

# **Rheology and Viscoelastic Properties of Fluids**

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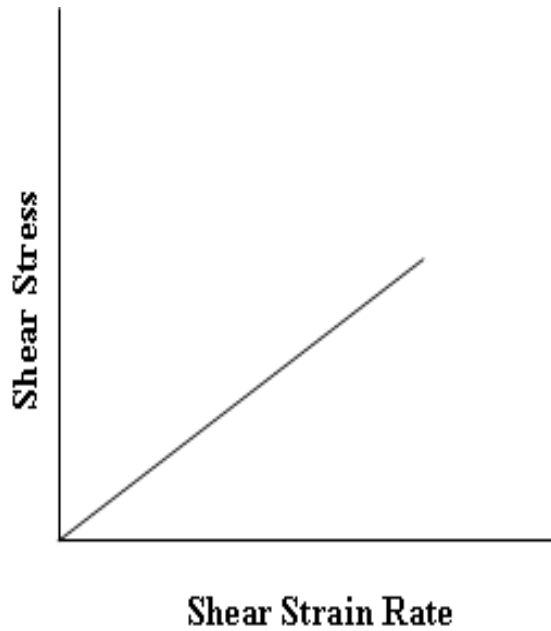
***Memorial University***

# Outlines

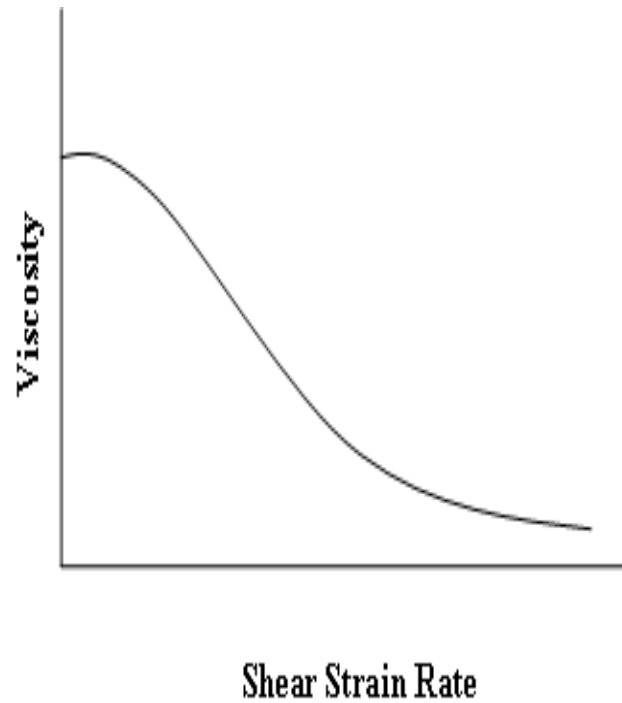
- Liquid behaviour.
  - Newtonian liquid.
  - Non-Newtonian liquid.
- Colloidal systems and suspensions.
  - Definition and classification.
- Rheometers.
  - Concentric Cylinder Rheometer.
  - Capillary Rheometer.
- Applications.
- Conclusion.

# Liquid Behaviour

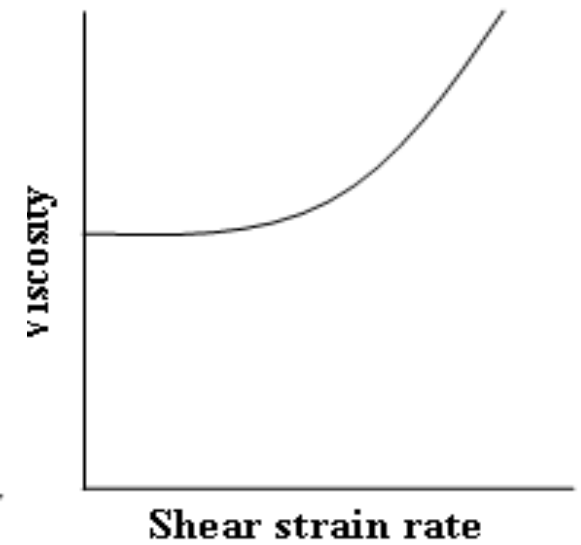
Newtonian liquids



The shear thinning liquids



The shear thickening liquids



# **Colloidal systems and suspensions**

- Colloidal systems.
- Classification.
- Why colloidal systems?

