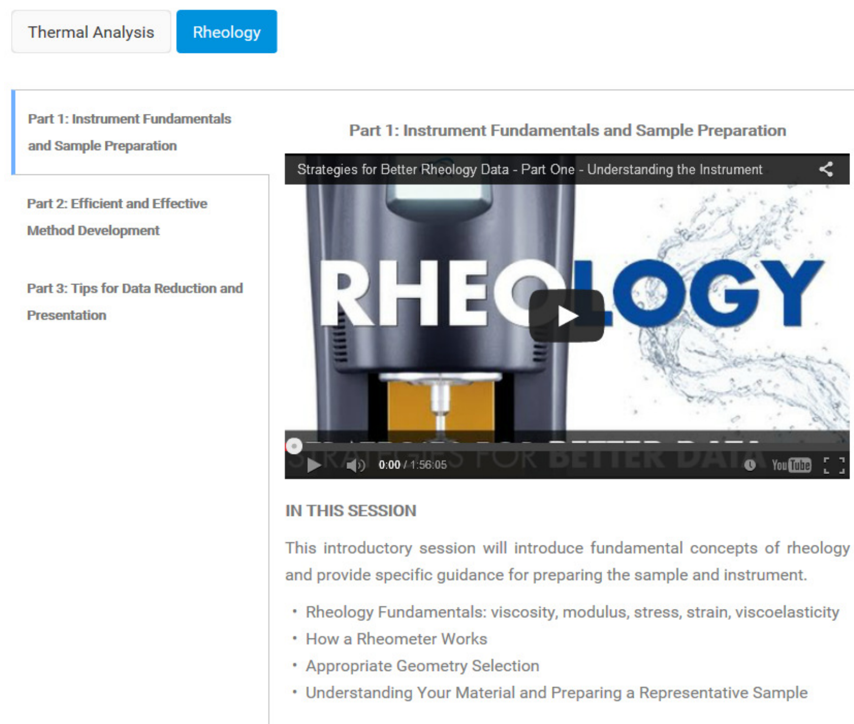
Instructional Video Resources

Quickstart e-Training Courses





Strategies for Better Data - Rheology



Avoid Testing Artifacts

- TA Webinar - Professor Randy H. Ewoldt

  http://www.tainstruments.com/randy-h-ewoldt-experimental-challenges-of-shear-rheology-how-to-avoid-bad-data-2/

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.

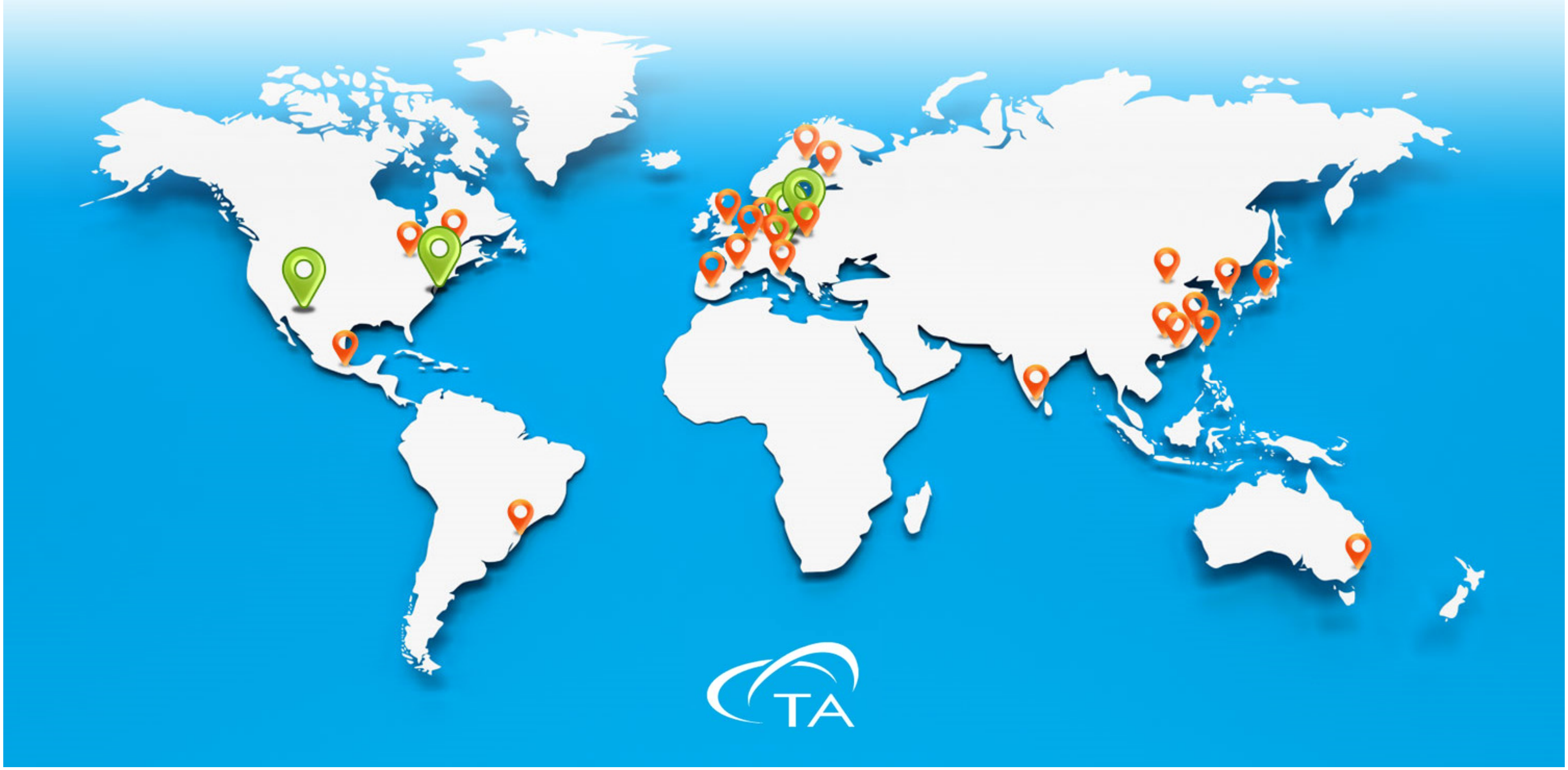
Ewoldt R.H., Johnston M. T., Caretta L.M., “Experimental challenges of shear rheology: how to avoid bad data”, in: S. Spagnolie (Editor), *Complex Fluids in Biological Systems*, Springer (2015) 1-36

What if I need help?

- TA Tech Tips
  - http://www.youtube.com/tatechtips
- On-site training & e-Training courses - see Website
- TA Instruments Applications Helpline available from the TA website
  - http://www.tainstruments.com/support/applications/applications-hotline/
- Service related queries
  - Email: servicehelpline@tainstruments.com
  - Ph: 302-427-4050
- Check out our Website
  - http://www.tainstruments.com/

Thank You

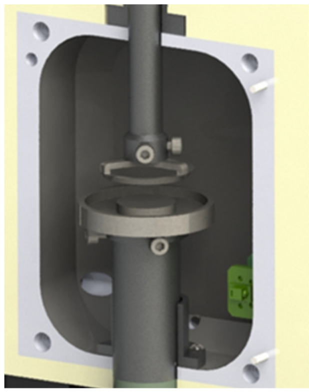
The World Leader in Thermal Analysis, Rheology, and Microcalorimetry



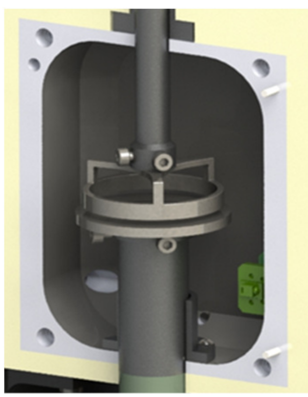
Applications of Rheology

Advanced Accessories

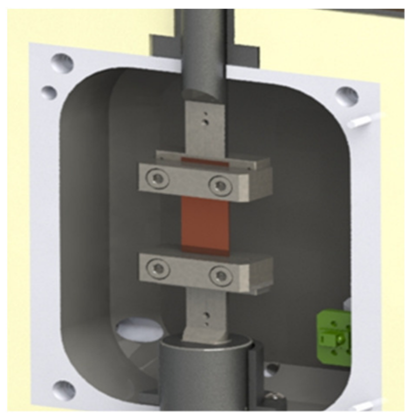
DHR Humidity Accessory



▪ Surface Diffusion



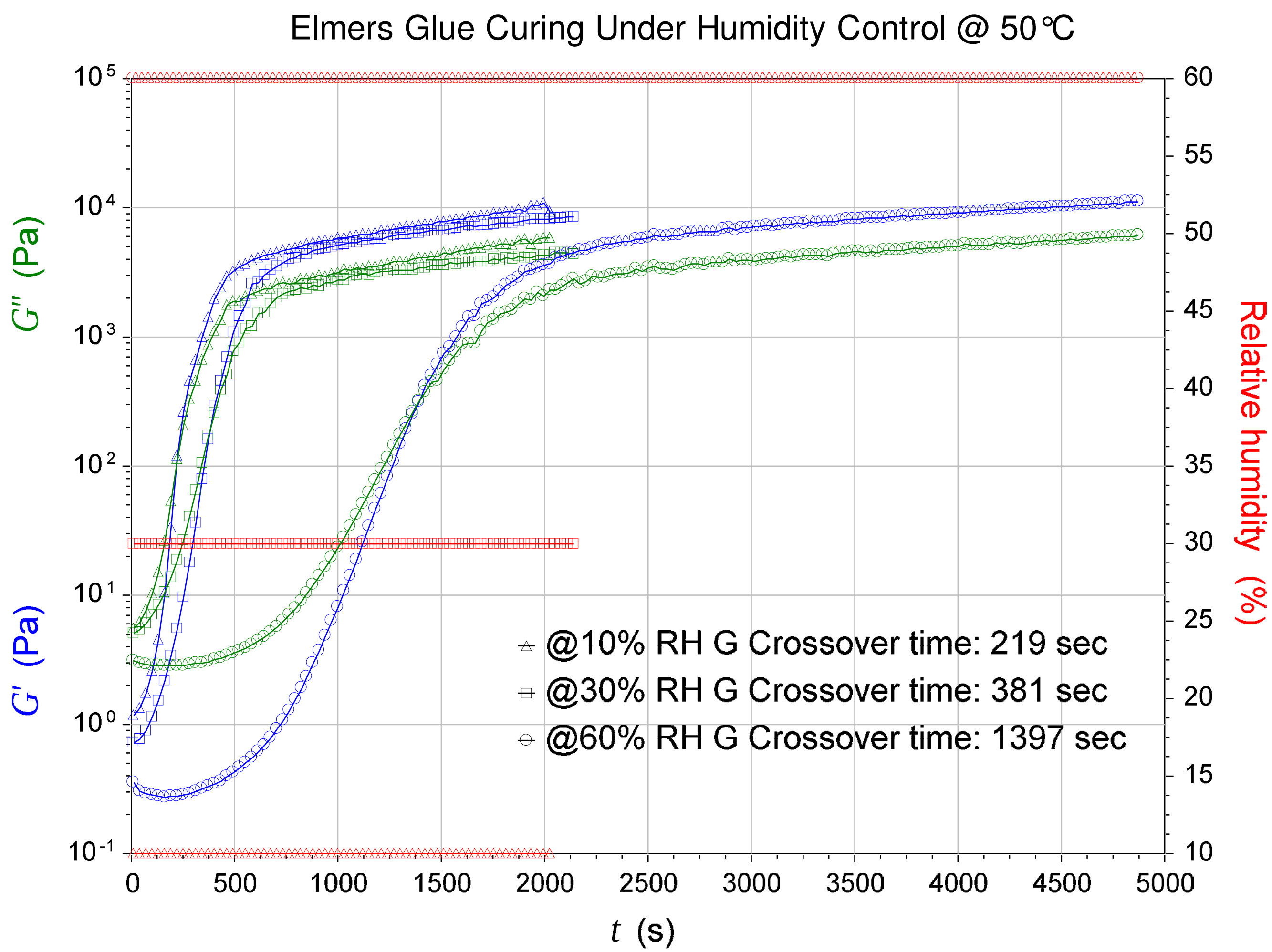
▪ Bulk Diffusion



▪ Film/fiber Tension

Temperature Range 5 ℃ – 120 ℃
Temperature Accuracy ±0.5 ℃
Heating/Cooling Rate ±1 °C/min maximum
Humidity Range 5- 95%
Humidity Accuracy 5-90%RH: ±3% RH >90%RH: ±5% RH
Humidity Ramp Rate ±2% RH/min increasing or decreasing

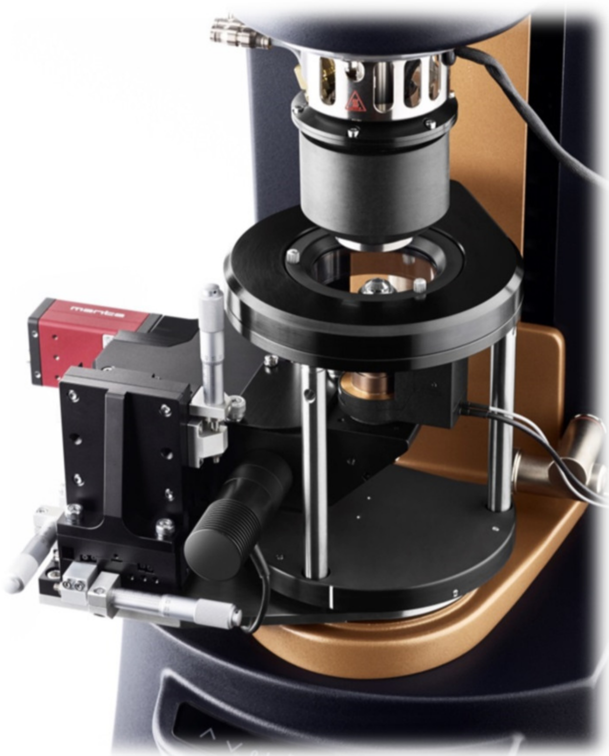
DHR Humidity Accessory

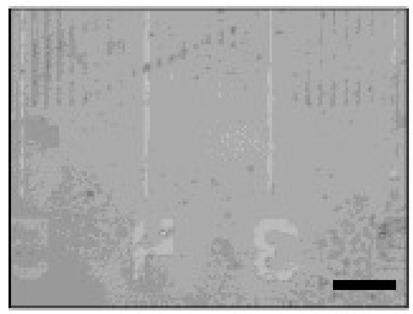


- Bulk diffusion geometry at 50°C and constant RH (10%, 30% and 60%)
- The test frequency - 1.0 rad/s and oscillation torque - 5 µN·m

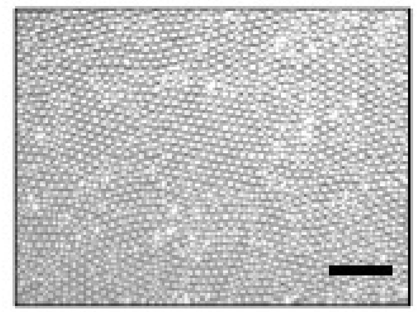
Modular Microscope Accessory (DHR)

