Rheology
–Principles & Application

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Outline

What is the position of rheology?

Classification of non-Newtonian fluids

Rheological Parameters

- Steady Shear
- Oscillatory Sear
- Extensional Flow

Examples

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What is the position of rheology? What Is Rheology?

- Rheology is the study of the Deformation and Flow of matter
- Rheology is the study of the flow of materials that behave in an interesting or unusual manner.
  - Oil and water flow in familiar, normal ways
  - Mayonnaise, peanut butter, chocolate, bread dough and silly putty flow in complex and unusual ways.
  - Mayonnaise *vs*. Honey

Generally, the Rheology focuses on the
Resistance of Material against Flow

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The two types of material resistances against flow (I)

Frictional Resistance (Viscosity) η

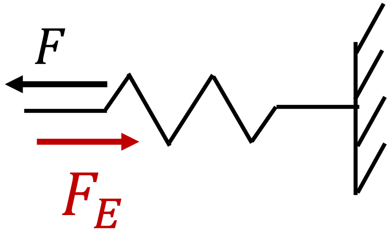
- Consider a brick on an asphalt surface.
- Once a force F is applied, the brick will resist against it with friction F_f.
- This is a frictional resistance.
- Viscosity is the material resistance that emerges due to friction between the layers of the fluid.

For the materials that only show frictional resistance against flow, that resistance is called the "Viscosity".

The two types of material resistances against flow (II)

❑ Elastic Resistance (Elastic Modulus) G

- Consider a spring attached to the wall.
- Once a force F is applied, the spring will resist against it with an elastic force F_E.
- This is an elastic resistance.



For the materials that have elastic behavior, not considering the elastic resistance means ignoring one side of the material properties, which will cause issues in applications and end-use properties of the materials.

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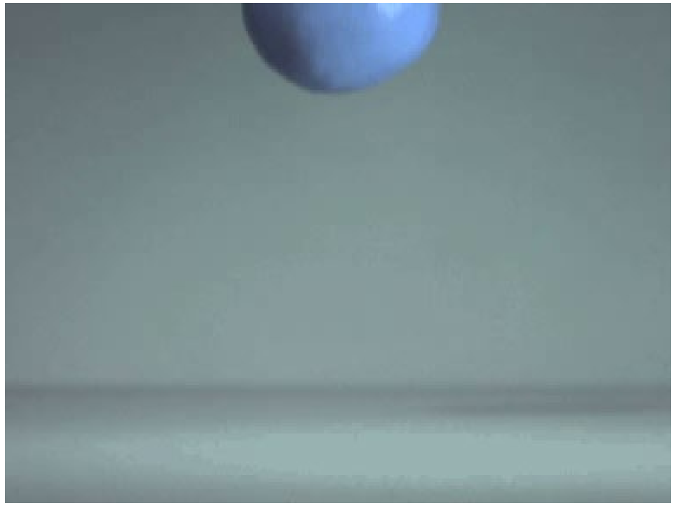
Characteristics of each Material Resistance Type

❑ Frictional (Viscous) Resistance

- Wastes energy
- More relevant in slow processes

❑ Elastic Resistance

- Stores energy
- More relevant in fast processes



Viscoelasticity is the balance between the frictional (viscous) and elastic resistances of the material against the flow.

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Why Rheology?

- States of matter
  - Solid, Liquid and Gas
  - Plasma (at extremely high temperature)
  - Bose-Einstein Condensate (at extremely low temperature)
- Classical definition of "liquid" as opposed to "solid"
  - A "fluid" is any substance that deforms continuously under the application of an arbitrarily small shearing force
- With this definition
  - Mayonnaise is a solid, since it holds against gravity
  - Glass is a liquid (!), since it creeps, albeit ever so slowly, against forces even much weaker than gravity

Clearly the classical definition is inadequate.
That is why Rheology comes into the picture.

Definitions:

- Complex fluids are
  - substances that flow at modest stresses
- By flow, it is meant
  - a smooth deformation on a humanly accessible time scale

Examples:

- A piece of ceramic does not flow; it deflects under modest loads, and it fractures under great ones
- Peanut butter flows rather smoothly when a child pushes a butter knife across it

Many materials fall well within the given rough definition, and they are worthy of a title

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Complex Fluids

- Characteristic Feature of Complex Fluids
  - Much larger molecular/structural length scales than simple liquids and simple solids
  - Polymers
  - Polymer gels
  - Particulate suspensions
  - Particulate gels
  - Foams, emulsions and blends
  - Surfactant solutions
  - Block copolymers
  - Electro- and magnetoresponsive suspensions, etc.

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What Is Rheology Use? (I)

Rheology is a "TOOL" to

- Characterize various materials
  - Material fingerprint
- Classify various families of materials
- Formulate each material family
  - Constitutive Equations

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What Is Rheology Use? (II)

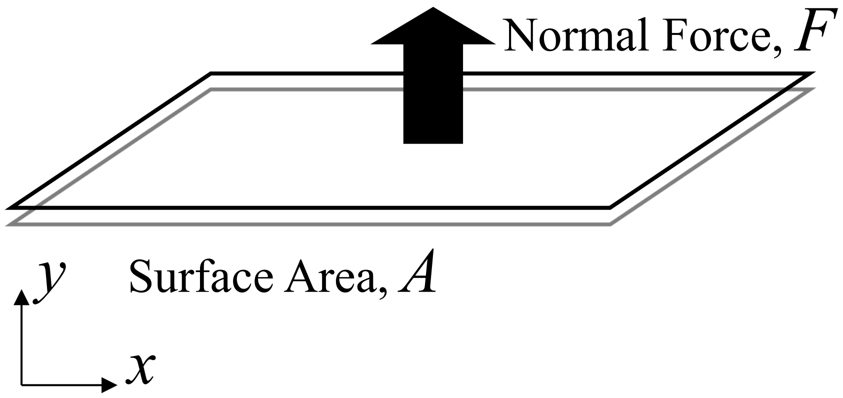
Rheology is a "BRIDGE"

- Molecular structure
  - Molecular Weight & MWD
  - Particle Size & PSD
  - Chain branching and cross-linking
  - Interaction of fillers with matrix polymer
  - Single or multiphase structure
- Rheological Properties (as a function of)
  - Force
  - Relative motion
  - Temperature
- Runnability (Processibility) & Product Performance

Material Characterization

Stress, Force per Area

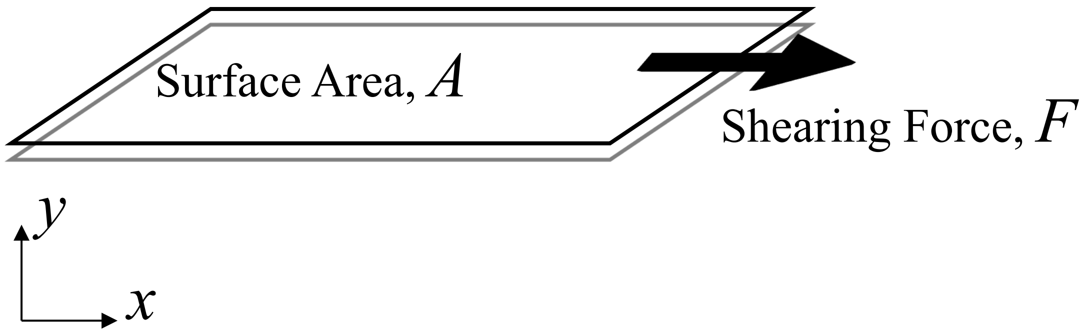
Normal Stress



$$\frac{F}{A} = \text{Normal Stress}$$

$$\frac{F_y}{A_y} = \text{Normal Stress} = \tau_{yy}$$

Shear Stress



$$\frac{F}{A} = \text{Shear Stress}$$

$$\frac{F_x}{A_y} = \text{Shear Stress} = \tau_{yx}$$

Units of Stress [Pa] ≡ [N/m^2] ≡ [10 dynes/cm^2]

