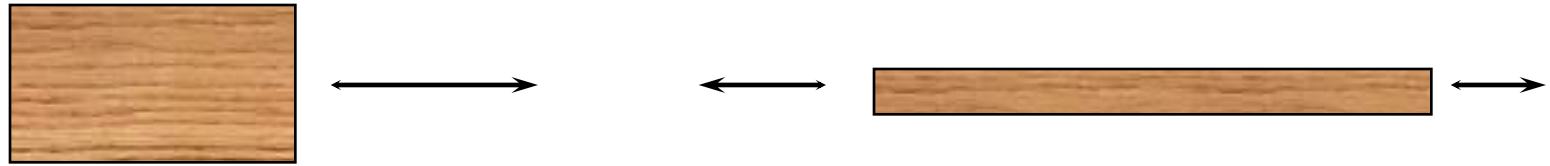# Understanding Rheology

Ross Clark

Distinguished Research Fellow

San Diego R&D

- **CP Kelco makes carbohydrate based water soluble polymers**
  - Fermentation
    - Xanthan
    - Gellan
  - Plant derived
    - Pectin
    - Cellulose gum
    - Carrageenan
- **Thirty two years!**
  - Rheology
  - Particle characterization (zeta potential, sizing)
  - Microscopy
  - Sensory science
  - Unusual properties

- **Strain – Deformation or movement that occurs in a material. Expressed as the amount of movement that occurs in a given sample dimension this makes it dimensionless.**
  - Translation: How much did I move the sample?
- **Stress – Force applied to a sample expressed as force units per unit area, commonly dynes/cm^2 or N/m^2.**
  - Tranlation: How hard did I push, pull or twist the sample?
- **Viscosity –The ratio of shear stress/shear strain rate.**
  - Translation: How much resistance is there to flow?
- **Modulus – The ratio of stress / strain, expressed in force units per unit area (since strain has no dimensions).**
  - Translation: How strong is the material?
- **Extensional viscosity – The resistance of a liquid to being pulled**
- **Dynamic testing – The application of a sinusoidally varying strain to a sample**

➢ **Shear** - A sliding deformation that occurs when there is movement between layers in a sample, like fanning out a deck of cards. May also be called torsion.

➢ **Compression** - A pushing deformation that results from pushing on two ends of a sample, like squeezing a grape.

➢ **Tension** - A pulling deformation that occurs as you stretch a sample, like pulling on a rubber band. May also be called extension.
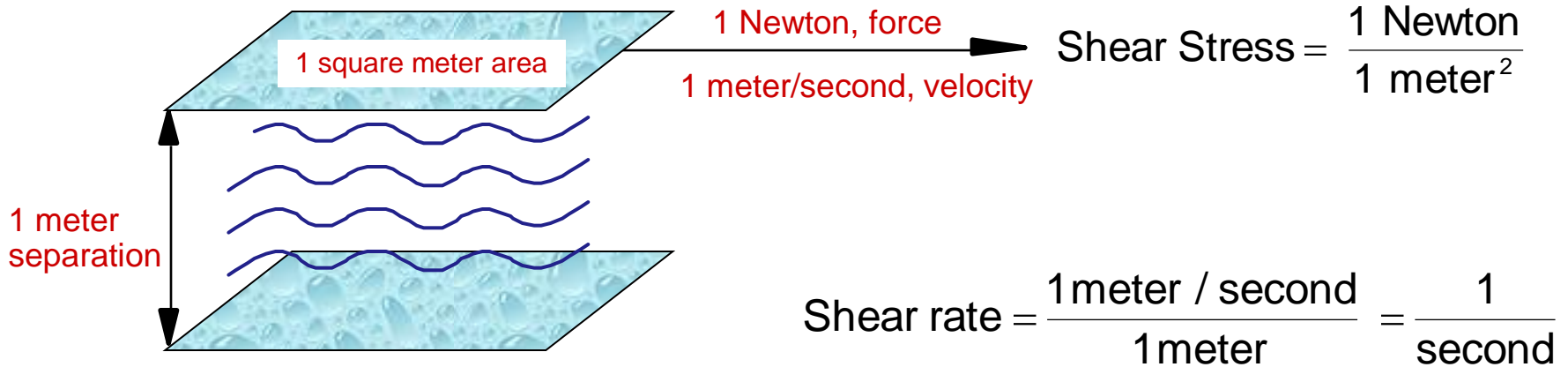
Extension (Tension)

Bending

Simple Shear

1 square meter area

1 Newton, force

1 meter/second, velocity

$$\text{Shear Stress} = \frac{1 \text{ Newton}}{1 \text{ meter}^2}$$

1 meter separation

$$\text{Shear rate} = \frac{1 \text{meter / second}}{1 \text{meter}} = \frac{1}{\text{second}}$$

Since viscosity is defined as shear stress/shear rate, the final units (in the SI system) for viscosity are Newton•second / m^2. This can also be given as a Pascal•second since a Pascal is one Newton / m^2.

In the more traditional physics units, the units of viscosity are dynes•seconds / cm^2. This is defined as 1 Poise

1 mPa•s (milliPascal•second) is equivalent to 1 cP (centiPoise).

Density is sometimes included for gravity driven capillary instruments. This unit is a centiStoke.

➢ **Dynamic Mechanical Analysis – Typically, a solid material is "pushed" in bending, tugging, or sliding in a repetitive manner.**

➢ **Common symbols used:**

| Type of deformation:	Modulus values	Strain	Stress
Shear	G, G', G" G*	γ	τ
Compression /tension	E, E', E", E*	ε	σ

➢ **Tan delta – The tangent of the phase angle, delta. Obtained as the ratio of G' and G" or E' and E"**

   – Still used but actual phase angle (δ) seems more logical
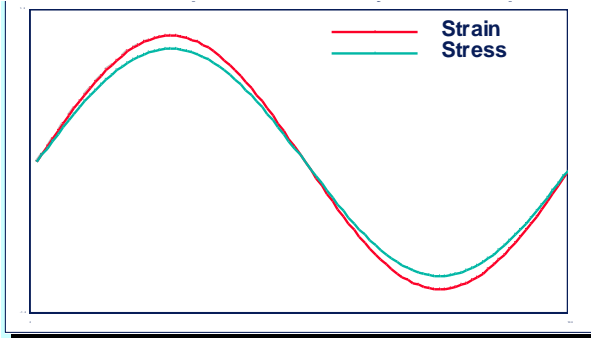
Elastic materials, like a steel spring, will always have stress and strain when tested in dynamic test. This is because the material transfers the applied stress with no storage of the energy.
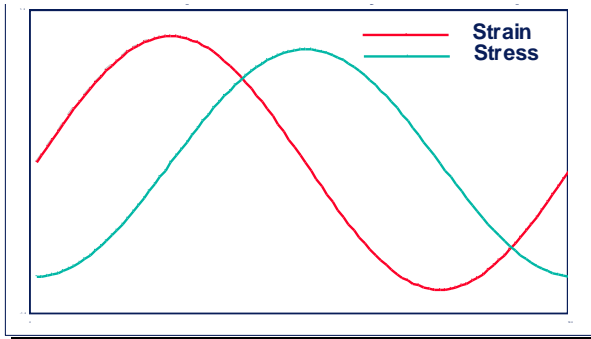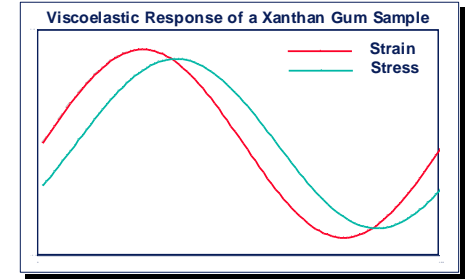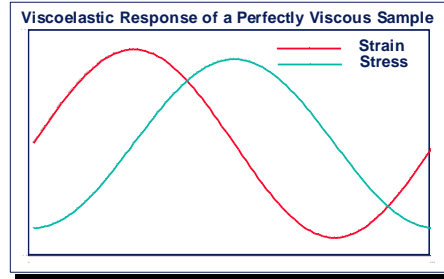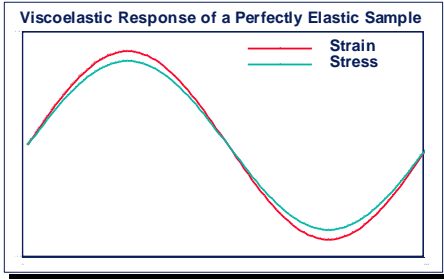
Viscous materials, like water or thin oils, will always have stress and strain shifted 90° from each other. This is because the most resistance to movement occurs when the rate of the movement is the greatest.
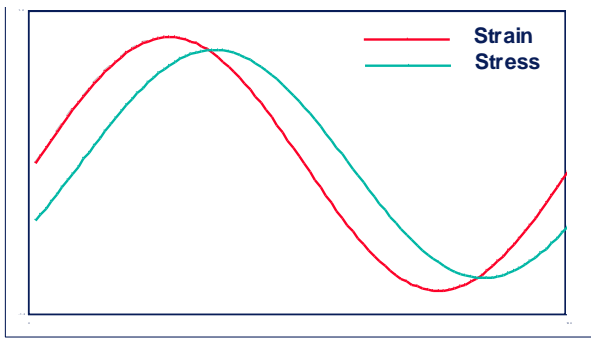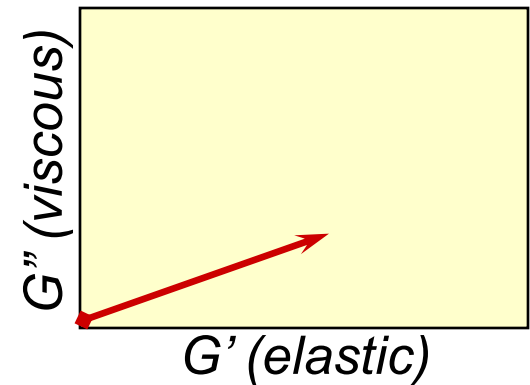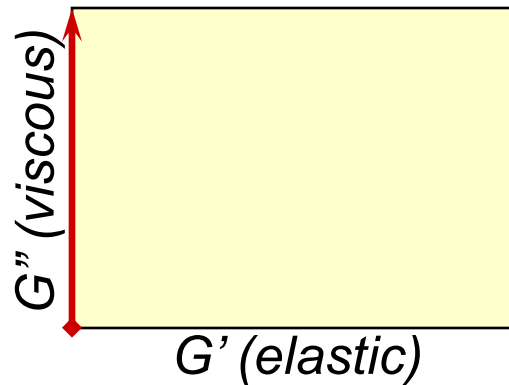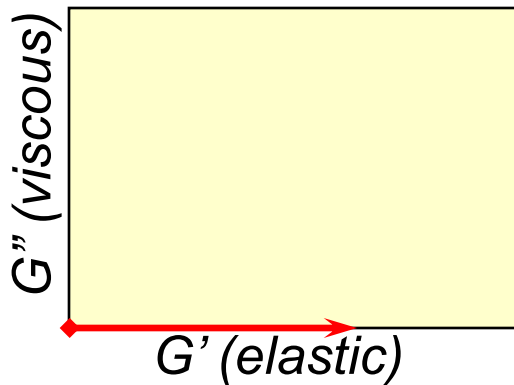
Most of the world is viscoelastic in nature and so shares characteristics of elastic and viscous materials. The phase shift (δ) will always be between 0° and 90°.

Where do G' and G'' come from?

Viscoelastic Response of a Perfectly Elastic Sample
Strain
Stress

Viscoelastic Response of a Perfectly Viscous Sample
Strain
Stress

Viscoelastic Response of a Xanthan Gum Sample
Strain
Stress

Convert to phase angle (δ) and magnitude and then from polar to rectangular coordinates

G'' (viscous)

G' (elastic)

G'' (viscous)

G' (elastic)

G'' (viscous)

G' (elastic)

What is the use of viscoelasticity?

➢ **As crosslinks form in a material, it shows more and more elasticity.**

➢ **As molecular weight increases, most systems become more entangled, this results in more elasticity, especially at high deformation rates.**

➢ **Samples with a high degree of viscous response tend to not stabilize and suspend as well.**

➢ **Processing of samples that are too elastic can often be difficult.**

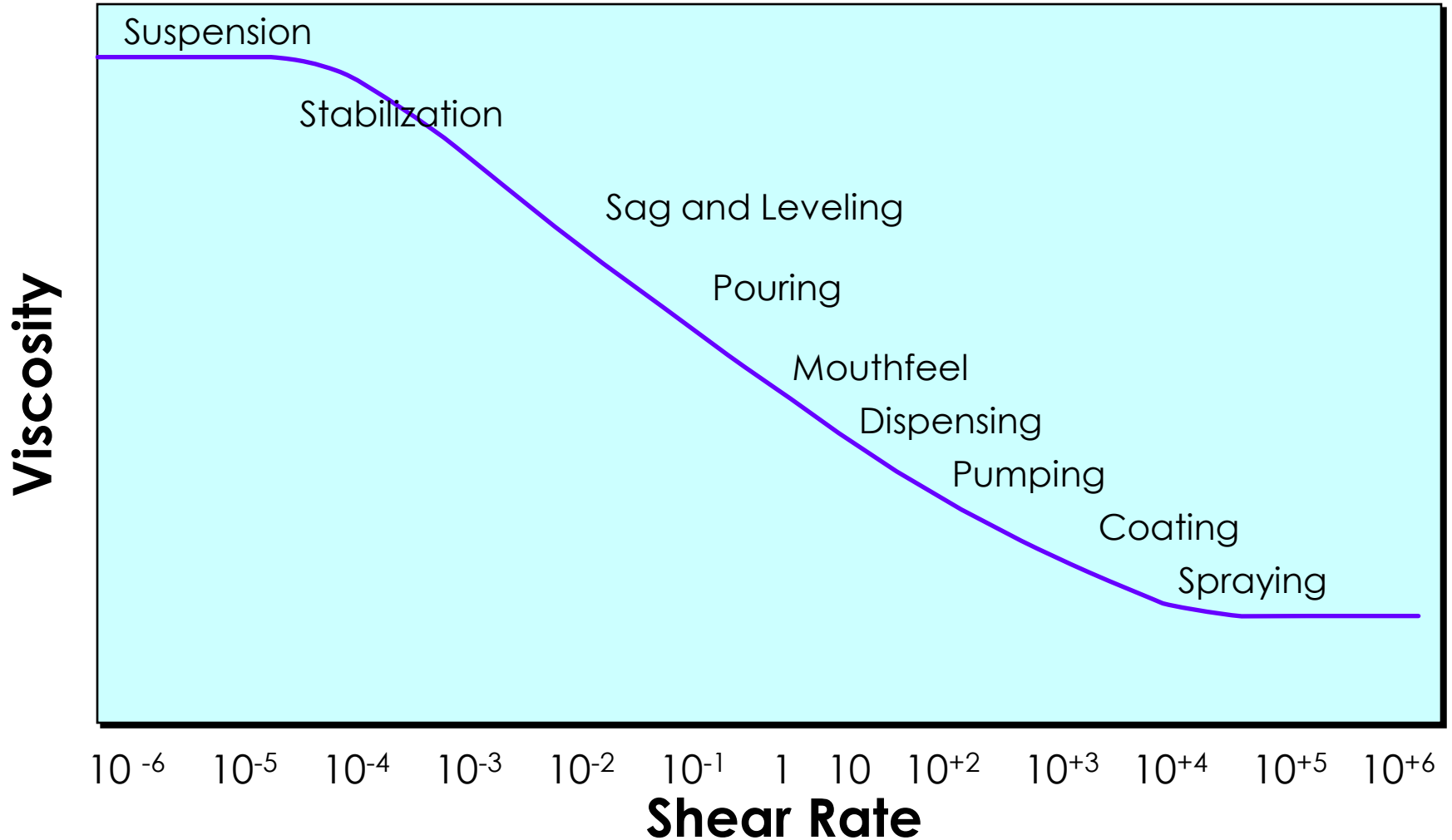➢ **Rate dependent effects (how fast you shear)**
- A sample that decreases in viscosity as rate increases is **pseudoplastic**
  - ➢ Alignment of chains due to flow field decreases resistance
- Unusual samples can increase in viscosity as the rate goes up, these are **dilatent**
  - ➢ Almost always are highly loaded suspensions with many particles that lock together as the rate increase; can't get out of the way
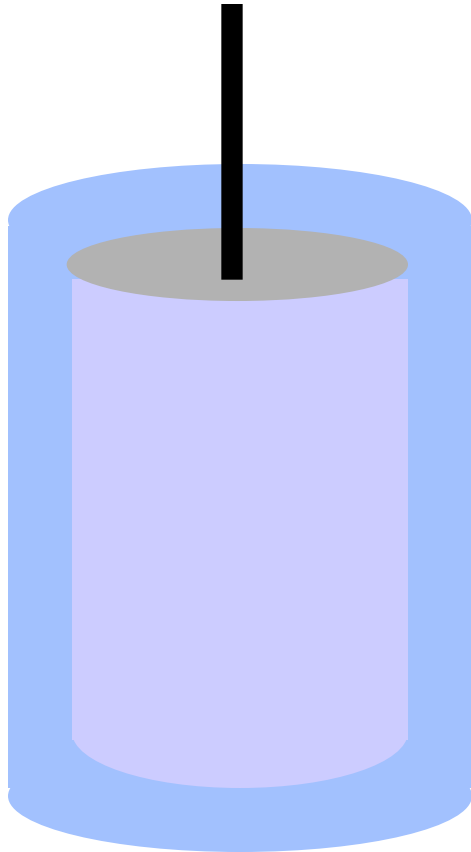
➢ **Time dependent effects (how long you shear)**
- When viscosity goes down this is **thixotropy**; may or may not be reversible after shear stops
  - ➢ If the network is robust, it is reversible
- Increasing viscosity is very rare, it is called **rheopectic** flow. You may never see it!