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

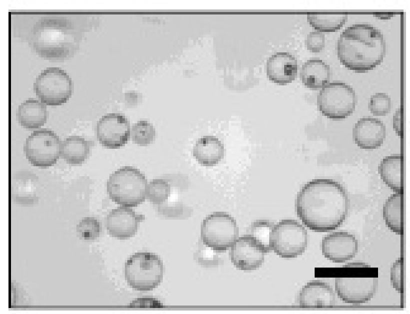




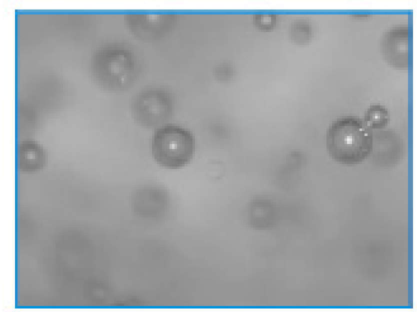
Calibration Grid, 20X



7 µm Fluorescent PS Spheres, 20X



Glass Spheres in PDMS, 20X

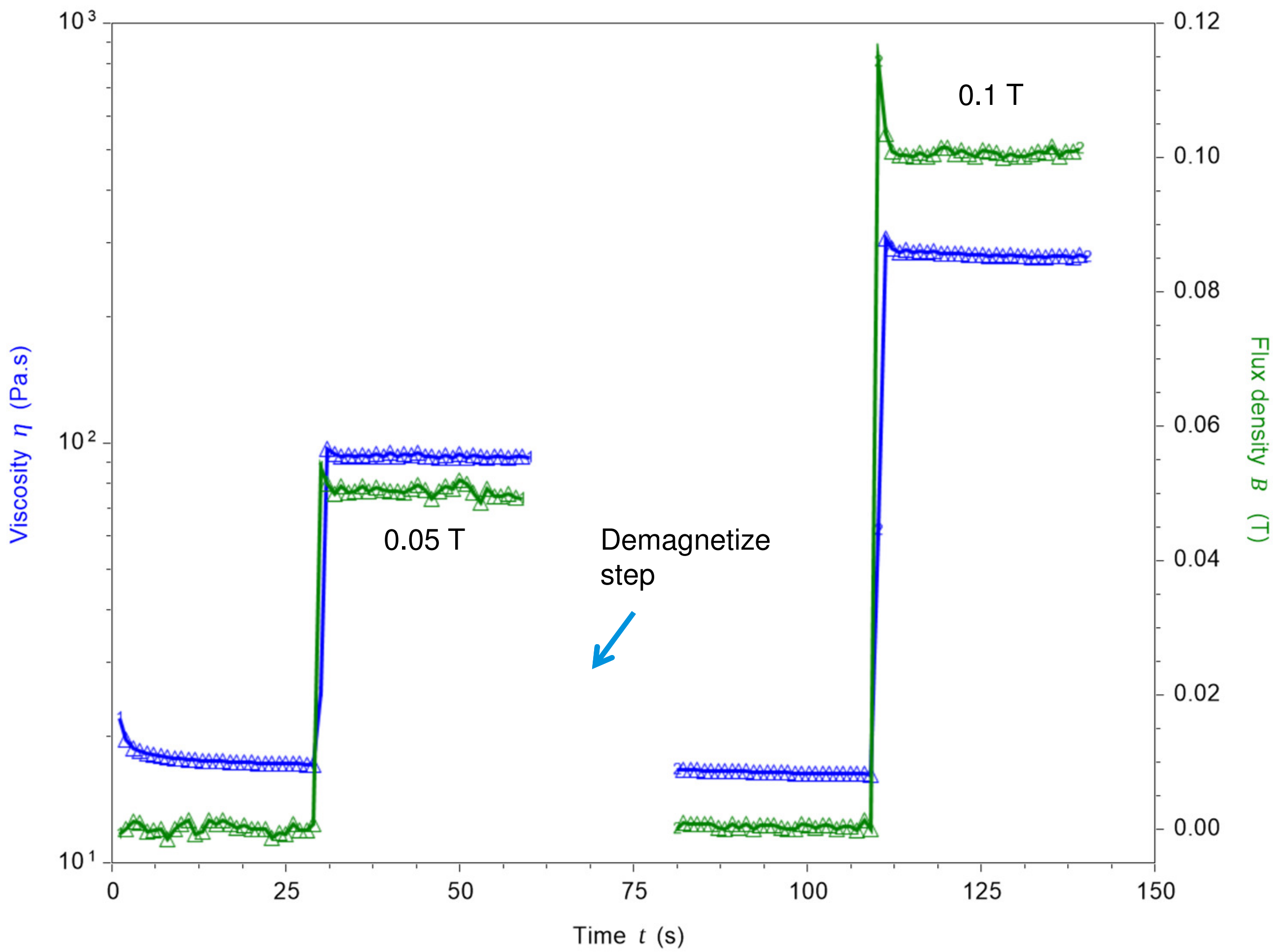


3D scan of hollow glass spheres, 20X

MagnetoRheology Accessory (DHR)

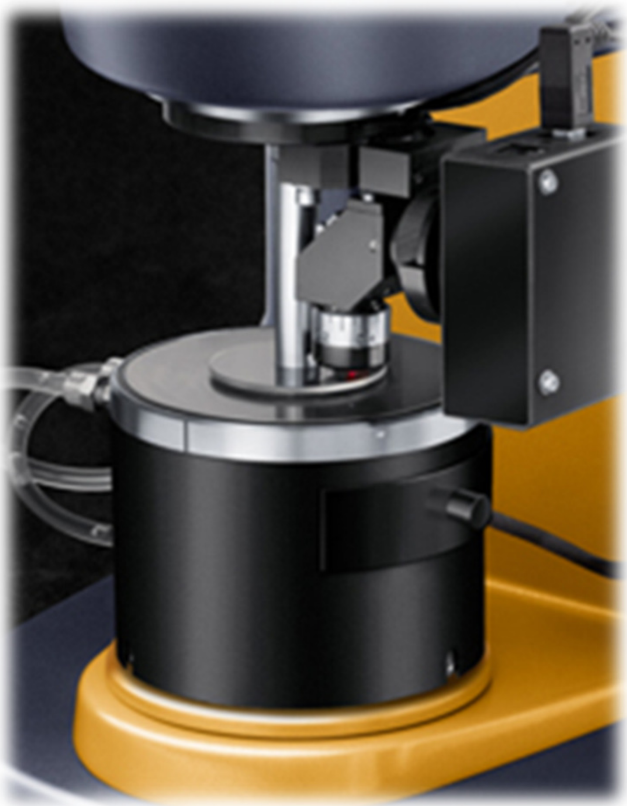
- The MR Accessory enables characterization of magneto-rheological fluids under the influence of a controlled field
- Applied fields up to 1 T with temperature range of -10 ℃ to 170 ℃ (standard and extended temperature options)
- The system accommodates an optional Hall probe for real-time measurement and closed-loop control of the sample field

Magneto Rheology Accessory (DHR)



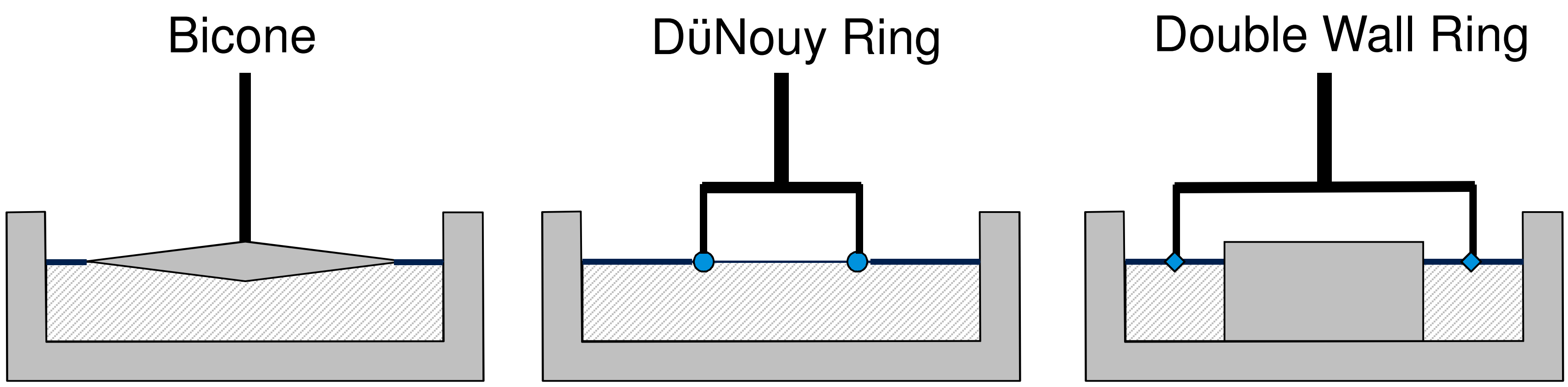
- Lord MR Fluid MRF-140CG (081610) – 300µm gap at 20°C

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



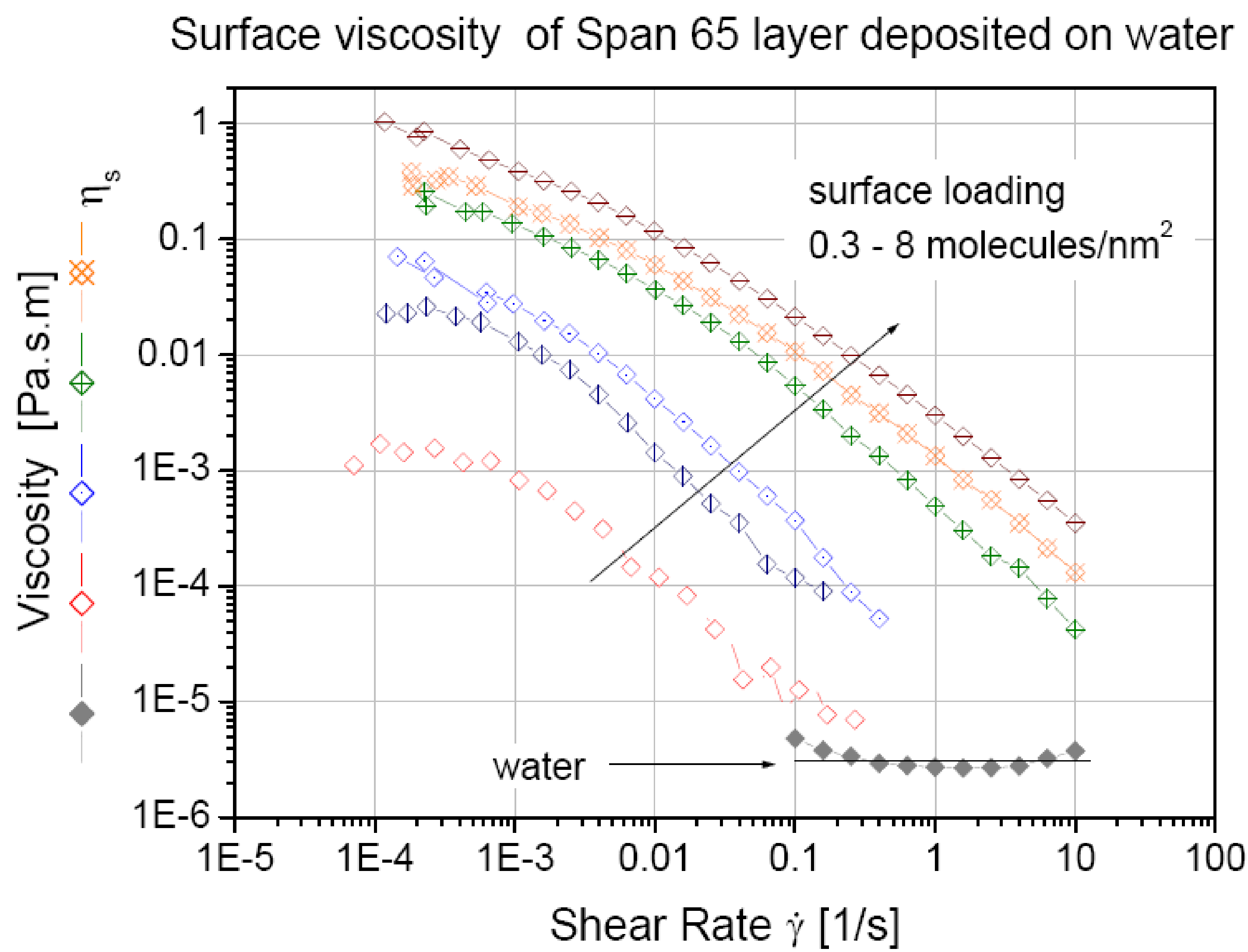
Steady Shear Viscosity at air/liquid and liquid/liquid interface.

Qualitative Viscoelastic measurements at air/liquid and liquid/liquid interface.

Quantitative Viscoelastic measurements at air/liquid and liquid/liquid interface.

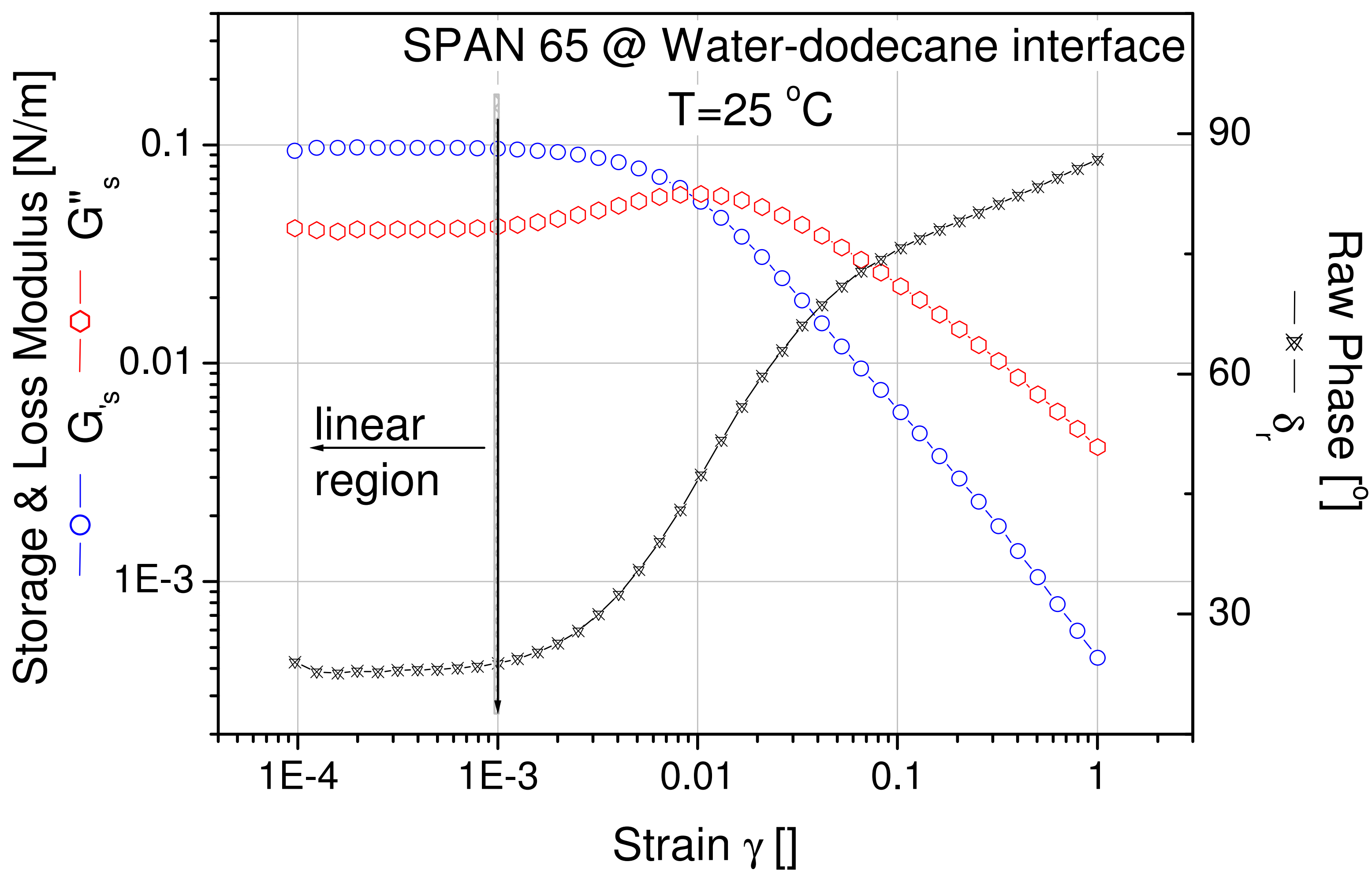
- Interfacial shear rheology of thin layers at liquid-liquid or liquid-gas interfaces
- Effect of particles, surfactants or proteins at the interface
- Applications: food, biomedical, enhanced oil recovery