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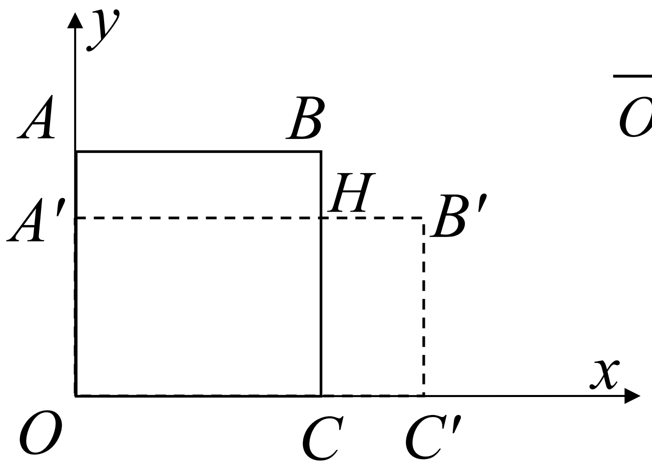
Extensional Strain & Extensional Rate

Extensional (Elongational) Strain

- (Intensity of) Extensional Deformation

$$\text{Extensional Deformation} = HB' = du_x = \text{Extensional Displacement}$$



$$\frac{HB'}{OC(=AB)} = \text{Extensional Deformation Intensity}$$

$$= \text{Extensional Strain}$$

$$= \varepsilon$$

$$= \frac{du_x}{dx}$$

Extensional (Elongational) Rate

- Rate of change of Extensional strain with time

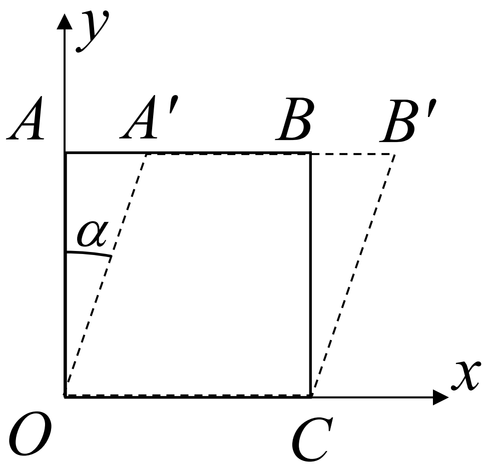
$$\dot{\varepsilon} = \frac{d\varepsilon}{dt} = \boxed{\frac{d}{dt}\left(\frac{du_x}{dx}\right) = \frac{d}{dx}\left(\frac{du_x}{dt}\right)} = \frac{dv_x}{dx}$$

Shear Strain & Shear Rate

Shear Strain

- (Intensity of) Shear Deformation

Shear Deformation $= AA' = du_x =$ Shear Displacement



$$\frac{AA'}{OA} = \text{Shear Deformation Intensity}$$

$$= \text{Shear Strain}$$

$$= \tan\alpha \cong \alpha\,(\text{rad}) \qquad \text{for } \alpha < 5°$$

$$= \gamma$$

$$= \frac{du_x}{dy}$$

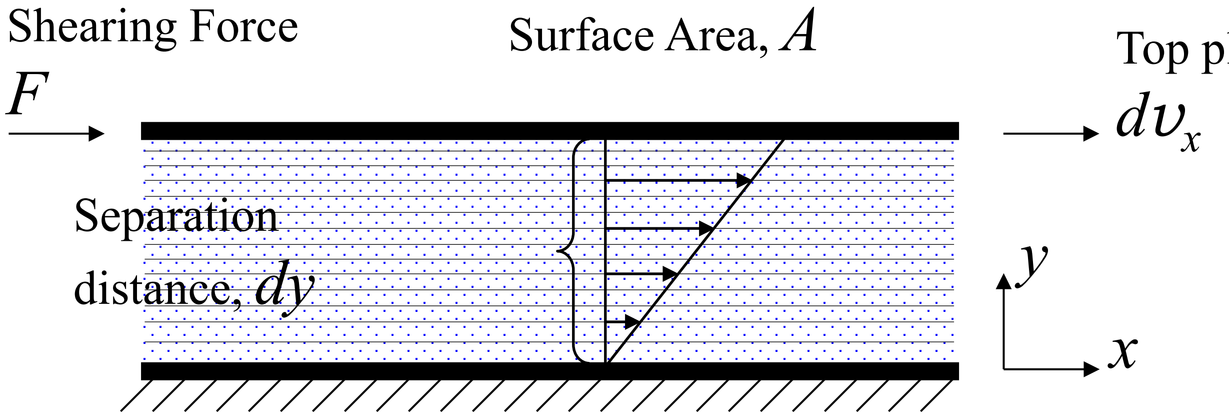
Unit of Strain:	[no unit]
Unit of Rate of Strain:	$[s^{-1}]$

Shear Rate

- Rate of change of shear strain with time

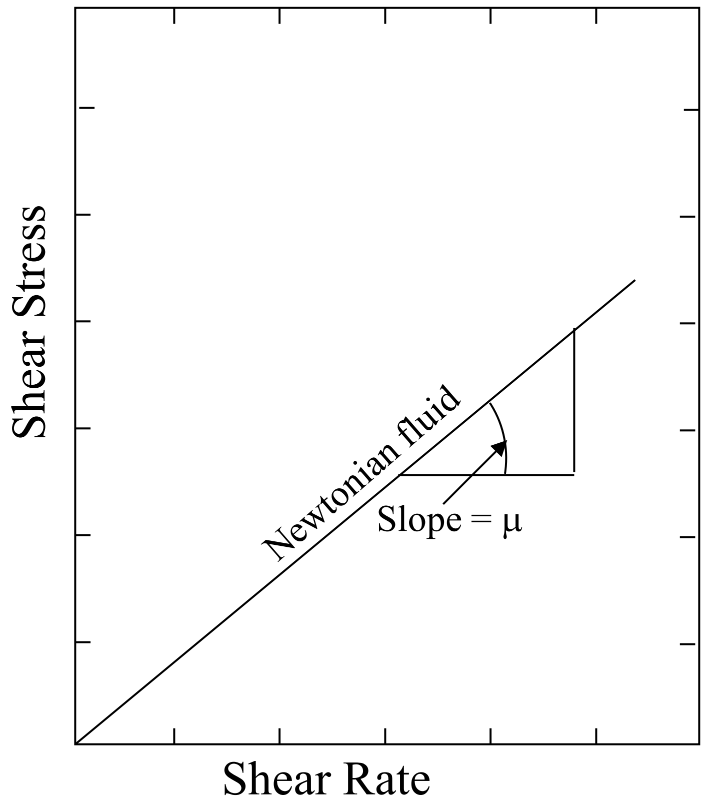
$$\dot{\gamma} = \frac{d\gamma}{dt} = \frac{d}{dt}\left(\frac{du_x}{dy}\right) = \frac{d}{dy}\left(\frac{du_x}{dt}\right) = \frac{dv_x}{dy}$$

Newtonian Fluid



$$\frac{F}{A} = \tau_{yx} = \mu \frac{dv_x}{dy} = \mu \dot{\gamma}_{yx}$$

Shear Stress   Shear Rate



Units of Viscosity [Pa.s] ≡ [10 Poise]
[N.s/m^2] ≡ [10 dynes.s/cm^2]
[mPa.s] ≡ [c. P.] ≡ [centi Poise]

