

viscosity \rightarrow resistance to flow \rightarrow even though it might not be the correct parameter for some materials (solids).

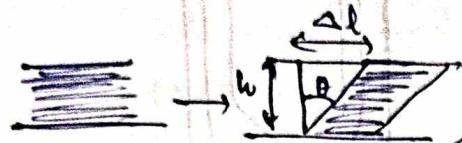
soft matter: anything that can deform (or flow)

Newtonian fluid $\rightarrow \sigma = \eta \frac{\partial v_x}{\partial y}$ $\dot{\gamma} = \frac{\partial v_x}{\partial t}$

uniform viscosity (μ)

shear strain $\equiv \dot{\gamma}$

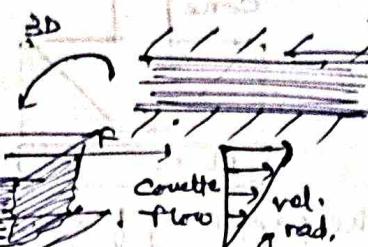
strain rate $= \dot{\gamma}$



$$\theta = \tan^{-1}\left(\frac{\Delta l}{h}\right)$$

Strain
rate.

Prove that
 $\dot{\gamma} = \frac{\partial v_x}{\partial y}$



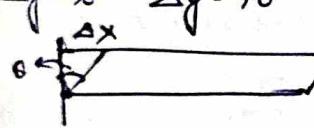
Force (Tangential)
if we assume
that there
is no slip cond.
the liquid molecules
in contact with
lower plate don't
move and upper
plate move so
we have a rel.



We don't want our h to be $h > \gg l$ gradient.

We want it to be comparable with Δl .

So, we look at Local strain.

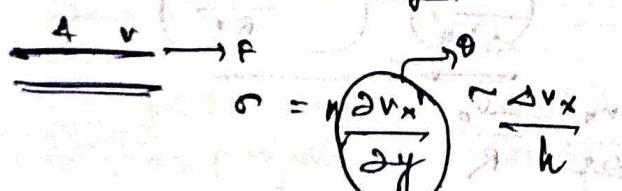


Local strain $\rightarrow \epsilon = \theta = \lim_{\Delta y \rightarrow 0} \frac{\Delta x}{\Delta y} = \tan \theta$

$\tan \theta = \frac{\Delta x}{\Delta y}$

$$\frac{\partial v_x}{\partial x}$$

elongation flow $\rightarrow \dot{\epsilon}_x$ \rightarrow stretching of soft matter
or particles moving apart in
opposite x direction.



$$\sigma = \eta \frac{\partial v_x}{\partial y}$$

$$\sigma = \frac{F}{A} \rightarrow \eta = \frac{F/A}{\dot{\epsilon}} = \frac{F/A}{u/h}$$

(for finding viscosity)

\hookrightarrow viscosity is measured using a rheometer

\rightarrow while measuring viscosity we can control only one parameter of the system.

\rightarrow for more precision the gap should be less.

\rightarrow if strain is to be found stress can be controlled and vice versa.

\rightarrow If expt. needs to be carried out for more time, dimensions of the plates should be very large (impractical) \rightarrow so rheometer is designed with circular plates.

Newton's Law of viscosity
applicable on not just Newtonian fluids but other as well. Thus, does not guarantee that the fluid it is applied on is a Newtonian fluid.



$\sigma \propto \gamma$

$\sigma = \eta \gamma$

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

$\sigma = \eta \frac{\partial v_x}{\partial y}$

$\sigma = \eta \frac{\partial v_x}{\partial t}$

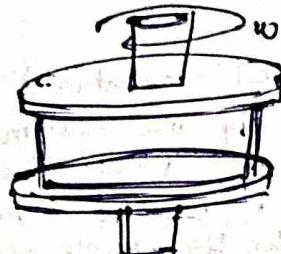
PIV (Particle Image Velocimetry)

use of fluorescent particles to get the vel. profile
using particle local $\frac{\partial v_x}{\partial y}$, more precision in μ

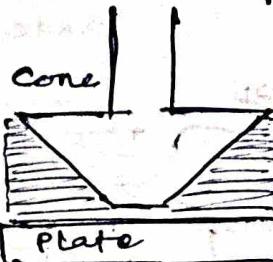
Rheometry

(structure property relationship of soft matter)

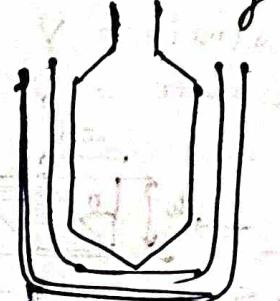
parallel plate rheometry



cone and plate rheometry



cup and bob rheometry



we can measure the property from which we can access the structures

$$\text{Reynolds no.} = \frac{\text{Inertial force}}{\text{viscous force}} = \frac{\rho v d}{\mu}$$

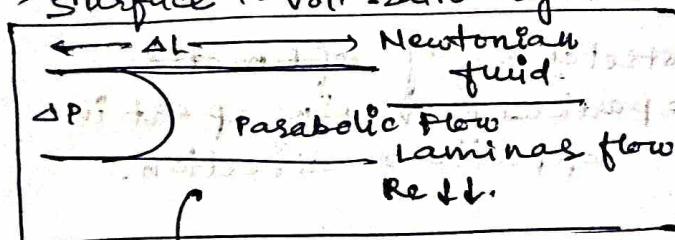
Re depends on surface-to-vol. ratio

applied by wall → kinetic Δ

in microchannels, the flow is always laminar

Re no. is very low due to increased viscous forces.

Surface to vol. ratio high



Hagen Poiseuille flow is parabolic :-

$$v_x = \frac{\Delta P}{\frac{8 \eta L}{R^2}} \left(R^2 - r^2 \right)$$

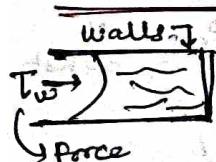
$$v_x = v_0 \left(1 - \frac{r^2}{R^2} \right)$$

$$\frac{\partial v_x}{\partial r} = \frac{2v_0}{R}$$

$$w_s = f(\Delta P, L, \mu)$$

$$\frac{\partial v_x}{\partial r} = \frac{2v_0}{R}$$

Wall shear → stress applied by fluid on the walls of the pipe / whatever vessel it is flowing through.



$$T_w (\text{wall force}) = \Delta P \pi R^2$$

$$T_w = \frac{\Delta P R}{2L}$$

Microfluidic Approach! — We are approximating the viscosity of the fluid by saying that the wall μ is roughly equal to the μ of bulk.

$$\text{Viscosity} = \frac{\text{stress}}{\text{strain rate}}$$

$$\eta = \frac{(\Delta P) R}{2L} \times \frac{1}{\frac{2}{R} \left(\frac{\Delta P}{L\eta} \right)^{R^2}}$$

→ everything will cancel
independently to find viscosity η .

$$v_o = \frac{\Delta m}{t} = \frac{\dot{m}}{t} = \rho A v_{avg} \Rightarrow \text{we'll find } v_{avg}$$

$$v_{avg} = \frac{\dot{m}}{\rho A} \Rightarrow v_{avg} = \frac{v_o}{2}$$

$$v_o = 2 v_{avg}$$

$$\text{So } v_o = \frac{2\dot{m}}{\rho A}$$

$$\text{Fluid at wall} = \frac{\Delta P R}{2L} \cdot \frac{(\frac{\dot{m}}{\rho A}) \times \frac{1}{R}}{\frac{2}{R}} = \frac{\Delta P R^2 \rho A}{8L} \quad (A = \text{Area of cross section})$$

Constitutive eqn → Eqn which governs fluid behaviour. Any constitutive eqn relates 2 terms. (stress & strain, strain rate or higher derivatives of strain)

$$\sigma = f(\gamma, \dot{\gamma}, \ddot{\gamma}, \dots)$$

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

any constant

$$\sigma = G \gamma$$

elastic & viscous particle

viscoelastic → complex fluids

Weissenberg effect → rod climbing effect

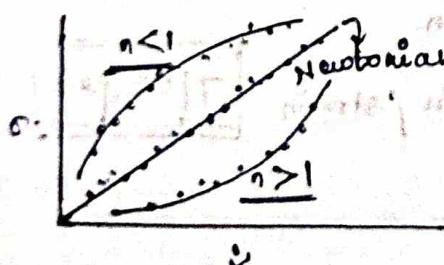
Power Law fluid ⇒ $\sigma = \mu(\dot{\gamma})^n$

When $n=1$ ⇒ Newtonian fluid.

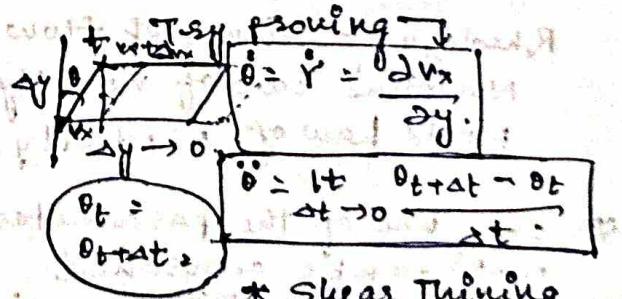
$n < 1$ ⇒ shear thinning fluid.

$n > 1$ ⇒ shear thickening fluid

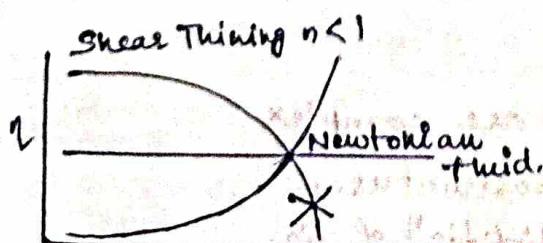
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σ vs $\dot{\gamma}$
graph is not
very
intuitive.



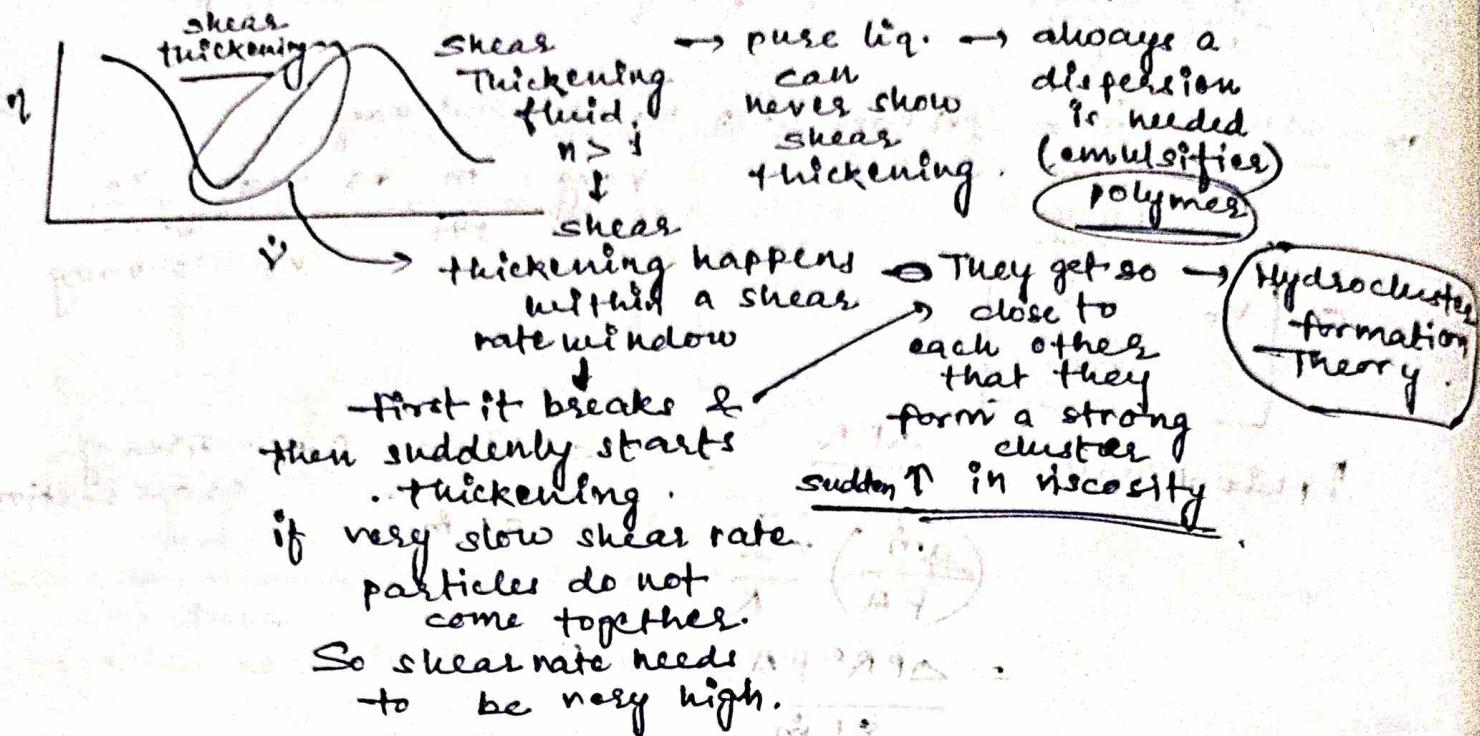
* Shear Thinning means when force applied μ ↓ (viscosity ↓)



$$\dot{\gamma} | \sigma | \frac{\sigma}{\dot{\gamma}} = \eta$$

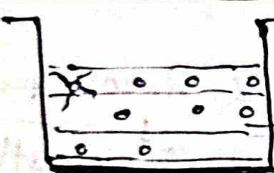
* we don't need extra data. We can use the data to build σ vs $\dot{\gamma}$ to build η vs $\dot{\gamma}$ graph.