Surface Concentration Effects on Interfacial Viscosity



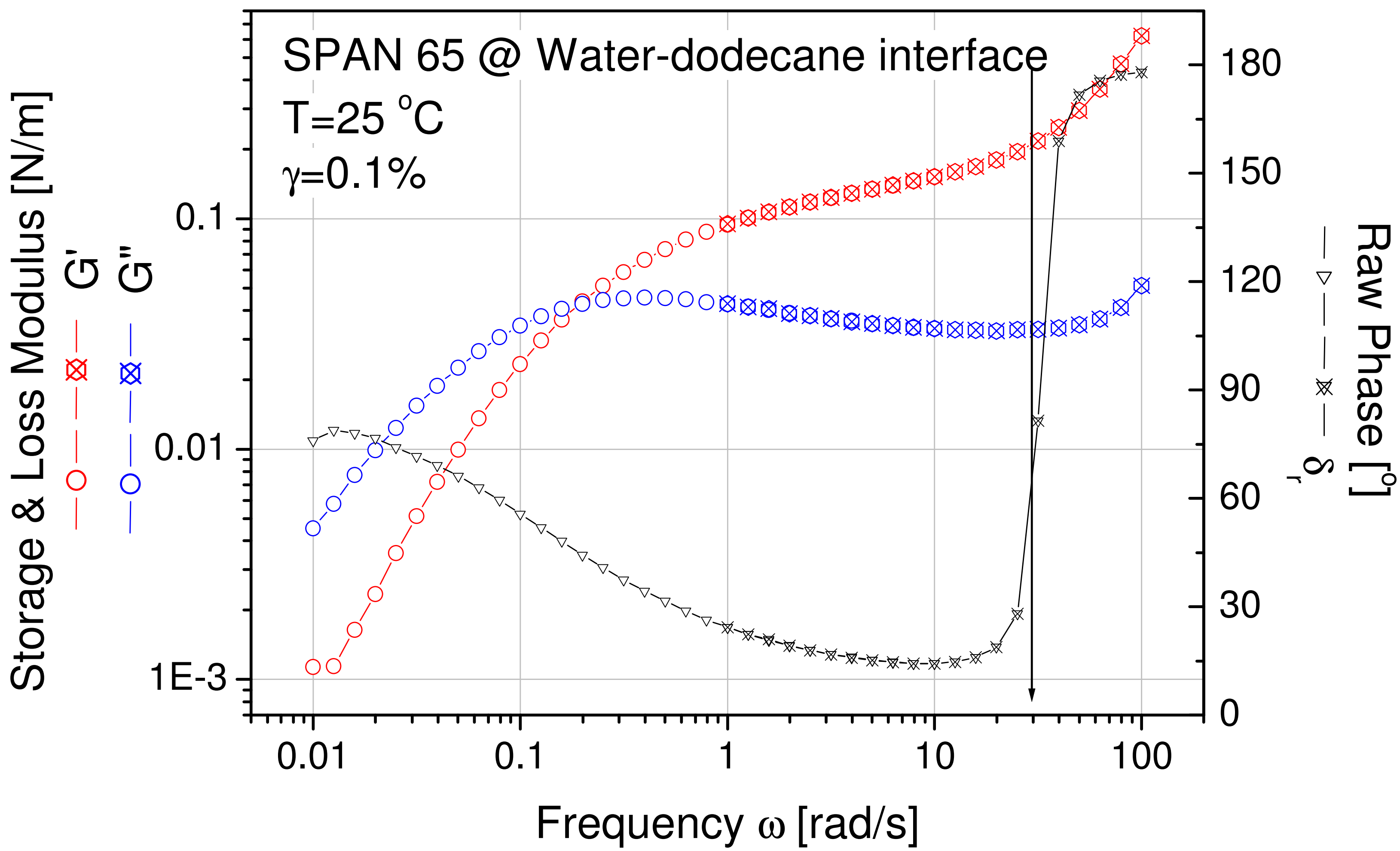
SPAN65® Water-Dodecane Interface

Interfacial properties Span65 @ water-dodecane interface



SPAN65® Water-Dodecane Interface

Interfacial properties Span65 @ water-dodecane interface

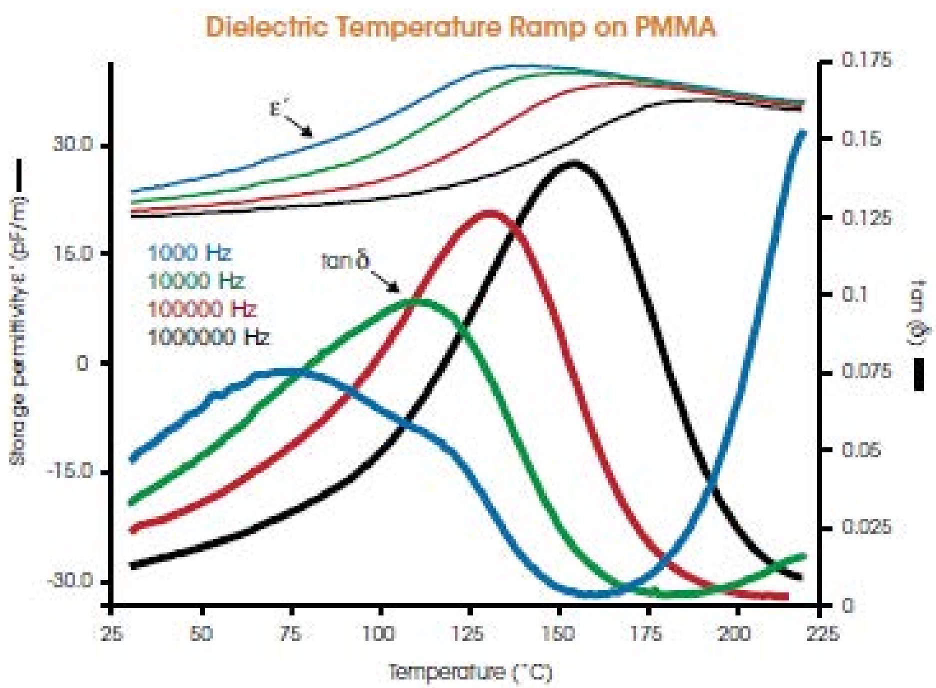


Dielectric Accessory

Agilent E4980A LCR meter

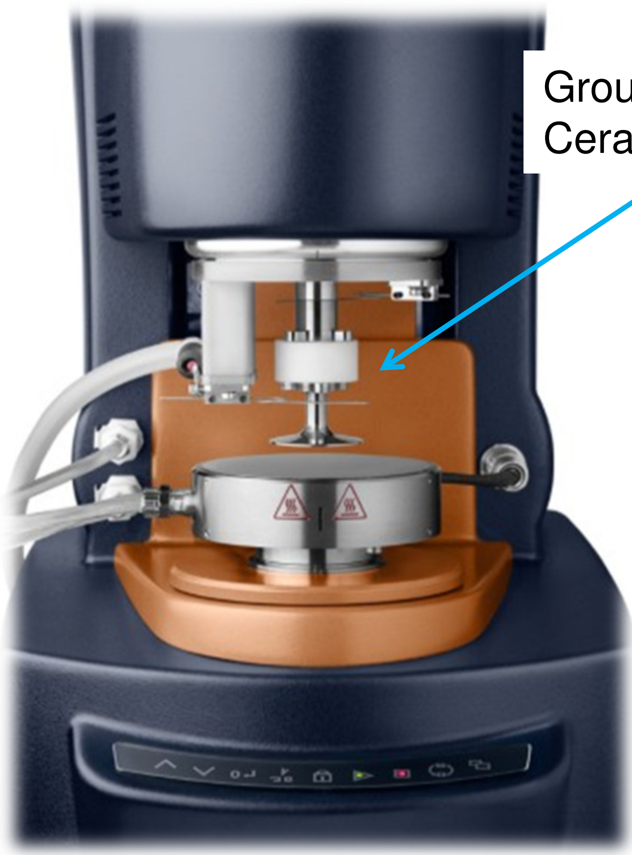
Ground Geometries with Ceramic Insulator
(standard or disposable)

Dielectric Accessory

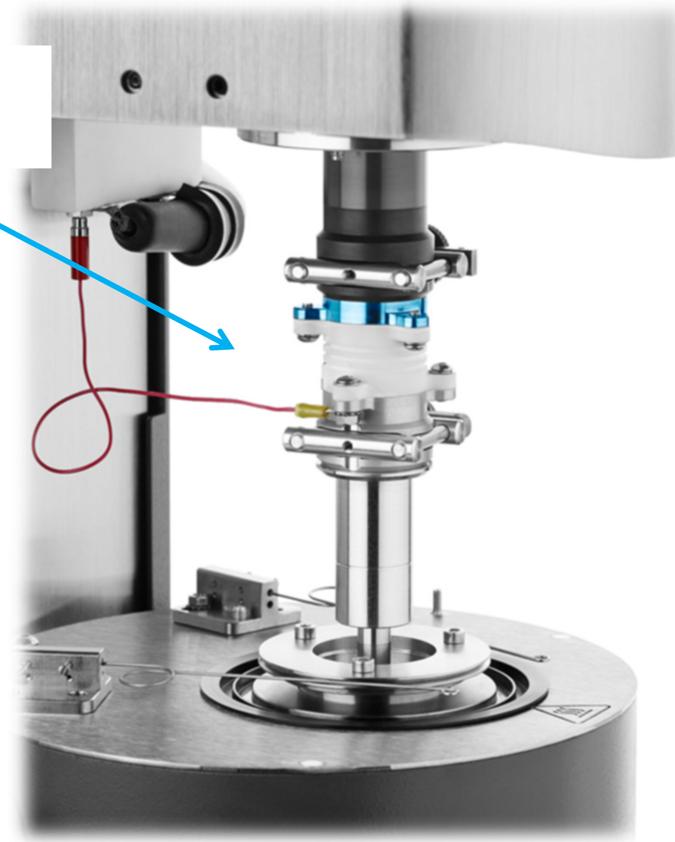


- Stand-alone or combined Dielectric-rheology
- LCR Fully programmable from TRIOS
- Wide temperature range: -160 to 350 ℃
- Applications: Characterize polar materials such as PVC, PVDF, PMMA, PVA

Electro-Rheology (ER) Accessory

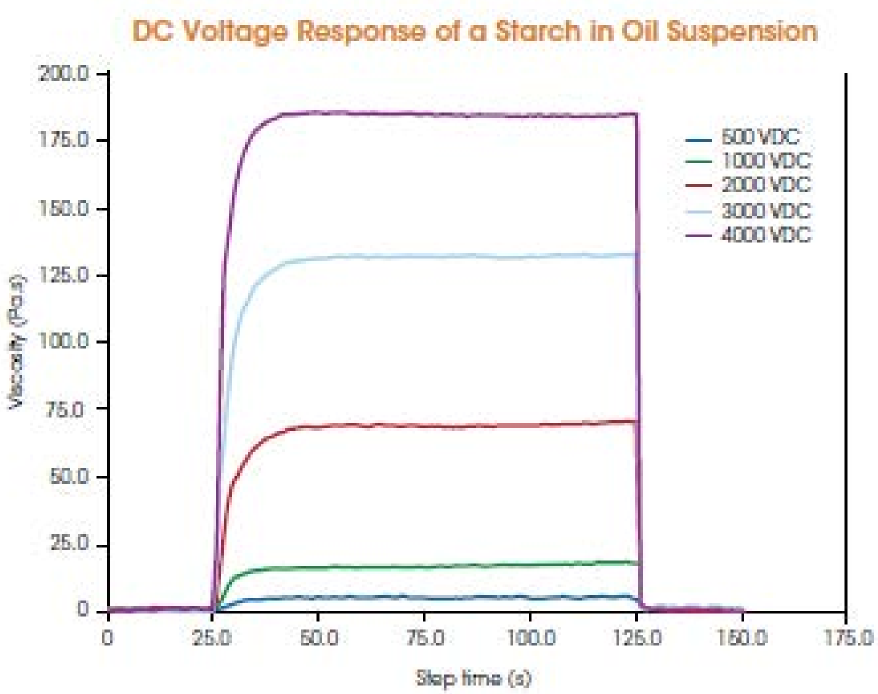


Ground Geometries with
Ceramic Insulator



- Plates and DIN concentric cylinders

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

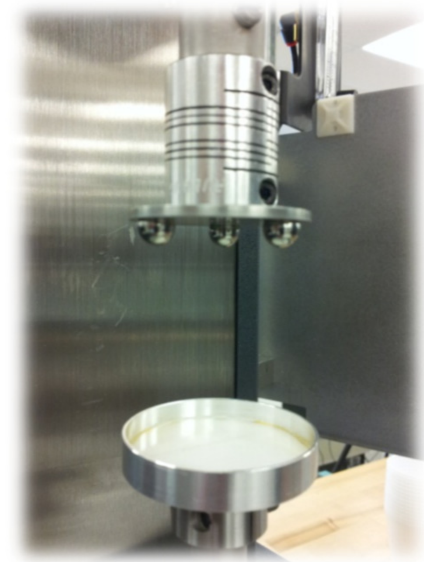
ARES G2 FCO and APS Tribology Accessory

Ring on Plate

Ball on 3 Plates

4 Balls

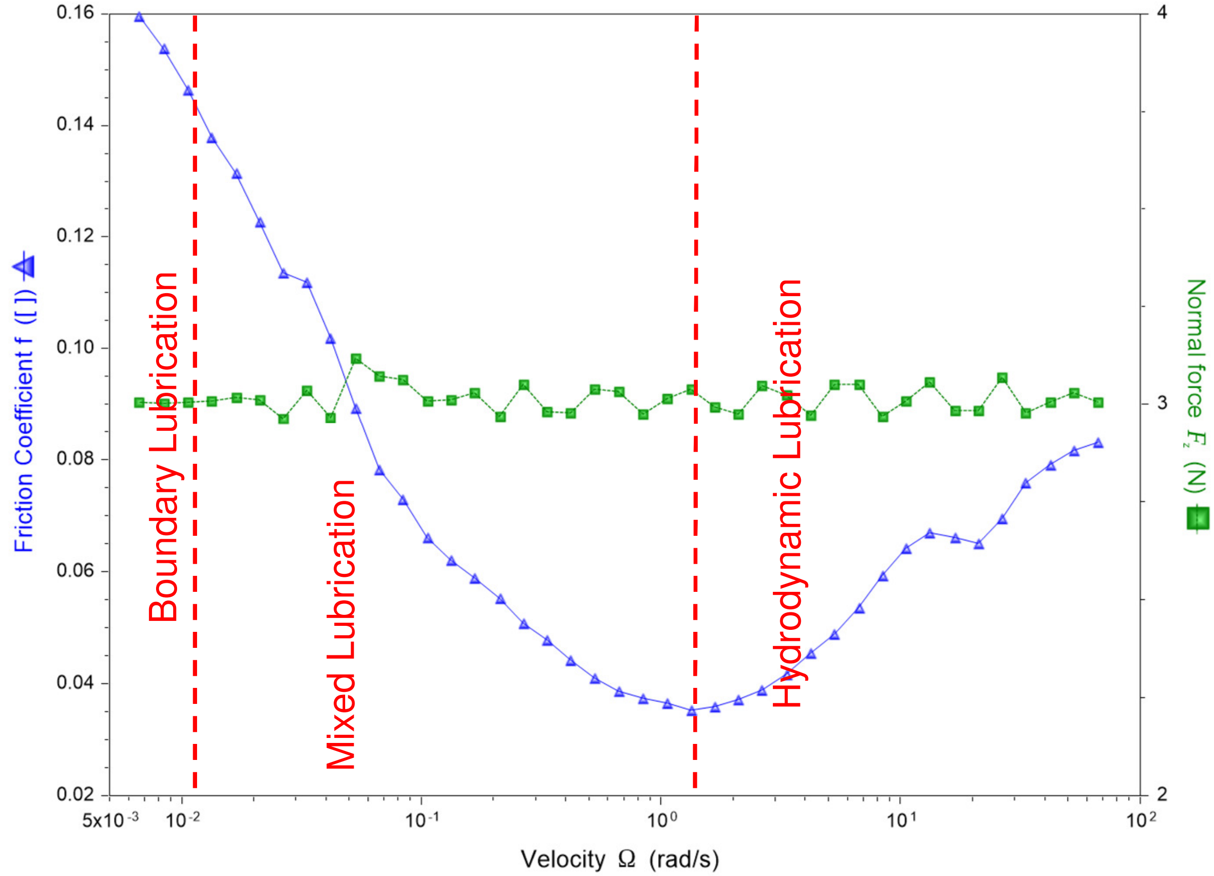
3 Balls on Plate

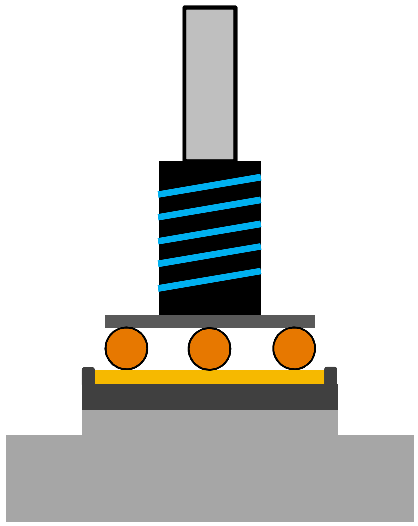


- High temperature with FCO
  - Applications: Automotive, High temp. greases/oils, Asphalt, Rubber
- Close to Room Temperature - APS and Plate
  - Applications: Personal care products, Lubricants, Foods