Typical Viscosity Values

Substance	Newtonian Viscosity at Room Temp. μ (mPa.s or cP)
Air	10^{-2}
Water	1
Olive oil	100
Castor oil	600
100% Glycerin (20 °C)	1500
Honey	10^{4}
Corn syrup	10^{5}
Molten polymers	10^{6}
Bitumen	10^{11}
Molten glass	10^{15}
Glass	10^{43}

cP : centiPoise

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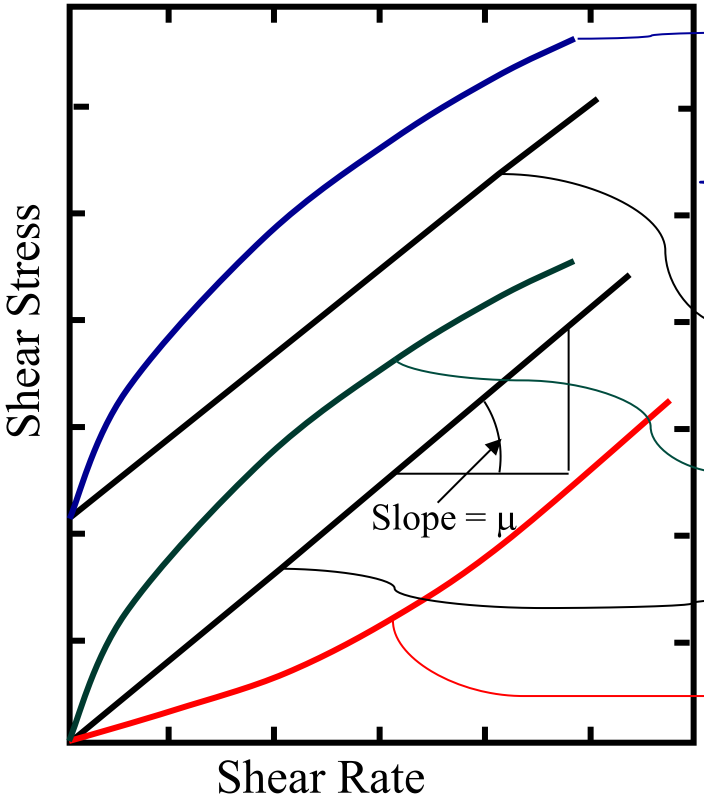
Non-Newtonian Fluids Classification – Time-Independent Fluids

Non-Newtonian Fluids

- Time-Independent Fluids
  - Shear Thinning (Pseudoplastic)
  - Shear Thickening (Dilatants)
  - Viscoplastic Fluids
- Time-Dependent Fluids
- Viscoelastic



Viscoplastic Fluids

Casson Model $\tau^{1/2} = \tau_y^{1/2} + \eta_\infty^{1/2}\dot{\gamma}^{1/2}$

Herschel-Bulkley $\tau = \tau_y + K\dot{\gamma}^n$

Bingham Plastic $\tau = \tau_y + \eta_\infty\dot{\gamma}$

Pseudo-plastic fluid $\tau = K\dot{\gamma}^n \quad n < 1$

Newtonian fluid $\tau = \mu\dot{\gamma}$

Dilatant fluid $\tau = K\dot{\gamma}^n \quad n > 1$

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Non-Newtonian Fluids Classification – Time-Dependent Fluids

Non-Newtonian Fluids

- Time-Independent Fluids
- Time-Dependent Fluids
  - Thixotropic Fluids
  - Rheopectic Fluids
- Viscoelastic

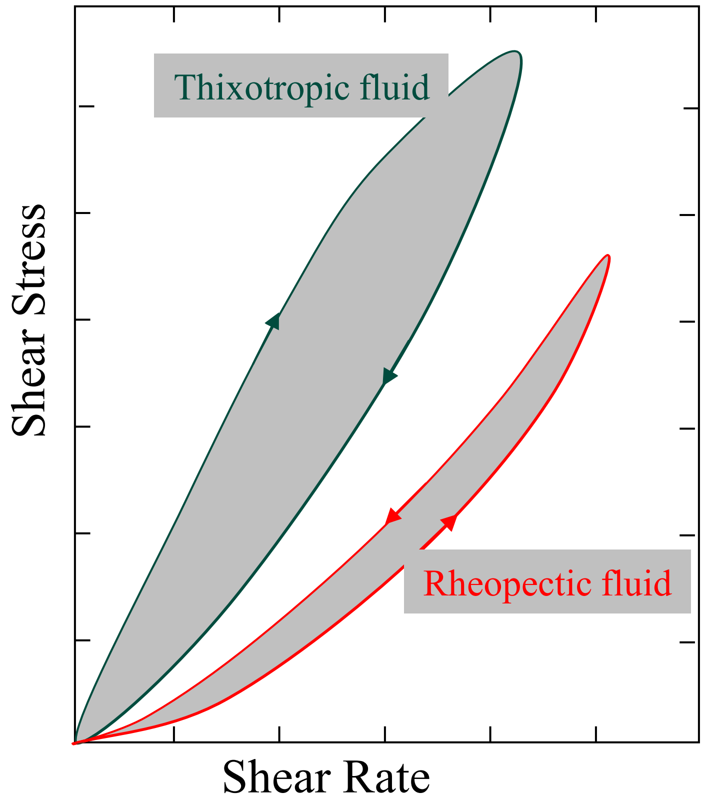
Thixotropy Model

λ : Structural Parameter showing the degree of ***jamming*** of material microstructure

$$\frac{d\lambda}{dt} = \frac{1}{\theta} - \alpha\dot{\gamma}\lambda$$

α, θ : material constants

$$\text{Restructured status} \underset{\text{Structure buildup}}{\overset{\text{Structure breakup}}{\rightleftarrows}} \text{Destructed status}$$



Tests on time-dependent structured materials require preconditioning.

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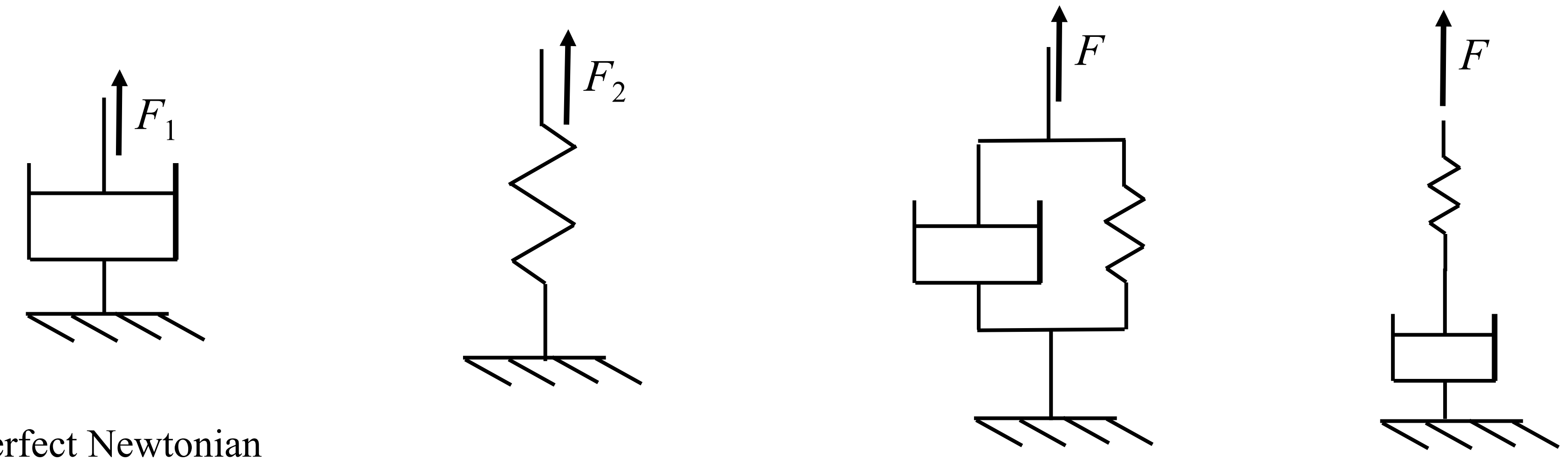
Non-Newtonian Fluids Classification – Viscoelastic Fluids