➢ **Did you see shear thinning? No!**

Viscosity vs. Shear Rate

- Suspension
- Stabilization
- Sag and Leveling
- Pouring
- Mouthfeel
- Dispensing
- Pumping
- Coating
- Spraying

Shear Rate: 10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}, 1, 10, 10^{+2}, 10^{+3}, 10^{+4}, 10^{+5}, 10^{+6}

Couette, coaxial cylinder or cup and bob

- This type of "geometry" is commonly used for materials that contain suspended solids

- Providing the gap between the cup and bob is small, the exact shear rate can be determined

- Easy to control evaporation with an oil layer on top

- Higher shear rates result in unstable flow due to centrifugal force

Measured parameters: speed of rotation (rpm), torque (T), bob radius (R_b), bob height (H_b) and cup radius (R_c)
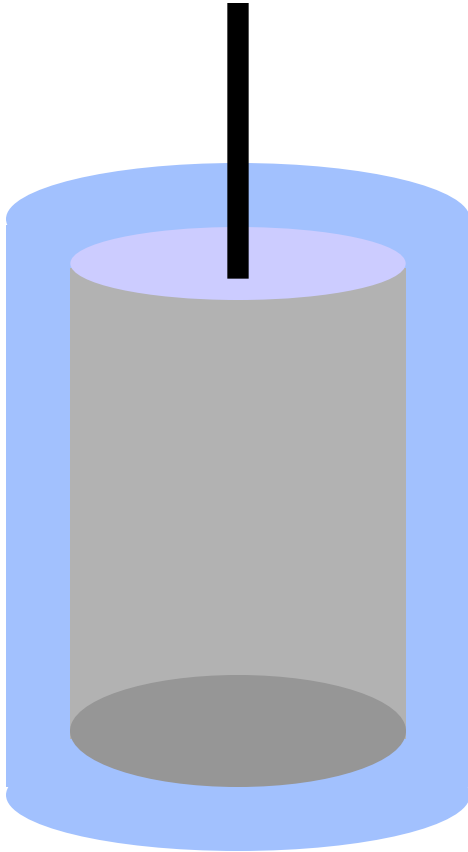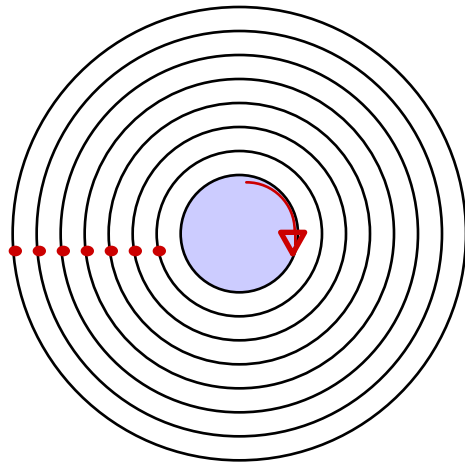
$$\tau = \frac{T}{2 * \pi * R_b^2 * H_b}$$
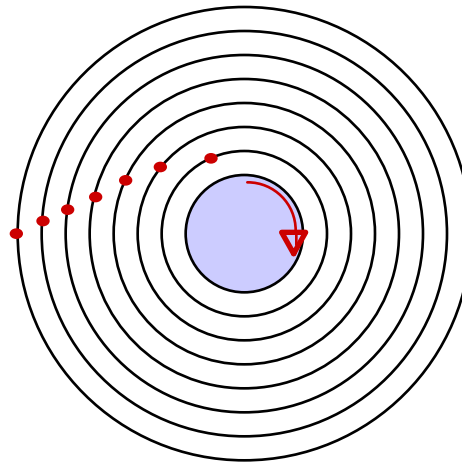
$$\dot{\gamma} = 2 * \frac{2 * \pi * rpm}{60} * \frac{R_c^2}{R_c^2 - R_b^2}$$

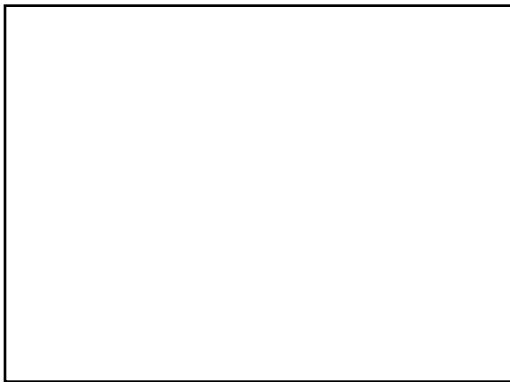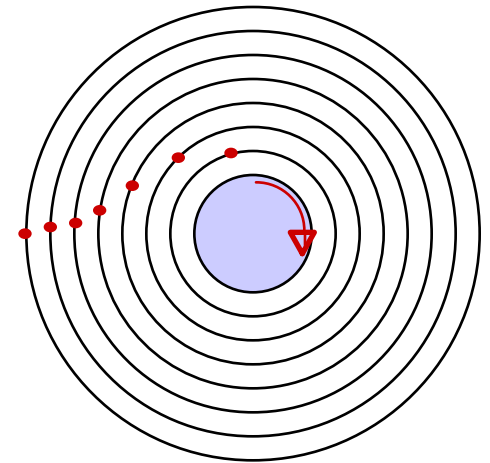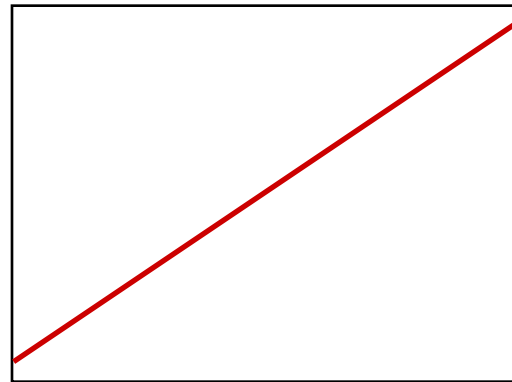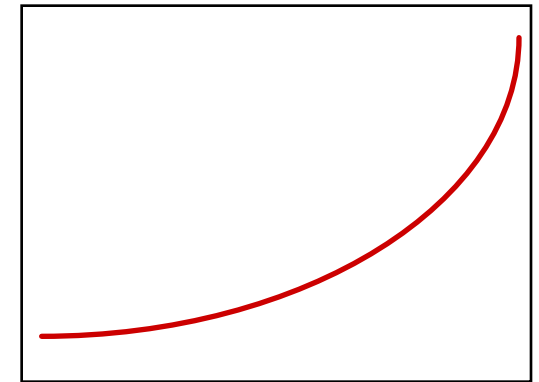*Newtonian flow assumed, corrections will need to be made for non-Newtonian fluids*

Initial, t=0

Newtonian

Pseudoplastic

Cup Wall ⟶ Bob Wall

Cup Wall ⟶ Bob Wall

Cup Wall ⟶ Bob Wall

For all cases except where the gap between the cup & bob is very small, that is Rc/Rb > 0.95, we must correct for the flow field in the gap. When a more pseudoplastic fluid is tested, the shear rate in the gap tends to be the highest near the rotating member (the bob in the case of the Brookfield). This is because the shear stress is at a maximum at this point and the fluid tends to flow faster under high shear stress values.

In any event, we need to correct for this flow profile in the gap. This is most commonly done by assuming that the material will obey the power law, that is $\tau = K \cdot \gamma^n$.

Below, a step by step procedure is listed for correction of the shear rate for non-Newtonian fluids in Couette viscometers: .

Step #1, calculate the shear stress, τ on the bob using the equation for Newtonian fluids.

Step #2, calculate the value of ω for each of the speeds used.

Step #3, make a log–log plot of τ and ω. Calculate the value of n (slope) and b (intercept).

Step #4, determine the correction factor, λ as: $\lambda = \dfrac{1 + [\ln (s) / n]}{\ln (s)}$ where $s = \sqrt{\dfrac{R_c^2}{R_b^2}}$

Step #5, determine the "K" value as $K = b / \lambda^n$

Step #6, determine the shear rate, $\dot{\gamma}$ as $\dot{\gamma} = \omega \cdot \lambda$

Step #7, determine the viscosity, η as $\eta = \tau / \dot{\gamma}$
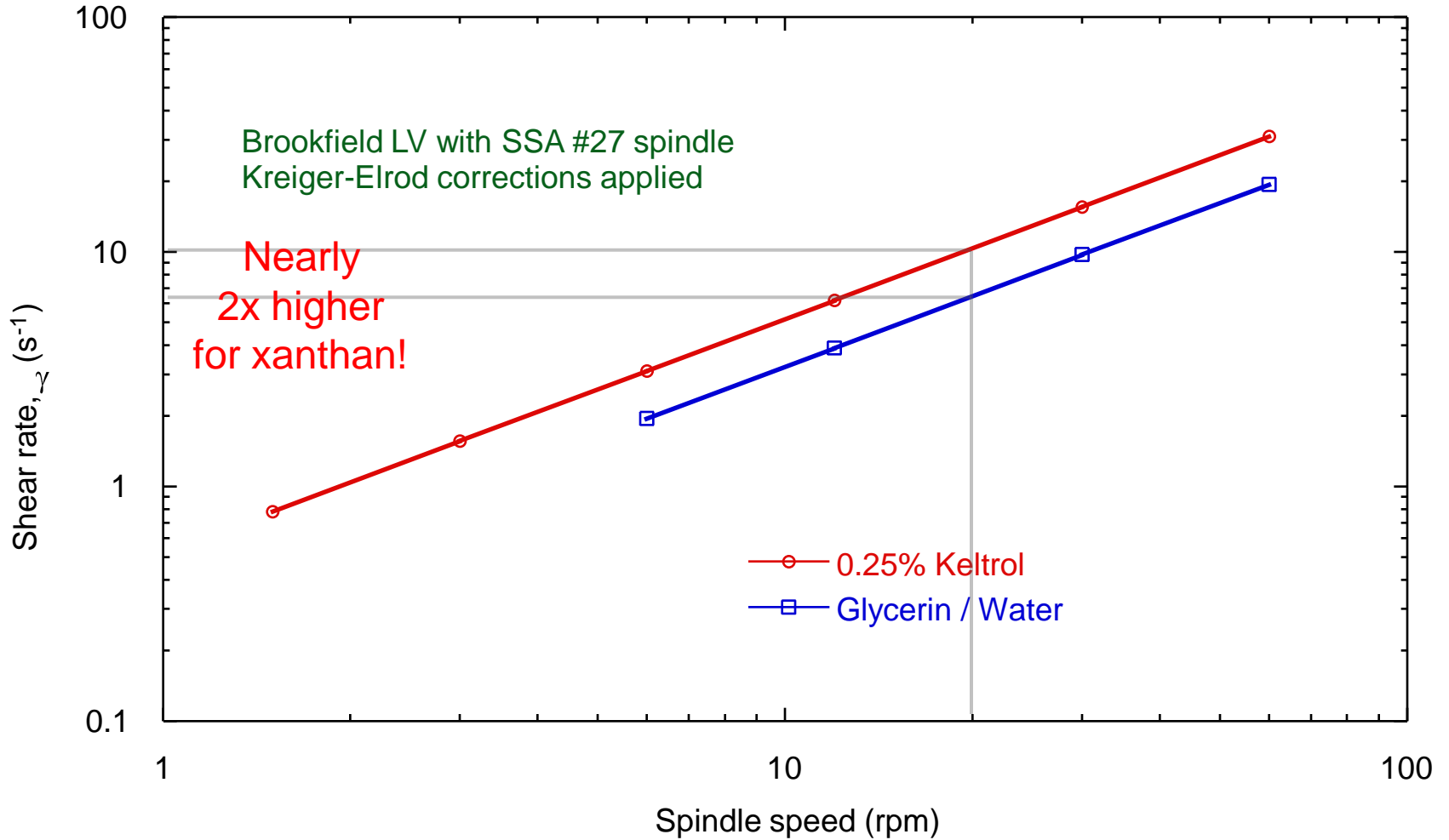
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In the table given below, the shear rate and errors associated with the Newtonian calculation of shear rate for two different theoretical pseudoplastic fluids are given. In each case the speed of the viscometer is the same (0.3 rpm) and the Rb/Rc calculation is given for the three different viscometer gaps.