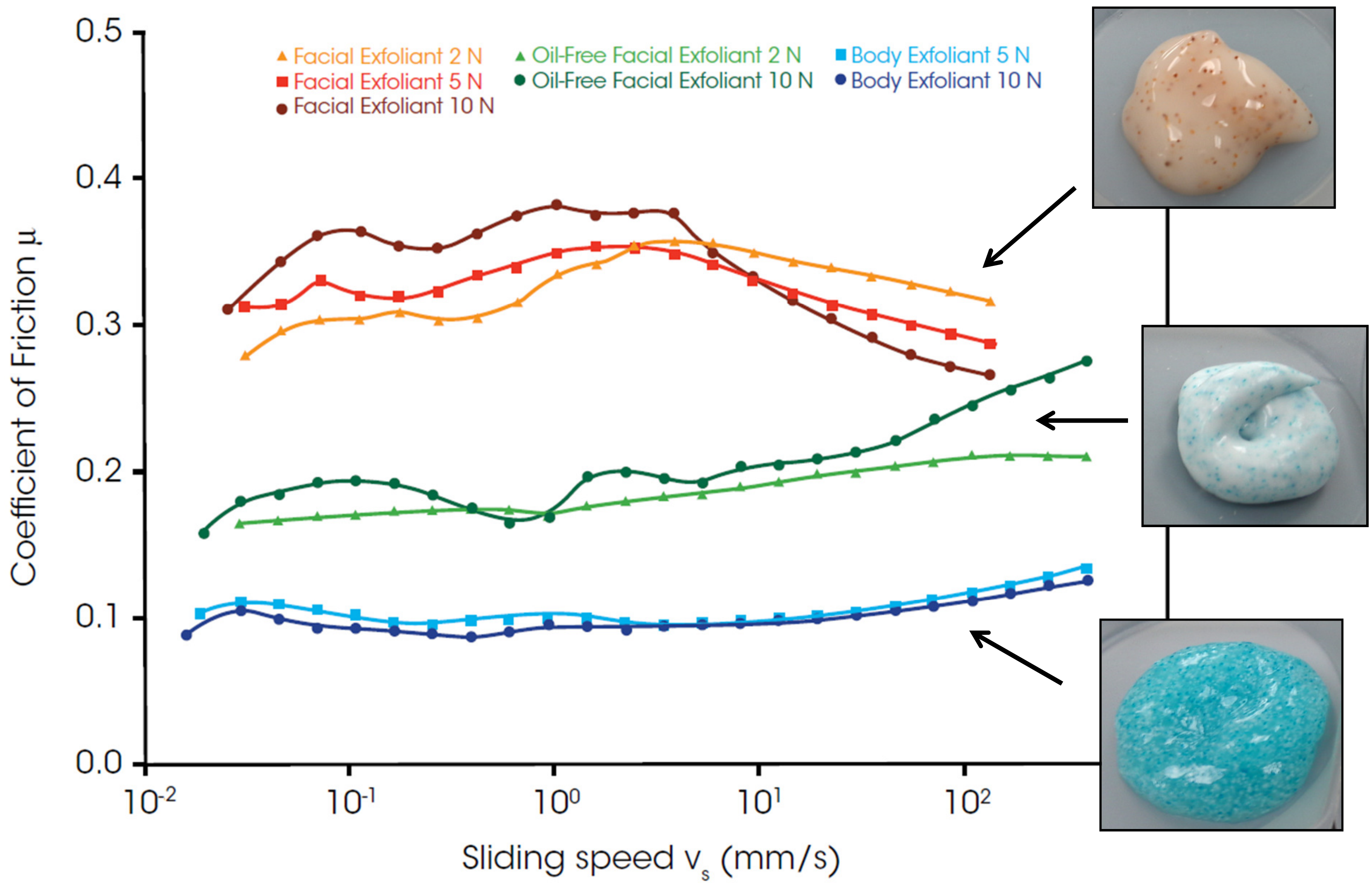
Coefficient of Friction Measurement

PVC on Steel with 2.0 Pa.s oil as lubricant
Geometry: 3 Balls on Plate
Temperature: 25℃, Procedure: Flow ramp



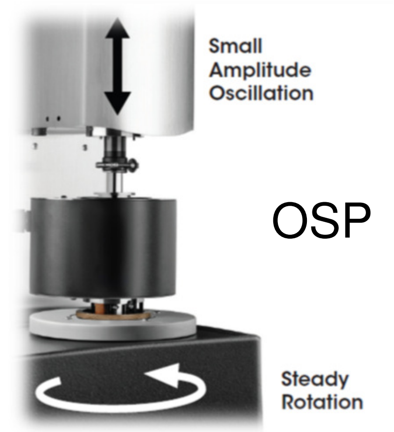


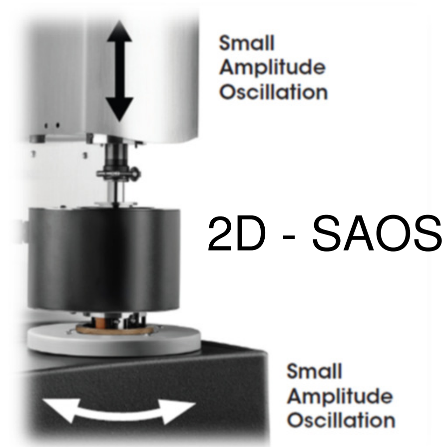
Tribo-Rheometry: Exfoliants



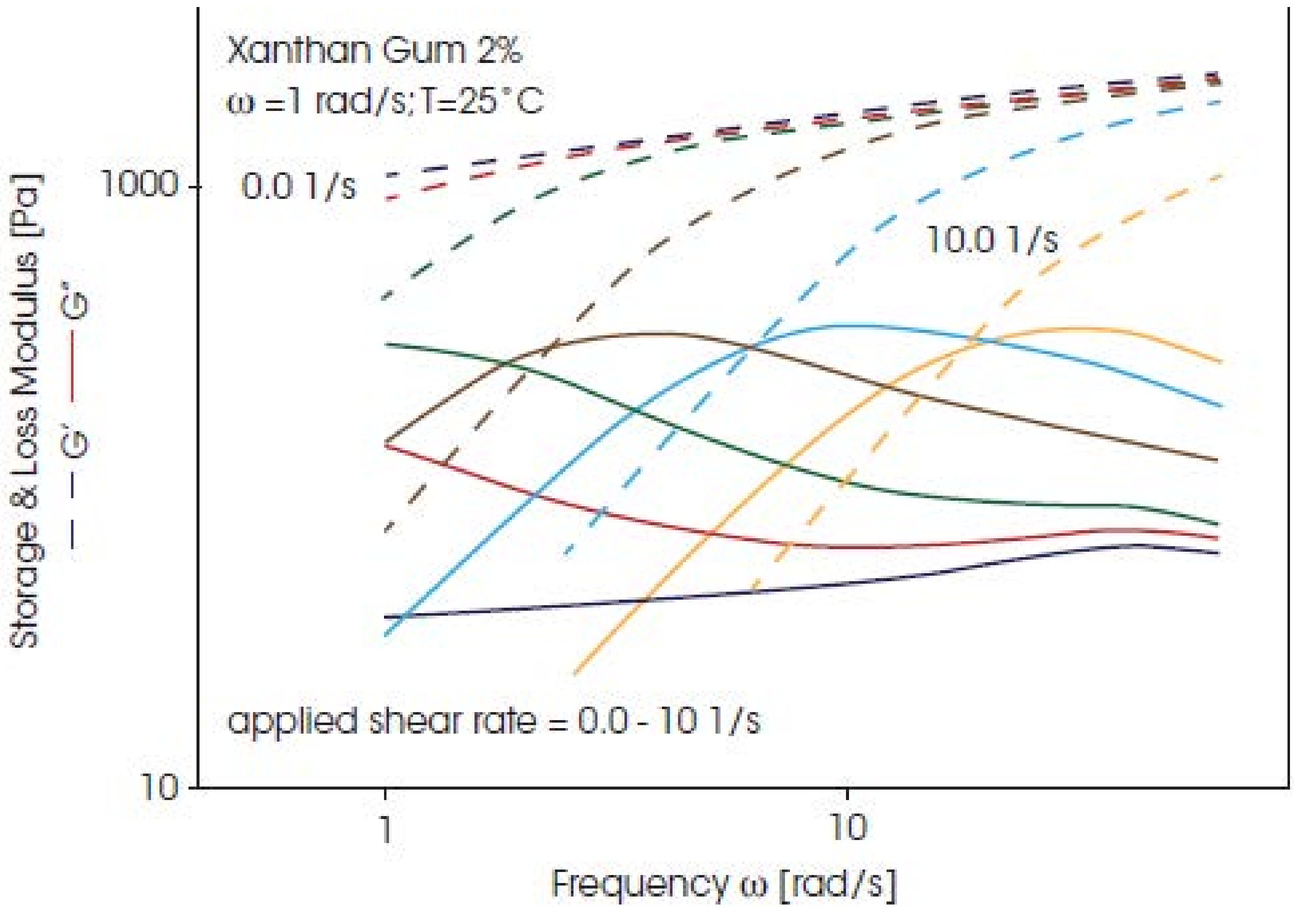
Orthogonal Superposition Features on ARES G2

- OSP on steady shear to monitor structural changes in materials (alternative to LAOS measurements)
- 2D-SAOS measurments 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,...