Non-Newtonian Fluids

- Time-Independent Fluids
- Time-Dependent Fluids
- Viscoelastic



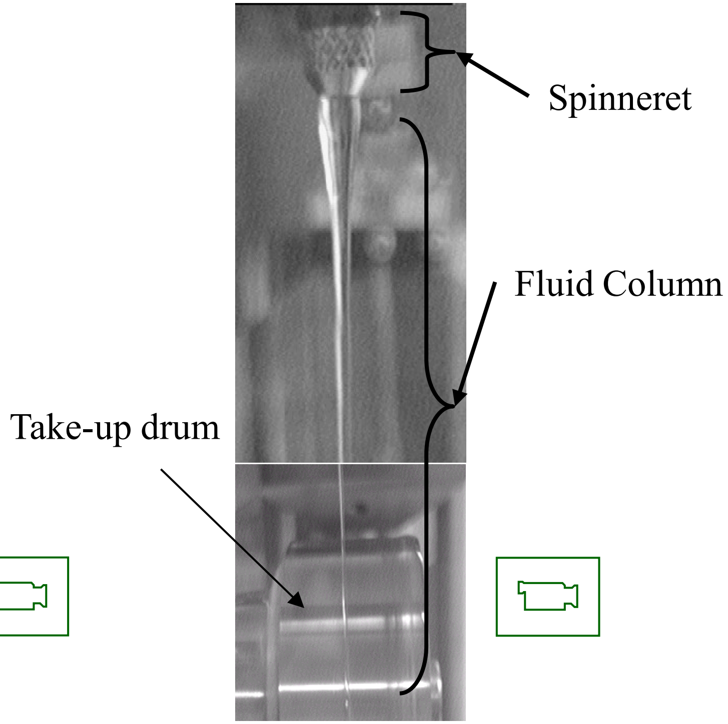
Perfect Newtonian Viscous Fluid (Dashpot System)	Perfect Hookian Elastic Spring	Voigt / Kelvin Viscoelastic Solid	Maxwell Viscoelastic Fluid
$\frac{F_1}{A} = \tau_1 = \eta \frac{dv_x}{dy} = \eta\dot{\gamma}$	$\frac{F_2}{A} = \tau_2 = G\frac{du_x}{dy} = G\gamma$	$\frac{F_1 + F_2}{A} = \tau = \eta\dot{\gamma} + G\gamma$	$\dot{\gamma}_1 + \dot{\gamma}_2 = \dot{\gamma} = \frac{\tau}{\eta} + \frac{\dot{\tau}}{G}$

Non-Newtonian Fluids Classification – Viscoelastic Fluids

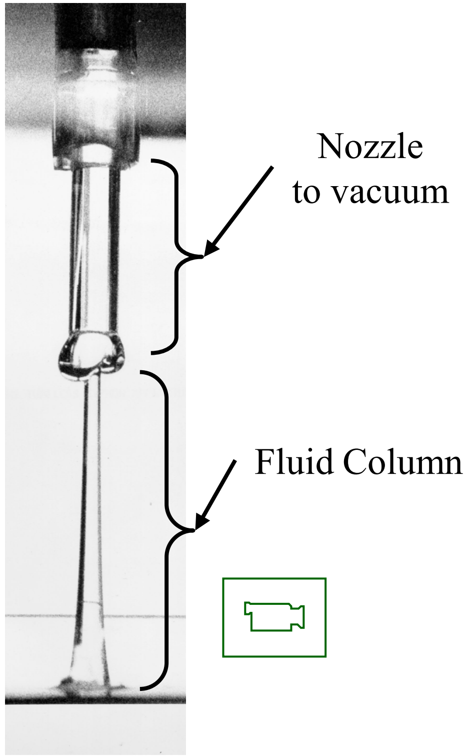
Non-Newtonian Fluids

- Time-Independent Fluids
- Time-Dependent Fluids
- Viscoelastic

Rod-Climbing Effect



Fiber-Spinning Experiment



Tubeless Siphon (Fano) Flow

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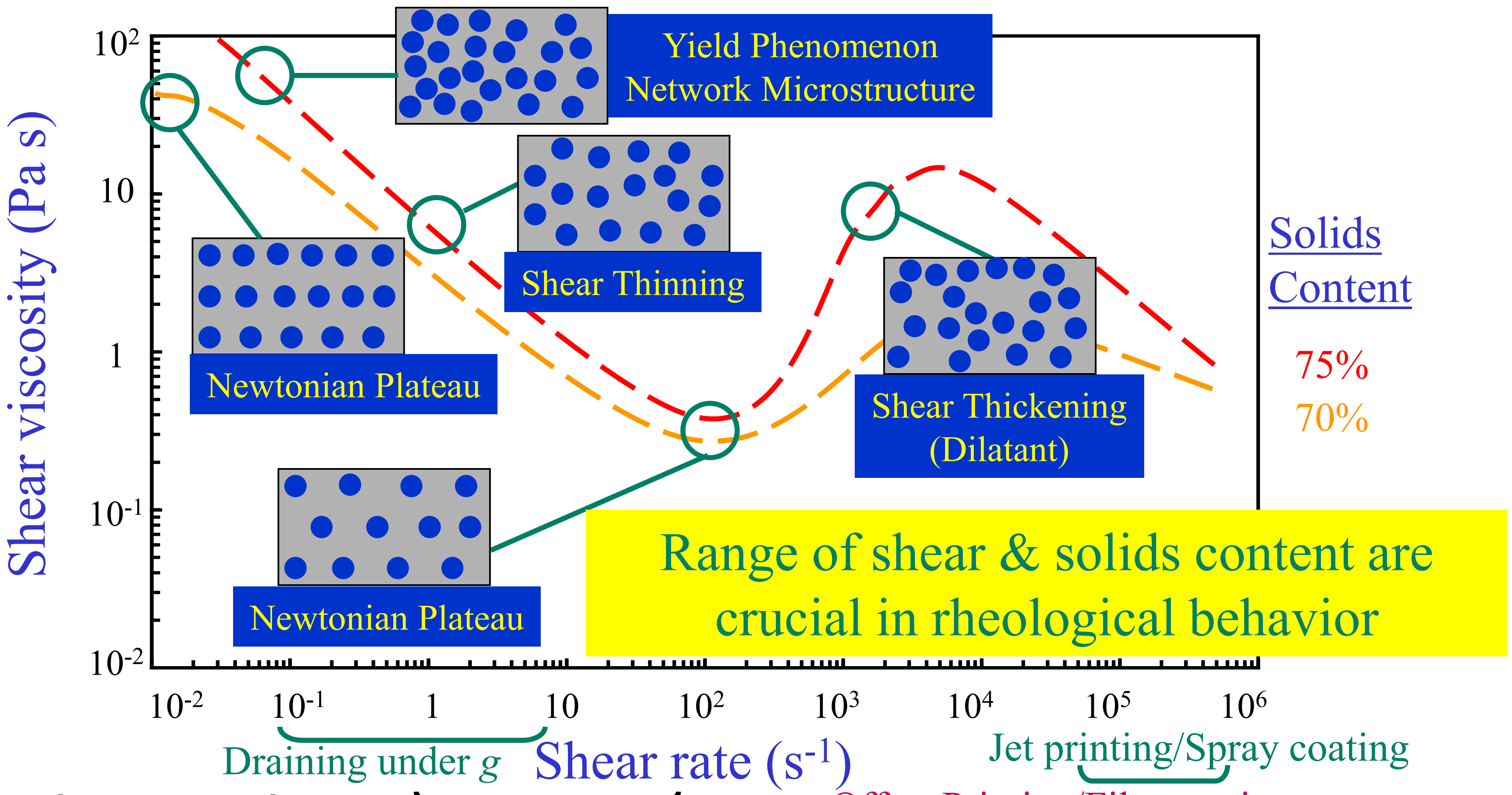
Rheology & Material Microstructure – Application Ranges