# Colloidal Systems

- It is a uniform distribution of large solute size particles (1nm to 1000 nm) inside a solvent phase.
- **The main forces:**
  1. **Electrostatic force (Repulsive):**  
It is a simple Coulomb interaction between the same charged suspended particles.
  2. **Polymer stabilization force (Repulsive):**  
Created due to existence of adsorbing polymer on the surface of colloidal particles.
  3. **Depletion force (Attractive):**  
Created due to the existence of non-adsorbing polymers in the solution.
  4. **Hydrodynamic force:**  
Suspended colloidal particles are influenced by the flow of the solution which results due to a movement of a colloidal particle.

# Classification

## Aerosols

- Dispersion of liquid droplets in a gas. [**Fog**].
- Dispersion of solid particles in a gas. [**Smoke**]



## Emulsions

- Dispersion of one liquid in another one (two immiscible liquids). [**Milk**]



## Suspensions

- Dispersion of solid particles in a liquid medium. [**paint**]



# Why colloidal systems?

- They are used to produce many of industrial and food products which are used in our daily life such as : cheese, ink, milk, paint etc.....

# Rheometers

- Uses:

1. Viscosities.
2. Shear stress with respect to shear strain rate behaviour.
3. Pressure gradient of the fluid.
4. Velocity profile.
5. Storage and Loss modulus.



# Rheometers

- Concentric Cylinder Rheometer

- The narrow gap concentric cylinder rheometer.
- The wide gap concentric cylinder rheometer.

- Capillary Rheometer

# Concentric Cylinder Rheometer

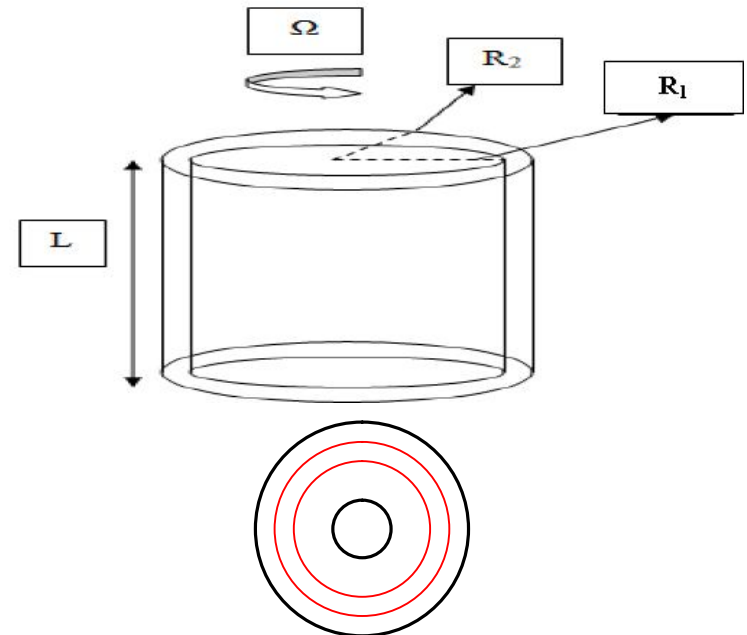
- Two concentric cylinders of radii  $R_1$  and  $R_2$ .
- A relative angular velocity ( $\Omega$ ) of one cylinder with respect to another one.
- The shear stress ( $\sigma$ ) at any cylindrical surface of radius ( $r$ ) is:

$$\sigma = \frac{G}{2\pi r^2}$$

**G** : "is the torque per unit length acting on the liquid cylindrical surface of radius  $r$ ".

- The strain rate:  $\dot{\gamma} = r \frac{d\omega}{dr}$

$\omega$  : Is the relative angular velocity between i.e.: the inner cylinder and the liquid cylindrical surface of radius ( $r$ )



# Concentric Cylinder Rheometer

- The narrow gap concentric cylinder rheometer:

- The length (L) of the cylinders is much larger than the radii ;  $L \gg R_1, R_2$
- The ratio of inner cylinder to outer cylinder radii is greater than 0.97.