What happens if $\dot{\gamma} > 0$
We do not know, high precision device needed for $\dot{\gamma}$ as less than 10^{-3}



Complex \rightarrow complex microstructures

fluids (somewhere in b/w macro level and molecular level)
oil in water emulsion:



What happens is eventually the oil molecules coalesce to form a single cluster. \downarrow phase segm.

To sustain this emulsion, we need to add emulsifier (surface active agents)

3D Network \rightarrow b/w (e.g. - casein) oriented protein molecules. By - cheese. air trapped inside \rightarrow foam \rightarrow gas entrapped inside 3-D of liq. network

Rheology — Science of flow.

Newton's Law of viscosity: Stress \propto strain rate

Hooke's Law of Elasticity: Stress \propto strain.

only one of the parameters (stress / strain / strain rate) can be controlled.

$$\sigma = f(\tau, \delta, \ddot{\delta}, \ddot{\ddot{\delta}}, \text{material properties})$$

flow curve

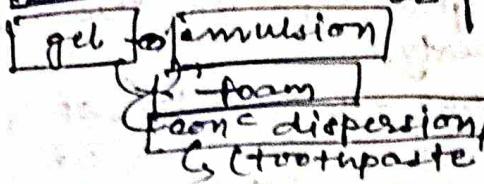
constitutive eqⁿ

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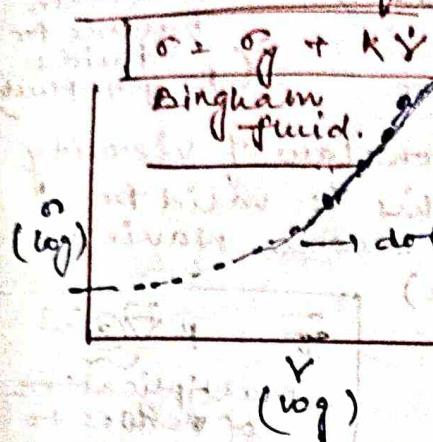
Complex fluids \rightarrow constitutive eqⁿ are complex
complex microstructures.

Cushion \rightarrow Solid foam \rightarrow Solidification of liq.

Liquid crystal \rightarrow complex fluids \rightarrow atleast a combo. of 2 polymers or fluids.



Constitutive eqn:-



$\dot{\gamma} \rightarrow 0$ (we cannot make rate of change 0)

We are controlling the shear rate
(rate of change of σ is being controlled)



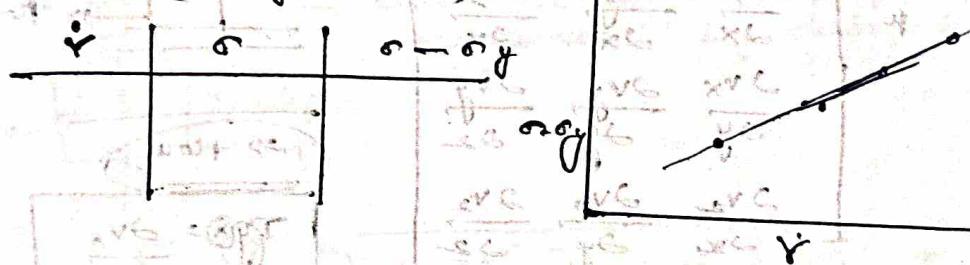
Torque is being applied to maintain the software then gives stress

cause \rightarrow effect

$k \rightarrow$ material property

If the rate of deformation is very very small, then also there will be stress (residual stress), we need to overcome it to make the fluid / material flow.

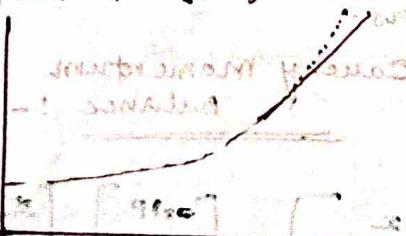
$$(\sigma - \sigma_y) = k(\dot{\gamma})$$



Herschel Berkley fluid

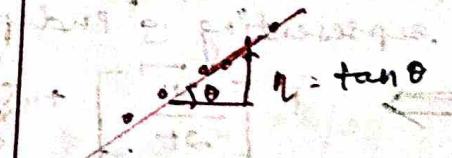
$$\sigma = \sigma_y + k(\dot{\gamma})^n$$

when $n = 1$ fluid is Bingham.



Power Law fluid:-

$$\sigma = k(\dot{\gamma})^n$$



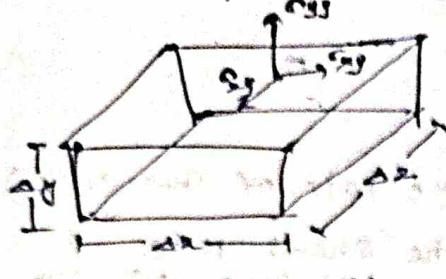
Visco Elasticity (elastic + viscous)

Stress \rightarrow Tensor

8/08/23

$$\begin{aligned} \frac{\partial u_x}{\partial t} + u_x \frac{\partial u_x}{\partial x} + u_y \frac{\partial u_x}{\partial y} + u_z \frac{\partial u_x}{\partial z} &= \frac{1}{\rho} \left(-\frac{\partial P}{\partial x} + \frac{\partial T_{xx}}{\partial x} + \frac{\partial T_{xy}}{\partial y} + \frac{\partial T_{xz}}{\partial z} \right) + g_x \\ \frac{\partial u_y}{\partial t} + u_x \frac{\partial u_y}{\partial x} + u_y \frac{\partial u_y}{\partial y} + u_z \frac{\partial u_y}{\partial z} &= \frac{1}{\rho} \left(-\frac{\partial P}{\partial y} + \frac{\partial T_{yx}}{\partial x} + \frac{\partial T_{yy}}{\partial y} + \frac{\partial T_{yz}}{\partial z} \right) + g_y \\ \frac{\partial u_z}{\partial t} + u_x \frac{\partial u_z}{\partial x} + u_y \frac{\partial u_z}{\partial y} + u_z \frac{\partial u_z}{\partial z} &= \frac{1}{\rho} \left(-\frac{\partial P}{\partial z} + \frac{\partial T_{zx}}{\partial x} + \frac{\partial T_{zy}}{\partial y} + \frac{\partial T_{zz}}{\partial z} \right) + g_z \end{aligned}$$

We want to define stress at a pt. but that is not possible. So, mathematically, we say that stress is defined on a very small cube which is almost the size of a pt. and nine vectors just represent this cube. (Tensor representation) n dimensional property.



$$\sigma_{xx} \frac{\partial u_x}{\partial x} + 4\sigma_{xy} \frac{\partial u_x}{\partial y} + \sigma_{yy} \frac{\partial u_x}{\partial y} + 4\sigma_{xz} \frac{\partial u_x}{\partial z} = \frac{1}{V} \left(-\frac{\partial P}{\partial x} + \frac{\partial T_{xx}}{\partial x} + \frac{\partial T_{xy}}{\partial y} + \frac{\partial T_{xz}}{\partial z} \right) + \rho g_x \rightarrow \text{Cauchy Momentum Balance for fluids (for gen. fluid)}$$

$$\begin{bmatrix} \frac{\partial}{\partial x} & [u_x \ u_y \ u_z] \\ \frac{\partial}{\partial y} & \\ \frac{\partial}{\partial z} & \end{bmatrix} = 3 \times 3$$

When we plug this Newton's Law of Viscosity in above eqⁿ. Since this is valid for a Newtonian fluid, it becomes Navier Stokes Eqⁿ (special case)

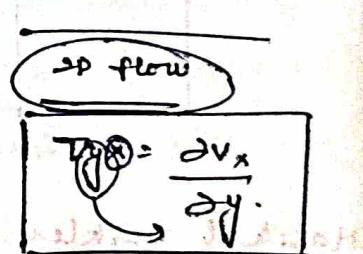
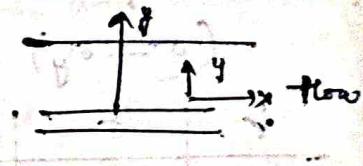
$$\begin{bmatrix} T_{xx} & T_{xy} & T_{xz} \\ T_{yx} & T_{yy} & T_{yz} \\ T_{zx} & T_{zy} & T_{zz} \end{bmatrix} = \mu \begin{bmatrix} \frac{\partial v_x}{\partial x} & \frac{\partial v_x}{\partial y} & \frac{\partial v_x}{\partial z} \\ \frac{\partial v_y}{\partial x} & \frac{\partial v_y}{\partial y} & \frac{\partial v_y}{\partial z} \\ \frac{\partial v_z}{\partial x} & \frac{\partial v_z}{\partial y} & \frac{\partial v_z}{\partial z} \end{bmatrix}$$

(Newton's Law of viscosity)

$$\overline{T} = \mu \overline{\nabla} \otimes \overline{v}$$

multiplication of vectors to give tensor
Dyadic product

$$\mu \begin{bmatrix} \frac{\partial v_x}{\partial x} & \frac{\partial v_y}{\partial x} & \frac{\partial v_z}{\partial x} \\ \frac{\partial v_x}{\partial y} & \frac{\partial v_y}{\partial y} & \frac{\partial v_z}{\partial y} \\ \frac{\partial v_x}{\partial z} & \frac{\partial v_y}{\partial z} & \frac{\partial v_z}{\partial z} \end{bmatrix}$$



$$T_{xz} = \frac{\partial v_x}{\partial z}$$

T_{xz} → (means force in z dirⁿ on x plate.)

RHS → Shear force + pressure force + Body force.