Draining under *g*

Jet printing/Spray coating

Offset Printing/Film coating

Gravity leveling

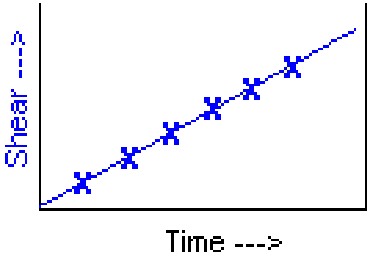
Pumping

Mixing

Lithographic printing/ Blade coating

Air Knife coating

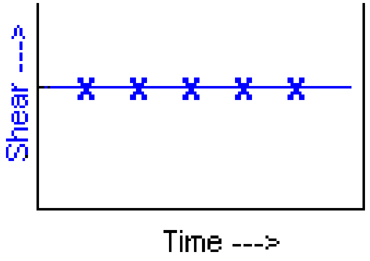
Shear Flow Tests



Ramp Test

Continually increasing the shear from a lower value to a higher one in a given time.

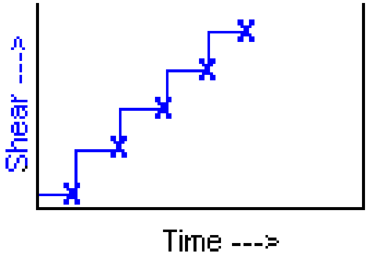
Mainly used to get the hysteresis loop to determine a quick measure of thixotropy.



Creep/Startup Test

Holds the shear at a constant given value.

Used to get startup data (in rate control tests) or creep data (in stress control tests).



Stepped Flow Test

Applying successive shear values in an increasing or decreasing path. Data collected over the last x seconds.

Used to get steady-state flow curves in rate control or stress control modes. Also used to get the hysteresis loop to determine a measure of thixotropy.

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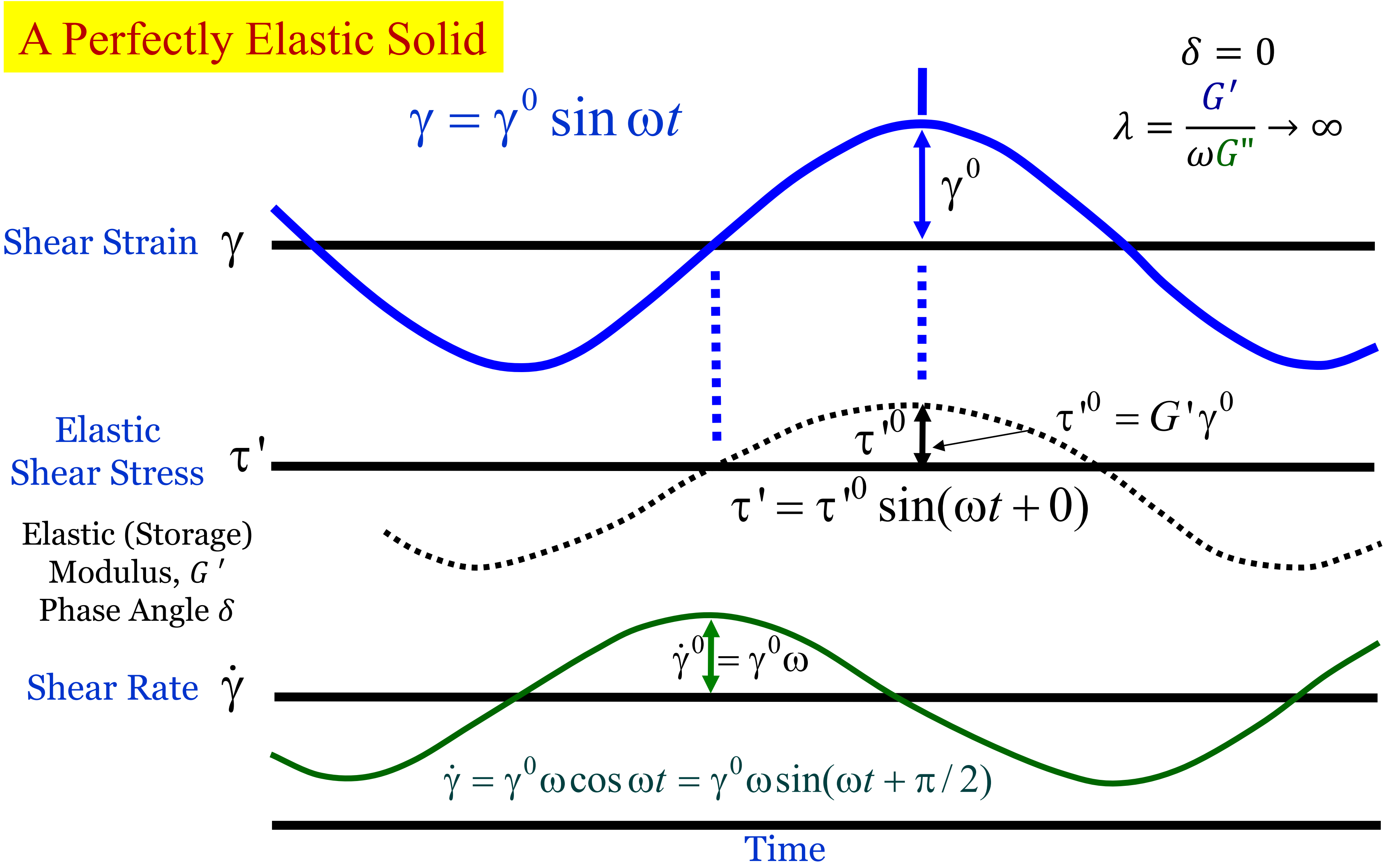
Oscillatory Shear (Dynamic) Test