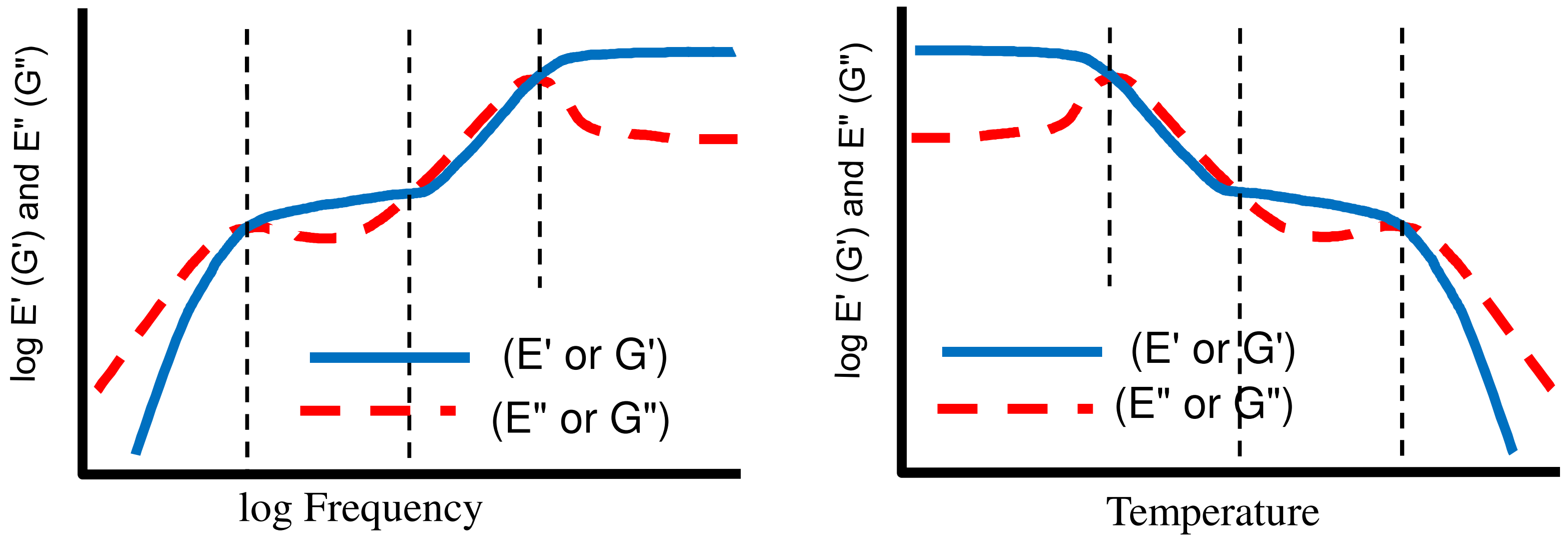
Structure breakdown monitored by OSP



Steady shear breaks downs 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

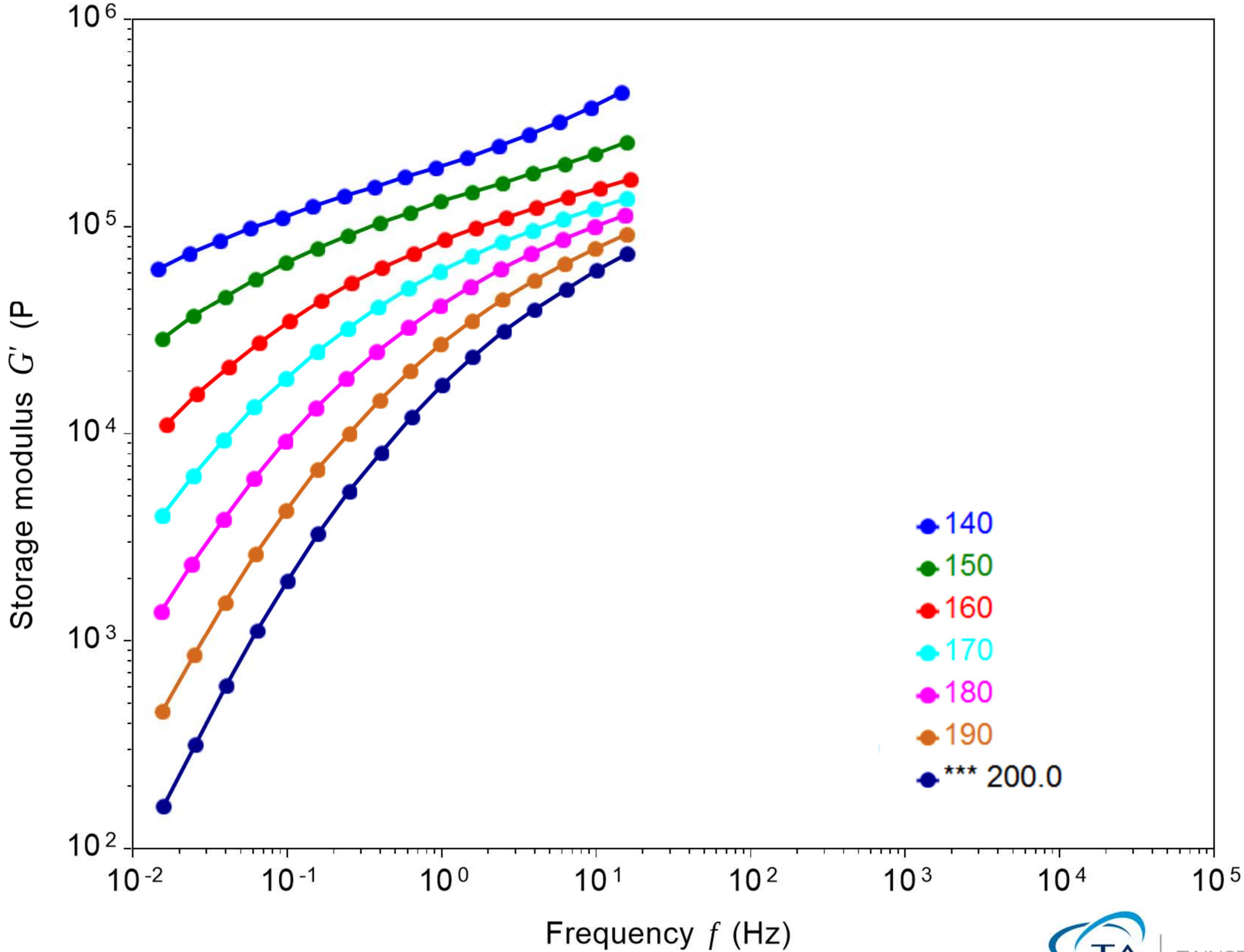
When Not to Use TTS

- 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



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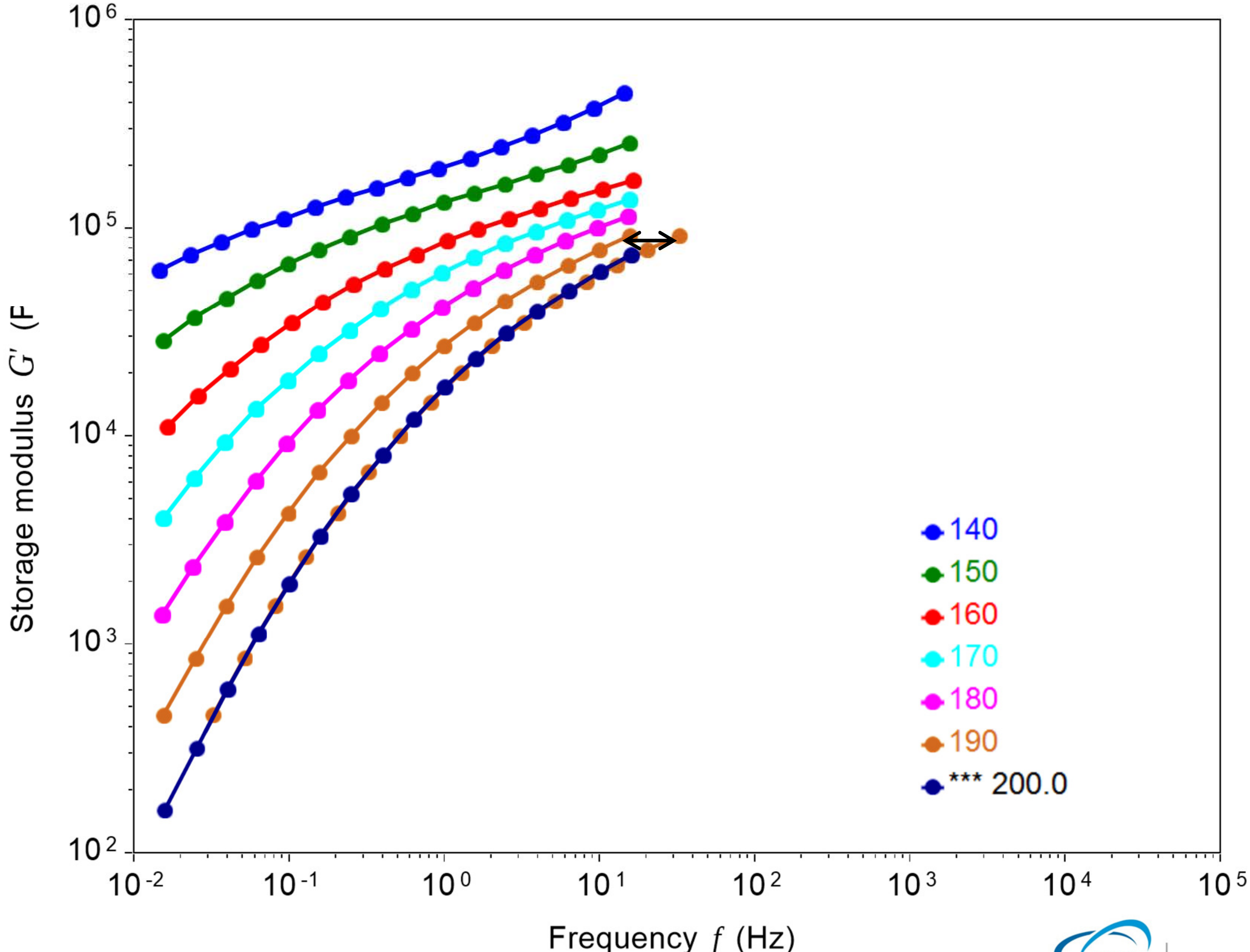
TTS Shifting



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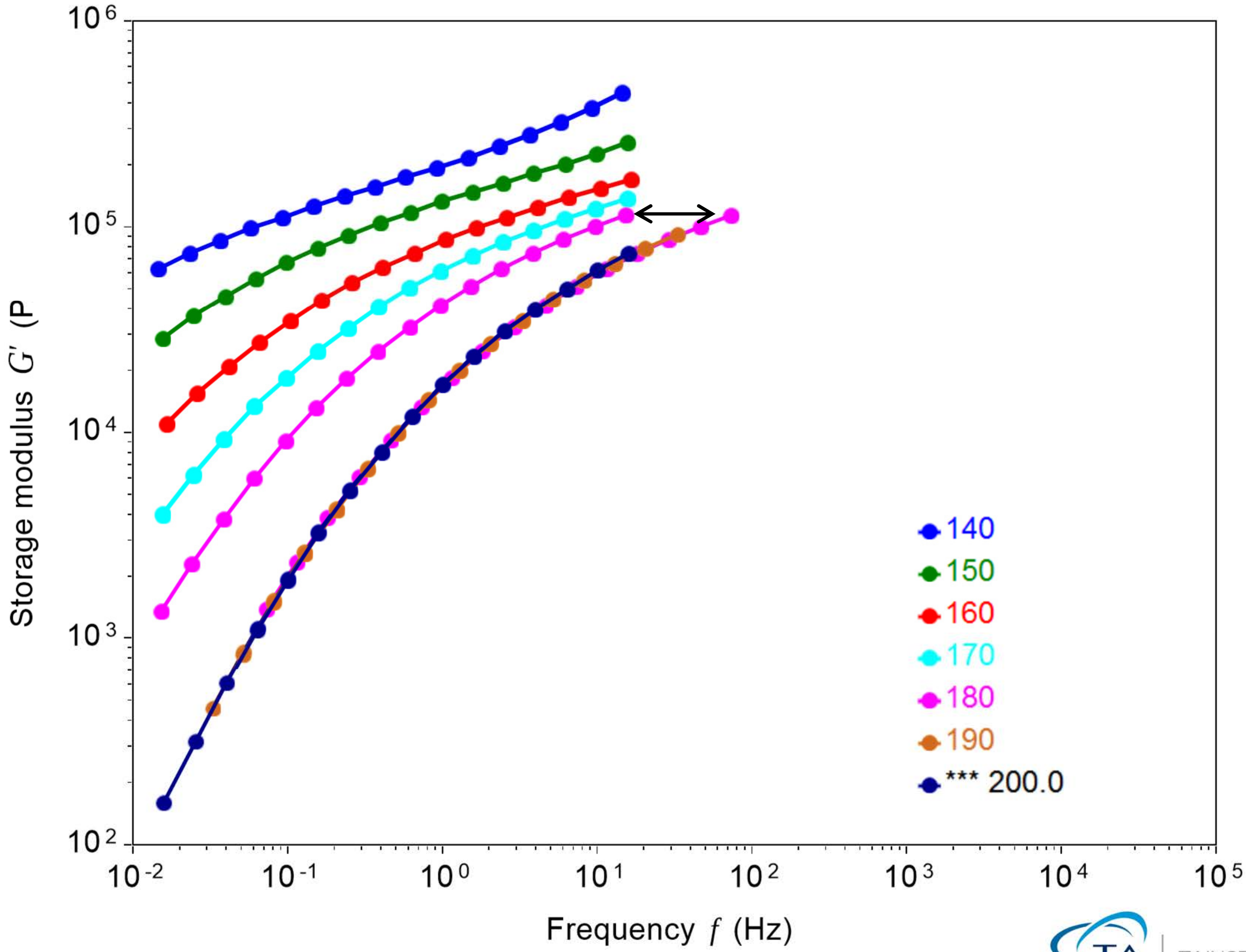
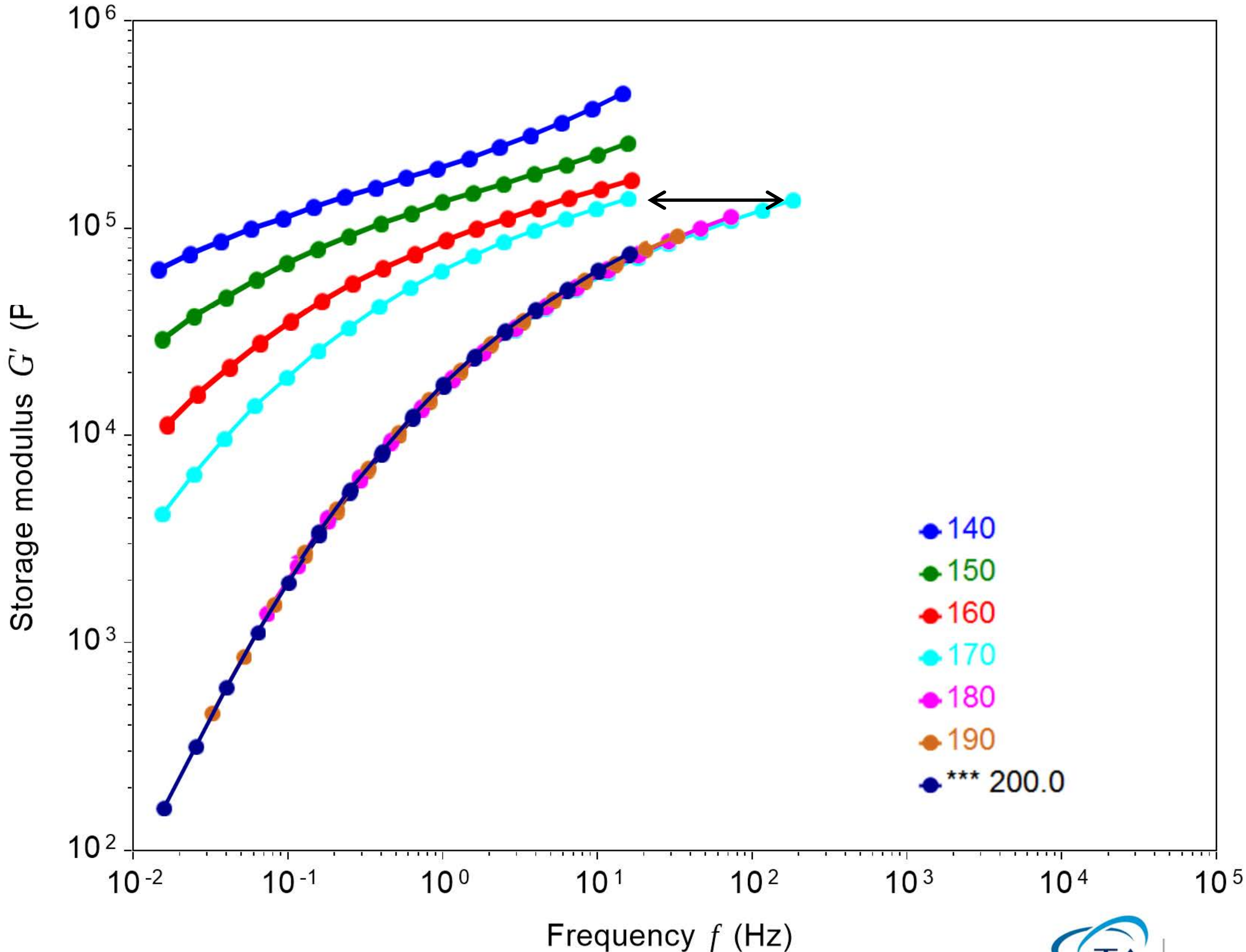
TTS Shifting



TTS Shifting



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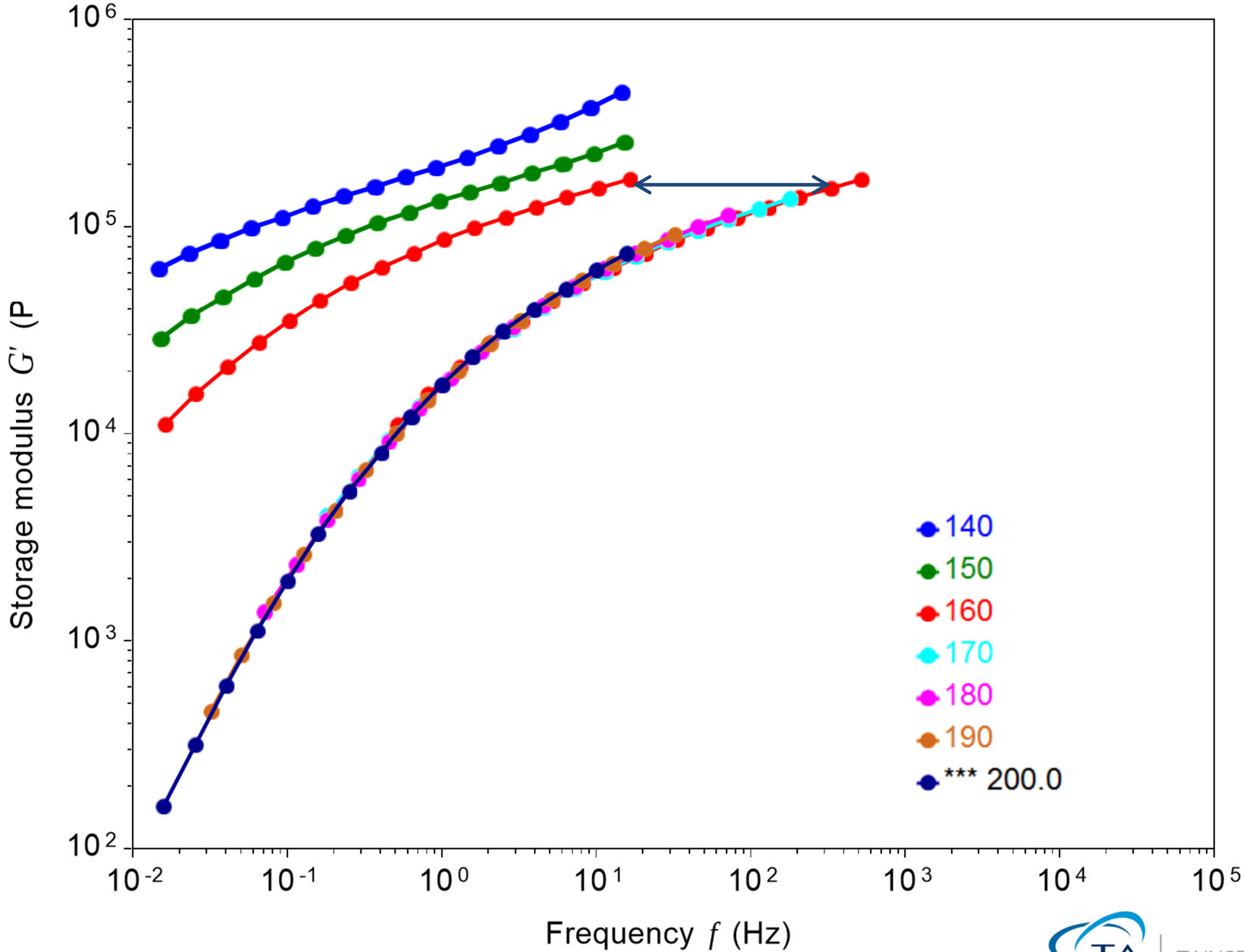
TTS Shifting