* There is no physical meaning of Tensor. It is just a way of representing 9 independent relations.

$$\Rightarrow \rho \left[\frac{\partial u}{\partial t} \right] + \mu \nabla \otimes \overline{u} \rightarrow \text{scalar operator}$$

Cauchy Momentum Balance :-

$$\Rightarrow \rho \begin{bmatrix} \frac{\partial v_x}{\partial t} \\ \frac{\partial v_y}{\partial t} \\ \frac{\partial v_z}{\partial t} \end{bmatrix} + \begin{bmatrix} u_x \frac{\partial u_x}{\partial x} + u_y \frac{\partial u_x}{\partial y} + u_z \frac{\partial u_x}{\partial z} \\ u_x \frac{\partial u_y}{\partial x} + u_y \frac{\partial u_y}{\partial y} + u_z \frac{\partial u_y}{\partial z} \\ u_x \frac{\partial u_z}{\partial x} + u_y \frac{\partial u_z}{\partial y} + u_z \frac{\partial u_z}{\partial z} \end{bmatrix} = \begin{bmatrix} \frac{\partial P}{\partial x} \\ -\frac{\partial P}{\partial y} \\ -\frac{\partial P}{\partial z} \end{bmatrix} + \begin{bmatrix} \frac{\partial T_{xx}}{\partial x} & \frac{\partial T_{xy}}{\partial x} & \frac{\partial T_{xz}}{\partial x} \\ \frac{\partial T_{yx}}{\partial y} & \frac{\partial T_{yy}}{\partial y} & \frac{\partial T_{yz}}{\partial y} \\ \frac{\partial T_{zx}}{\partial z} & \frac{\partial T_{zy}}{\partial z} & \frac{\partial T_{zz}}{\partial z} \end{bmatrix}$$

$$\left(\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} \right) \Rightarrow (\vec{u} \cdot \vec{\nabla}) \begin{bmatrix} u_x \\ u_y \\ u_z \end{bmatrix} = (u_x \hat{i} + u_y \hat{j} + u_z \hat{k}) \left(\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} \right)$$

$$\frac{\partial \vec{u}}{\partial t} + (\vec{u} \cdot \vec{\nabla}) \vec{u} = -\nabla p + \vec{\nabla} \cdot \vec{\tau} + \vec{g}$$

* Product of a vector and tensor is tensor $\rightarrow f(r, \dot{r}, r..)$

$$\frac{\partial \vec{u}}{\partial t} + (\vec{u} \cdot \vec{\nabla}) \vec{u} = -\nabla p + \vec{\nabla} \cdot \vec{\tau} + \vec{g}$$

divergence vector

Shear rate \uparrow viscosity \uparrow

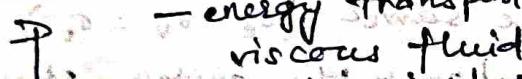
$\sigma = \eta \dot{\gamma} + k(\dot{r})^n \rightarrow$ Hooke's law give some idea of the viscosity & flow of fluids.

$\sigma = \eta \dot{\gamma} + k \dot{r} \rightarrow$ Bingham

But we need other viscoelastic models to get a better idea.

Maxwell Model: — more interest in the microstructure (complexity)

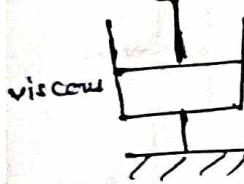
— energy transport to the spring gets dissipated



viscous fluid

— mechanical fluid

— elastic component is represented by a spring and viscous comp' by dashpot



Dashpot
 $\sigma = \eta \dot{v}$

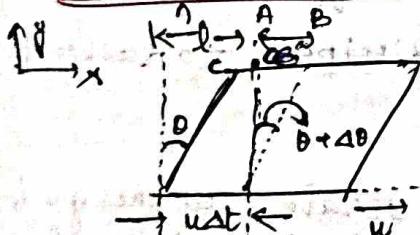
$$\sigma = \eta \dot{v} + \frac{\partial \sigma}{\partial t}$$

10/08/23

$$\frac{\partial (\rho \vec{V})}{\partial t} + \vec{\nabla}(\rho \vec{V} \vec{V}) = \rho \vec{J} + \vec{\nabla} \cdot \sigma_{ij}$$

Shear flow:

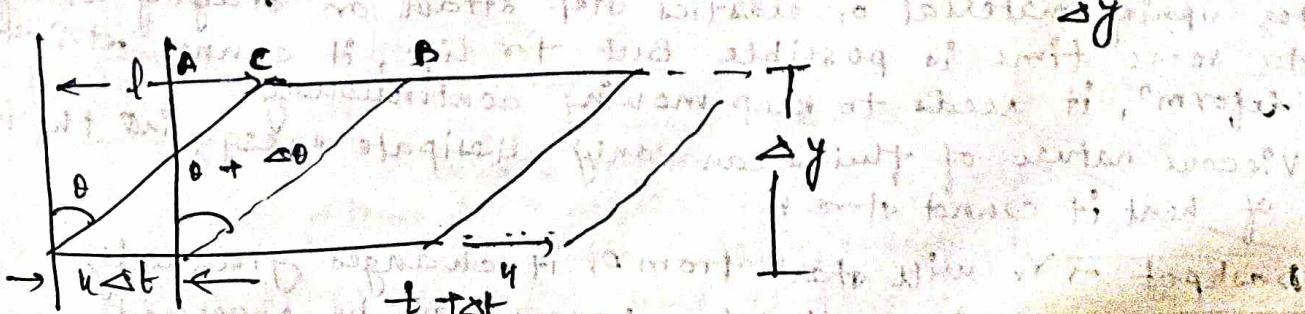
$$\text{Shear rate} = \dot{\gamma}_{xy} = \frac{\partial u_x}{\partial y}$$



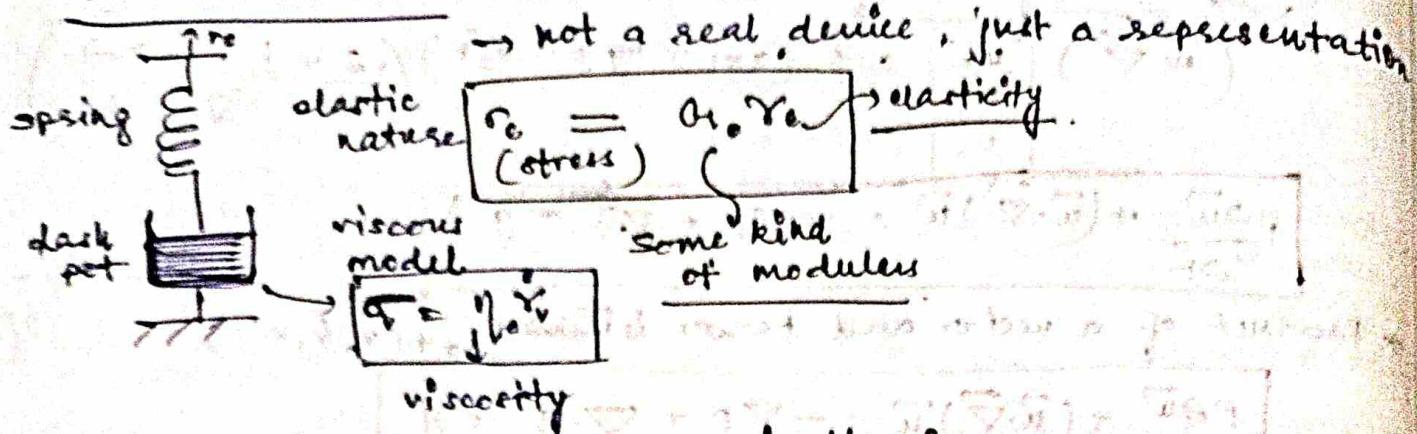
$$\dot{\gamma}_t = \theta_t = \frac{l}{dy}$$

$$\dot{\gamma}_{t+\Delta t} = \theta_{t+\Delta t} = AB/dy = \frac{AC+CB}{dy}$$

$$= (l - u \Delta t) + u \Delta t + \frac{\partial u}{\partial y} \Delta y \Delta t$$



Mechanical Models :-



Why series? Not a parallel combination?



In real expt, what are the parameters we can control? → strain rate $\dot{\gamma}$

$$\gamma_0 = \gamma_e + \gamma_v$$

strain is divided b/w elastic and viscous.

sel b/w γ_e & γ_v → They are same ($\sigma_e = \sigma_v = \sigma_0$)

There should be uniform throughout the system, otherwise the spring will break.

$$\sigma = \gamma_e + \gamma_v \quad (\text{in case of no strain})$$

$$\sigma = \frac{\gamma_e}{G_0} + \frac{\sigma_0}{\eta_0} \Rightarrow \frac{\sigma_0}{G_0} + \frac{\sigma_0}{\eta_0} = 0$$

$$\frac{1}{G_0} \frac{d\sigma}{dt} + \frac{\sigma}{\eta_0} = 0$$

$$\Rightarrow \frac{d\sigma}{dt} = -\frac{G_0}{\eta_0} \sigma \Rightarrow \ln \sigma = -\frac{G_0 t}{\eta_0} \rightarrow \sigma = \sigma_0 e^{-\frac{G_0 t}{\eta_0}}$$

at $t=0$ Whole energy → spring. Then dissipates to dashpot
 $t=0, \gamma = \gamma_0$

~~$\sigma = \sigma_0 e^{-\frac{G_0 t}{\eta_0}}$~~

$\gamma_0 = \gamma_{e,t=0}$ → only spring is facing strain (all energy is stored in the spring, $t=0$)

for spring material or elastics step strain or staying at deform for some time is possible. But for liq., it cannot "stop at deform", it needs to keep moving continuously.

Viscous nature of fluids can only dissipate energy in the form of heat it cannot store it.

Dashpot → γ_v will start from 0, it changes gradually.

re immediately changes can be expressed immediately.

$$t=0, \sigma = \sigma_0, \dot{\sigma}_e = \dot{\sigma}_0, \dot{\sigma}_0 = 0$$

$$\int_{\sigma_0}^{\sigma} \frac{d\sigma}{\sigma} = - \int_0^t \frac{G_0 \dot{\sigma}_e}{\eta_0} dt \rightarrow \ln\left(\frac{\sigma}{\sigma_0}\right) = - \frac{G_0 t}{\eta_0}$$

$$\Rightarrow \sigma = \sigma_0 e^{-\frac{G_0 t}{\eta_0}} \rightarrow \sigma = \sigma_0 e^{-(t/\tau)}$$

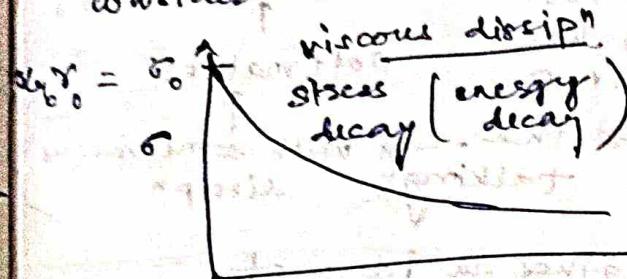
$$T = \frac{\eta_0}{G_0} = \text{timescale}$$

$$\boxed{\tau_0 = G_0 \tau_0}$$

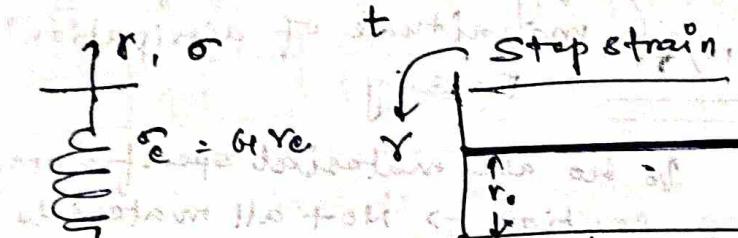
(Dashpot resists deformn)

$$\sigma(t) = G_0 \tau_0 e^{-(t/\tau)}$$

considers viscous part like inductor (resists change in strain)



14/08/23



$$\text{IC } t=0 \rightarrow \sigma = \sigma_0 = G_0 \tau_0$$

$$\tau = \tau_e = \tau_0 + \tau_0 = G_0 \tau_0$$

$t > 0$ first stage

~~viscous~~

Special expt. where we keep $\dot{\gamma} = 0$

~~viscous~~

~~viscous~~

$\dot{\gamma} = \dot{\gamma}_0 + \dot{\sigma}_0 = 0$
not modulus G_0 , η_0 not the actual viscosity
some kind of model parameters (material property)

$$\dot{\gamma} = \frac{1}{G_0} (\dot{\sigma} + \frac{\sigma}{\eta_0})$$

Relaxation

Energy dissipation due to viscous nature of the material.