- The shear stress :

$$\sigma = \frac{G}{2\pi R_a^2}$$

$R_a$ : represents "some average radius" which can be equal  $[(R_1+R_2)/2]$

- The shear strain rate:

$$\dot{\gamma} = \frac{R_a \Omega}{R_2 - R_1}$$

- The viscosity:

$$\eta = \frac{G(R_2 - R_1)}{2\pi R_a^2 \Omega}$$

# Concentric Cylinder Rheometer

- The wide gap concentric cylinder rheometer:

- The viscoelastic behaviour; shear strain-shear stress relationship for suspensions of large particles.

- For the power law model fluids:  $\eta = K_2 (\dot{\gamma})^{n-1}$

shear strain rate

Shear stress

$$\dot{\gamma} = \frac{2\Omega}{n(1-b^{2/n})}$$

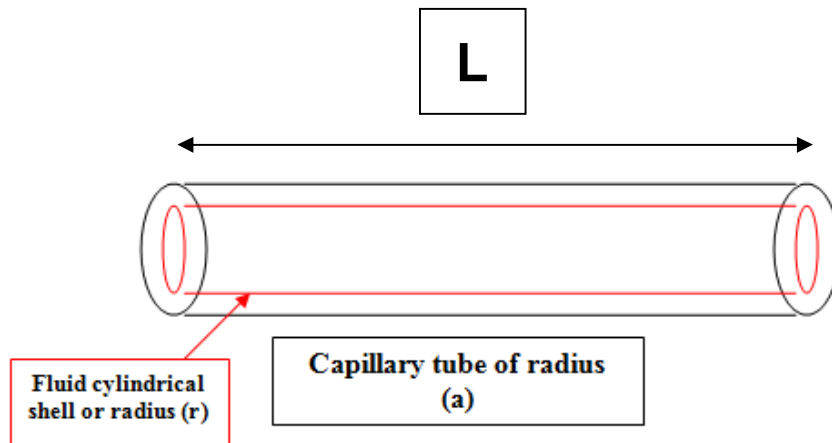
$$\sigma = \frac{G_1}{2\pi R_1^2}$$

$$b = \frac{R_1}{R_2}$$

$G_1$ : is the torque per unit length acting on the inner cylinder

# Capillary Rheometer

- It consists of Capillary tube of radius (a) and length (L).



# Capillary Rheometer

- **Newtonian fluid:**

1. The pressure gradient depends on the volume flow rate of fluid.
2. The velocity profile , shear stress, and the value of shear strain depends mainly on the radius of liquid cylindrical layer.