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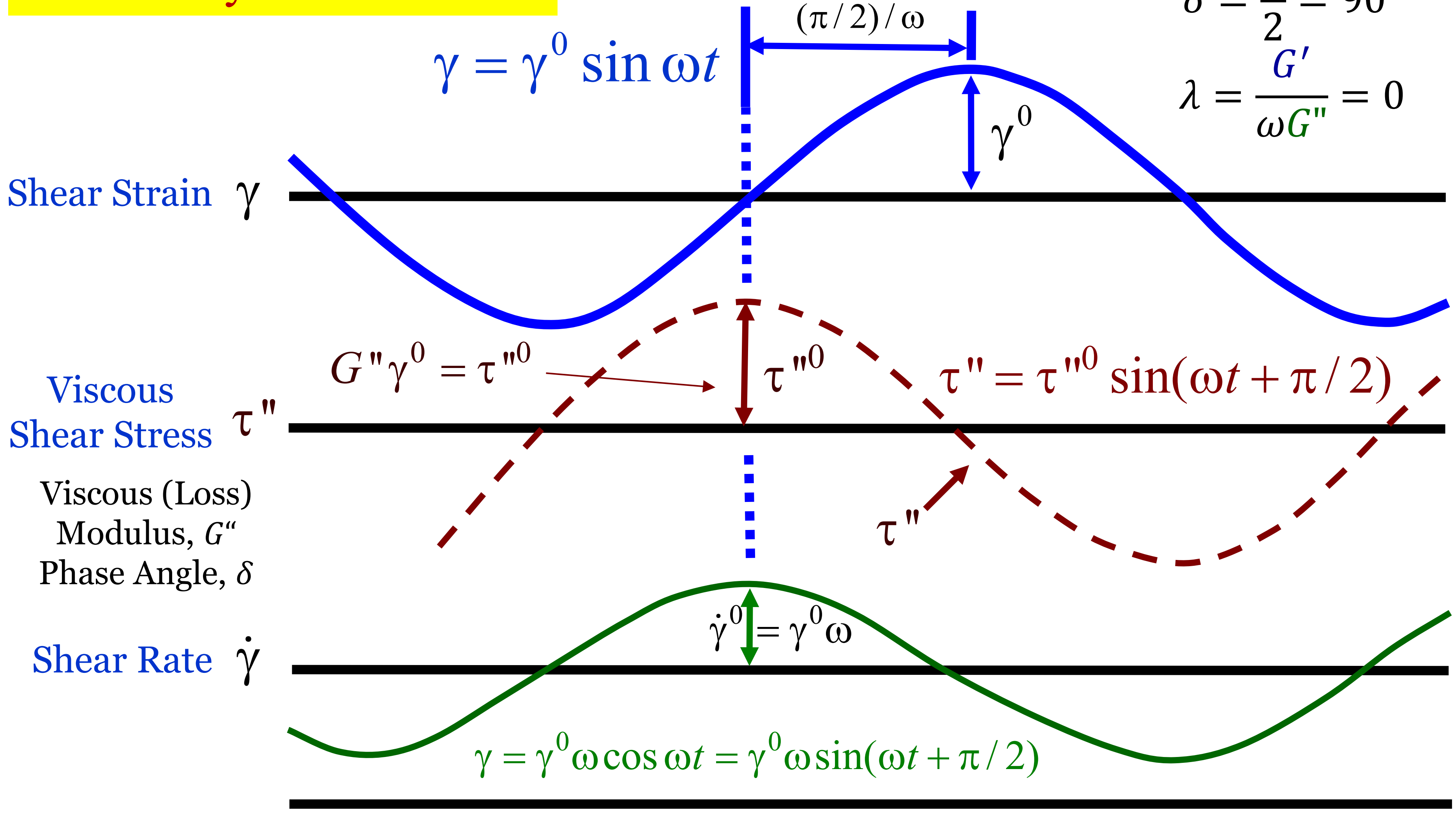
Oscillatory Shear (Dynamic) Test

A Perfectly Viscous Fluid

$$\delta = \frac{\pi}{2} = 90^\circ$$

$$\lambda = \frac{G'}{\omega G''} = 0$$



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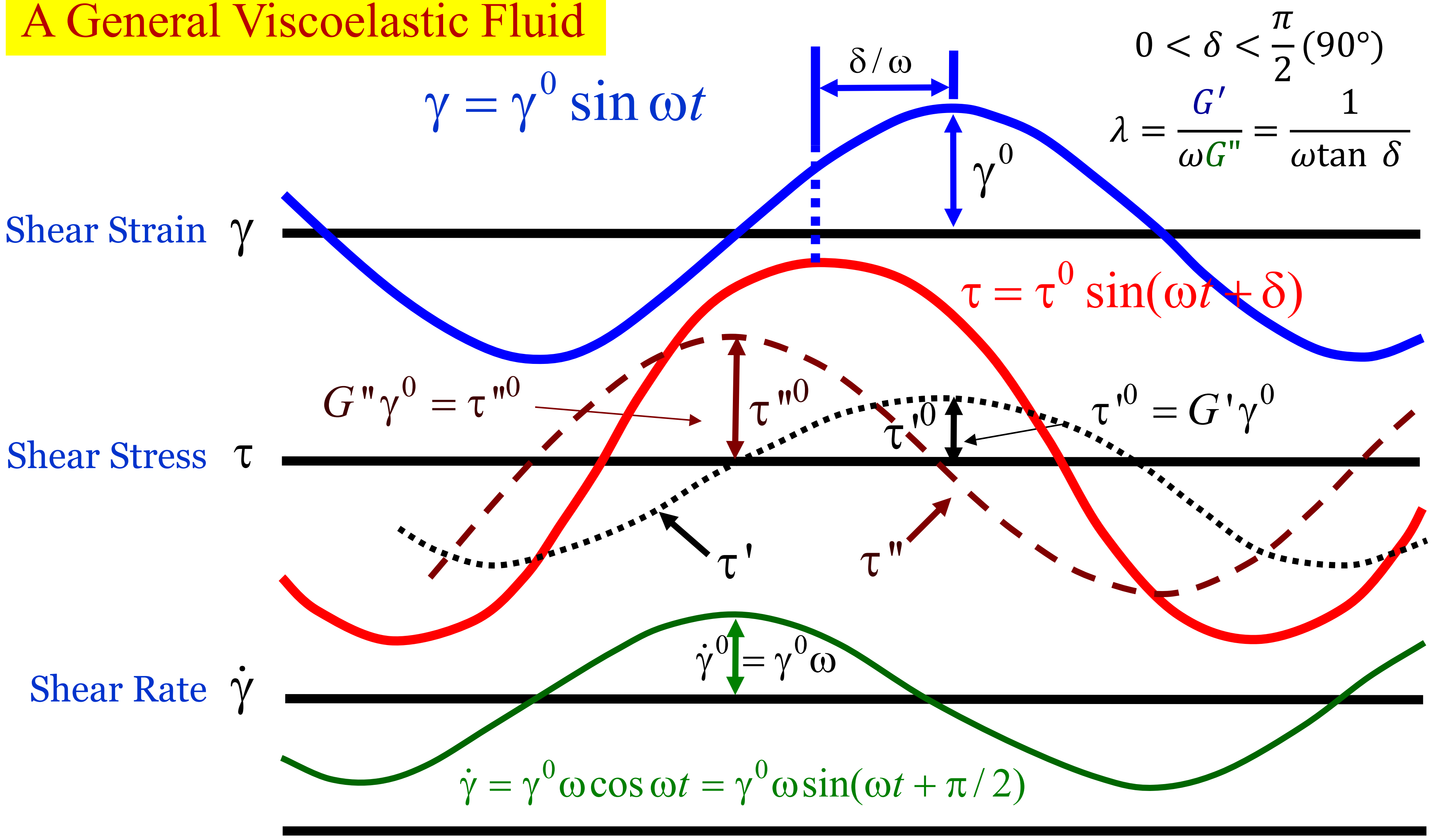
Oscillatory Shear (Dynamic) Test

A General Viscoelastic Fluid



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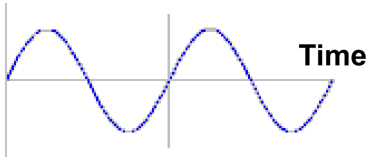
Oscillatory Flow Tests

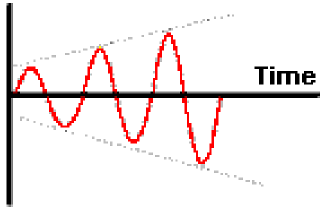


Time/Temperature Sweep Test

Holding the stress/strain amplitude and frequency at constant given values and

- ❑ varying time
- ❑ increasing/decreasing temperature.