It can be seen that the errors become very large for pseudoplastic fluids in wide gap instruments. This is one reason to avoid the use of small spindles in the Brookfield small sample adapter or any other viscometer.
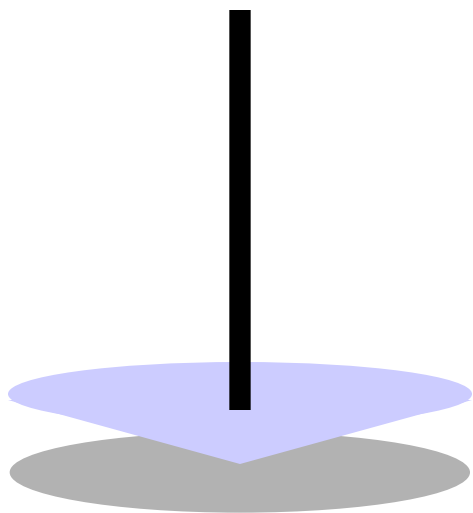
Couette Gap	Newtonian n=1	Pseudoplastic n=0.658	Error (%)	Pseudoplastic n=.261	Error (%)
Narrow 0.967	0.974	0.99	1.64%	1.063	9.14%
Moderate 0.869	0.255	0.271	6.27%	0.344	34.90%
Wide 0.672	0.11	0.127	15.45%	0.199	80.91%

An example of some of the dimensions for various Brookfield attachments is given in the table below. As you can see, the error associated with even the "best" conditions (#18 bob with the small sample adapter or the UL) is still significant, especially when the degree of pseudoplasticity of most of our fluids is taken into account.

	Bob Radius (mm)	Cup Radius (mm)	Rb/Rc
Small Sample Adapter, #18 bob	8.7175	9.5175	0.916
Small Sample Adapter, #27 bob	5.8600	9.5175	0.616
UL Adapter	12.5475	13.8000	0.909

Effect of Couette corrections

Brookfield LV with SSA #27 spindle
Kreiger-Elrod corrections applied

Nearly
2x higher
for xanthan!

Shear rate, $\dot{\gamma}$ (s^{-1})

Spindle speed (rpm)

—○— 0.25% Keltrol
—□— Glycerin / Water

Cone and plate

- This type of "geometry" is commonly used for clear fluids without solids

- If the angle of the cone is less than about 3°, there will be a uniform shear rate in the gap

- Mind the gap! Particles can interfere since a common gap is 50 microns

- A variation of this is the parallel plate; a compromise in accuracy for ease of use
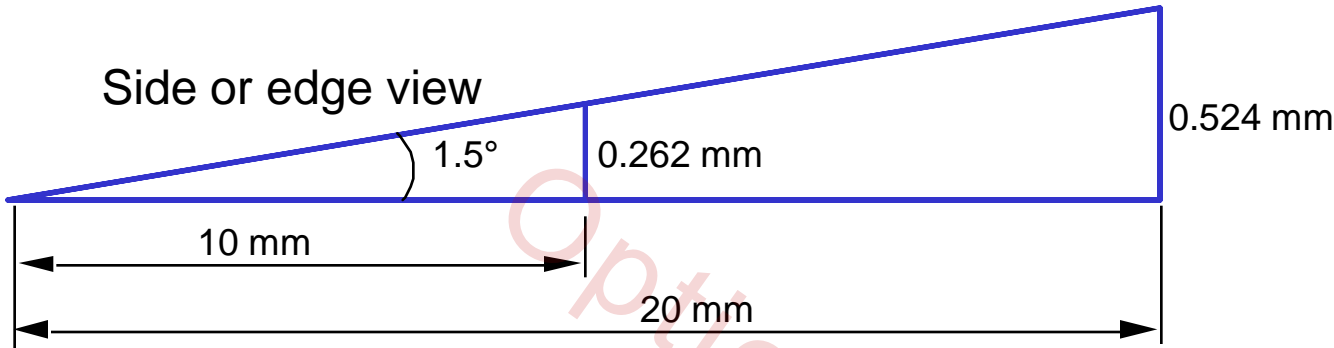
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Measured parameters: speed of rotation (rpm), torque (T), cone angle (θ) and cone radius (R_c)
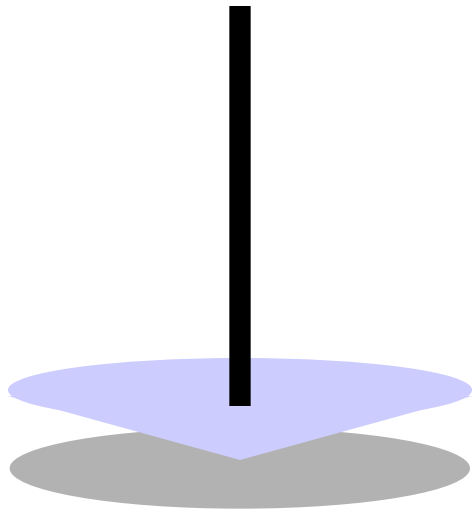
$$\tau = \frac{T}{2/3 * \pi * R_c^3}$$
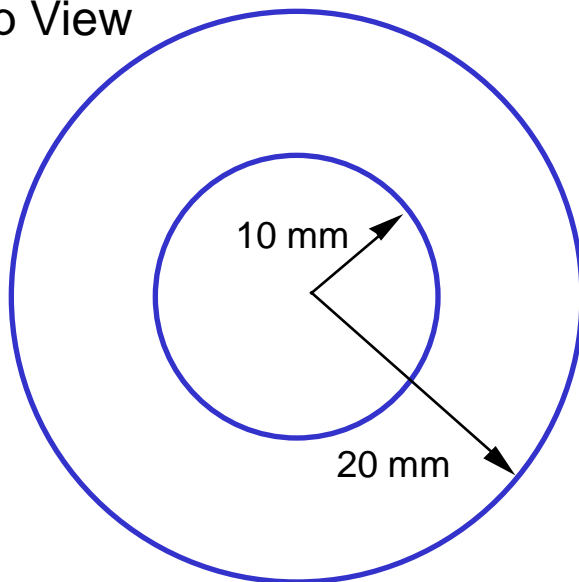
$$\dot{\gamma} = 2 * \frac{2 * \pi * rpm / 60}{\sin(\theta)}$$

* Calculations are valid for Newtonian and non-Newtonian materials

Side or edge view

0.524 mm

1.5°   0.262 mm

10 mm

20 mm

In this example, we have a cone with angle, θ and a radius, r. Providing that the cone angle is <~4°, the following equations give the shear stress and shear rate.

Top View

10 mm

20 mm

$$\tau = \frac{\text{Torque}}{2/3 \cdot \pi \cdot r^3} \qquad \dot{\gamma} = \frac{2 \cdot \pi \cdot (\text{rpm} / 60)}{\text{sine}(\theta)}$$

If we assume a speed of 12 rpm or 1.26 rad/s:

Linear velocity @ 10 mm = 12.6 mm/sec
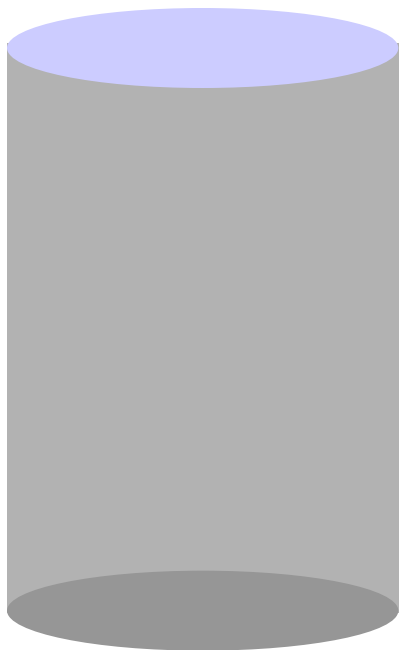Linear velocity @ 20 mm = 25.2 mm/sec.
The shear strain rate is given by the velocity / separation:

Shear strain rate @ 10 mm = 48.1 s^{-1}
Shear strain rate @ 20 mm = 48.1 s^{-1}.

By the equation given above for shear rate we get 48.0 s^{-1}.

Capillary or pipe flow

- This type of "geometry" can be used with either clear fluids or ones with solids

- The device can be driven by a constant pressure or a constant volumetric flow

- Gravity driven glass instruments are traditional for polymer Mw

- Excellent oscillatory instrument is the Vilastic www.vilastic.com. Superb accuracy for low viscosity

Measured parameters: capillary radius (Rc), capillary length (Lc), volumetric flow rate (Q) and pressure drop ($\triangle$p)
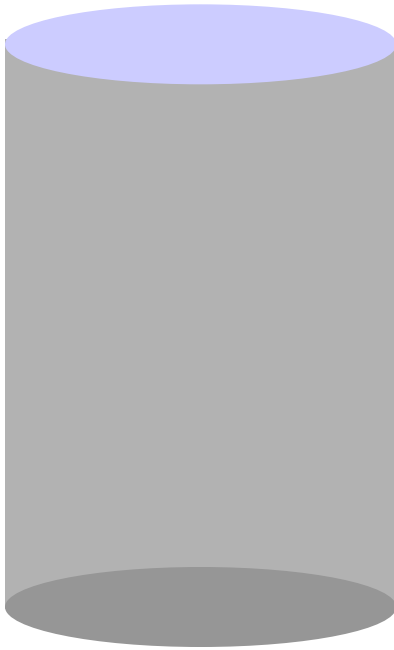
$$\tau = \frac{\triangle p * R_c}{2 * L_c}$$

$$\dot{\gamma} = 2 * \frac{4 * Q}{\pi * R_c^3}$$

* Newtonian flow assumed, corrections will need to be made for non-Newtonian fluids

Steady shear rheological models

- **Used to "reduce" the data to a standard equation.**
- **May provide insight into molecular processes.**
  - Yield stress
  - Association or crosslink half life
- **Are useful to engineers needing data to plug into standard formulas (pumping, pressure drop, pipe size).**

Equation: $\tau = K * \dot{\gamma}$
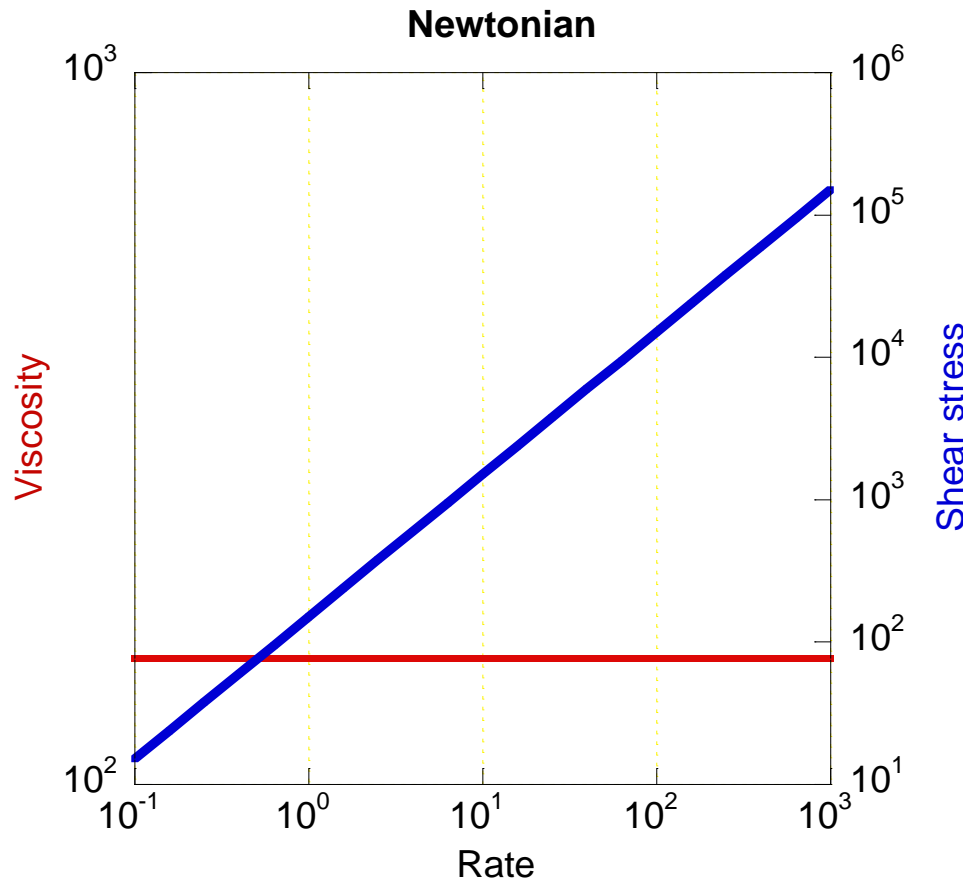
For this graph:

K = 150

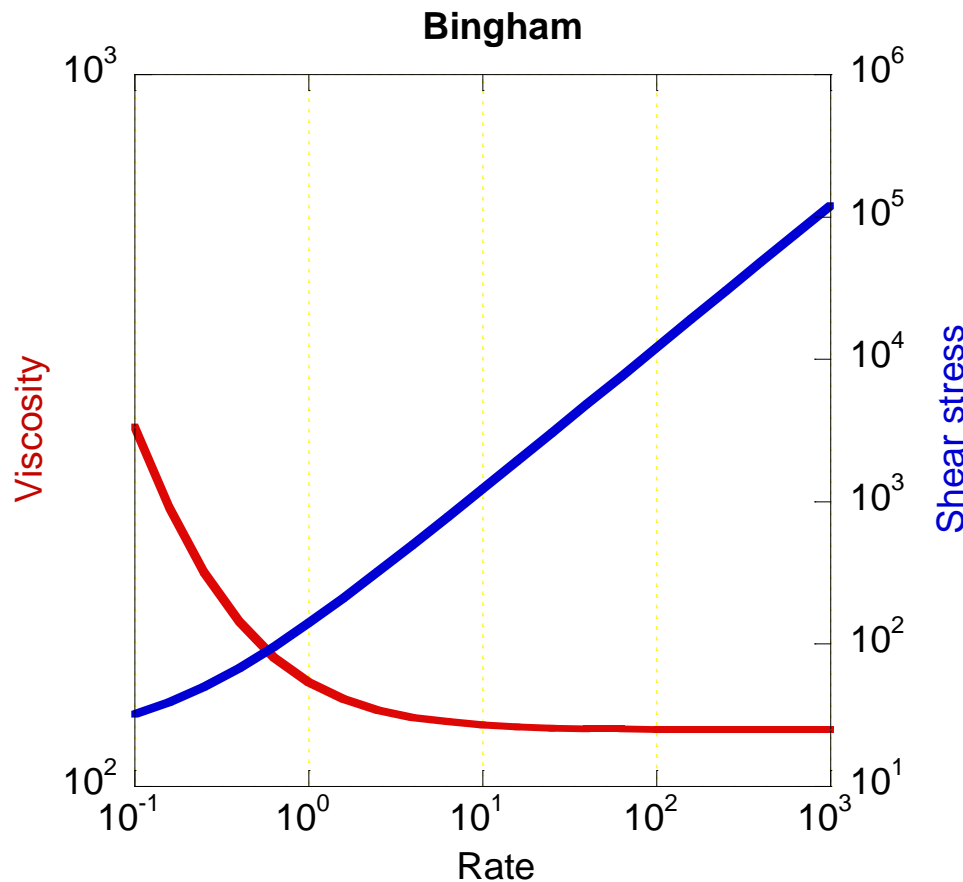Newtonian fluids are rare. Low molecular weight oils and some small water soluble polymer molecules.