η_0, G_0 are model parameters.

$$\sigma(t) = G_0 \tau_0 e^{-t/(\eta_0/G_0)}$$

$$\frac{\eta_0}{G_0} = T = \text{relaxation time scale}$$

initially:-

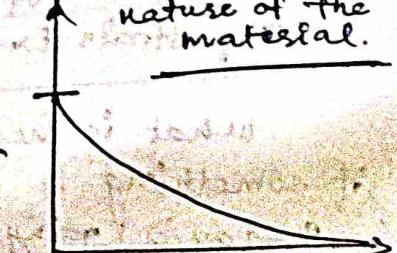
σ_0 = stress stored in the spring.

σ_0 = stress is decaying.

Whenever we are putting step strain, energy

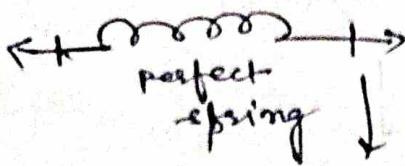
is getting stored in spring but at the same time we have viscous component. So, what is

happening is viscous dissipation of energy



Energy \leftrightarrow Stress \rightarrow energy is decaying \rightarrow stress is decaying
 either it remains const. or it dissipates (decays) \rightarrow takes form of other forms of energy which is not helpful for us)

(6) \rightarrow Total output \rightarrow Total stress experienced by the system.



some energy will get stored

and it will remain forever

So relax' timescale $\rightarrow \infty$.

Ex. Water & similar fluids have relax' timescale $\rightarrow \infty$.

Somewhere in between are the materials about which we are talking with some viscous dissipation

elastic part \leftrightarrow
 (spring) stores energy
 viscous part
 dissipates energy

Ex. $T = \text{loss for } 10^3$

σ as compared to σ_0

$$\sigma = \sigma_0 e^{-t/\tau}$$

$\rightarrow T$ gives an idea of magnitude of dissipation of energy.

$$\sigma_{\text{actual}} = f(\sigma_0, t^*)$$

strain energy

\rightarrow uses of (dissip'')

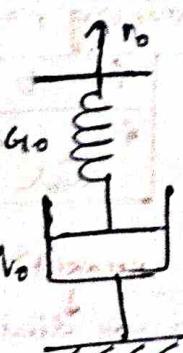
\rightarrow connects to a new form

\rightarrow No two are material specific property
 caution \rightarrow Not all materials behave like these $\rightarrow \sigma_0 e^{-t/\tau}$
 stress decaying exponentially.

Step strain Test

Input \rightarrow const. strain \rightarrow stress

Output \rightarrow Stress.



$$\sigma = \frac{\sigma_0}{\tau} e^{-t/\tau}$$

$\tau = \text{relax' time scale}$

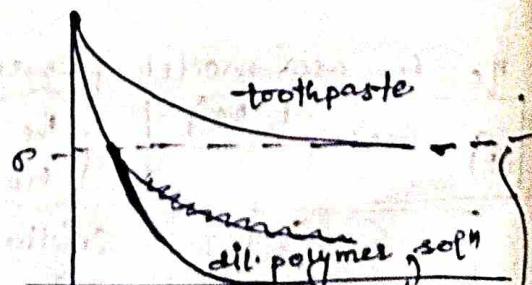
Higher relax' time scale signifies relaxation process is slow

17/08/23

$$\text{Stop strain Expt.} \rightarrow \sigma = f(t) = \sigma_0 + \int \sigma_0 / \tau \cdot t$$

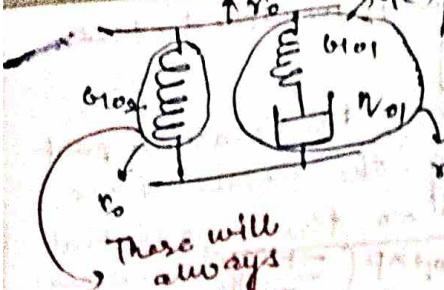
what is measurable? $\rightarrow T$

if something is very viscous, lots of energy is going to dissipate but the timescale will vary (depends)



only this much dissipation is possible the rest of the energy is going to remain for quite longer period of time (maybe ∞)

Tooth Paste Model :-

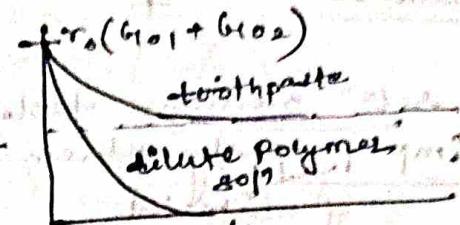


$$\sigma_i(t) = r_{i0} \exp(-t/\tau_i)$$

$\sigma(t) = \sigma_0 + \sigma_1(t) + \sigma_2(t)$

$$\sigma(t) = r_0 + r_{01} \exp(-t/\tau_1) + r_{02} \exp(-t/\tau_2)$$

$$t \rightarrow 0, \quad \sigma_0 = r_0 (r_{01} + r_{02})$$



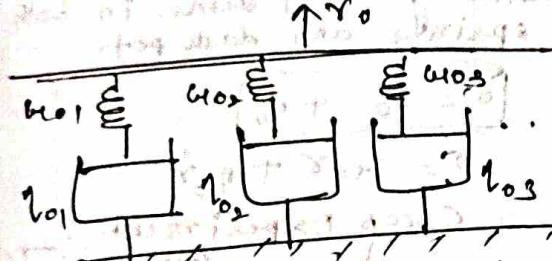
These will always be energy stored in this spring.

This is the case for all real

fluids instead of one

Relaxation time distribution: — multiple relax' time scales work in real fluids instead of one τ , there are a no. of τ s which cumulatively decide the decay behaviour of the fluid.

$$\sigma(t) = \sum_{i=1}^n \sigma_i(t)$$



$$\sigma_i(t) = r_{i0} \exp\left(-\frac{t}{\tau_i}\right)$$

$$\sigma(t) = \sum_{i=1}^n r_{i0} \exp\left(-\frac{t}{\tau_i}\right)$$

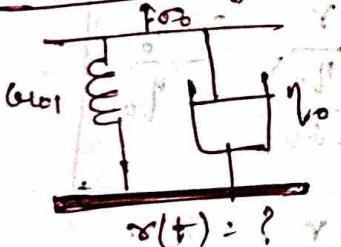
Includes the combined effect of multiple substances

+ ∞ energy that stays in the system

Kelvin - Voigt Model :-

Stress ($\sigma(t)$) decays

when we apply step strain.



$$\sigma(t) = \left(\sum_{i=1}^n r_{i0} \right) \exp\left(-\frac{t}{\tau_i}\right)$$

$t \rightarrow \infty$ (some const. stress remaining to represent we use a perfect spring)



Single Maxwell Element :-

$$\sigma = r_0 \exp\left(-\frac{t}{\tau}\right)$$

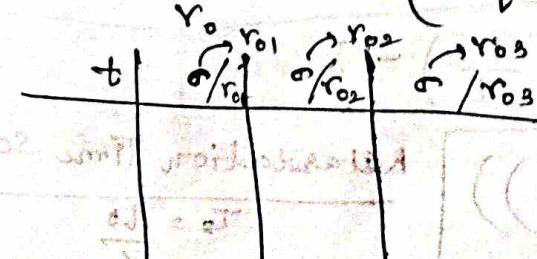
changing in the graph beside.

Different step strain

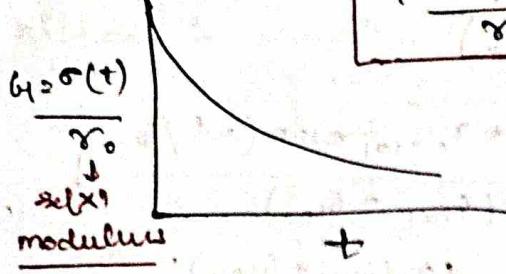
t

$$\sigma(t) = \exp\left(-\frac{t}{\tau}\right)$$

if we plot σ/r_0



We get a master curve (all the single curves we are getting (r_0, r_0, r_0) collapse into one) for the representation of material property



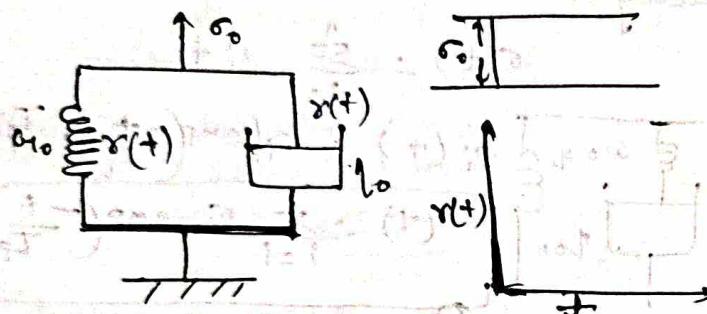
$$\sigma_0 = \frac{\sigma_0(t)}{\tau_0} \rightarrow \text{relaxation modulus} \rightarrow \text{Normalized stress}$$

We generally eliminate the plateau part while constructing the curve as we want to focus on the exponential part $\sigma(t) = \sigma_0 e^{-t/\tau_0}$ generalized Maxwell model.

relaxation modulus tells about the nature of the material. It is an imp. property which decays with time during stress relaxation of material.

Kelvin Voight Model :-

Charging a resistor with a capacitor



Initially $\sigma(t)$ same in both spring and dash pot

$$\sigma = \sigma_0 + \eta_0$$

$$\sigma = \sigma_0 + \eta_0$$

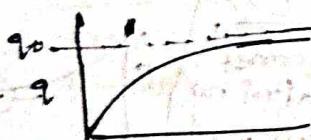
Creep Experiment aim.

(get some property)

$$\epsilon = iR + \frac{q}{C}$$

$$\epsilon = \frac{dq}{dt} R + \frac{q}{C}$$

$$q = q_0 \left(1 - \exp\left(-\frac{t}{RC}\right) \right)$$



If there is a viscous element in parallel, strain at $t=0$ should be zero.

$$\frac{dr}{dt} + \frac{r}{\tau_0} = \frac{\sigma_0}{\eta_0}$$

$$\frac{dr}{dt} + \frac{r}{\tau_0} = \frac{\sigma_0}{\eta_0}$$

$$r \exp\left(\frac{t}{\tau_0}\right) \Big|_{t=0}^t = \int_0^t \frac{\sigma_0 \exp\left(\frac{t}{\tau_0}\right)}{\eta_0} dt$$

$$r(t) \exp\left(\frac{t}{\tau_0}\right) - r_{t=0} \exp\left(\frac{0}{\tau_0}\right) = \frac{\sigma_0}{\eta_0} \exp\left(\frac{t}{\tau_0}\right)$$

$$r(t) \exp\left(\frac{t}{\tau_0}\right) = \frac{\sigma_0}{\eta_0} \exp\left(\frac{t}{\tau_0}\right) - \frac{\sigma_0}{\eta_0} \exp\left(\frac{0}{\tau_0}\right)$$

$$r(t) \exp\left(\frac{t}{\tau_0}\right) = \frac{\sigma_0}{\eta_0} \left[\exp\left(\frac{t}{\tau_0}\right) - 1 \right]$$

$$r(t) = \frac{\sigma_0}{\eta_0} \left(1 - \exp\left(-\frac{t}{\tau_0}\right) \right)$$

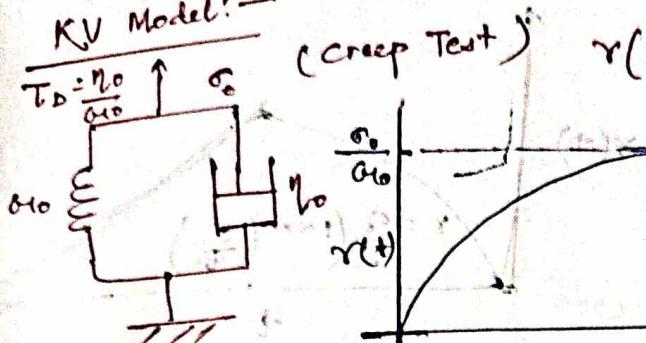
Retardation Time Scale

$$\tau_0 = \frac{\eta_0}{G_0}$$

* Strain at $t=0$ is σ_0/G_{10} for Maxwell model.
 * Strain takes some time to reach its max. value bcoz of the viscous nature of liq. (energy dissipⁿ occurs over a time scale). $T_D \rightarrow$ dissipⁿ \rightarrow retardⁿ time scale.