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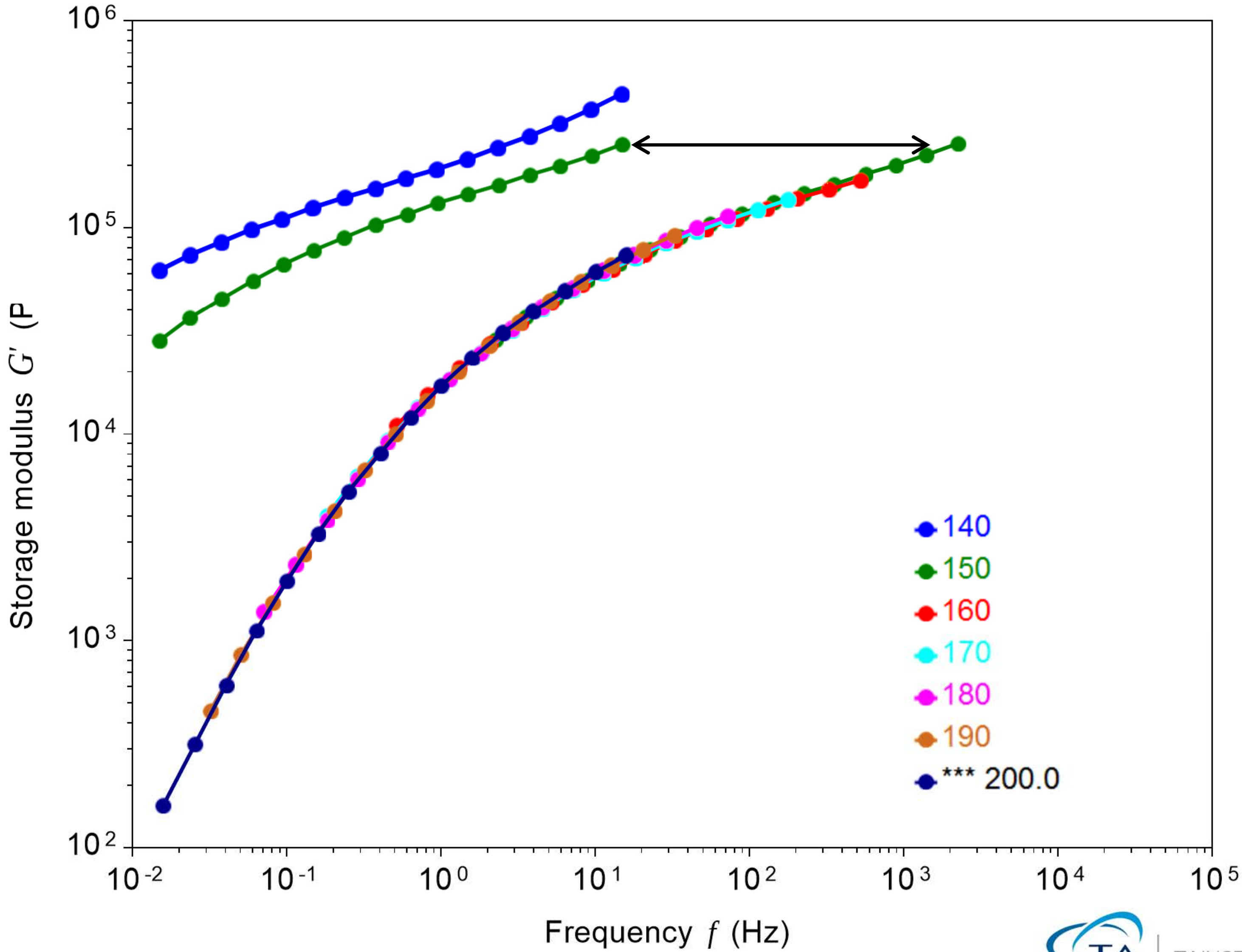
TTS Shifting



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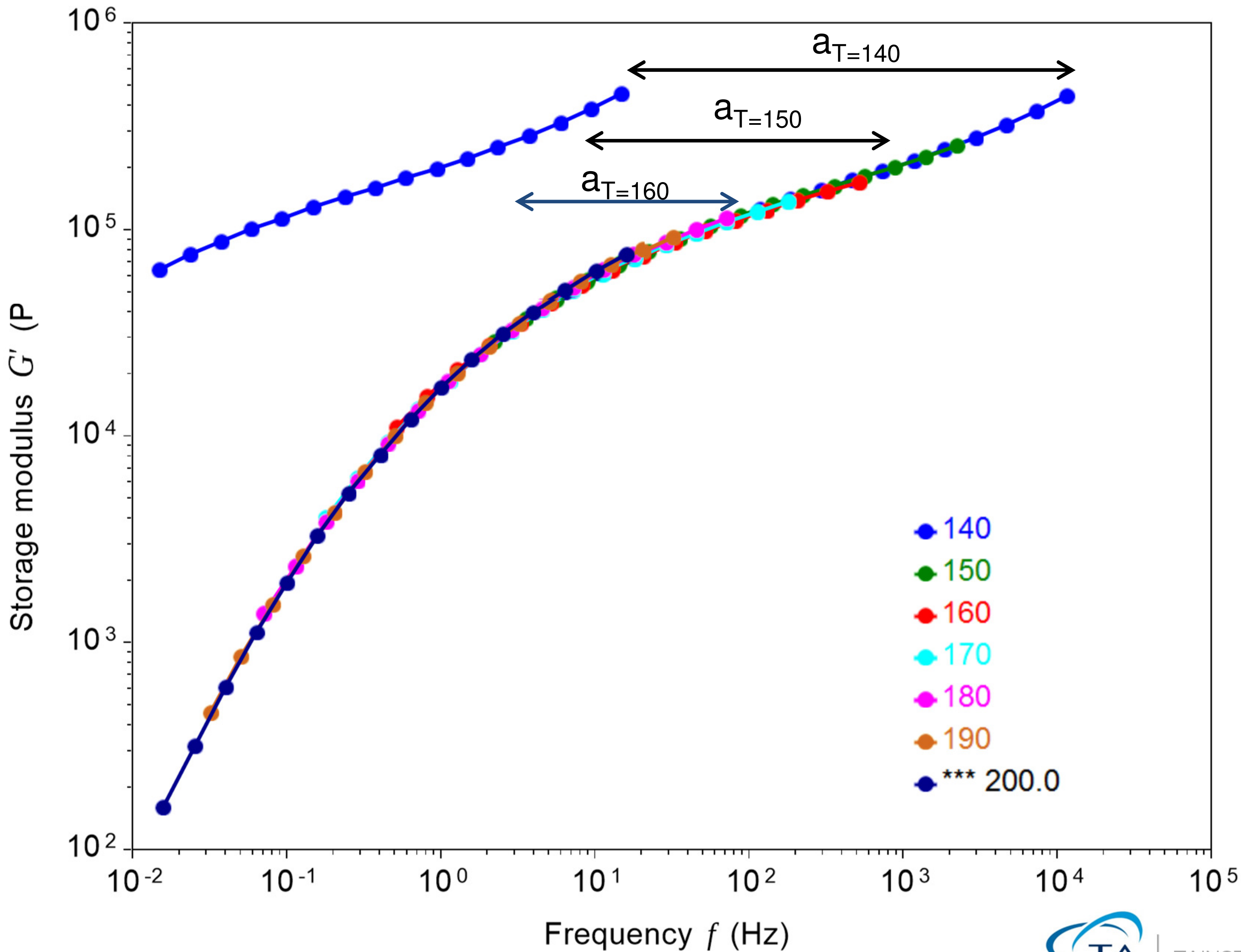
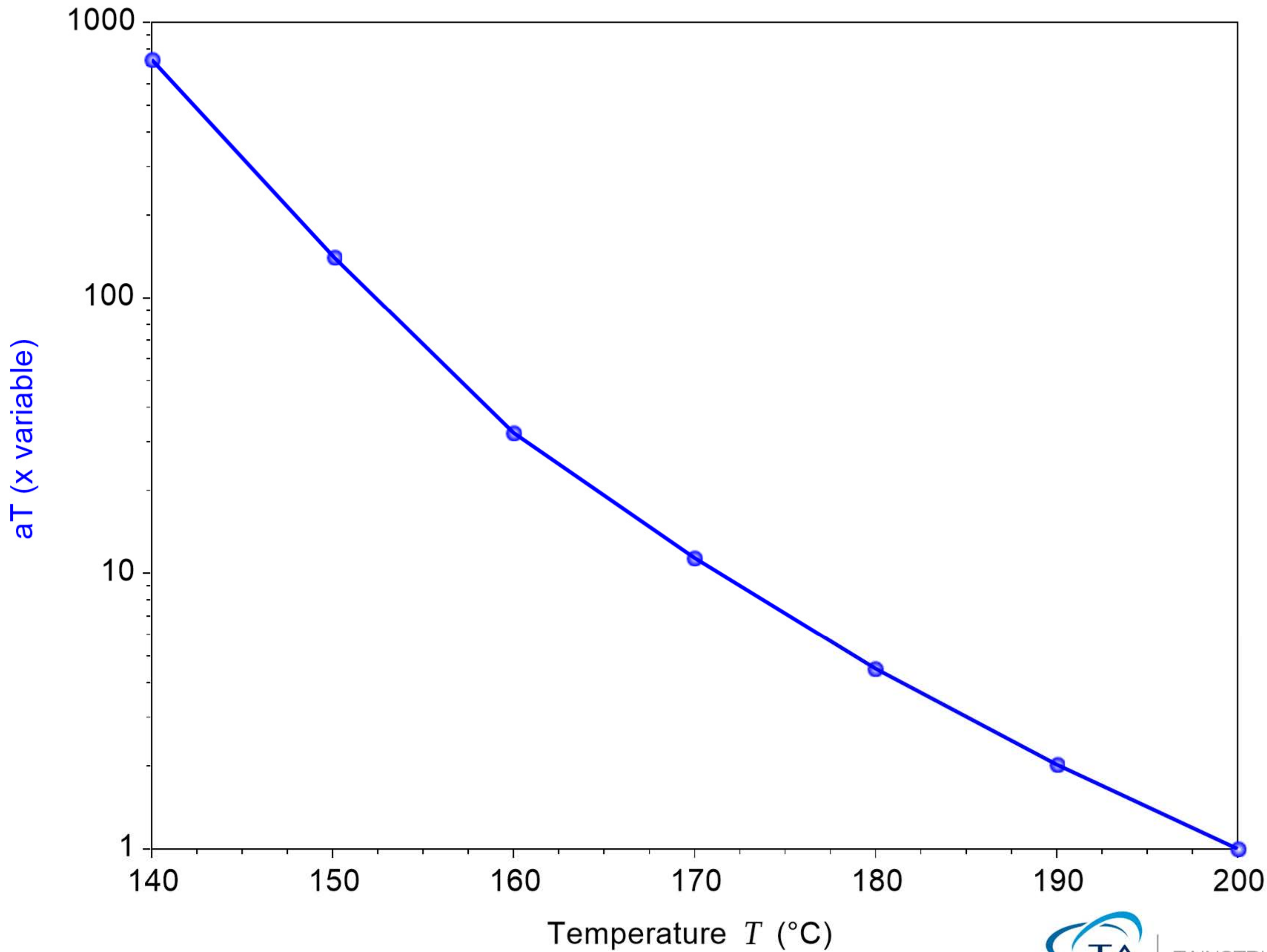
TTS Shifting



Shift Factors a_T vs Temperature



Shift Factors: WLF Equation

- 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

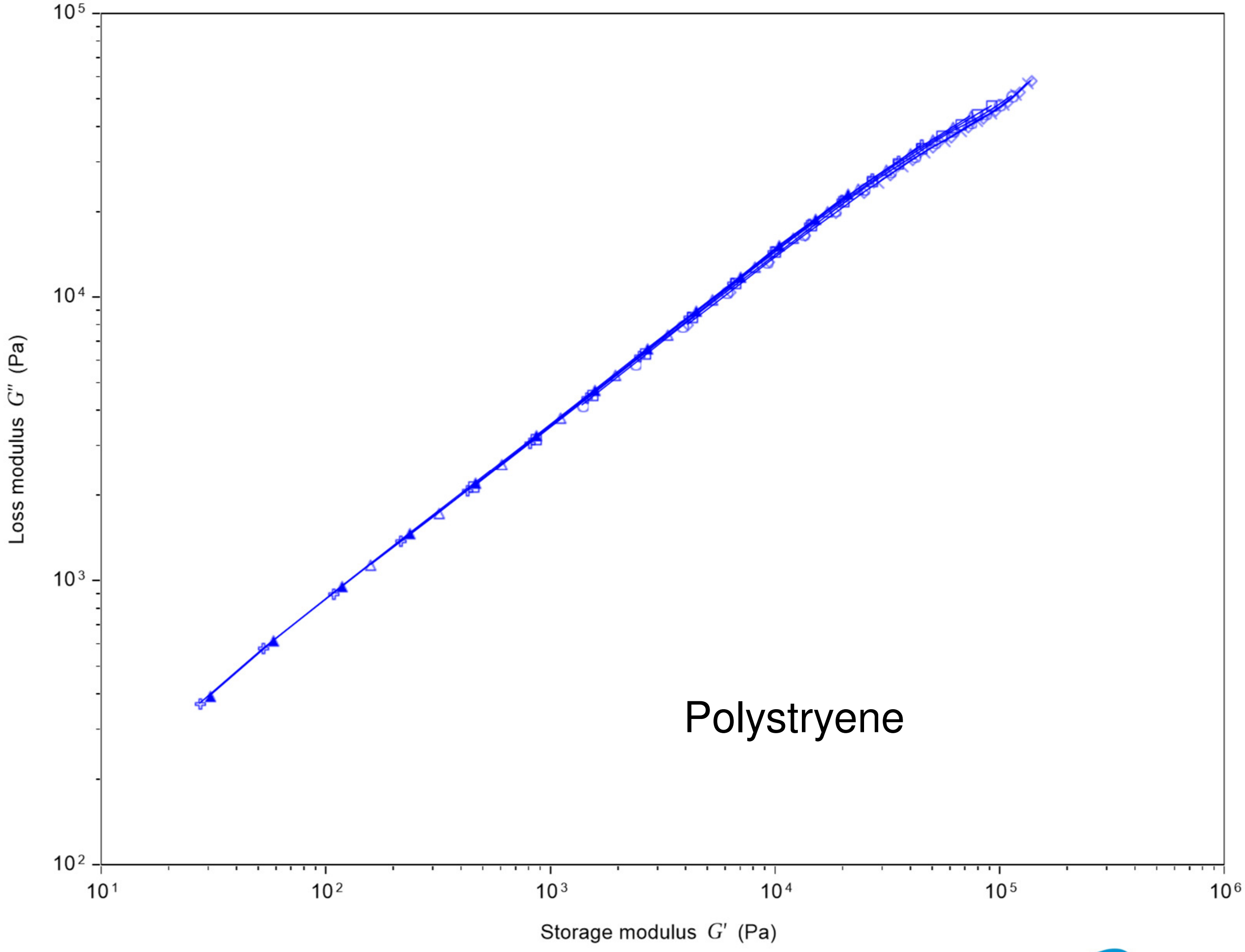
- Sometimes you shouldn't use the WLF equation (even if it appears to work)
- If $T > T_g + 100°C$
- If $T < T_g$ and polymer is not elastomeric
- If temperature range is small, then c_1 & c_2 cannot be calculated precisely