- **Non-Newtonian fluid:**

**For Power Law Model Liquid:**  $\eta = K_2 (\dot{\gamma})^{n-1}$

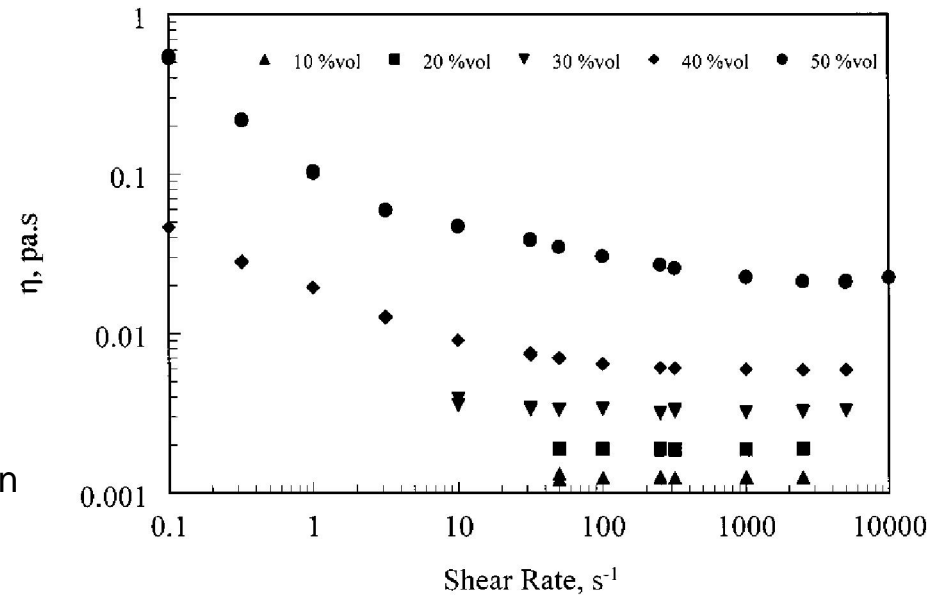
1. The pressure gradient depends mainly on the properties of the fluid.
2. The velocity profile depends on both the radius of liquid cylindrical shell layer and the properties of the liquid.

# Applications

- Capillary Rheometer was used to study and detect the viscosity behaviour of a colloidal silica suspension at different polyethylene oxide (PEO) concentrations.

# Applications

- **Newtonian behaviour** up to 30 % VF.
- **Non-Newtonian shear thinning** behaviour at both 40 % and 50 % VF.
- **By increasing the volume fraction of silica particles:**
  1. More obvious shear thinning behaviour appears.
  2. the value of shear rate at which a transition occurs from non-Newtonian to Newtonian region becomes larger.



**Viscosity Vs Shear strain rate** at different colloidal silica volume fractions for suspensions of 0.6  $\mu\text{m}$  silica particle radius dispersed in a solution contains 2.5 mg/g (solid) of PEO ( $M_w=7500$  g/mole) and 0.01 M of  $\text{NaNO}_3$ .



# Applications

## • Explanations:

- **Layered structure:**  
Electrostatic repulsion force and polymer stabilization force are dominant.

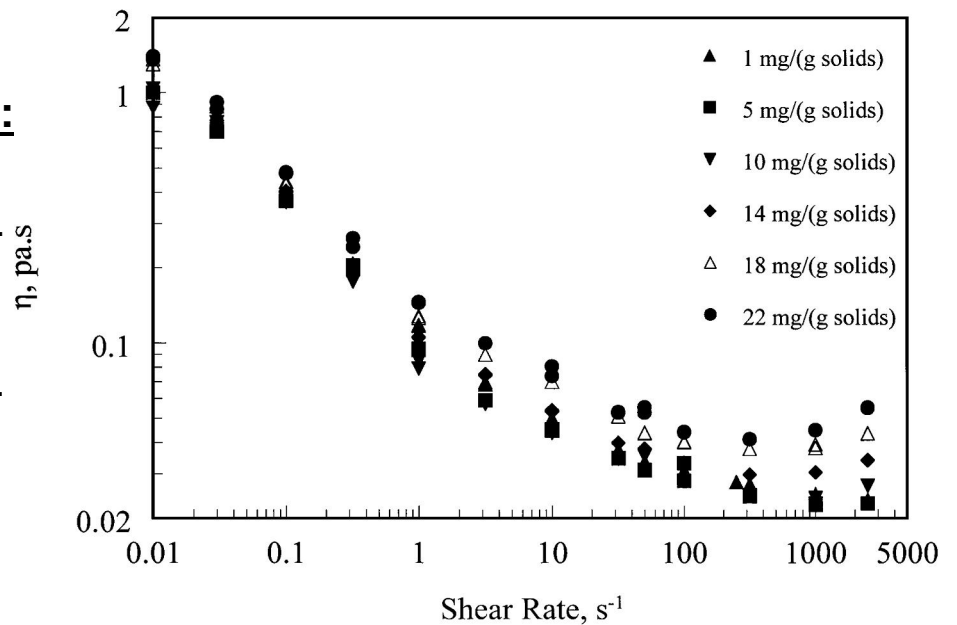
Transition



- **Disordered structure:**  
Hydrodynamic interaction that is created due to the shearing process is dominant.