[22/08/23]

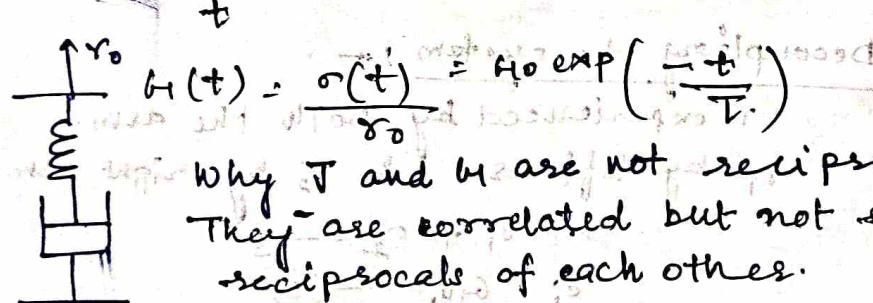
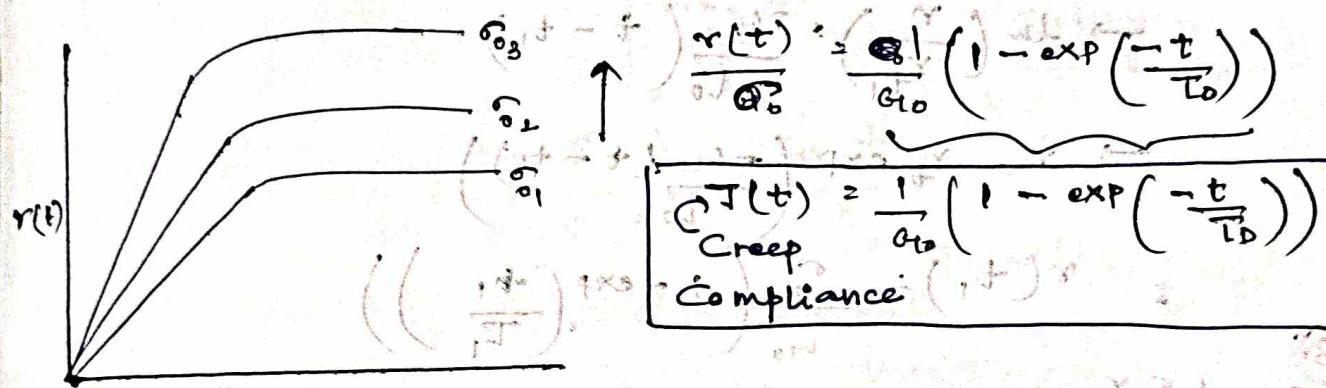
KV Model:-



→ if the spring is not there, no delay in response.

→ But here the process is creepy (lagging), bcoz of the spring.

→ There is a retardation in strain evolution



Why T and G are not reciprocals?

They are correlated but not straight-forward reciprocals of each other.

⇒ We cannot do creep test with Maxwell model const stress σ_0 , bcoz we will not get something useful out of it

Maxwell model

$$\dot{\gamma} = \dot{\gamma}_e + \dot{\gamma}_v = \frac{d\gamma_e}{dt} + \dot{\gamma}_v = \frac{d(\sigma_0/G_{10})}{dt} + \frac{\sigma_0}{\eta_0}$$

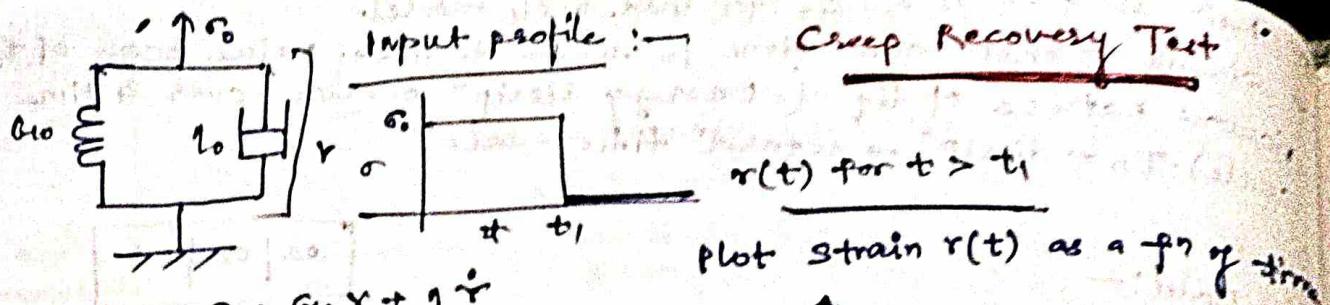
$$\frac{d\gamma}{dt} = \frac{\sigma_0}{G_{10} + \eta_0}$$

Linear stress is applied. Linear evolution of stress const²

$$\frac{d\gamma}{dt} = \frac{\sigma}{G_{10}} + \frac{\sigma}{T D_{10}}$$

Trivial solⁿ
 $\eta_0 \& G_{10}$ const

Non Trivial solⁿ
 $\eta_0(t) \& G_{10}(t)$
 $\gamma(t)$



$$\sigma = G_{10} \gamma + \eta_0 \dot{\gamma}$$

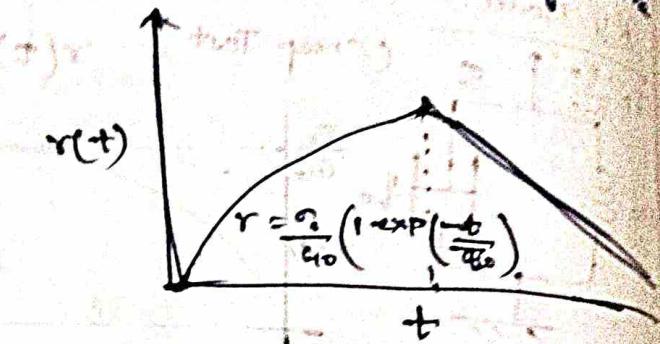
$$\sigma = G_{10} \gamma + \eta_0 \dot{\gamma}$$

$$\begin{aligned} \sigma &= G_{10} \gamma + \eta_0 \dot{\gamma} \\ \dot{\gamma} &= -\frac{G_{10}}{\eta_0} \gamma \end{aligned}$$

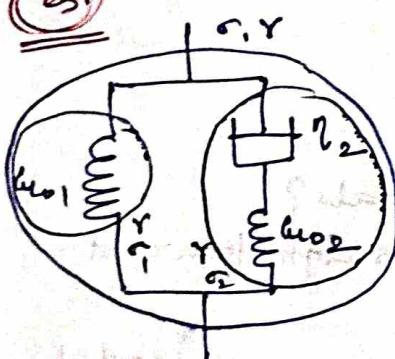
$$\rightarrow \ln\left(\frac{\gamma}{\gamma_{t_1}}\right) = \frac{-G_{10}}{\eta_0}(t - t_1)$$

$$\rightarrow \gamma = \gamma_{t_1} \exp\left(\frac{-G_{10}}{\eta_0}(t - t_1)\right)$$

$$\therefore \gamma(t_1) = \frac{\gamma_0}{G_{10}} \left(1 - \exp\left(\frac{-t_1}{T_1}\right)\right)$$



Q3.



Decoupling the system :-

γ experienced by both the arms
 σ_1 by left arm & σ_2 by right arm
 $\sigma = \sigma_1 + \sigma_2 \quad @$
 $\sigma_1 = G_{101} \gamma \quad b$

$$\begin{bmatrix} \ddot{\gamma}_1 \\ \ddot{\gamma}_2 \end{bmatrix} = \begin{bmatrix} \ddot{\gamma}_{12} + \frac{\eta_1}{G_{101}} \dot{\gamma}_1 \\ \ddot{\gamma}_{12} + \frac{\eta_2}{G_{102}} \dot{\gamma}_2 \end{bmatrix} \quad c$$

$$\sigma = G_{101} \gamma + \sigma_2 \rightarrow \sigma_2 = \sigma - G_{101} \gamma$$

$$\dot{\sigma}_2 = \dot{\sigma} - G_{101} \dot{\gamma}$$

$$\dot{\gamma} = \frac{\dot{\sigma} - G_{101} \dot{\gamma}}{G_{102}} + \frac{\dot{\sigma}_2}{\eta_2} \rightarrow \dot{\gamma} = \frac{\dot{\sigma} - G_{101} \dot{\gamma}}{G_{102}} + \frac{\sigma - G_{101} \gamma}{\eta_2}$$

Constitutive eqn

$$\frac{\sigma}{\eta_2} + \frac{\dot{\sigma}}{G_{102}} = \dot{\gamma} \left(1 + \frac{G_{101}}{G_{102}}\right) + \frac{G_{101} \gamma}{\eta_2}$$

after stress relax' test (const strain applied)

step strain test $\rightarrow \dot{\gamma} = 0$

$$\Rightarrow \frac{\sigma}{\eta_2} + \frac{\dot{\sigma}}{G_{102}} = \left(1 + \frac{G_{101}}{G_{102}} \right) + \frac{G_{102} \gamma_0}{\eta_2}$$

$$\Rightarrow \frac{\sigma}{\eta_2} + \frac{\dot{\sigma}}{G_{102}} = \frac{G_{101} \gamma_0}{\eta_2} \quad (\gamma = \gamma_0)$$

$$\Rightarrow \frac{d\sigma}{dt} + \frac{G_{102} \dot{\sigma}}{\eta_2} = G_{101} G_{102} \gamma_0$$

$$\rightarrow \frac{d\sigma}{dt} = \frac{G_{102}}{\eta_2} (G_{101} \gamma_0 - \sigma)$$

$$\rightarrow \int \frac{d\sigma}{G_{101} \gamma_0 - \sigma} = \int \frac{-G_{102} t}{\eta_2} dt$$

out $\dot{\sigma} = 0 = (G_{101} + G_{102}) \gamma_0$
Spring only.

$$\rightarrow \ln \left(\frac{G_{101} \gamma_0 - \sigma}{G_{101} \gamma_0} \right) = \frac{-G_{102} t}{\eta_2}$$

$$\rightarrow G_{101} \gamma_0 - \sigma = e^{\frac{-G_{102} t}{\eta_2}} (G_{101} \gamma_0)$$

$$\rightarrow \sigma = G_{101} \gamma_0 (1 - e^{\frac{-G_{102} t}{\eta_2}})$$

$$\rightarrow \sigma = G_{101} \gamma_0 - (G_{101} \gamma_0 - G_{101} \gamma_0 e^{\frac{-G_{102} t}{\eta_2}})$$

$$= G_{101} \gamma_0 e^{\frac{-G_{102} t}{\eta_2}}$$

$$= G_{101} \gamma_0 e^{\frac{-G_{102} t}{\eta_2}}$$

$$\boxed{\sigma(t) = (G_{101} \gamma_0 - G_{101} \gamma_0 e^{\frac{-G_{102} t}{\eta_2}}) + G_{101} \gamma_0}$$

Ultimately no energy remains in the system. It gets dissipated into some other form.