Equation: $\tau = \tau_o + (K * \dot\gamma)$

Bingham

For this graph:

K = 120

$\tau_o = 20$

This modification of the Newtonian model allows for a yield stress. This is a force that must be exceeded before flow can begin.

A frequently used oil-field model ("YP" and "PV").

Equation: $\sqrt{\tau} = \sqrt{\tau_o} + \sqrt{K} * \sqrt{\dot{\gamma}}$

Casson model

For this graph:

K = 40
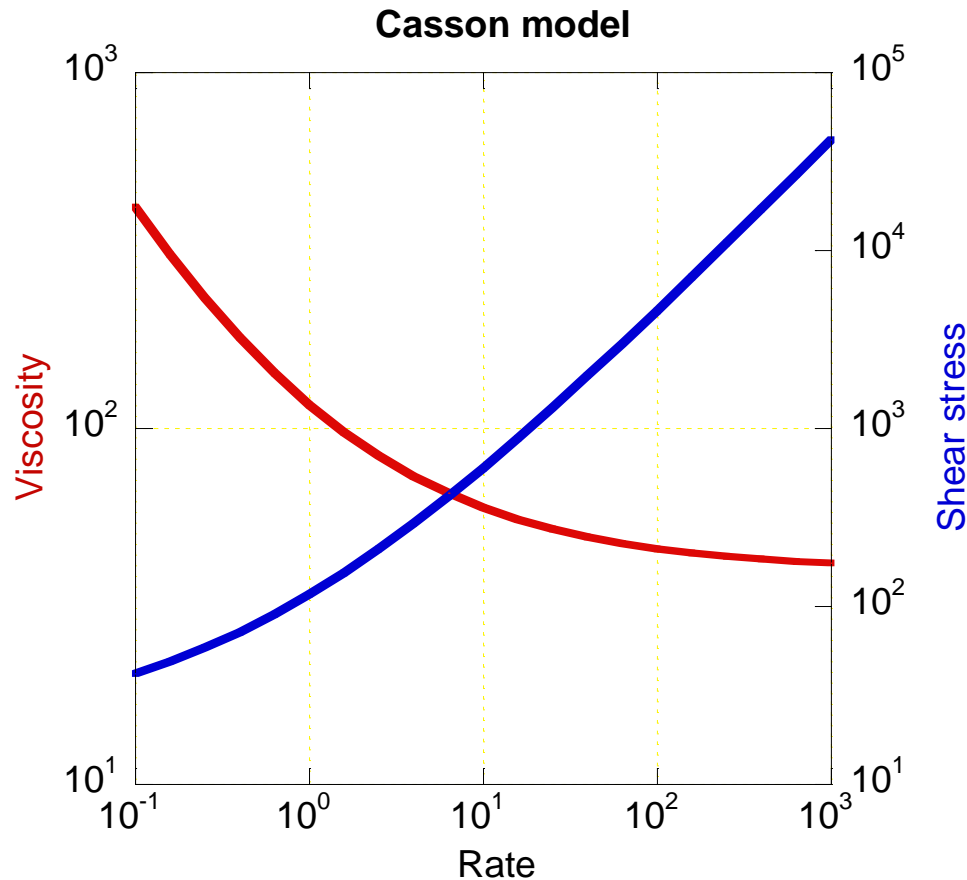
$\tau_o = 20$

This is a variation of the Bingham model. It is frequently used to extrapolate to a yield stress from low shear rate data. Has been successfully used with chocolate.

Equation: $\tau = K * \dot{\gamma}^{n}$
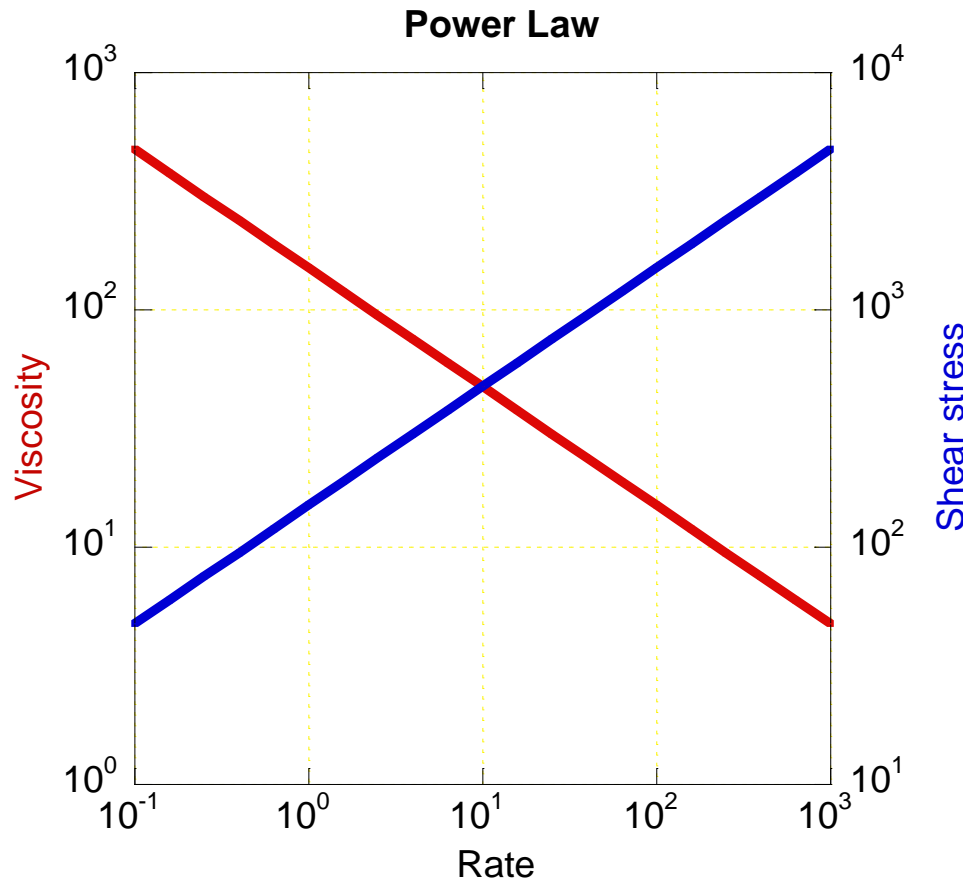
Power Law

For this graph:

K = 150

n = 0.5

The power law model is the most frequently used equation. It fits a wide range of water soluble polymers to a more or less acceptable degree. Xanthan gum is a "classic" power law fluid

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Equation: $\tau = \tau_o + K * (\dot{\gamma}^{\,n})$

Ellis or power law + yield stress
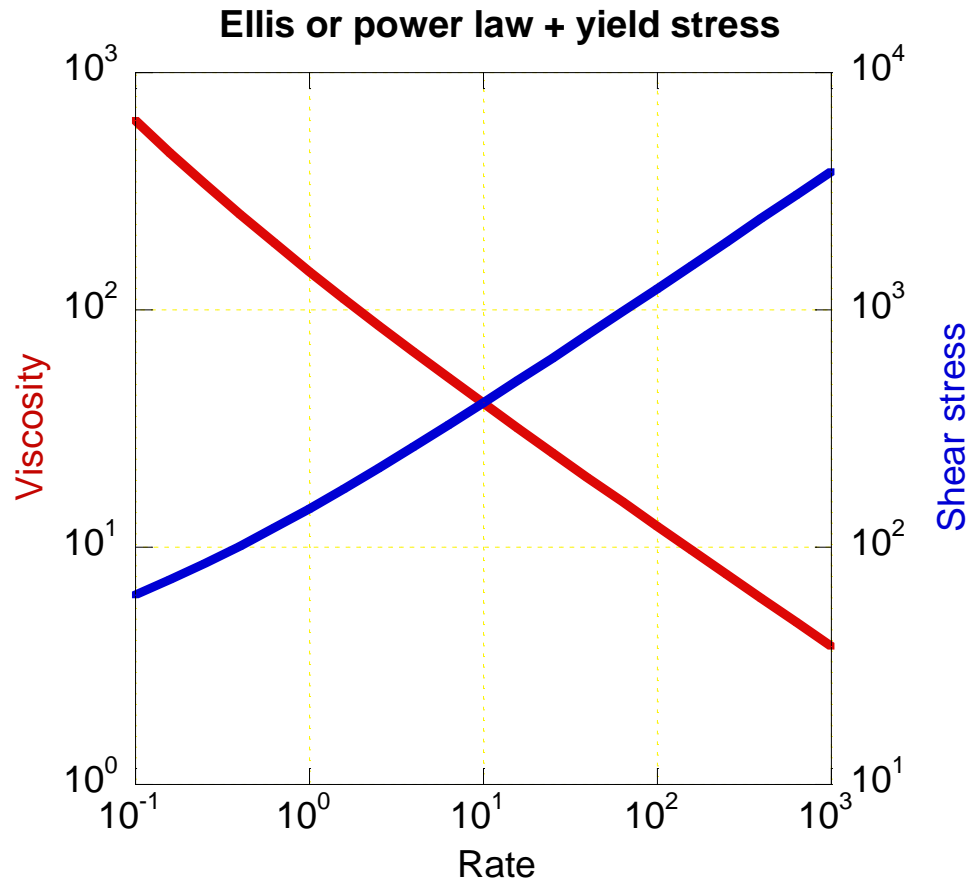
For this graph:

K = 120

n = 0.5

$\tau_o = 25$

This modification of the power law model allows for a yield stress like the Bingham. It is difficult to fit; 2 known parameters, 3 unknowns.

Equation: $\eta = \eta_\infty + \dfrac{\eta_o - \eta_\infty}{1 + K * (\dot{\gamma}^n)}$

Cross model
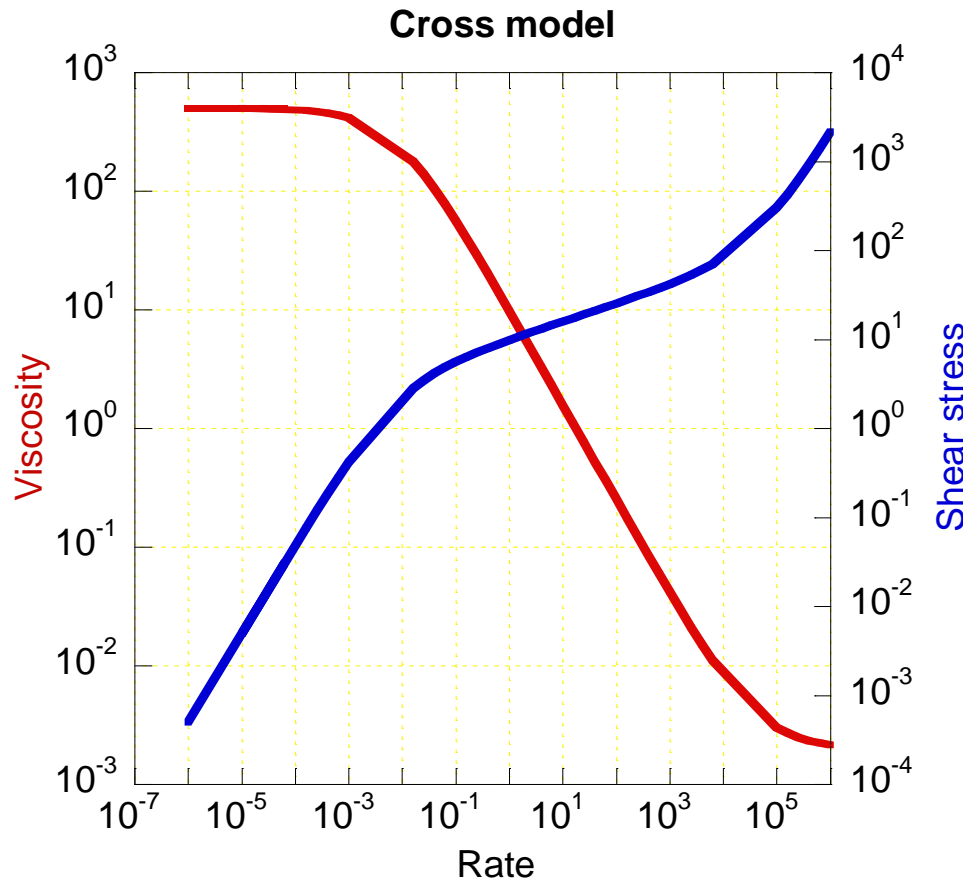
For this graph:

$\eta_\infty = 0.002$

$\eta_o = 500$

$K = 50$

$n = 0.8$

This model fits viscosity data rather than shear stress data. It allows for upper and lower Newtonian viscosity values. With 4 parameters, it requires non–linear methods.

1% Xanthan in 0.05 M NaCl

50 mm parallel plate, 0.5 mm gap

23ºC

10 rad/s

50% strain

ARES instrument
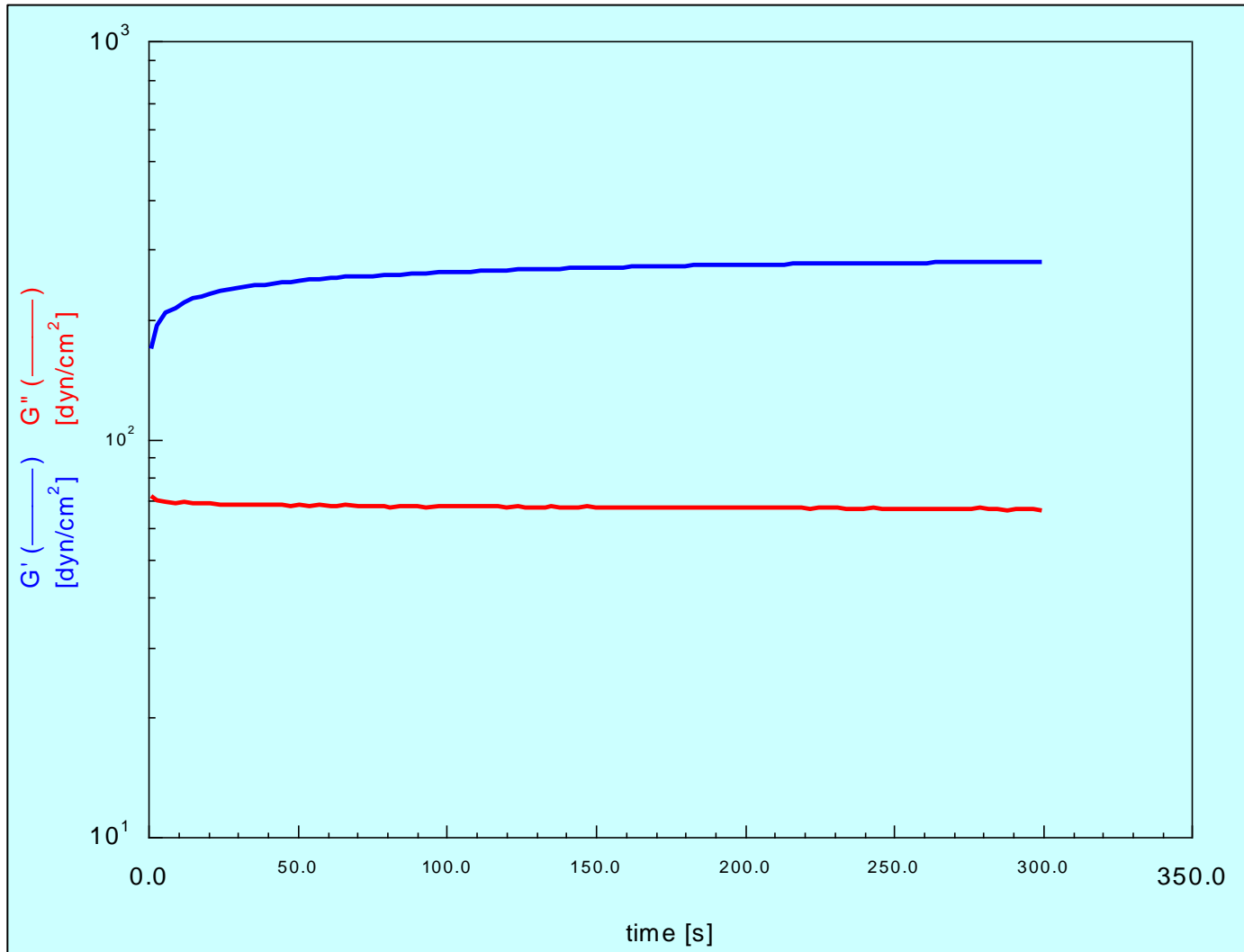
What is learned from a time sweep?