# Applications

- **Non-Newtonian shear thinning** behaviour over a shear rate range  $0.01$  to  $500 \text{ s}^{-1}$ .
- Over a shear rate rang larger than  $500 \text{ s}^{-1}$ :
  - **Newtonian:**  
[PEO]=  $1 \text{ mg}/(\text{g solid})$  to  $10 \text{ mg}/(\text{g solid})$ .
  - **Non-Newtonian shear thickening:**  
[PEO]= $14 \text{ mg}/(\text{g solid})$  to  $22 \text{ mg}/(\text{g solid})$ .



The viscosity Vs shear rate strain of  $0.6 \mu\text{m}$  silica colloidal suspension at different PEO concentrations and  $0.01 \text{ M}$  of  $\text{NaNO}_3$ .

# Applications

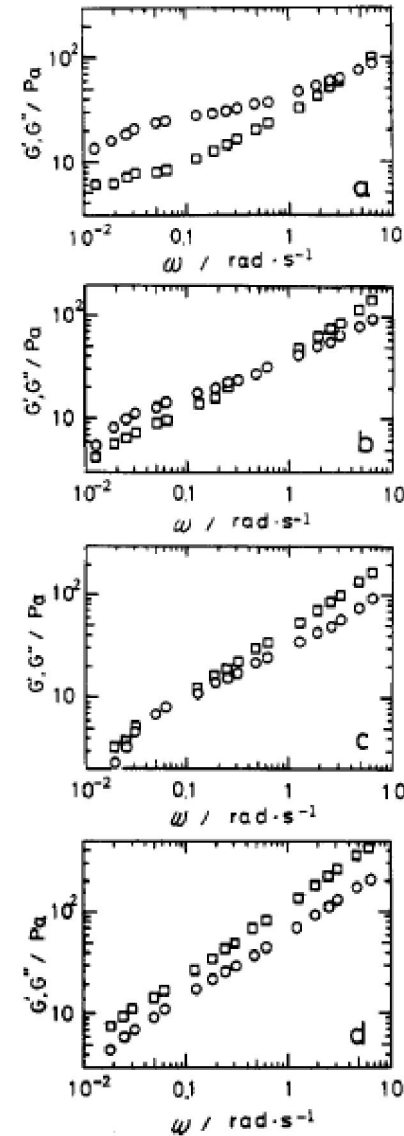
- Explanations:

At high PEO concentration, most of the added polymer do not adsorb on the colloidal particles such that **the concentration of free PEO molecules inside the solution increases** which causes an increase in the depletion forces between the particle in the solution which causes an increase in the viscosity of solution at higher PEO concentrations

# Applications

- Coaxial Cylinder Rheometer was used to study dynamic measurements which include storage modulus  $G'$  and loss modulus  $G''$  for a silica suspensions in an aqueous solutions consist of hydroxypropylmethyl cellulose (HPMC) at different silica and polymer concentrations.

- A plateau in the curve at lowest polymer concentration which is attributed to the formation of the gel-like structure (solid-like behaviour).
- $G'$  and  $G''$  curves for 1.25 %, 1.5 %, and 1.75 %, are intersect each other at specific frequency values.
- Intersection point represents a transition from solid-like to liquid-like behaviour.
- The value of frequency ;at which the intersection occurs; decreases by increasing the polymer concentration.