Oscillatory Rheology! —

24-8-2023

$$G(t) = \frac{\sigma(t)}{\gamma_0} \quad \begin{array}{l} \text{Relax modulus} \\ (\text{Relax time scale}) \end{array}$$

Normalised Stress

$$\tau(t) = \frac{\gamma(t)}{\omega_0} \quad (\text{Retardation Time Scale})$$

Cyclic compliance γ_0

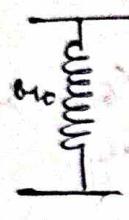
Oscillate in a controlled manner as we want to obtain some useful inform

$$\sigma = \sigma_0 \sin(\omega t)$$

angular frequency

$$f = \frac{\omega}{2\pi}$$

f = no. of cycles per second / per unit time (Hz)



$$\sigma = \sigma_0 \sin(\omega t) \rightarrow \text{in phase}$$

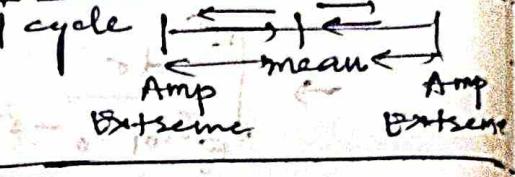
$$\gamma = \gamma_0 \sin(\omega t)$$

$$\sigma = \gamma_0 \tau_0$$

$$= \gamma_0 \tau_0 \omega \cos(\omega t)$$

$$= \eta_0 \tau_0 \omega \sin\left(\omega t + \frac{\pi}{2}\right) \quad \text{out of phase}$$

w = radian per sec.



in phase with elastic part

out of phase with viscous part (stress & strain out of phase)

elastic σ , γ are in phase means $\phi = 0$ $\phi \rightarrow$ phase angle

$$\text{viscoelastic: } \sigma = \sigma_0 \sin(\omega t + \phi) \quad 0 < \phi < \pi/2$$

$$\sigma = \sigma_0 \sin \omega t$$

$$\sigma = \sigma_0 \sin(\omega t + \phi)$$

$$\sigma = \underbrace{\sigma_0 (\cos \phi \sin \omega t)}_{\text{in phase}} + \underbrace{\sigma_0 (\sin \phi \cos \omega t)}_{\text{out of phase}}$$

elastic nature

time const. dependent

out of phase viscous nature

models are valid only for linear regime (small deflections) if stress/strain are changed very rapidly or are very large it fails.

ALL LAWS are linear (dependence is linear). So Models fail in a non-linear system.

Water has no elasticity

Models: —

$$(Storage or Elastic Modulus) \quad G' = \frac{\sigma_0 \cos \phi}{\gamma_0}$$

$$G'' = \frac{\sigma_0 \sin \phi}{\gamma_0} \quad (\text{Loss or Viscous modulus})$$

Loss Tangent

$$\frac{\text{Storage}}{\text{Loss}} = \frac{G'}{G''}$$

$$G^* = G' + iG''$$

G^* → Complex Modulus

(No physical meaning)

$$G^* = \frac{\Delta \sigma}{\Delta \gamma} = \frac{\sigma(+ + \Delta t) - \sigma(+)}{\gamma(+ + \Delta t) - \gamma(+)}$$

stress & strain complex

$$\text{Input } \gamma = \gamma_0 \sin(\omega t) \Rightarrow \gamma_0 e^{i\omega t} + \gamma_0 e^{-i\omega t} = \gamma_0 (\cos \omega t + i \sin \omega t)$$

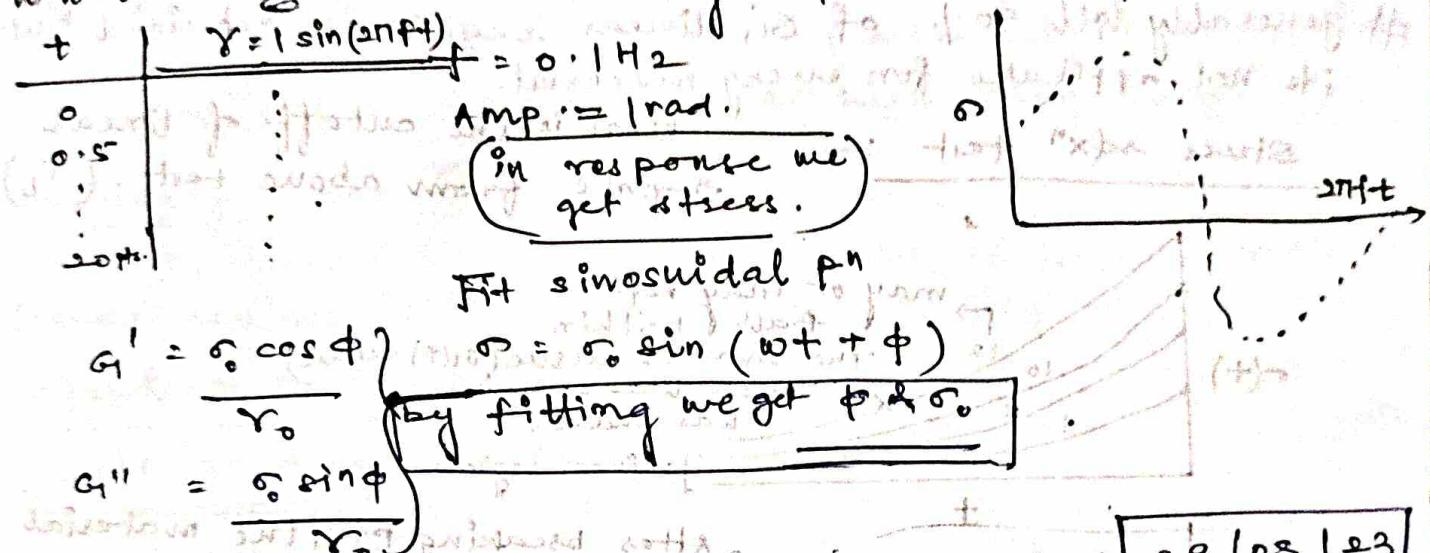
$$G'' = \frac{\gamma_0 e^{i\omega t} (e^{i\omega(t+\tau)} - e^{-i\omega t})}{\gamma_0 (e^{i\omega(t+\tau)} - e^{i\omega t})} = \frac{\gamma_0 e^{i\omega t}}{\gamma_0}$$

$$= \frac{\gamma_0 (\cos \omega t + i \sin \omega t)}{\gamma_0}$$

$$G'' = \left(\frac{\sigma_0 \cos \phi}{\gamma_0} \right) + \left(i \left(\frac{\sigma_0 \sin \phi}{\gamma_0} \right) \right)$$

$$G' = \underbrace{\frac{\sigma_0 \cos \phi}{\gamma_0}}_{G'_1} + \underbrace{i \left(\frac{\sigma_0 \sin \phi}{\gamma_0} \right)}_{G''_1}$$

What do we measure during expt? how to get G' & G'' ?



29/08/23

$G'' = \frac{d\sigma_0}{dt} = G'_1 + iG''_1$ (only for mathematical convenience)

The previous models don't give complete picture. Relaxation time scale is very high for both viscous & elastic dominated material.

(1) $\eta_0 = \frac{G_0}{G''_1}$ → Just model → See it as parameters of a whole (not exactly viscosity and other modulus)

Oscillatory Rheology kind of gives us a complete picture

Linear regime:

The deformations are very small & stress/strain are additive in nature

Upto what stress value is it possible to get $J(t)$?

These is a cutoff after which non linear regime starts.

How do we find out the linear regime for a material?

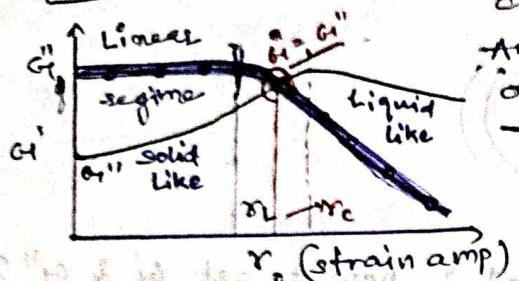
Linear regime?

Linear regime \leftarrow Strain Amplitude Sweep Test

$$\gamma = \gamma_0 \sin(2\pi f t)$$

Let say f is fixed.

$$\begin{aligned}\gamma_0 &= 0.1 \rightarrow \gamma = \gamma_1 \\ \gamma_0 &= 0.2 \rightarrow \gamma = \gamma_2 \\ &\vdots \quad \vdots\end{aligned}$$



So, the variable of interest which we are controlling is γ_0 .

γ_0 is very small (deformations very small) if nothing is happening to material why change in G' ?

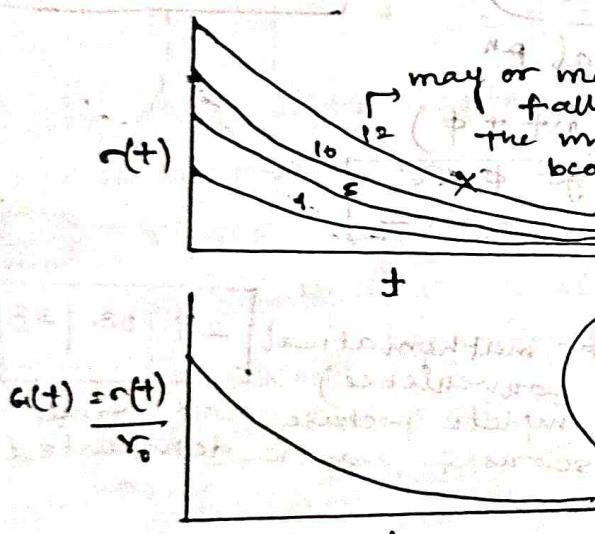
And how small the deformations are depends on the material.

The pt. of sudden decrease in G' (or elastic modulus) \rightarrow breaking pt. in this expt., at each γ_0 the avg. G' is taken & plotted for each cycle.

generally till 90% of G' , linear regime is retained but it's not applicable for every material.

Stress Relaxation Test

What is the cutoff of linear regime from above test. (γ_L)



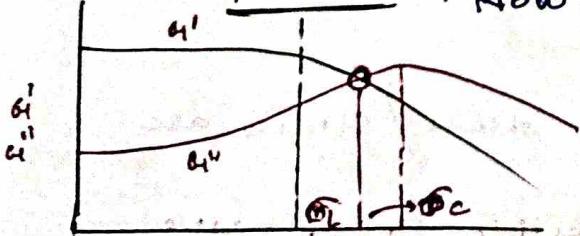
may or may not fall within the master curve ($G(t)$ curve)
bcz linear regime was ended.
↳ linear regime

After breaking pt.; the material becomes more like earlier it was more solid like. \rightarrow going from elastic dominated regime to viscosity dominated regime ($G'' > G'$)

rate of loss of energy \uparrow with γ_0 up to a limit.

To be proved in future; - rate of loss of energy $= f(G'')$ & should change near the breaking pt. bcoz if the material is same & does not change. (f should not change)

Stress - Amplitude Sweep Test! Now, our input $\rightarrow \sigma_0 \sin \omega t$



σ_0 (stress amp)
for 1 cycle

We don't need to do separate tests. We can just put Strain Amplitude instead of only strain. (same for stress) and if we know our γ_L we can get our σ_L . So for σ_0 every γ_0 we can get σ_L . We are only interested in amplitude

Frequency $\rightarrow \gamma = \gamma_0 \sin(\omega t)$

\Rightarrow The timescale over which viscous dissipation of energy takes place \rightarrow Relaxation Time Scale \rightarrow take energy and try to take a new form (configuration)

Relaxation Time scale \rightarrow (belongs to material)

$$T_{\text{exp}} = \frac{1}{f} \quad \begin{array}{l} \text{experimental} \\ \text{Time} \\ \text{Scale} \end{array}$$

$f = 0.1 \text{ Hz}$

↳ 10 seconds to complete 1 cycle

every cycle is identical to previous cycle if material remains intact.