➢ **This is an essential first test to do on a material that is unknown.**

➢ **Tells you how long to wait to allow the sample to recovery after loading.**

➢ **Tells you how long you may need to wait between linked tests.**

➢ **Provides insight into recovery processes**

➢ **Used with initial controlled shear to monitor recovery after a process such a filling.**

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1% Xanthan in 0.05 M NaCl

50 mm parallel plate, 0.5 mm gap

23ºC

10 rad/s

1 to 1000% strain

ARES instrument

Linear viscoelastic region

Strain [%]

G'' (———) [dyn/cm^2]

G' (———) [dyn/cm^2]
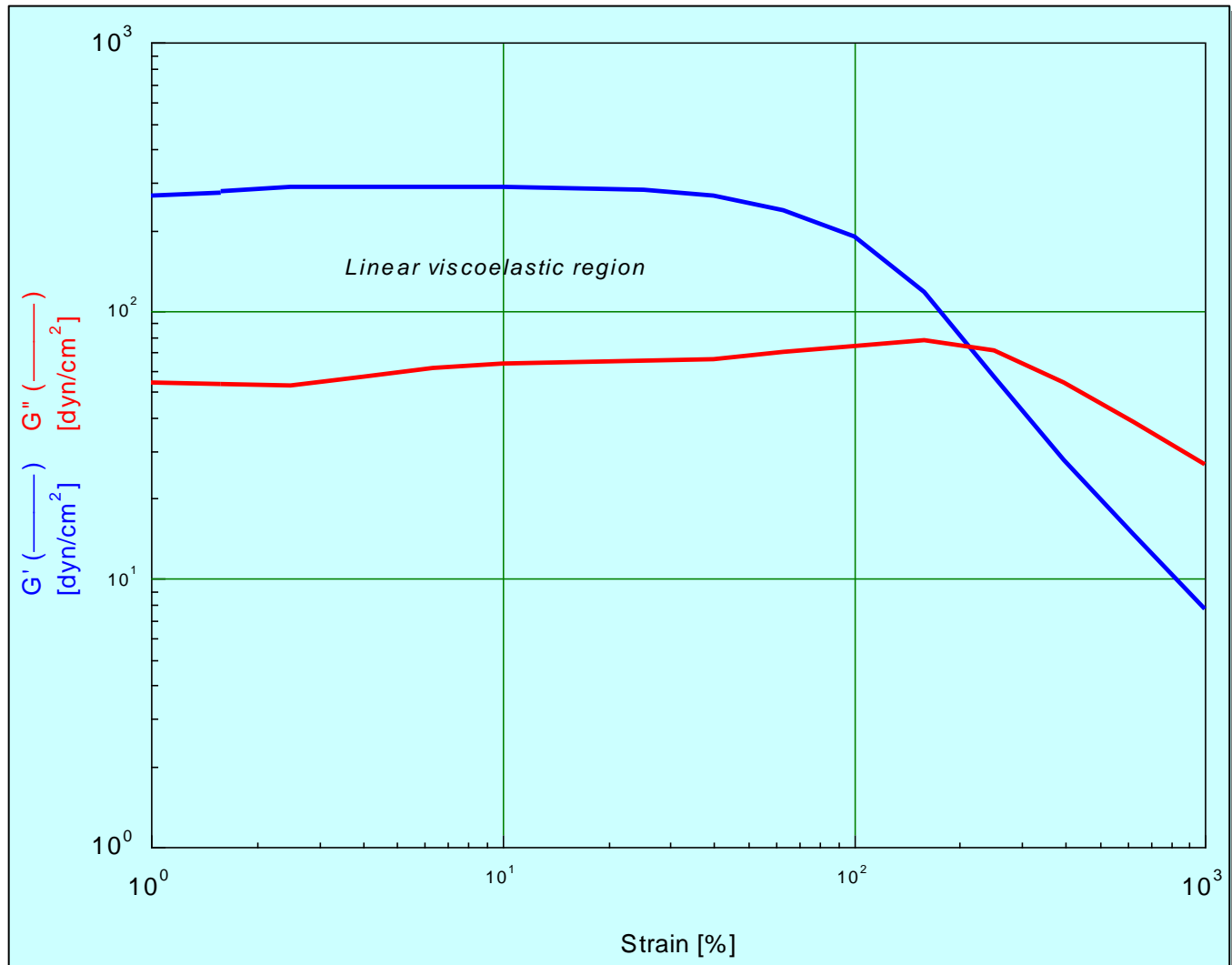
➢ **How does applied strain effect the sample.**

  – Where does the structure begin to breakdown

  – How quickly does it breakdown

➢ **Does the material have a linear viscoelastic region.**

  – Most do, that is where you normally do all further tests.

  – How wide is this range?

1% Xanthan in 0.05 M NaCl

50 mm parallel plate, 0.5 mm gap

23ºC

0.01 to 100 rad/s

50% strain

ARES instrument
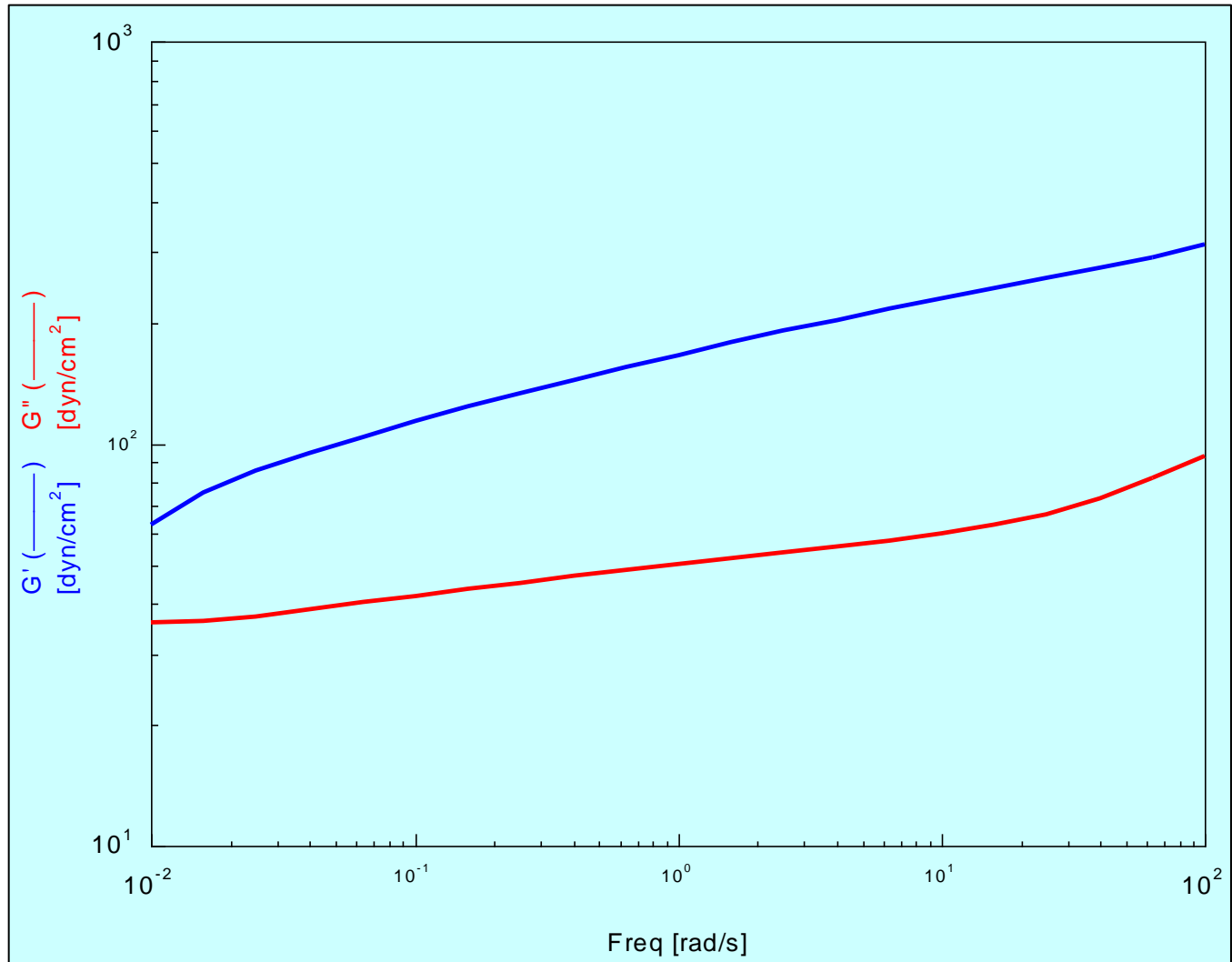
➢ **Tells us how time effects the sample.**

- Materials usually become stronger (modulus increases) as the rate increases or the measurement time decreases (rate = 1/time).

- If you can look at a material over a wide enough time range, most things are the same.

- Cross over points for E' and E" are commonly used as an indication of the sample's relaxation time (elastic and viscous values are equal).

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1% bacterial cellulose in tap water

50 mm parallel plate, 0.5 mm gap

23ªC

Stress ramp from 0 to 100 dynes/cm^2 over a 120 second period

SR-2000 instrument

Yield stress:(20.59 dynes/cm^2 @ 139.57% strain)

$\gamma(t)$ (——) [%]

$\tau(t)$ [dyn/cm^2]
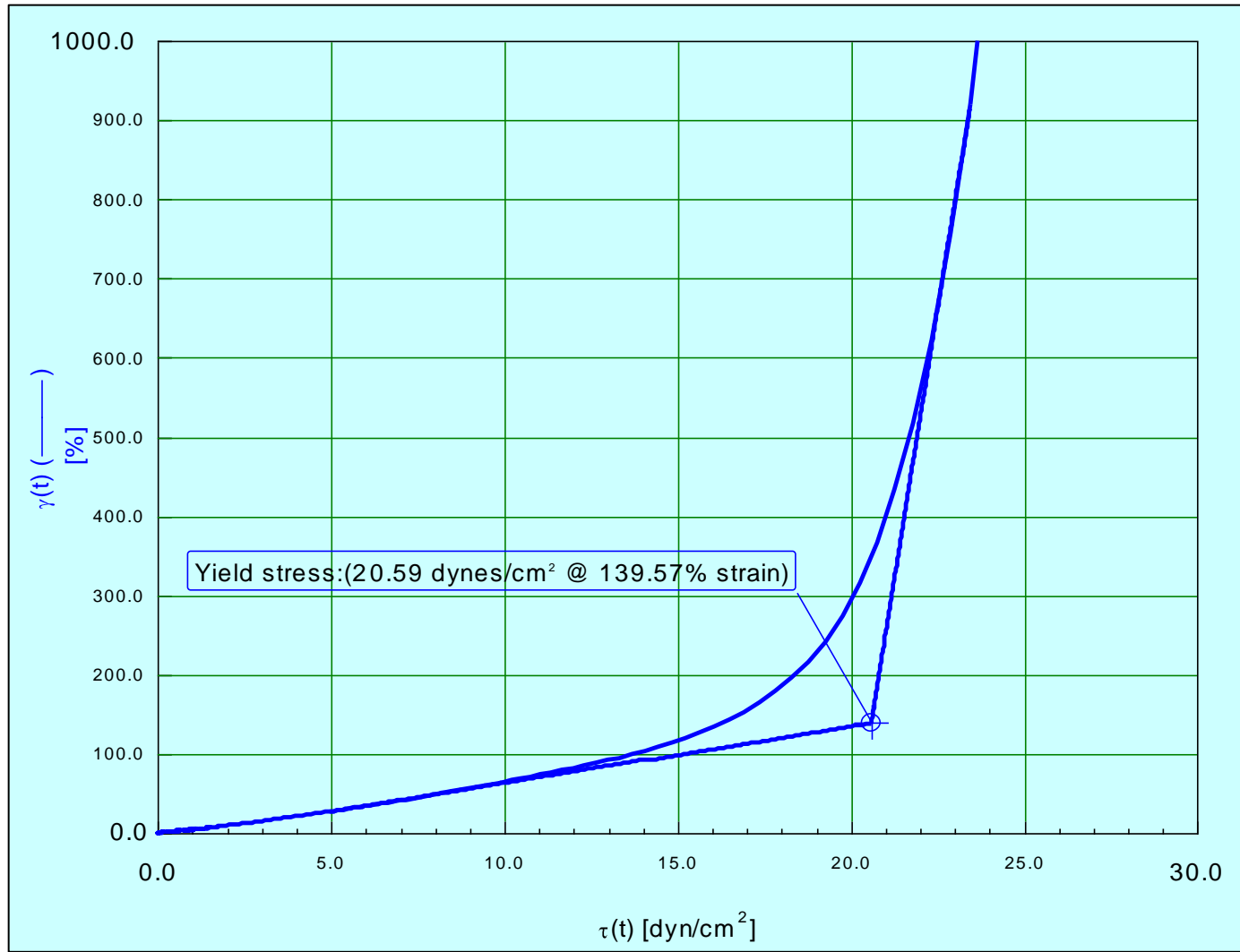
➢ **Best way to find a yield stress (catsup).**

- By continually increasing the applied stress from zero to some value that will get the material to flow, we can look for a break in the curve.