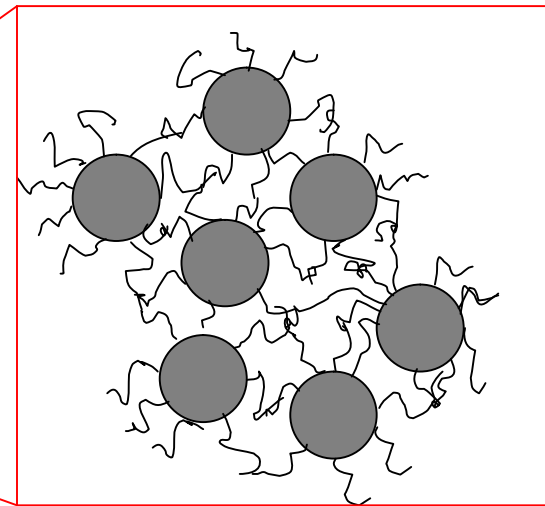
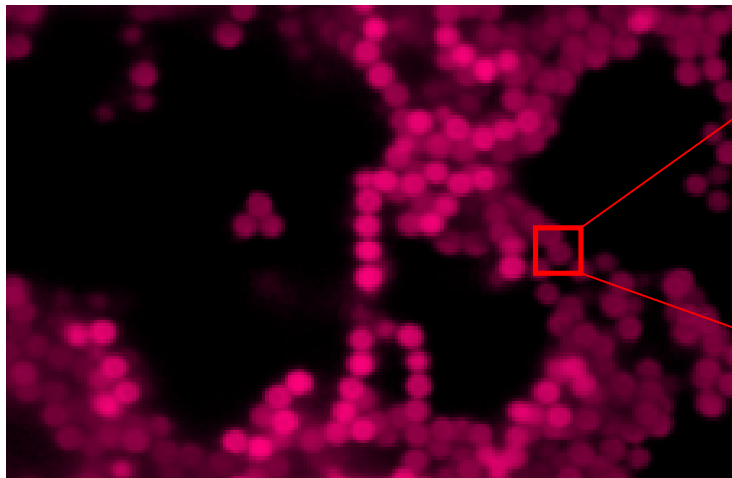
*Yoshitaka Ryo, Yasuhiro Nakai, and Masami Kawaguchi. Viscoelastic Measurements of Silica Suspensions in Aqueous Cellulose Derivative Solutions. Langmuir 1992,8, 2413-2416.*

**Log-Log Plots of  $G'$  and  $G''$  Vs frequency** for 5% silica suspensions at various HPMC concentrations: a, 1.25%; b, 1.5%; c, 1.75%; d, 2.0%

# Applications

- Explanations:

- Plateau at lowest HPMC concentration is attributed to the formation of gel structure (solid-like structure) in which the silica particles attached to each other via polymer chains which adsorb on the surface of silica particles.