Used to check the stability of material by time/temperature

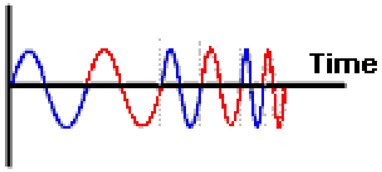


Amplitude Sweep Test

Applying successive stress/strain amplitude values in an increasing or decreasing path.

Used to find various structural regions of the material.

- ❑ Linear viscoelastic region
- ❑ Solid-Liquid transition
- ❑ Very good test for dispersions



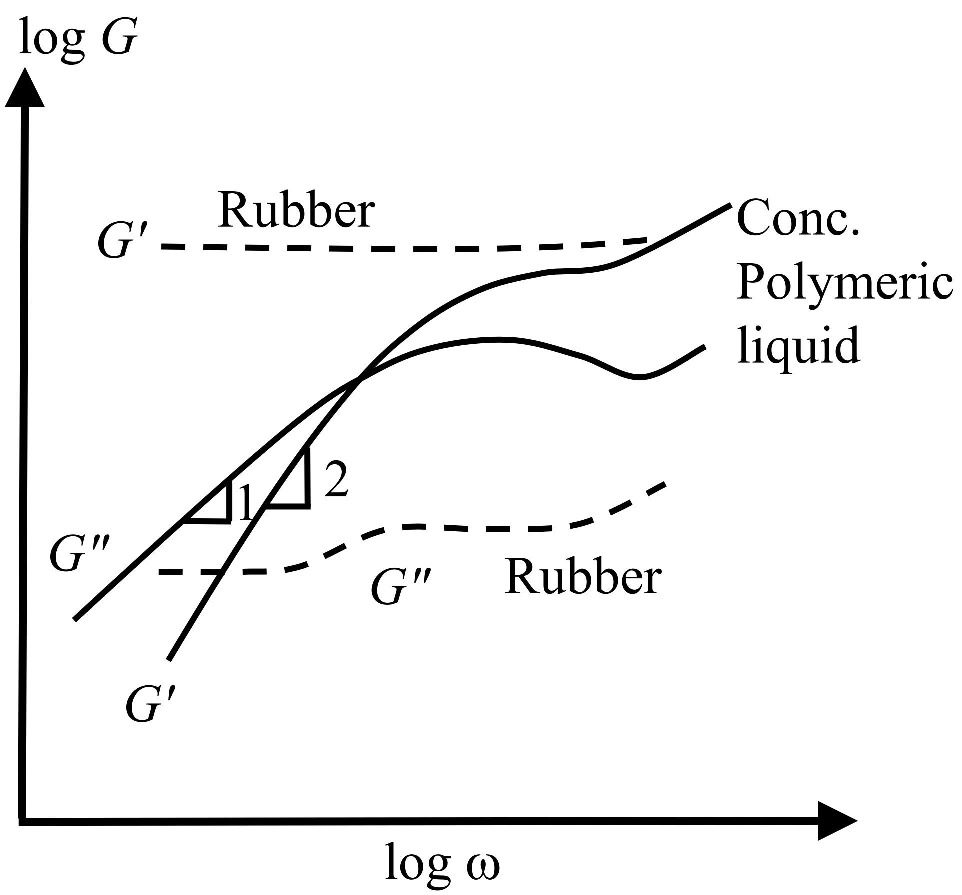
Frequency Sweep Test

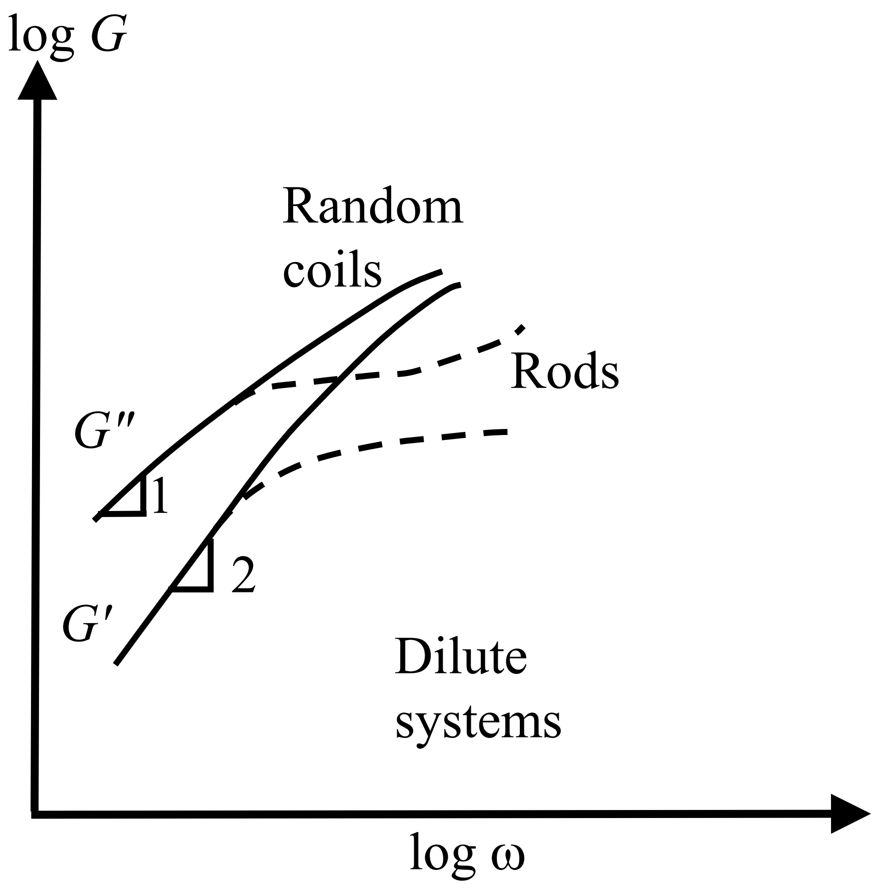
Holding the stress/strain amplitude at a constant given value and varying the frequency in an increasing or decreasing path.

Mainly used for non-thixotropic materials.

- ❑ Amorphous polymer melts
- ❑ Polymer solutions
- ❑ Assumed each point in linear viscoelastic region