- This break indicates when the material structure was substantially broken.

➢ **Both the yield stress and yield strain are important.**

➢ **Yield strain should be a little larger than the LVR limit.**

Temperature sweep test

0.5% gellan gum in 4 mM $CaCl_2$

50 mm parallel plate, 0.5 mm gap

23ºC

Dynamic test at 10 rad/s and 5% strain

ARES instrument with Peltier heating / cooling

Chart legend:
- Control $T_s \sim 97C$
- Treatment #1 T_s 82C
- Treatment #2 T_s 74C

Set temperature defined as G' value of 10 dynes/cm^2

G' (——) [dyn/cm^2]

Temp [°C]

<----- Cooling test run from high temp to low <-------
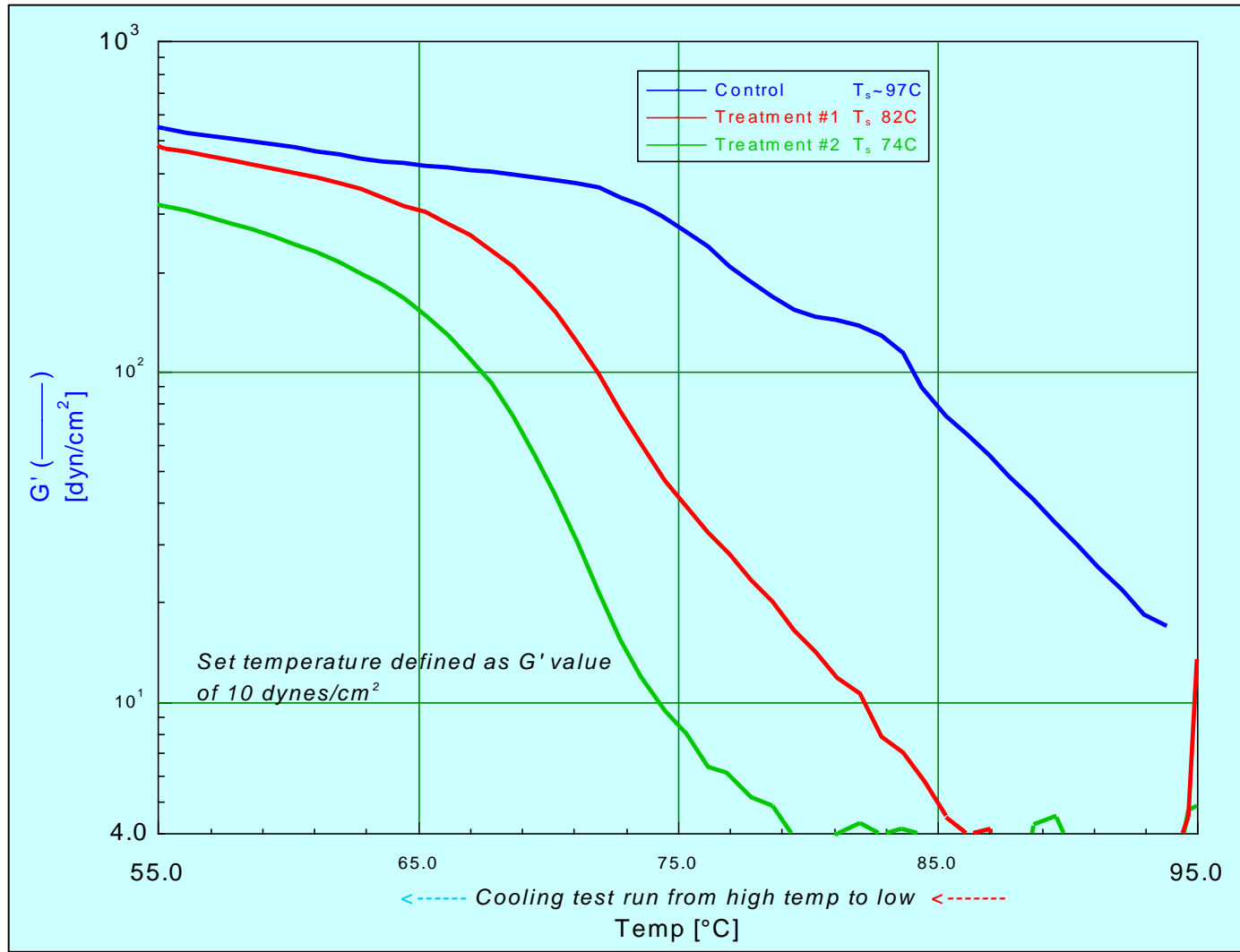
Why do a temperature sweep test?

➢ **Commonly used to find T_g in a material**

   – Point at which the structure changes due to temperature

➢ **Used to find melting temperatures of samples.**

   – Materials like gelatin can change from a liquid to a solid

➢ **Find the amount of thinning that occurs with heating to predict performance and design process equipment**

1% Xanthan in 0.05 M NaCl

50 mm parallel plate, 0.5 mm gap

23ºC

50 dynes / cm^2 stress
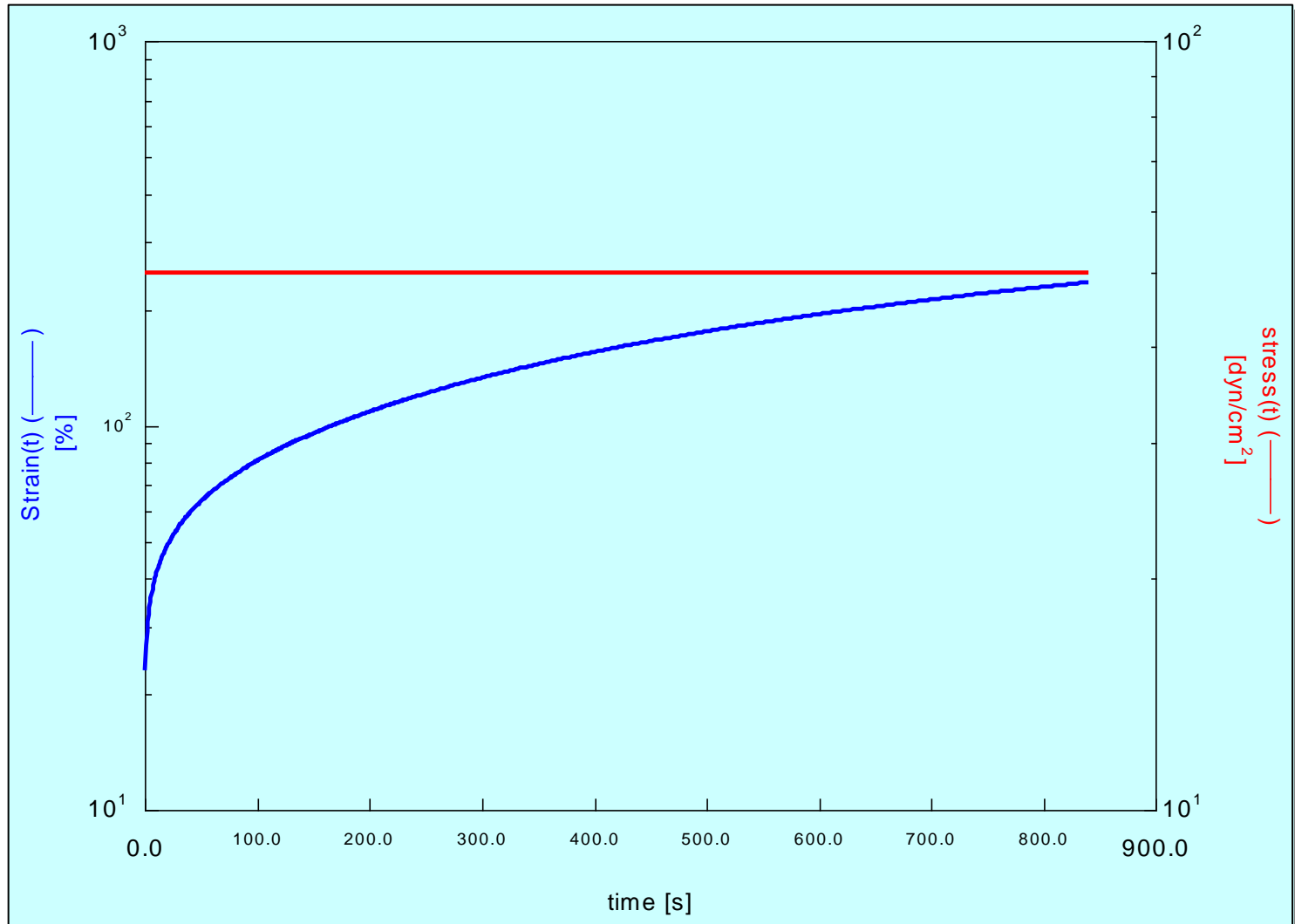
What is learned from a creep test?

➢ **When a material is subjected to a constant stress (force) it will flow easily if it has the characteristics of a liquid and less if it is solid-like.**

➢ **Can be used to fit data to spring-dashpot models.**

➢ **Materials with a high amount of creep may be too fluid-like (elastomers).**

➢ **Some materials that are very elastic may not store energy or dampen properly.**

Spring and dashpot models

Used to provide a physical model of a material's properties

Spring-represents a perfectly elastic element
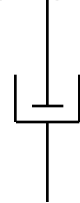
Dashpot-represents a perfectly viscous element
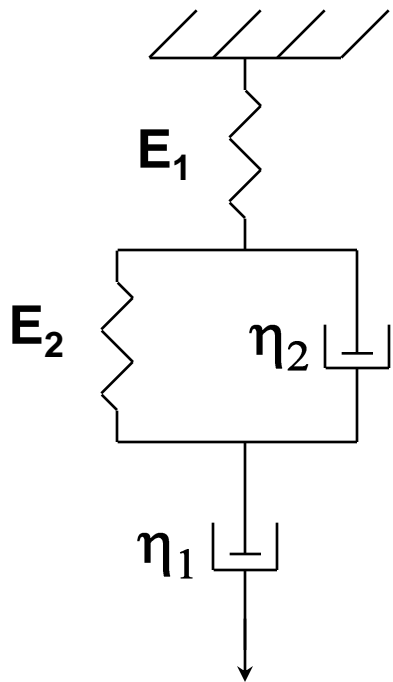
This represents an idealized creep curve with the data fitting a single relaxation or retardation time. E_1 represents the initial elastic deformation, η_1 represents the creep flow or steady state viscosity and the $E_2 + \eta_2$ combination provides a retarded flow that can be used to determine a characteristic time of a material.