- In these cases, the Arrhenius form is usually better

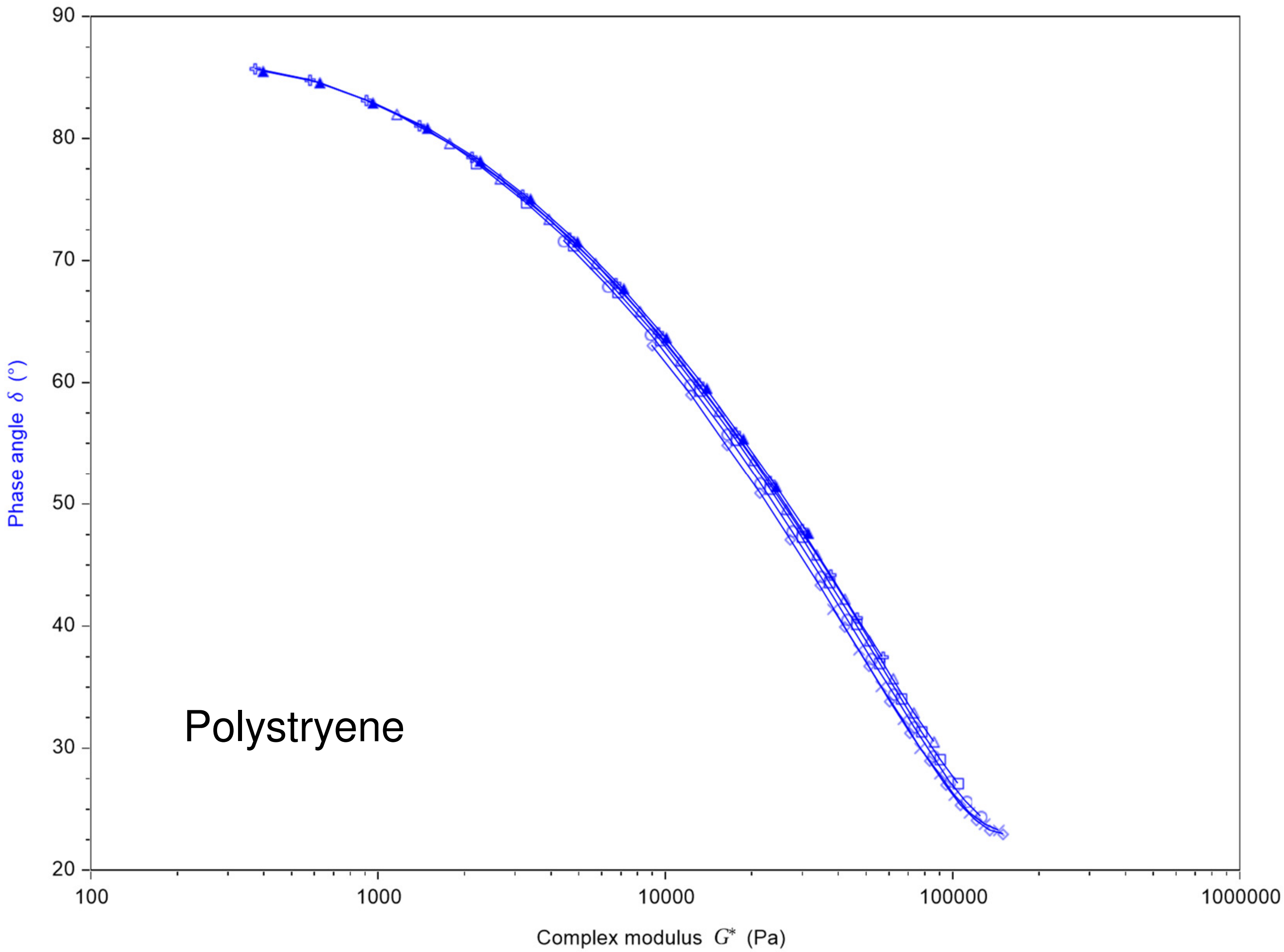
$$\ln a_T = (E_a/R)(1/T - 1/T_0)$$

  - 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



Verify Data for TTS



References for TTS

1) Ward, I.M. and Hadley, D.W., "*Mechanical Properties of Solid Polymers*", Wiley, 1993, Chapter 6.

2) Ferry, J.D., "*Viscoelastic Properties of Polymers*", Wiley, 1970, Chapter 11.

3) Plazek, D.J., "*Oh, Thermorheological Simplicity, wherefore art thou?*" Journal of Rheology, vol 40, 1996, p987.

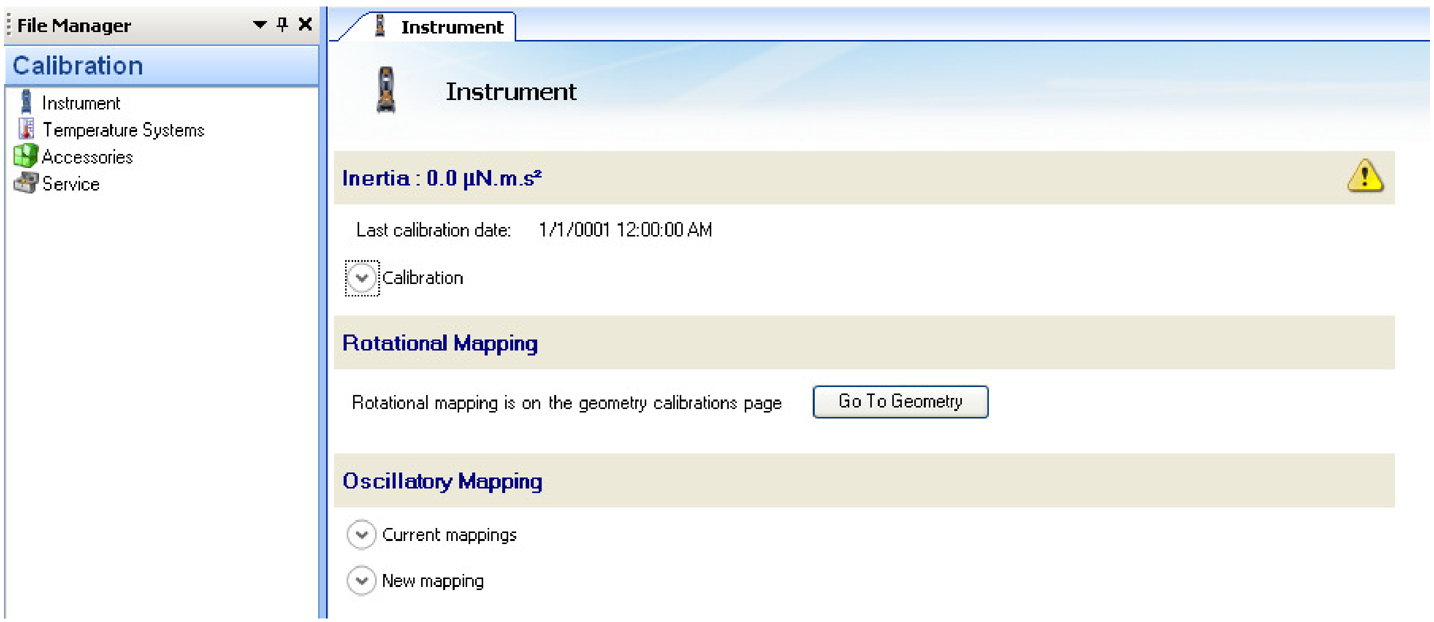
4) Lesueur, D., Gerard, J-F., Claudy, P., Letoffe, J-M. and Planche, D., "*A structure related model to describe asphalt linear viscoelasticity*", Journal of Rheology, vol 40, 1996, p813.

Appendix 2: Rheometer Calibrations

DHR and AR

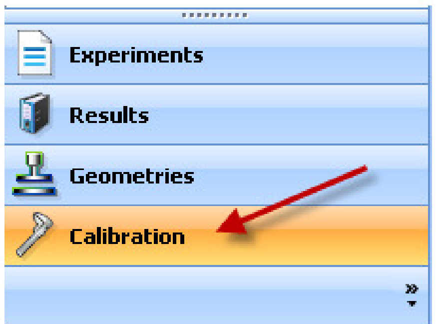
DHR – Calibration Options

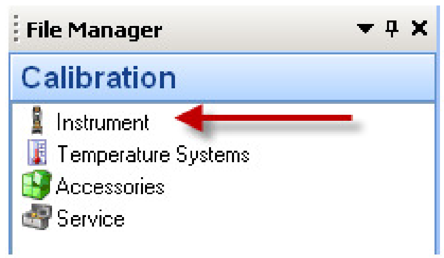
- Instrument Calibrations
  - Inertia (Service)
  - Rotational Mapping
  - Oscillation Mapping (recommended for interfacial measurements)

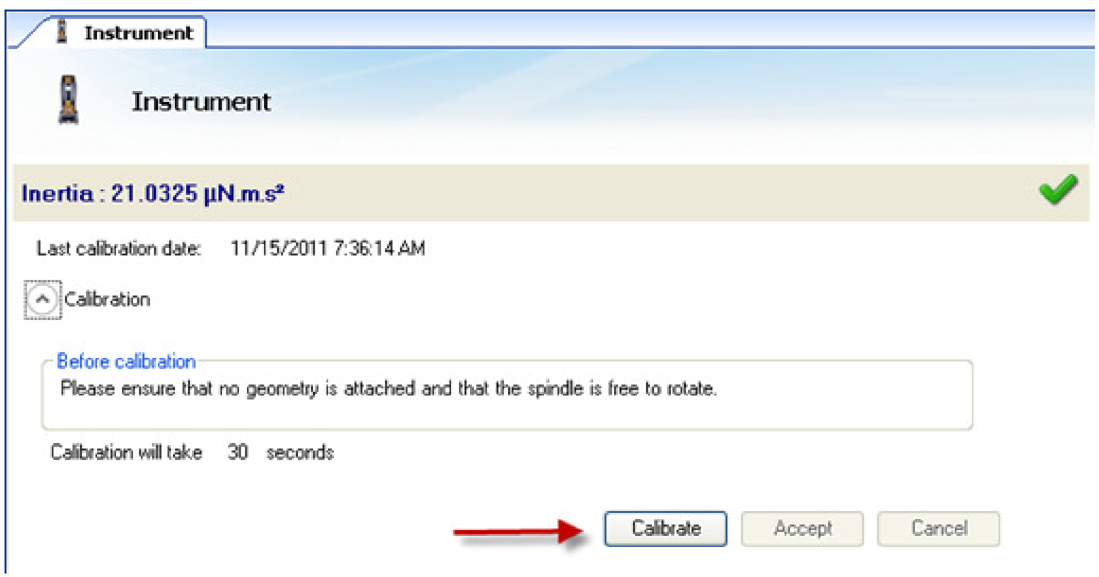


DHR – Inertia Calibration

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

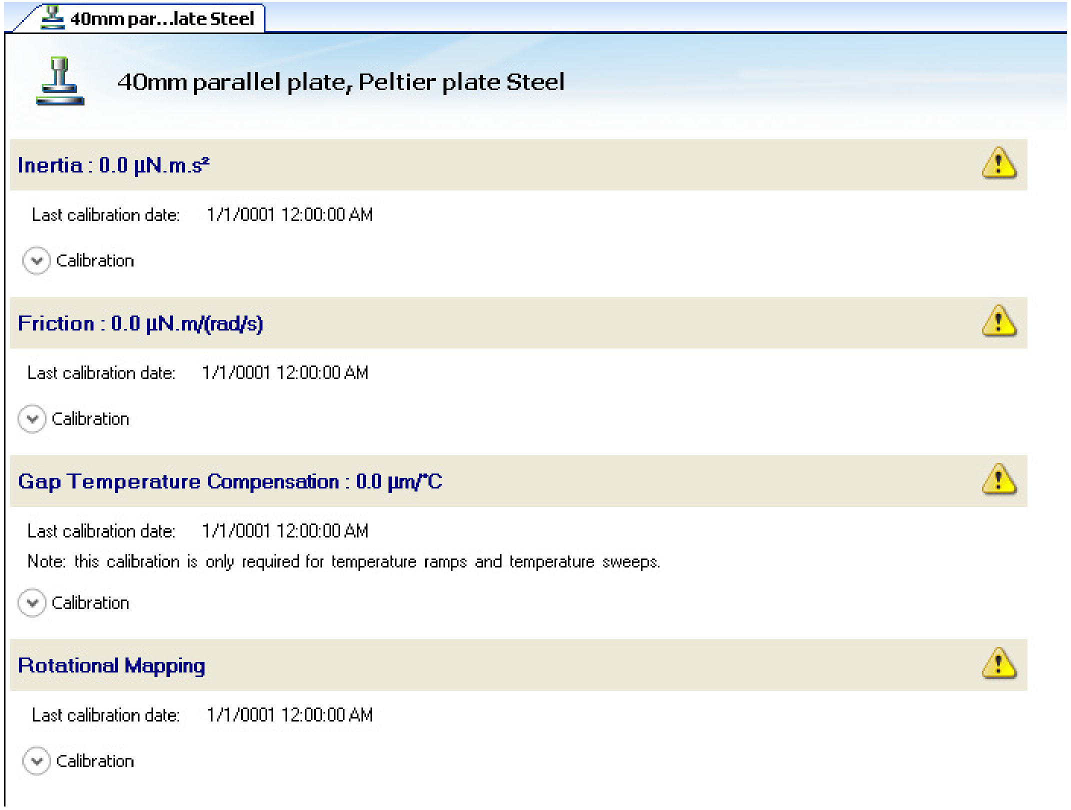




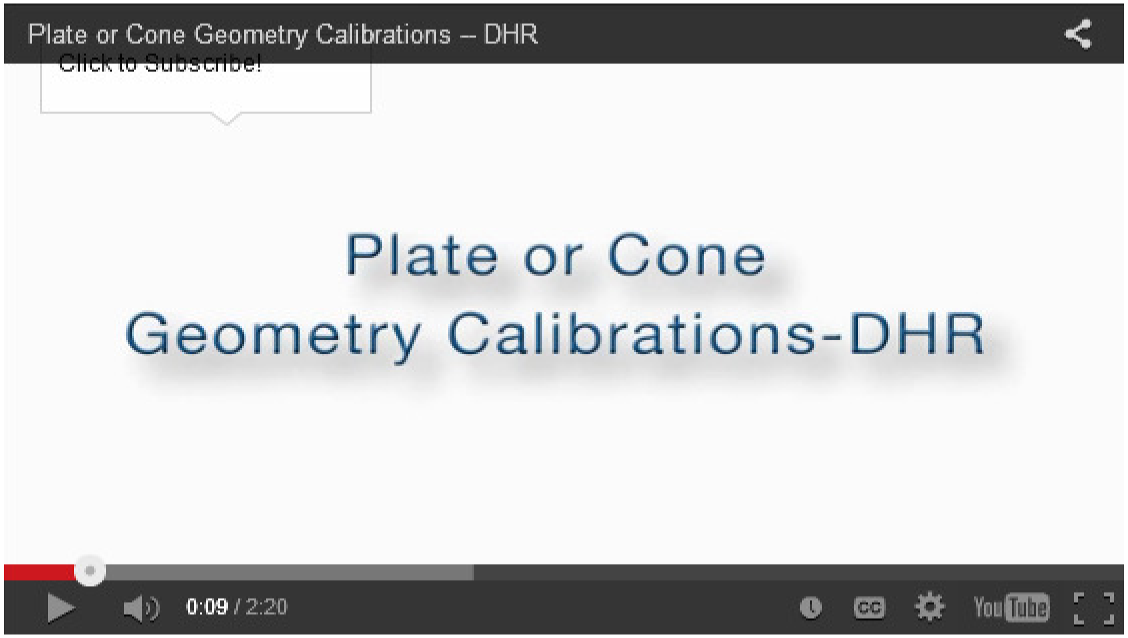


DHR – Geometry Calibration

- 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)