Let's compare T and T_{exp} :-

$T \ll T_{\text{exp}} \rightarrow$ Liquid like \rightarrow at very low frequency (relatively more liq. like)

$T \gg T_{\text{exp}} \rightarrow$ Solid like \rightarrow at high frequency.

frequency Sweep Test :-

$\gamma = \gamma_0 \sin(\omega t)$ $\gamma_0 \rightarrow$ avg. value in linear regime

Linear regime itself is dependent on frequency

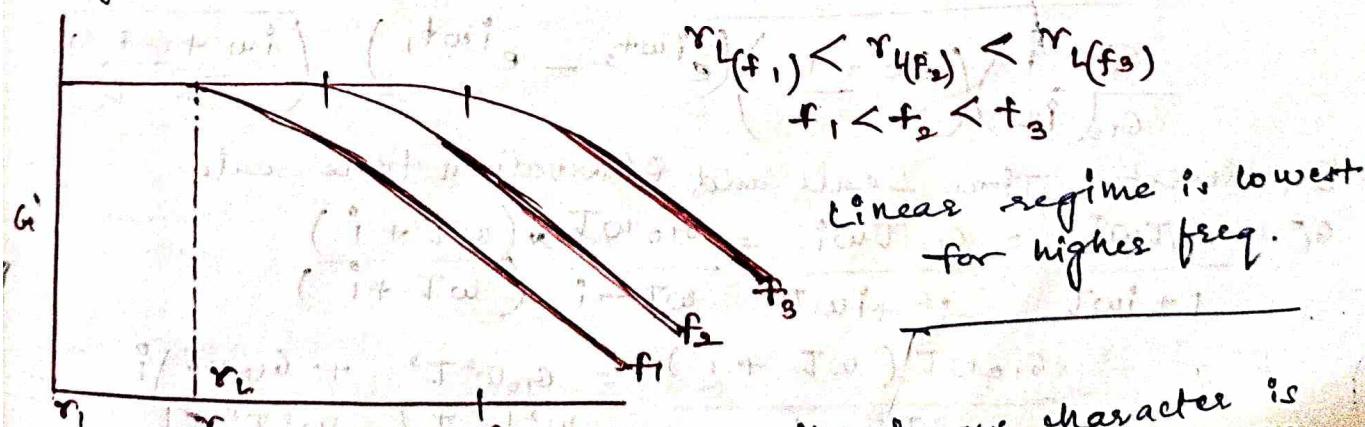
dependence of γ_0 on frequency :-

Strain-Amplitude Sweep Test :-

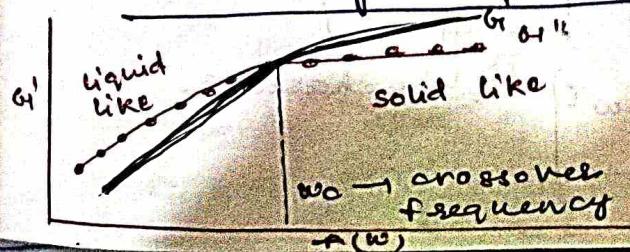
$$\gamma = \gamma_0 \sin(\omega t) \quad \gamma_1 < \gamma_0 < \gamma_3 \rightarrow f_1 < f_2 < f_3$$

$$\gamma = \gamma_0 \sin(\omega t) \quad \gamma_1 < \gamma_0 > \gamma_3$$

higher the freq. more will be the elasticity



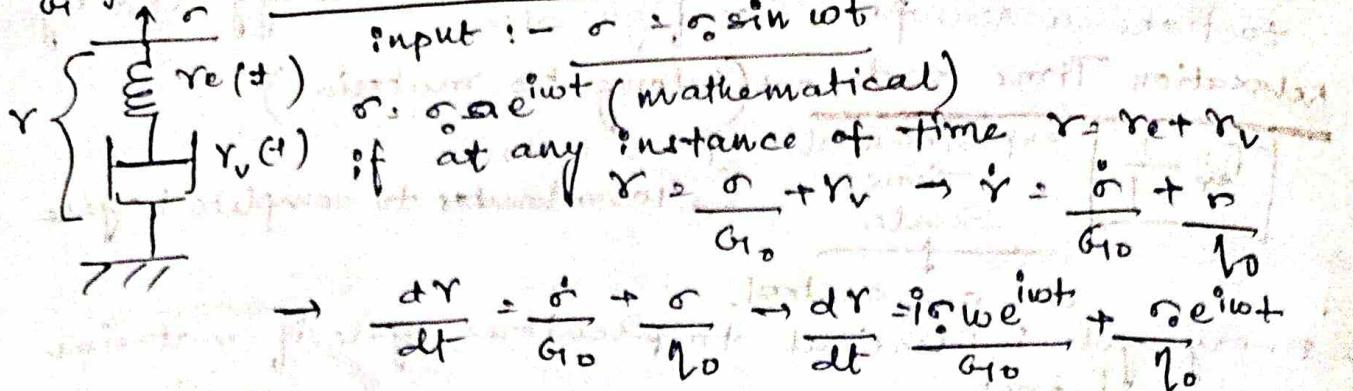
Frequency sweep Test :-



if viscous character is dominated at low freq., then $G'' \uparrow$ (will be higher at high freq. \rightarrow more elastic character)
 w_0 is representative of relaxation time scale because relaxation is energy dissipation $\uparrow w$, elasticity \uparrow

Mathematical Analysis of Freq. Sweep Test

$G''(f)$ Maxwell model :-



$$\Rightarrow \frac{dr}{dt} = \frac{\sigma_0 e^{i\omega t}}{G_{10}} \left(i\omega + \frac{1}{(\tau_0/G_{10})} \right) = \frac{\sigma_0 e^{i\omega t}}{G_{10}} \left(i\omega + \frac{1}{\tau} \right)$$

$$\Rightarrow \frac{dr}{dt} = \frac{\sigma_0 e^{i\omega t}}{G_{10}} \left(i\omega + \frac{1}{\tau} \right)$$

$$\alpha^* = \frac{\int_{t_1}^{t_2} dr}{t_2 - t_1} = \frac{\sigma(t_2) - \sigma(t_1)}{r(t_2) - r(t_1)}$$

$$\int_{t_1}^{t_2} dr = \int_{t_1}^{t_2} \frac{\sigma_0}{G_{10}} e^{i\omega t} \left(i\omega + \frac{1}{\tau} \right) dt = \Theta \left(\frac{\sigma_0 \cdot i\omega T + 1}{G_{10} \cdot \tau} \right) \int_{t_1}^{t_2} e^{i\omega t} dt$$

$$= \frac{\sigma_0}{G_{10}} \left(i\omega + \frac{1}{\tau} \right) \frac{1}{i\omega} (e^{i\omega t_2} - e^{i\omega t_1})$$

$$= \frac{\sigma_0}{G_{10}} \left(1 + \frac{1}{\tau i\omega} \right) (e^{i\omega t_2} - e^{i\omega t_1})$$

31/08/23

$$\alpha^* = \frac{\sigma_0 e^{i\omega t_2} - \sigma_0 e^{i\omega t_1}}{\frac{\sigma_0}{G_{10}} \left(\frac{1}{i\omega} \right) \left(i\omega + \frac{1}{\tau} \right) (e^{i\omega t_2} - e^{i\omega t_1}) \left(\frac{i\omega + \frac{1}{\tau}}{i\omega} \right)}$$

* Experimental Time Scale and Observation time scale.

$$G_T = \frac{G_{10} \tau \omega i}{1 + i\omega \tau} = \frac{G_{10} \tau \omega i}{-i^2 + i\omega \tau} = \frac{G_{10} \omega \tau \cdot (\omega \tau + i)}{\omega \tau - i} = \frac{G_{10} \omega \tau (\omega \tau + i)}{\omega \tau + i}$$

$$= \frac{G_{10} \omega \tau (\omega \tau + i)}{\omega^2 \tau^2 + 1} = \frac{G_{10} \omega^2 \tau^2 + G_{10} \omega \tau i}{\omega^2 \tau^2 + 1}$$

$$G'_1 = \frac{G_{10} \omega^2 \tau^2}{\omega^2 \tau^2 + 1}, \quad G''_1 = \frac{G_{10} \omega \tau}{\omega^2 \tau^2 + 1}$$

$\omega \tau \ll \ll 1$

$\rightarrow G'_1 \sim G_{10} \omega^2 \tau^2$

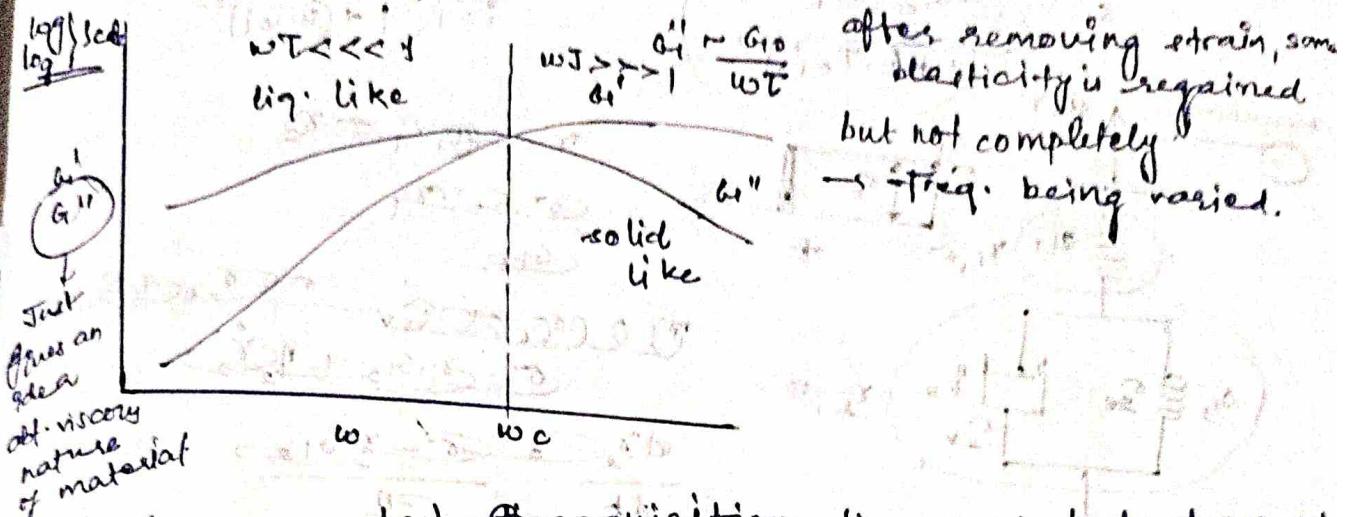
$G''_1 \sim G_{10} \omega \tau$

W.L.C. like character

initially $\omega_i > G_i''$ and it \uparrow rapidly. So both intersect, and then $\omega_i'' > G_i'$.

$\omega T \gg \omega$ \rightarrow solid like (classic nature dominance)

$$G' \approx G_0 \quad G'' \approx \frac{G_0}{\omega T}$$



$\omega T \gg 1$ $\rightarrow \omega_i'' \approx \frac{G_0}{\omega T}$ after removing strain, some elasticity is regained but not completely \rightarrow freq. being varied.

for freq sweep test, the acquisition time needs to be changed because of variation of f .

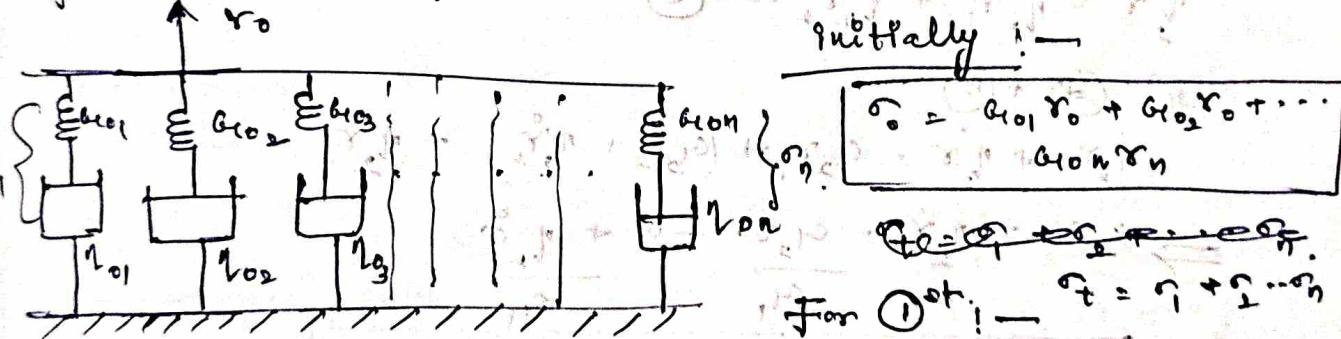
Generalized Maxwell model is needed as it will not work for every system.