E_1

E_2 η_2

η_1

η_1

strain

$E_2 + \eta_2$ - Relaxation time

E_1

time
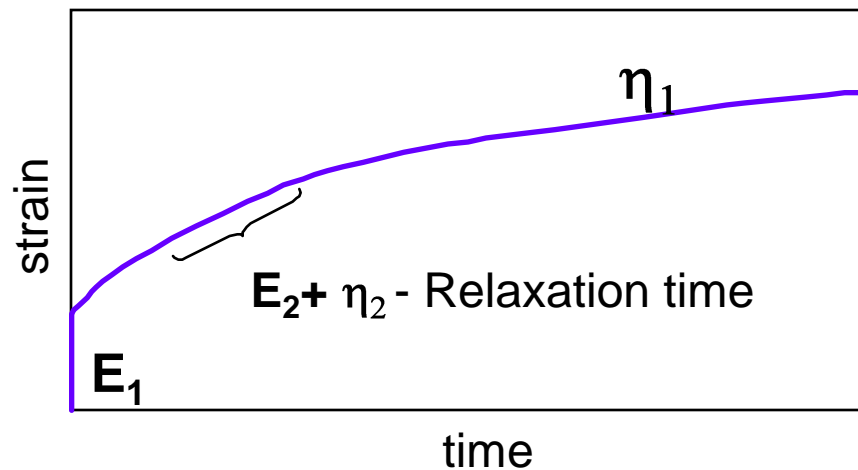
1% Xanthan in 0.05 M NaCl

50 mm parallel plate, 0.5 mm gap

23ºC

50% strain

ARES instrument
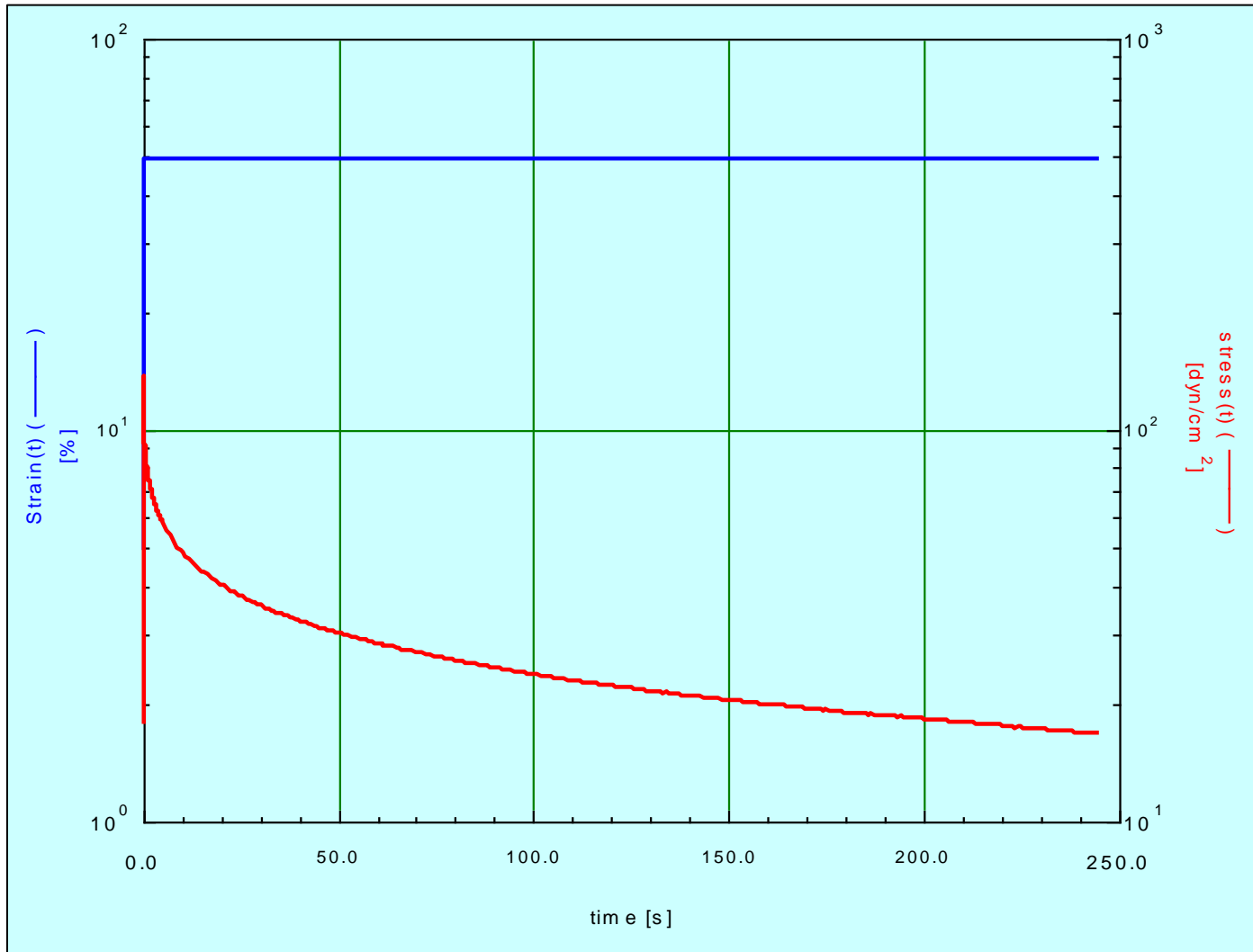
What is learned from a stress overshoot?
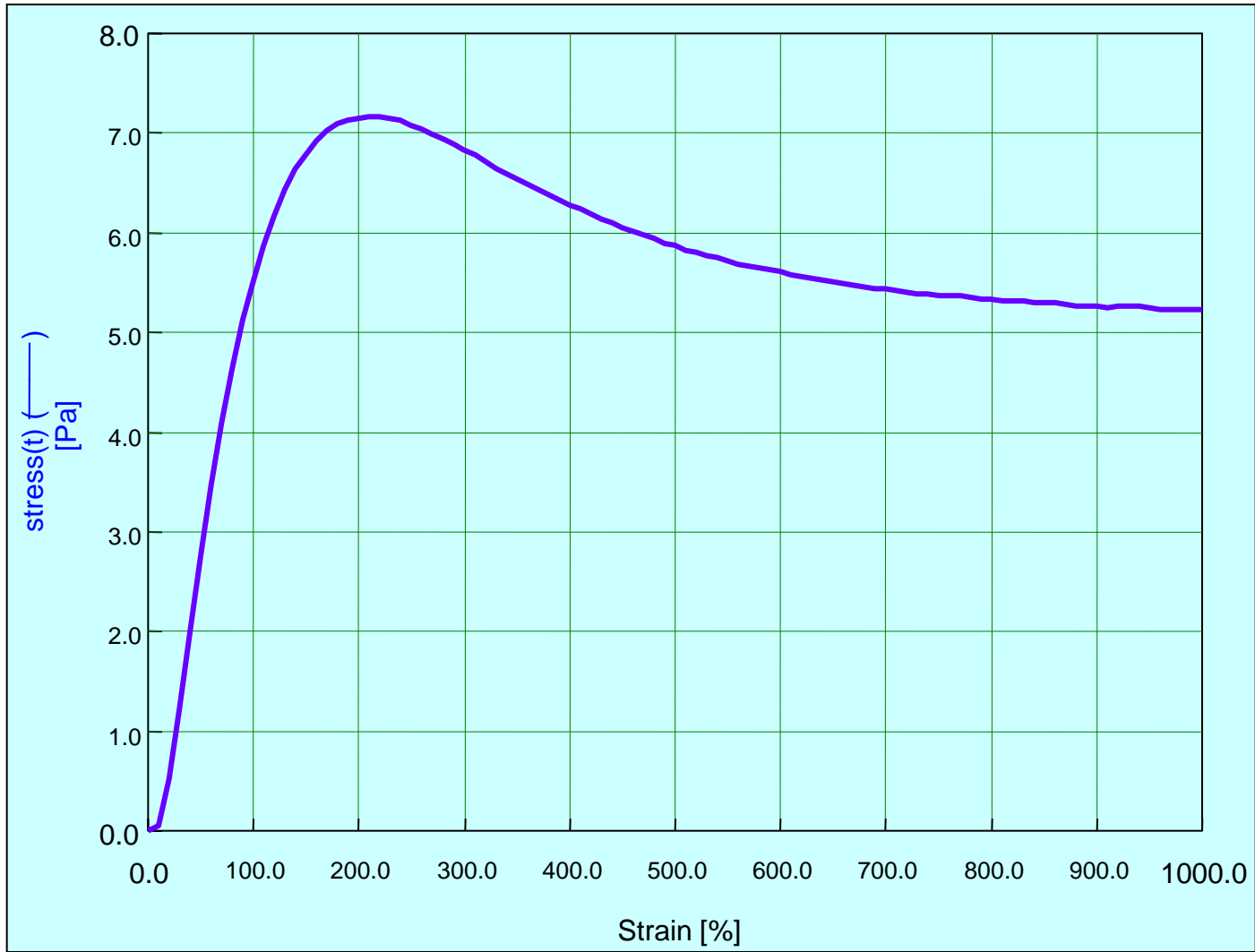
➢ **How does the sample behave as the structure is broken down by a large strain**

➢ **Comparable to a dynamic strain sweep**

  – The overshoot test is done in steady shear

  – Applies more strain than strain sweep

  – Strain is not oscillatory but steady

➢ **This mimics many filling and dispensing operations**

1% Xanthan in 0.05 M NaCl

50 mm parallel plate, 0.5 mm gap

23ºC

Frequency sweep data collected with auto stress adjust. Strain controlled from 20 to 50%

Creep data collected at 50 dynes / cm^2 stress

SR-2000 instrument

These data are from a frequency sweep curve

These data are from a transformation of the creep curve data.

G" (▽) [dyn/cm^2]

G' (△) [dyn/cm^2]

Freq [rad/s]

Why use a creep → freq. transform?

- ➢ **Creep tests provide data at longer times.**

- ➢ **Two tests (creep and frequency) + transformation can give more data in less time that a single longer frequency test.**

- ➢ **Use an applied stress that yields a creep strain roughly the same as what was applied in the frequency sweep.**

- ➢ **Use in reverse to predict creep from frequency sweep data. Useful in your instrument is not controlled stress.**

Relaxation → frequency transform
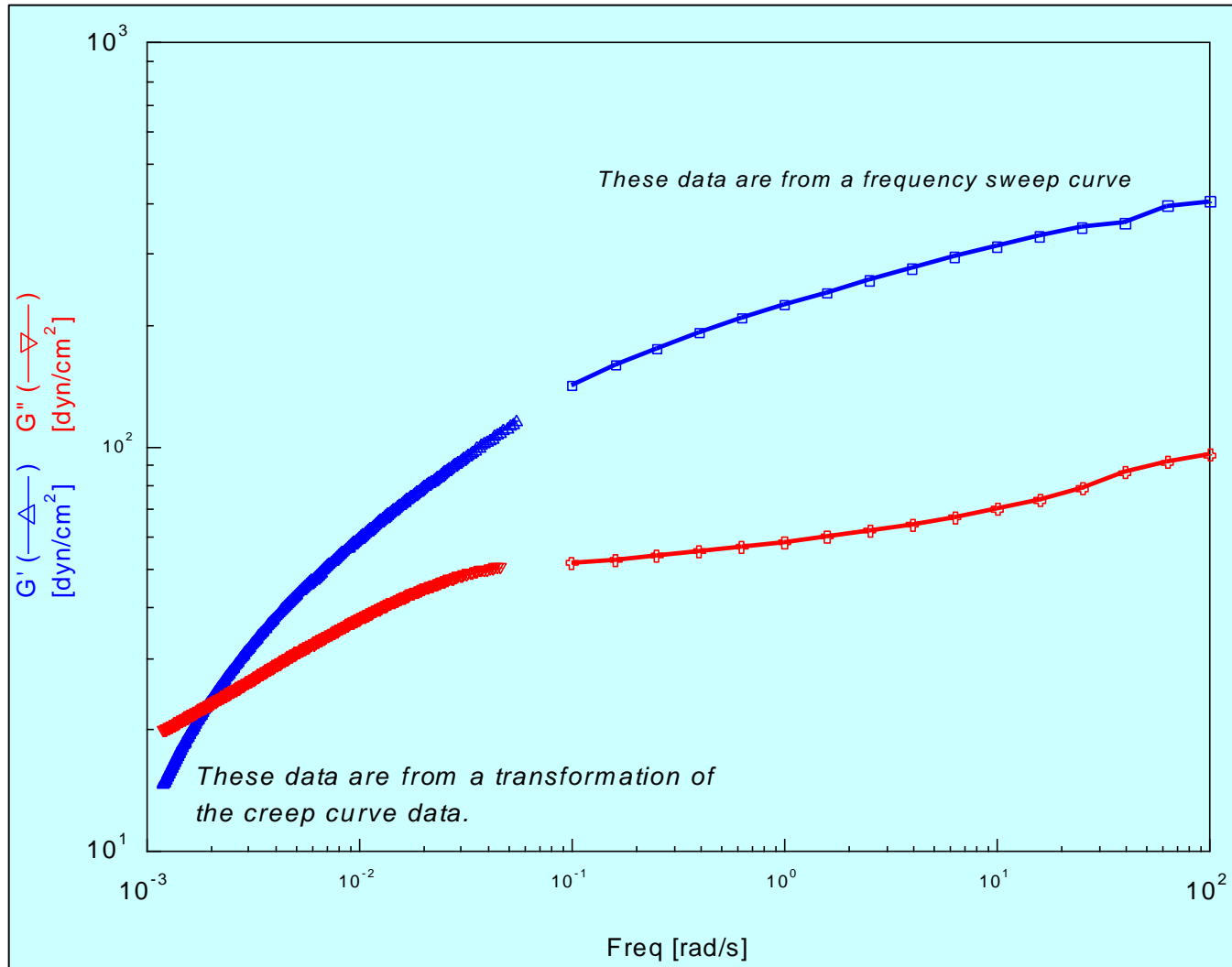
1% Xanthan in 0.05 M NaCl

50 mm parallel plate, 0.5 mm gap

23ºC

Frequency sweep data collected with auto stress adjust. Strain controlled from 20 to 50%

Creep data collected at 50 dynes / cm^2 stress

SR-2000 instrument

Solid lines from relaxation data — *Dashed lines from frequency sweep*

Axis labels: G" (——) [dyn/cm^2], G' (——) [dyn/cm^2], Freq [rad/s]

Why use a relaxation → freq transform?
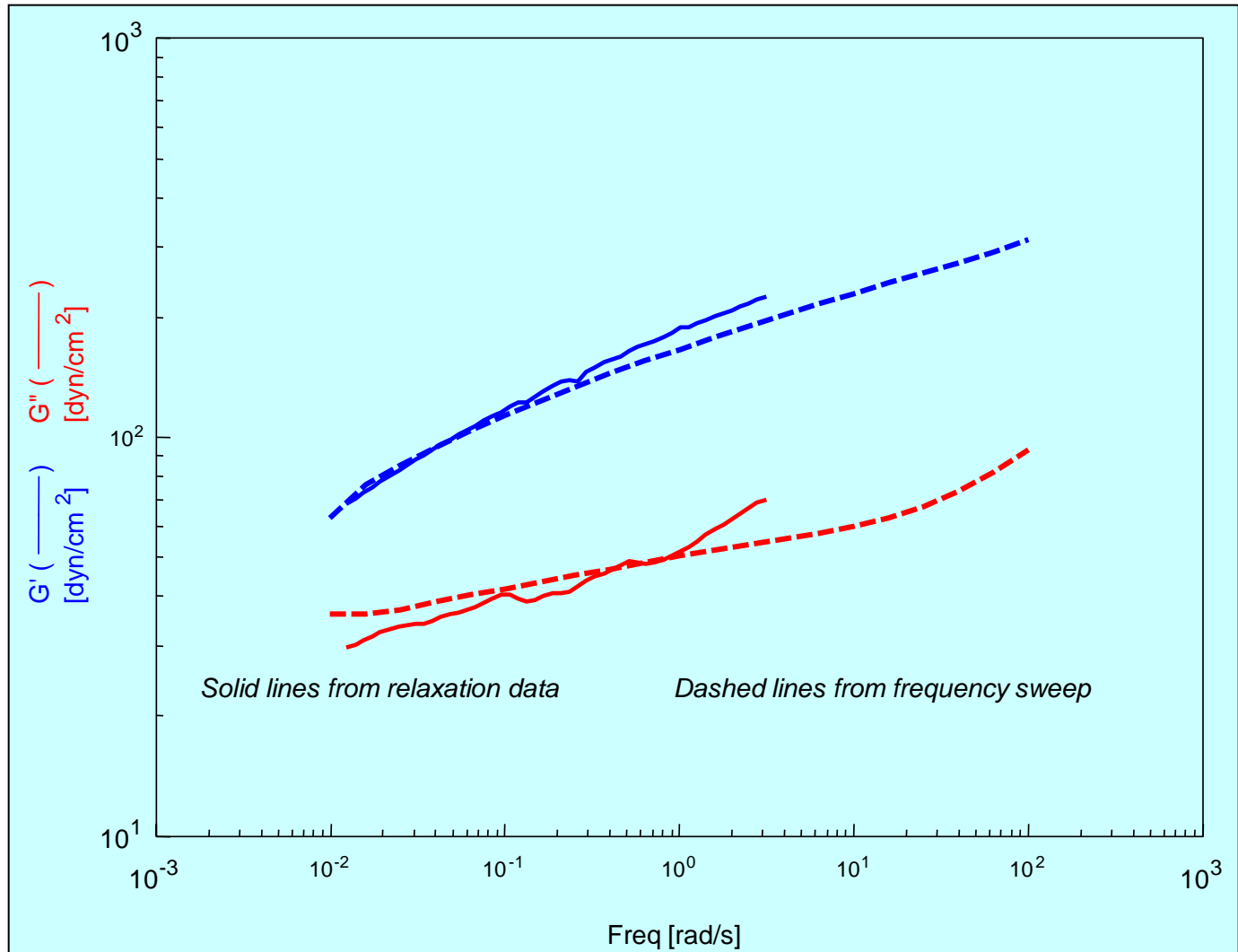
➢ **Sometimes relaxation tests can collect data a shorter times that other tests.**

➢ **Extending the data to shorter times aids understanding.**

➢ **This is a sort of "impact" test and can simulate some short time processes.**

➢ **Can serve as a confirmation of the data collected with another type of test.**

➢ **Use in reverse to obtain relaxation data from frequency sweeps.**

➢ **Characteristics of viscoelastic materials vary with both time and temperature.**

➢ **We can trade temperature for time and get more information quickly**

➢ **But…. Only if our material does not change state over the chosen temperature range**