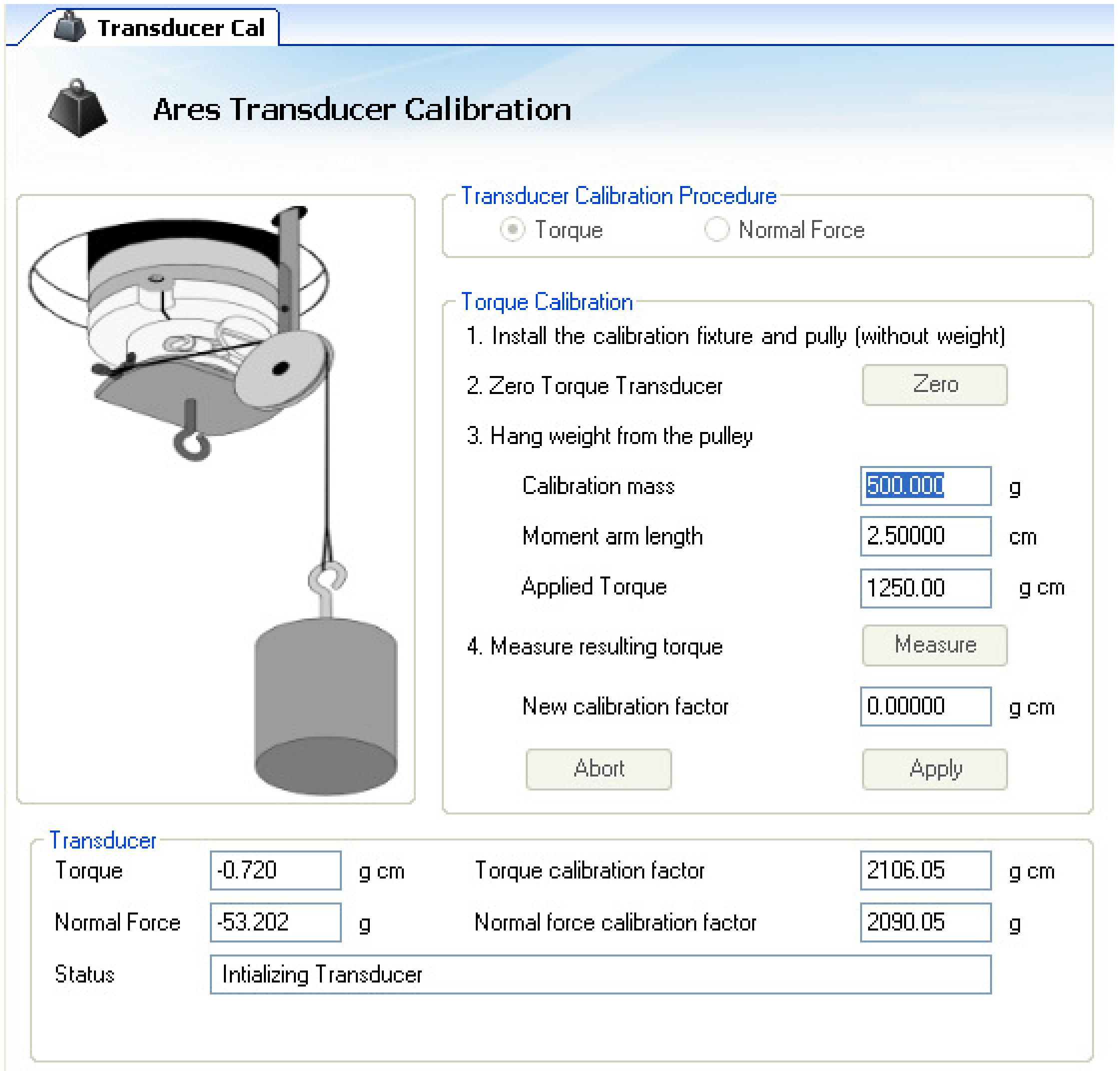
Appendix 2: Rheometer Calibrations

ARES-G2

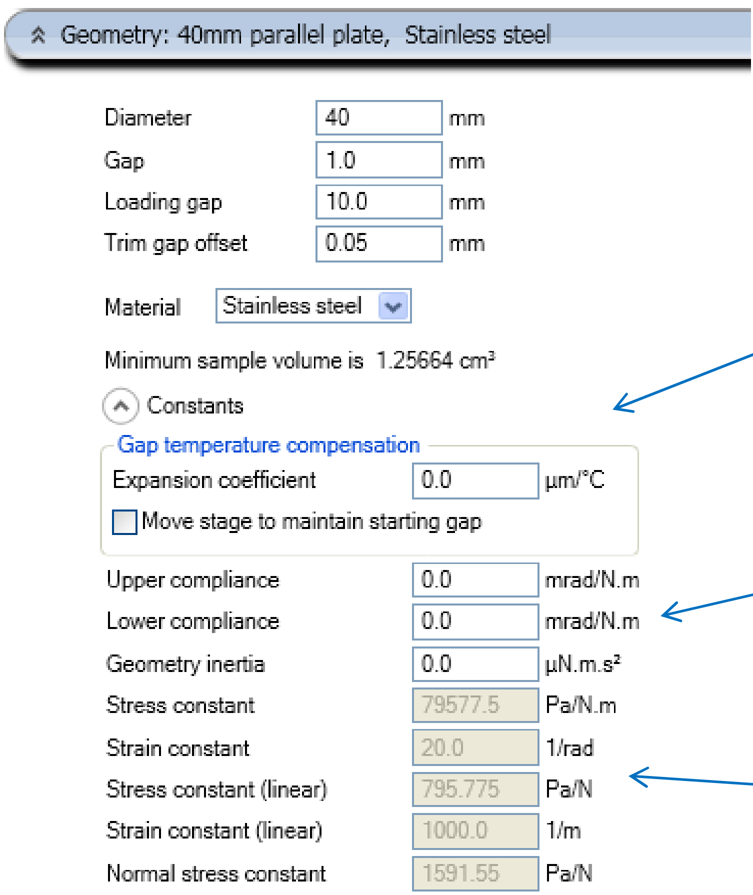
ARES-G2 – Calibration Options

- 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



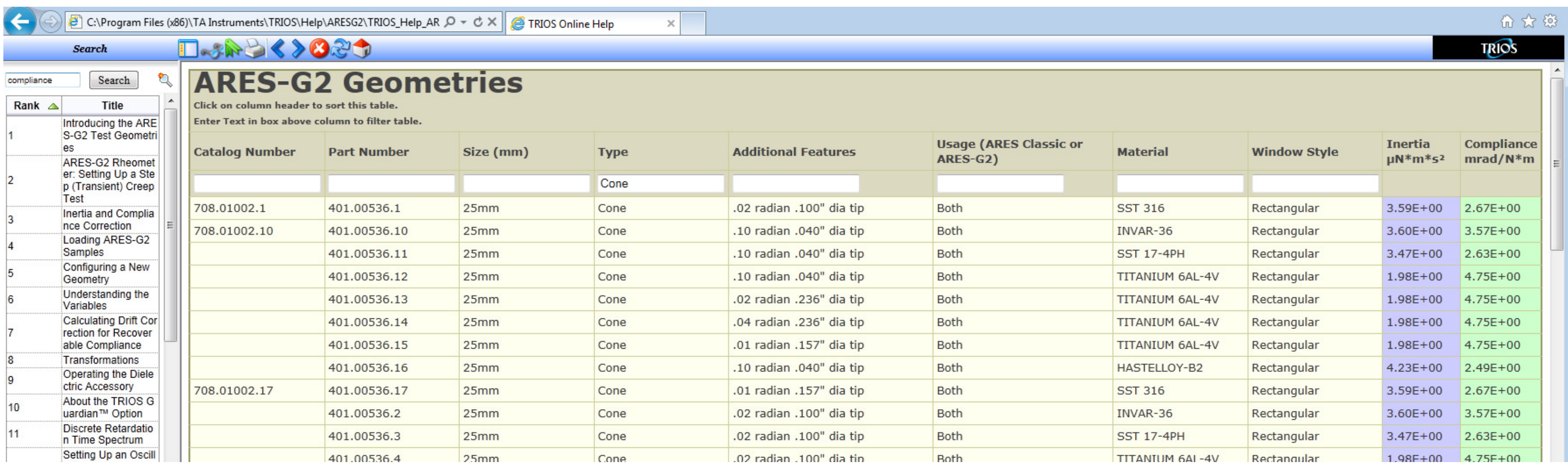
ARES-G2 – Geometry Calibration



- Gap Temperature Compensation
  - Enter manually or run calibration
- Compliance and Inertia
  - (from table in Help menu)
- Geometry Constants
  - Calculated based on dimensions

Geometry Inertia & Compliance- Help Menu

- Click here for a spreadsheet that contains the inertia, compliance, and gap compensation data for the majority of the ARES-G2/ARES tooling.



ARES-G2 Geometries

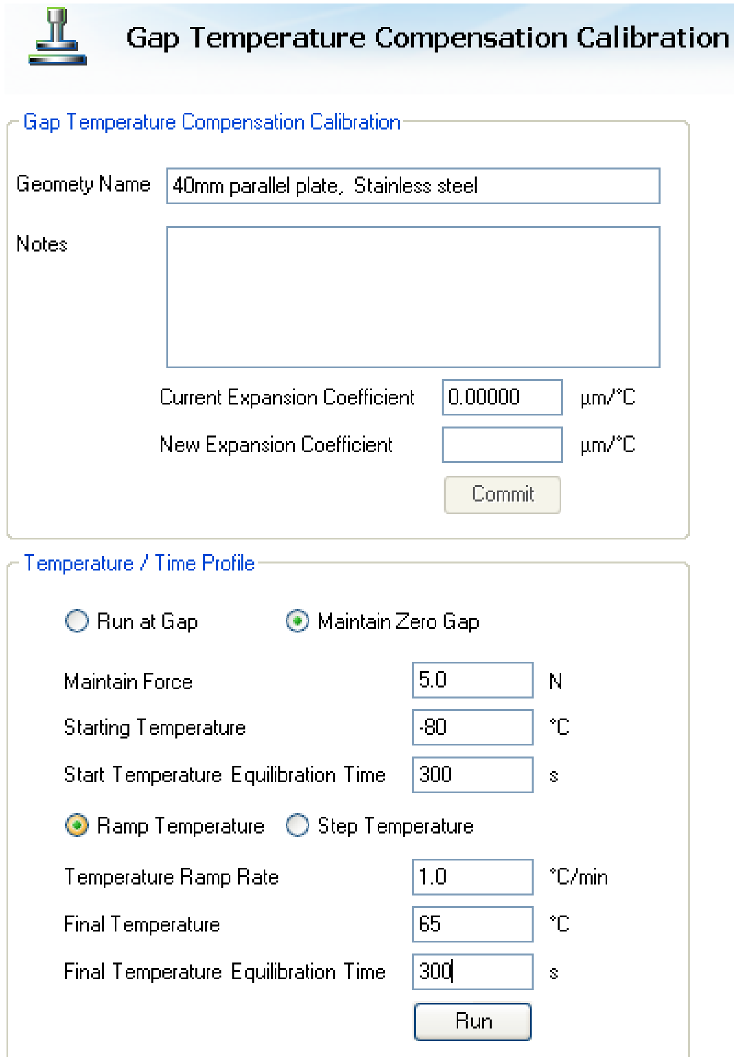
Click on column header to sort this table.
Enter Text in box above column to filter table.

Catalog Number	Part Number	Size (mm)	Type	Additional Features	Usage (ARES Classic or ARES-G2)	Material	Window Style	Inertia µN*m*s²	Compliance mrad/N*m
			Cone						
708.01002.1	401.00536.1	25mm	Cone	.02 radian .100" dia tip	Both	SST 316	Rectangular	3.59E+00	2.67E+00
708.01002.10	401.00536.10	25mm	Cone	.10 radian .040" dia tip	Both	INVAR-36	Rectangular	3.60E+00	3.57E+00
	401.00536.11	25mm	Cone	.10 radian .040" dia tip	Both	SST 17-4PH	Rectangular	3.47E+00	2.63E+00
	401.00536.12	25mm	Cone	.10 radian .040" dia tip	Both	TITANIUM 6AL-4V	Rectangular	1.98E+00	4.75E+00
	401.00536.13	25mm	Cone	.02 radian .236" dia tip	Both	TITANIUM 6AL-4V	Rectangular	1.98E+00	4.75E+00
	401.00536.14	25mm	Cone	.04 radian .236" dia tip	Both	TITANIUM 6AL-4V	Rectangular	1.98E+00	4.75E+00
	401.00536.15	25mm	Cone	.01 radian .157" dia tip	Both	TITANIUM 6AL-4V	Rectangular	1.98E+00	4.75E+00
	401.00536.16	25mm	Cone	.10 radian .040" dia tip	Both	HASTELLOY-B2	Rectangular	4.23E+00	2.49E+00
708.01002.17	401.00536.17	25mm	Cone	.01 radian .157" dia tip	Both	SST 316	Rectangular	3.59E+00	2.67E+00
	401.00536.2	25mm	Cone	.02 radian .100" dia tip	Both	INVAR-36	Rectangular	3.60E+00	3.57E+00
	401.00536.3	25mm	Cone	.02 radian .100" dia tip	Both	SST 17-4PH	Rectangular	3.47E+00	2.63E+00
	401.00536.4	25mm	Cone	.02 radian .100" dia tip	Both	TITANIUM 6AL-4V	Rectangular	1.98E+00	4.75E+00

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



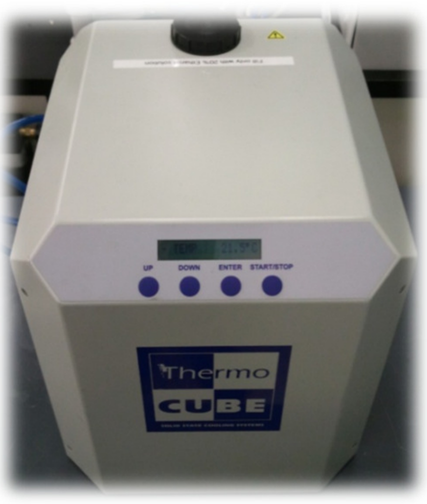
General Rheometer Maintenance

- 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.



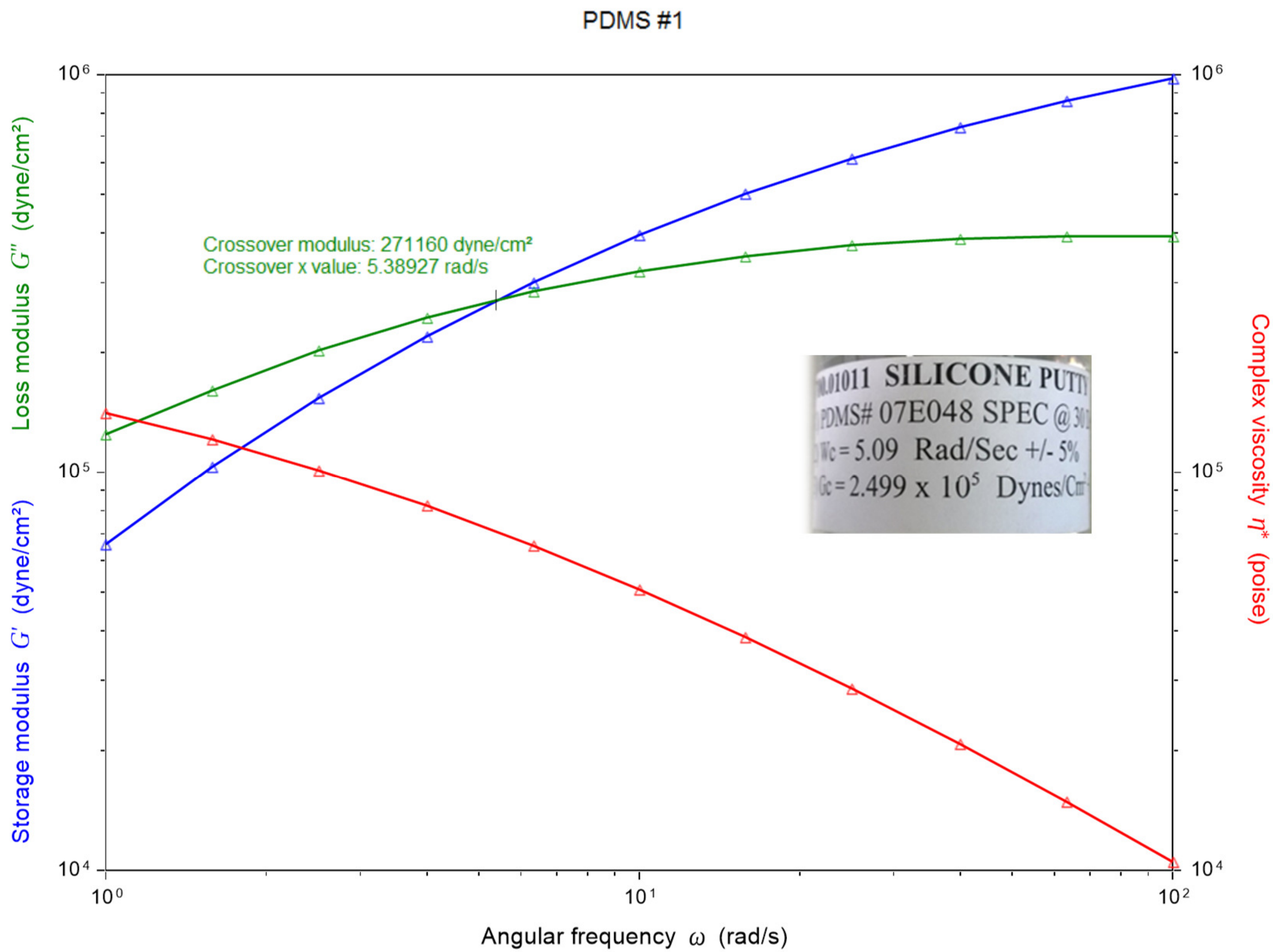
Verify Rheometer Performance

- 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



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)