General Trend for Polymeric Systems





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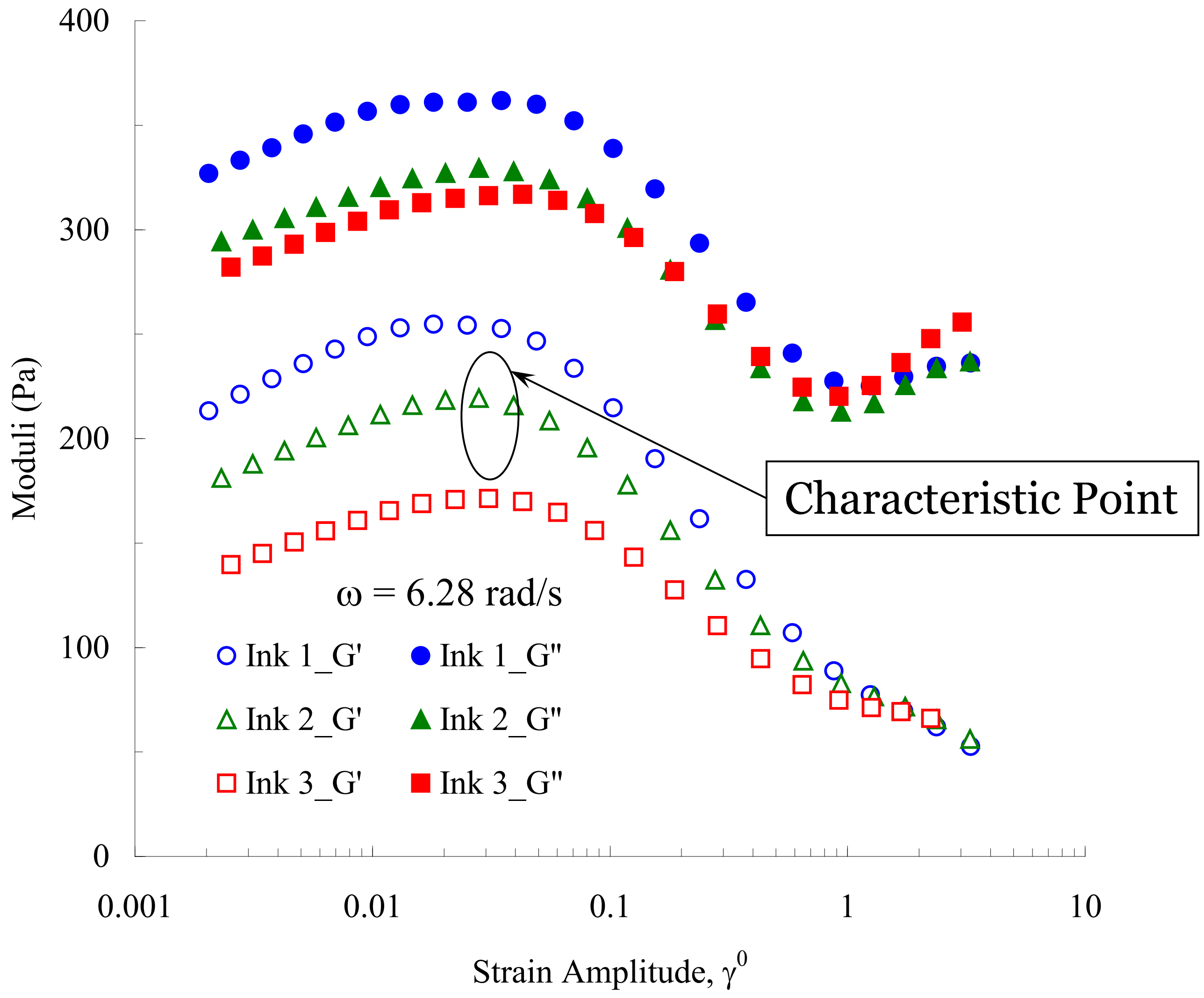
Experimental Data of a Paste Ink – Strain Amplitude Sweep Test



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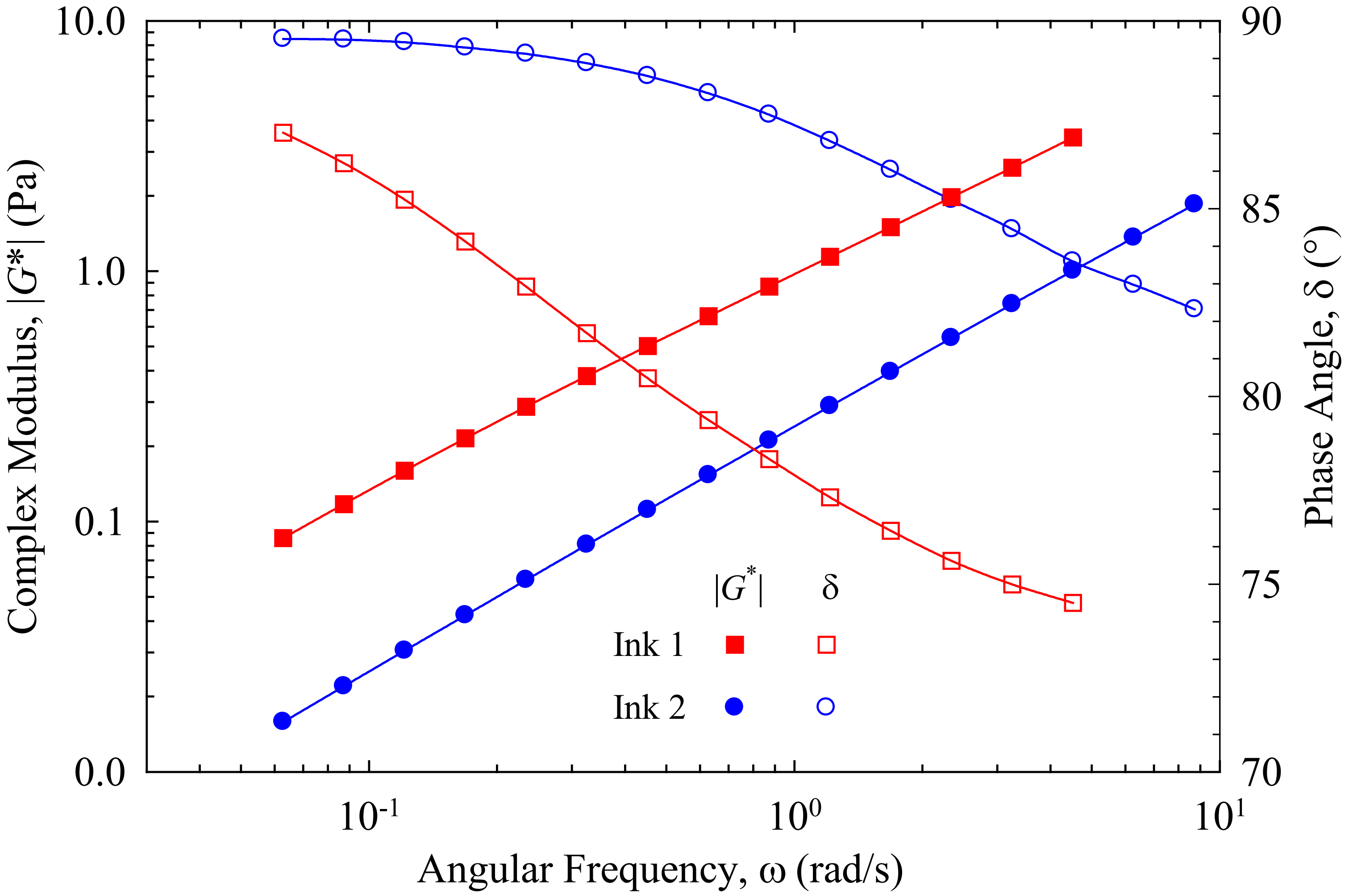
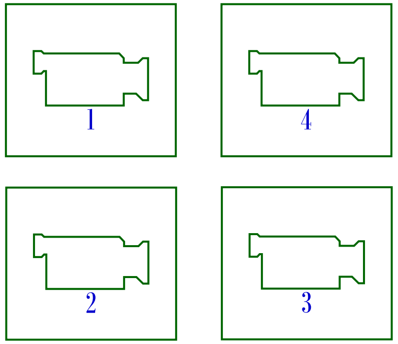
Experimental Data of a Liquid Ink – Frequency Sweep Test



Impact of Viscoelasticity

- Deborah number, *De*
  - Representing fluid elasticity wrt flow



$$De = \frac{\text{characteristic time of fluid}}{\text{characteristic time of flow}} = \frac{\lambda}{t_{\text{flow}}}$$

- Weissenberg number, *Wi*
  - Representing nonlinearity of viscoelasticity wrt flow

$$Wi = \text{characteristic time of fluid} \times \text{characteristic rate of deformation of flow}$$
$$= \lambda\dot{\gamma}$$

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Some Useful References

- Bird, R. B., Armstrong, R. C. and Hassager, O., *Dynamics of Polymeric Liquids, Vol. 1: Fluid Mechanics, 2nd Ed.*, (John Wiley & Sons, New York, NY, 1987).
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