0.5% gellan gum in 4 mM CaCl$_2$

25 mm parallel plate, 0.5 mm gap

-35 to +55ºC

Frequency sweep data collected at 10% strain

ARES instrument
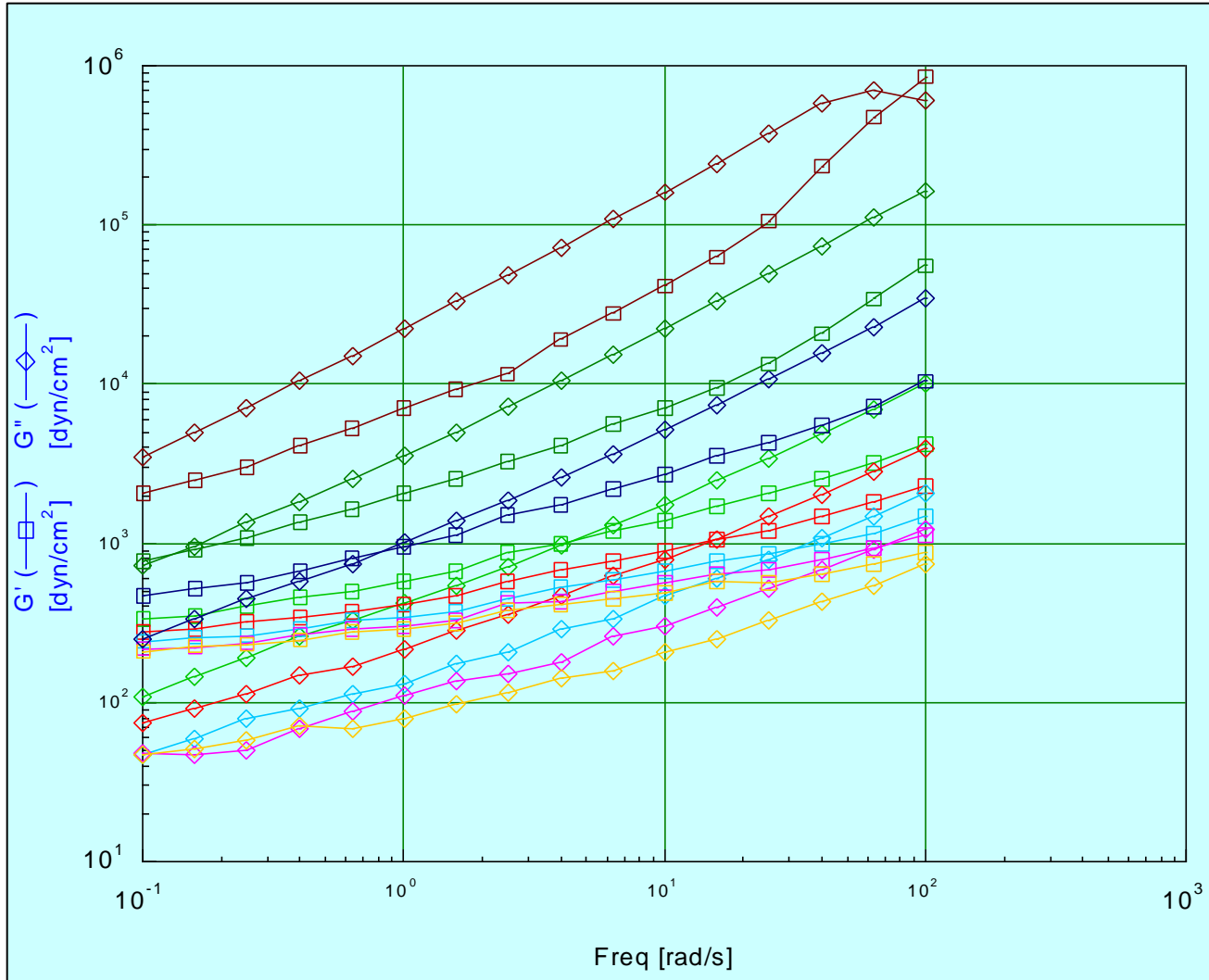
Data shifted with two dimensional residual minimization.

Cubic spline interploation

For more information concerning minimization methods developed by Brent and Powell, see W. H. Press, et. al., Numerical Recipes in C, Cambridge University Press, 1992, ISBN 0 521 43108
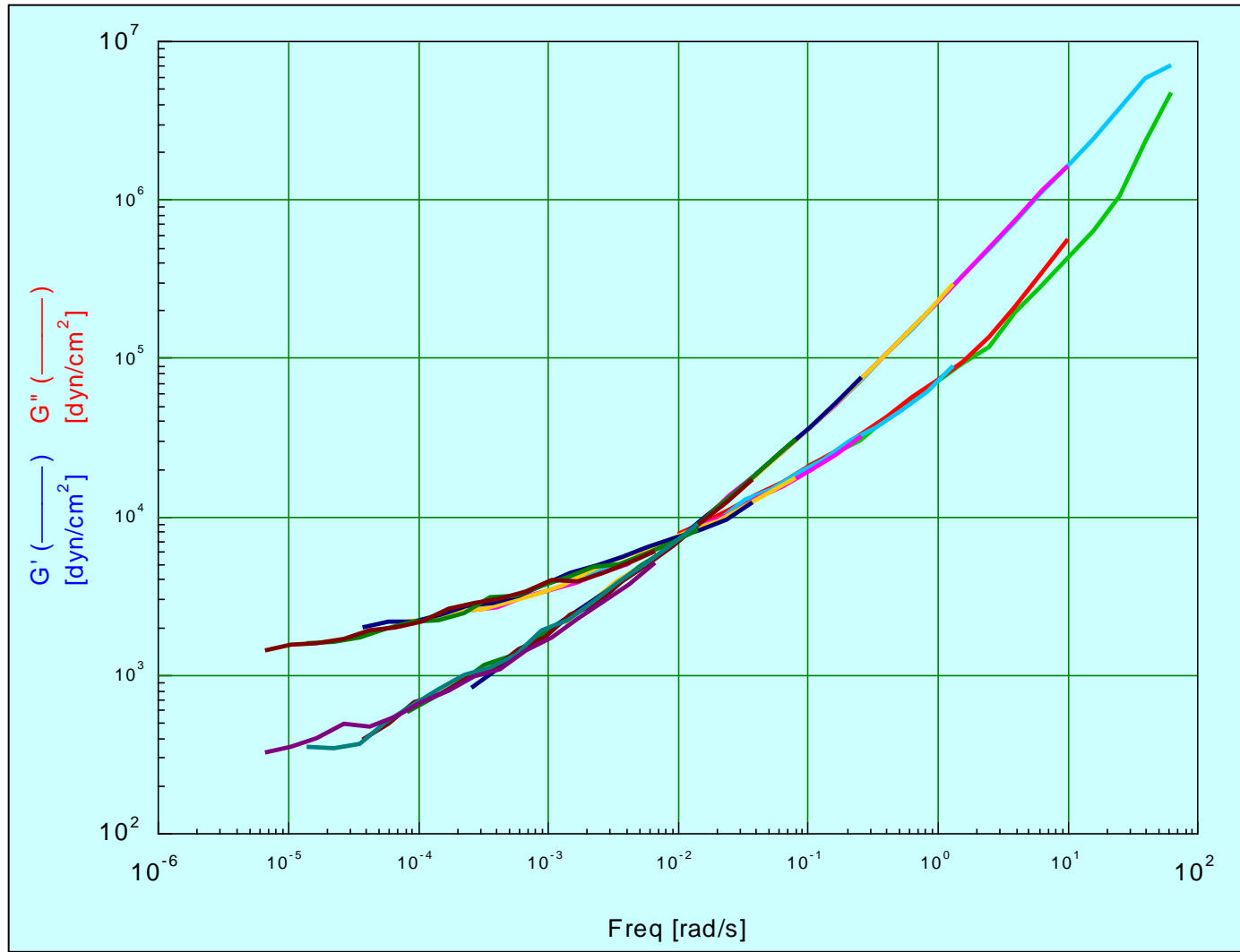
➢ **Know your instrument**

  – Torque limits

  ➢ Most manufacturers stretch the truth; confirm with standards!

  – Rotational speed limits

  ➢ Computerized instrument isolate the user; you need to know if you are asking the impossible
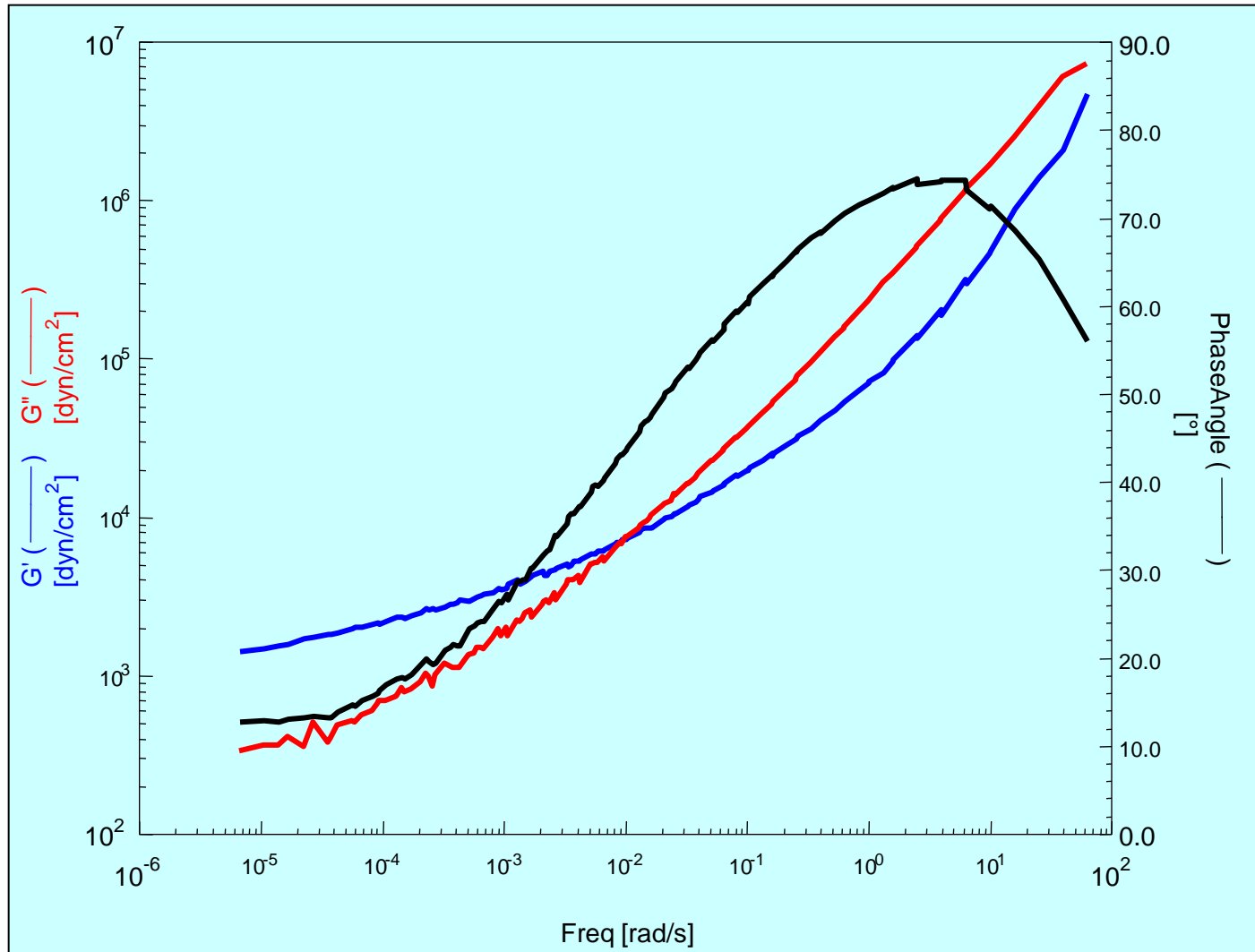
  – Frequency limits

  ➢ Very low frequencies might not be accurate

  ➢ High frequencies might have "roll off" in strain or inertial problems

  – Strain limits

  ➢ In a digital world there is a limit to the bits of resolution

  ➢ No substitute for being able to see the actual waveforms

  – Temperature accuracy

  ➢ Don't assume it is correct!

  ➢ Does the temperature controller over or undershoot

➢ **Controlled stress instruments are a problem**

  – Samples fundamentally react to strain

➢ **Pick the best test geometry**

– Cone and plate is ideal
- ➢ Small volume
- ➢ Uniform shear rate
- ➢ Can't be used with varying temperatures
- ➢ Can't be used if solid particles > 25% of the gap are present
  - – Common gap is 50 microns!

– Parallel plate a workable compromise
- ➢ Not a uniform shear strain or rate
- ➢ Relatively insensitive to temperature changes
- ➢ Handles solid particles better
  - – Common gap is 1 mm
- ➢ Reduce the gap to 50-100 microns to achieve a higher shear rate

– Couette is good for larger samples
- ➢ Usually need 5-20 ml samples
- ➢ Easier to control evaporation
- ➢ Needs corrections in most cases.
- ➢ Poor choice for high shear (Taylor instabilities)

➢ **Sample loading sensitivity**

  – Select the best way to load the sample

  ➢ Cast or form a gel in place

  ➢ Cut a gel and put between parallel plates

  ➢ Spoon or pipette

  – Use time sweeps to determine the effects of loading

  ➢ How long to wait before you begin testing

  – Determine if evaporation control is important

  ➢ Either recovery time or temperature are considered

➢ **Strain limits** (stay in the Linear Viscoelastic Region)

  – In most cases you have to work here

  ➢ Consider the LVR when picking frequency sweep parameters

  ➢ Can your instrument control strain?

  ➢ Does it back up and start over if the strain limit is exceeded?

  ➢ Consider the LVR strain when picking a creep stress

➢ **What are you really interested in?**

– Don't measure samples blindly; consider what is important

– This is not reading tea leaves! Be selective with testing

➢ **For a uniform type of sample with small variations:**

– No time or strain sweeps needed

– Mw and crosslinking can be measured with a frequency sweep

– Monitor modulus as a function of time?

– Is melt important?

➢ **If samples vary widely:**

– LVR strain is likely to vary; an important characteristic

– Network rearrangement can be measured with creep

– Setting or melting might be revealing

➢ **Creep (constant stress)**
  – How networks rearrange
  – Transformation to convert to frequency sweep

➢ **Step shear rate**
  – Low → High → Low for time dependency
  – ***Never***, ever, use a thixotropic loop test – ***Please***!

➢ **Temperature ramps**
  – Even if TTS is not used, can still find about phase changes
  – TTS cannot be used if there is a phase change!

➢ **Stress ramp**
  – Many materials have a functional yield stress
  – Philosopical arguments aside, yield stress is practically present in many materials

➢ **Oscillatory capillary test (Vilastic)**
  – Developed for biological fluids with weak structures

➢ **Flow curve (viscosity versus shear rate)**

  – Are steady shear tests even appropriate

  – Did thixotropy get covered up?

  – Increase or decreasing speed?

  – Steady increase (ramp) or stepwise (sweep)?

➢ **Thixotropic loop**

  – Ramp up and down

  – Area in between supposed to be thixotropy

  – Often is inertia in the instrument instead

➢ **Rheology is complex but understandable**
- – Experts often are not consulted (ask, we want to teach!)
- – Expertise is more important than intuition about what test to use

➢ **Tremendous evolution in the last 15 years**
- – Historical literature can be a disadvantage; start fresh

➢ **A great deal of misinformation in the literature**
- – For example, lack of strain control in "stress controlled" instruments
- – Manufacturers are not good sources of information
  - ➢ Some exaggeration and distortion

➢ **Still more tests available:**
- – Solids testing
- – Extensional properties of fluids
- – Optical rheology
- – Micro-rheology