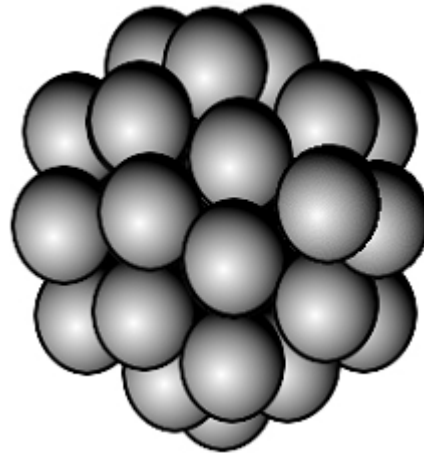


# Applications

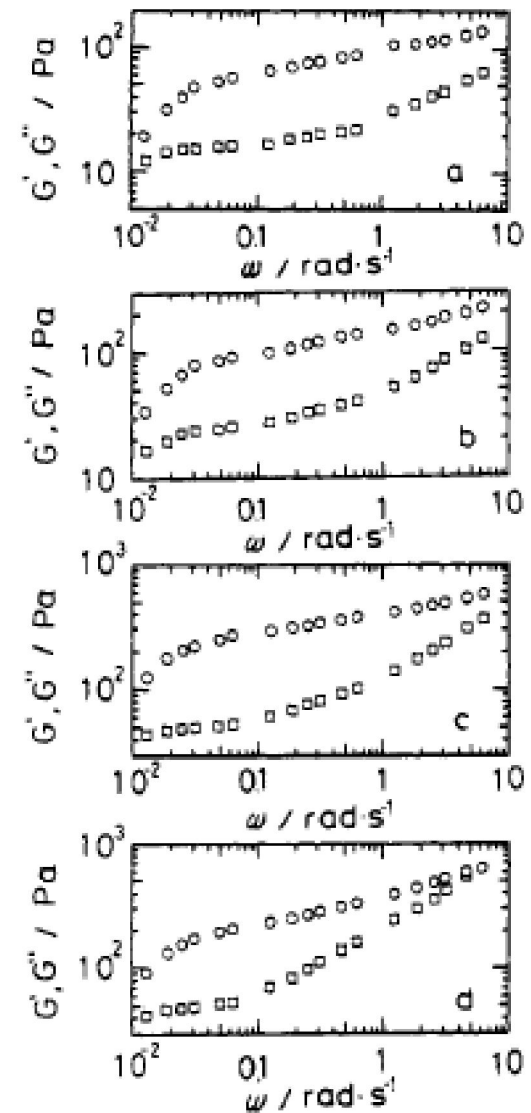
- Explanations:

The viscoelastic properties of the solution changes from solid to liquid-like behaviour by increasing polymer concentration since the concentration of non-adsorbing free polymer increases and then the depletion interaction between the suspended silica particles increases which creates

clusters [Aggregations of silica particles inside the solution]



- The value of  $G'$  is always larger than the value of  $G''$  for all polymer concentrations, which means that the solution has mainly solid-like behaviour due to the formation of gel structure.



*Yoshitaka Ryo, Yasuhiro Nakai, and Masami Kawaguchi. Viscoelastic Measurements of Silica Suspensions in Aqueous Cellulose Derivative Solutions. Langmuir 1992,8, 2413-2416.*

**Log-Log Plots of  $G'$  and  $G''$  Vs frequency for 7.5% silica suspensions at various HPMC concentrations: a, 1.25%; b, 1.5%; c, 1.75%; d, 2.0%**



# Conclusion

- We can use the rheological measurements to give an estimation about:
  1. The dominant interaction forces between the suspended colloidal particles in a solution.
  2. The main internal structure created by the suspended colloidal particles inside a solution.

# Question

- Is it enough to use rheological measurements to get information about the internal structure of the solution and to identify the interaction forces between the suspended particles ?

- **Answer :**

***No, it is not enough.***

We have to support our rheological results by using another techniques; such as NMR or Dynamic light scattering; in order to get more information about the main physical parameters; such as diffusion coefficients and relaxation times; that provide us with more accurate information about the internal structure and the mutual physical and chemical forces between the suspended particles inside the solution.



# Capillary Rheometer

- Newtonian fluid:

Pressure gradient

$$\frac{dP}{dL} = \frac{8Q\eta}{\pi a^4}$$

Velocity of a cylindrical shell of radius (r)

$$v(r) = (a^2 - r^2) \frac{1}{4\eta} \frac{dP}{dL}$$

Shear stress

$$\sigma = \eta \times \frac{dv}{dr} \propto \frac{r}{2} \frac{dP}{dL} = \frac{4\eta Q r}{\pi a^4}$$

Shear strain

$$\dot{\gamma} = \frac{dv}{dr} \propto \frac{r}{2\eta} \frac{dP}{dL} = \frac{4Qr}{\pi a^4}$$

**Q: the volume flow rate of the Newtonian liquid**

# Capillary Rheometer

- Non-Newtonian fluid

Satisfies power Law model

$$\eta = K_2 (\dot{\gamma})^{n-1}$$

The pressure gradient

$$\frac{dP}{dL} = \frac{2 K_2}{a} \left[ \frac{(3n + 1) Q}{\pi n a^3} \right]^n$$

The velocity profile

$$v(r) = \frac{Q(3n + 1)}{\pi a^2 (n + 1)} \left( 1 - \left( \frac{r}{a} \right)^{(n+1)/n} \right)$$