19/9/23

Generalized Maxwell model:-

Find expression of relax modulus for GMM. (G_{0i} , T_{0i})

Initially :-



$$V_0 = V_1 + V_2.$$

$$\Rightarrow \frac{\eta_1}{G_{01}} = \dot{V}_1 \quad \dot{V}_2 = \frac{\dot{V}_1}{R_{02}}$$

$$\dot{V}_1 + \dot{V}_2 = \dot{V}_0$$

$$\dot{V}_0 = \frac{\dot{V}_1}{G_{01}} + \frac{\eta_1}{R_{01}}$$

\rightarrow Similarly

$$\rightarrow 0 = \frac{d\eta_1}{dt} + \frac{\eta_1}{R_{01}} \rightarrow \frac{d\eta_1}{dt} = -\frac{G_{01}\eta_1}{R_{01}}$$

$$\rightarrow \ln\left(\frac{\eta_1}{\eta_{10}}\right) = \exp\left(-\frac{G_{01}t}{R_{01}}\right) \rightarrow \eta_1 = \eta_{10} \exp\left(-\frac{G_{01}t}{R_{01}}\right)$$

Similarly for $\eta_2 = \eta_{20} \exp\left(-\frac{G_{02}t}{R_{02}}\right)$

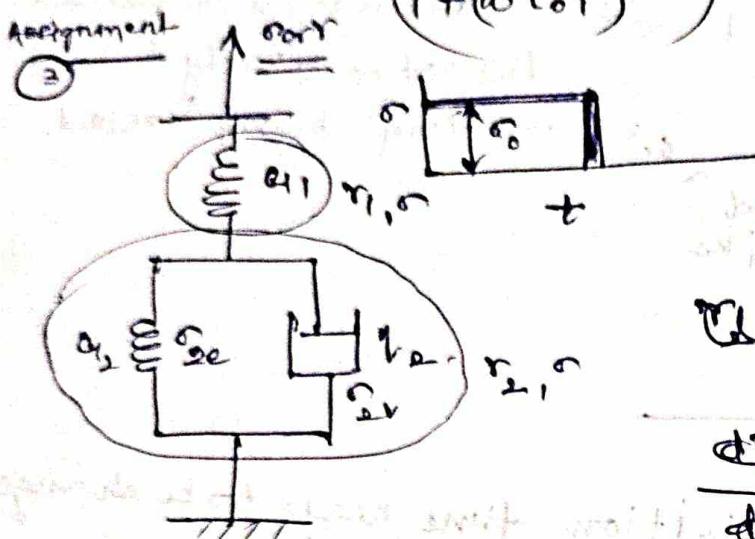
$$\eta_n = \eta_{n0} \exp\left(-\frac{G_{0n}t}{R_{0n}}\right)$$

$$\text{So } \sigma_t = \sigma_1 + \sigma_2 + \dots + \sigma_n$$

$$\sigma(t) = \sum_{i=1}^n \alpha_{10i} \exp\left(-\frac{t}{T_{10i}}\right) \text{ where } T_{10i} = \frac{10i}{G_{10i}}$$

To find α'_1 & $\alpha''_1 \rightarrow$ oscillatory strain Test

$$\alpha'_1 = \frac{\sum_{i=1}^n \alpha_{10i} (T_{10i} \omega)^2}{1 + (\omega T_{10i})^2} \quad \alpha''_1 = \frac{\sum_{i=1}^n (\alpha_{10i} T_{10i} \omega)}{1 + (\omega T_{10i})^2}$$



$$r = r_1 + r_2$$

$$\frac{\partial r}{\partial t} = \frac{\partial r_1}{\partial t} + \frac{\partial r_2}{\partial t}$$

Oscillatory Test

Castigliano's Rule

$$\frac{dr}{dt} = \frac{\partial \sigma}{\partial \gamma} \frac{\partial \gamma}{\partial t}$$

$$\sigma = G_1 \gamma_1 \quad \textcircled{a}$$

$$\sigma = G_1 \gamma_1 + G_2 \gamma_2 + l_2 \dot{\gamma}_2 \quad \textcircled{b}$$

$$\gamma = \gamma_1 + \gamma_2 \quad \textcircled{c}$$

$$G_2 \dot{\gamma} = G_2 \gamma_1 + G_2 \gamma_2 \quad \textcircled{d}$$

$$l_2 \dot{\gamma} = l_2 \dot{\gamma}_1 + l_2 \dot{\gamma}_2 \quad \textcircled{e}$$

eqⁿ $\textcircled{a} + \textcircled{b} :$

$$G_1 \gamma_1 + l_2 \dot{\gamma} = G_2 \gamma_1 + (G_2 \gamma_2 + l_2 \dot{\gamma}_2) + l_2 \dot{\gamma}_1$$

$$\Rightarrow G_1 \gamma_1 + l_2 \dot{\gamma}_2 = \frac{G_2 \gamma_1}{G_1} + \frac{G_2 \gamma_2}{G_1} + \frac{l_2 \dot{\gamma}_1}{G_1}$$

$$\Rightarrow \boxed{\sigma \left(1 + \frac{G_2}{G_1}\right) + \left(\frac{l_2}{G_1}\right) \dot{\sigma} = \alpha_1 \gamma_1 + \alpha_2 \gamma_2}$$

Boltzmann Superposition Principle:

5/09/23

$$\begin{aligned}
 & \gamma_i(+), \gamma_i(-) \quad \gamma = \frac{\dot{\sigma}}{G_{0i}} + \sigma \\
 & \sum_{j=1}^n \frac{d\sigma}{dt} + \frac{\sigma}{T_0} = G_{0i} d\gamma \\
 & \Rightarrow \sigma e^{t/T_0} \Big|_{-\infty}^t = \int_{-\infty}^t G_{0i} e^{t'/T_0} \dot{\gamma} dt' \\
 & \rightarrow \sigma e^{t/T_0} - (c)e^{-\infty/T_0} = \int_{-\infty}^t G_{0i} e^{t'/T_0} \dot{\gamma} dt' \\
 & \text{finite (we don't deal with } \infty \text{ quantities)} \\
 & \rightarrow \sigma e^{t/T_0} = \int_{-\infty}^t G_{0i} e^{t'/T_0} \dot{\gamma}(t') dt' \\
 & \rightarrow \sigma = \int_{-\infty}^t G_{0i} e^{t'/T_0} e^{-t/T_0} \dot{\gamma}(t') dt' \\
 & \rightarrow \sigma = \int_{-\infty}^t G_{0i} e^{(t-t')/T_0} \dot{\gamma}(t') dt' \\
 & = \int_{-\infty}^t G_{0i} e^{-(t-t')/T_0} \dot{\gamma}(t') dt'
 \end{aligned}$$

The above term will only remain if $\dot{\gamma}$ is being applied otherwise the whole term will become zero.

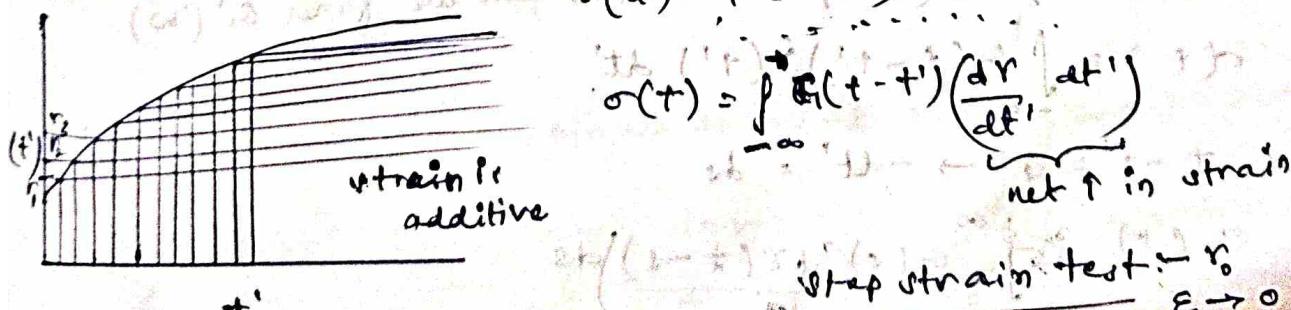
$$\sigma(t) = \int_{-\infty}^t G_{0i} e^{-(t-t')} \dot{\gamma}(t') dt' \Rightarrow \sum_{i=1}^n \sigma_i = \int_{-\infty}^t G_{0i} e^{-(t-t')} \dot{\gamma}_i dt'$$

$$\sigma(t) = \int_{-\infty}^t \sigma_i(t-t') \dot{\gamma}_i(t') dt' \rightarrow \text{All KV models in parallel.} \rightarrow \text{All Maxwell models in parallel.}$$

$$\gamma(t) = \int_{-\infty}^t \gamma_i(t-t') \dot{\gamma}_i(t') dt' \rightarrow \text{all KV models in series.}$$

$$t = \int_{-\infty}^t \sigma_i(t) \dot{\gamma}_i(t-t') dt', \quad r_2 = r_1 + dr, \quad r_3 = r_2 + dr$$

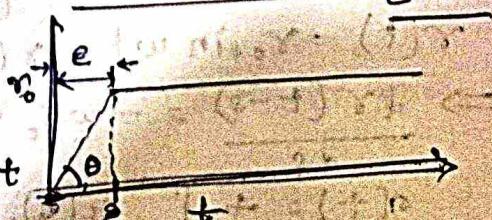
$$\sigma_i(t) = r_i \dot{\gamma}_i(t-t_1) + r_i \dot{\gamma}_i(t-t_2) + r_i \dot{\gamma}_i(t-t_3) + \dots$$



Linear strain field = sum of ∞ step strains.

$$\sigma(t) = \int_0^{\infty} G_i(t-t') \dot{\gamma}(t') dt' + \int_{E \rightarrow 0}^t \sigma_i(t-t') dt' \Leftrightarrow \sigma(t) = \int_{-\infty}^t \sigma_i(t-t') \dot{\gamma}(t') dt'$$

Step strain test: $\frac{r_0}{E \rightarrow 0}$



$$\sigma(t) = \int_0^t G_1(t-t') \gamma_0 dt' = \lim_{\varepsilon \rightarrow 0} \frac{\int_0^t G_1(t-\varepsilon) \gamma_0 dt'}{\varepsilon} = G_1(t) \gamma_0 \quad (1)$$

$$[\sigma(t) = r_0 \alpha(t)] \Rightarrow \sigma(t) = r_0 \alpha_0 \exp\left(-\frac{t}{T}\right)$$

∴ rel' b/w η and $G_1(t)$:-

Const. strain rate experiment :-

$$\dot{\gamma} = \text{const.} = \dot{\gamma}_0$$

$$\boxed{\eta = \frac{\sigma}{\dot{\gamma}}}$$

Newtonian fluid $\rightarrow \eta \text{ const.}$

$$\sigma(t) = \int_{-\infty}^t G_1(t-t') \dot{\gamma}_0 dt' \quad (\text{By B&P})$$

$$\Rightarrow \eta = \frac{\sigma(t)}{\dot{\gamma}} = \int_{-\infty}^t G_1(t-s) ds \quad \begin{matrix} (t-s = s) \\ (-ds = -ds) \end{matrix}$$

$$\Rightarrow \eta = - \int_{\infty}^0 G_1(s) ds = \sqrt{\frac{G_1(\infty)}{2\pi}} \rightarrow \text{time}$$

\Rightarrow rate of dissip'n of energy slow \rightarrow viscosity high.

? for a single Maxwell model :-

$$\eta = \int_0^\infty G_1 e^{-s/T_0} ds = [G_1 T_0 e^{-s/T_0}]_0^\infty = G_1 T_0$$



$$T_0 = \eta_0 / G_1$$

$$\boxed{\eta = \eta_0 = G_1 T_0}$$

viscosity of dashpot = viscosity of material [only for single Maxwell model]

$$G_1(\omega) \rightarrow G_1(t)$$

if we know of $G_1(t)$ of a material can we find $G_1(\omega)$.

$$\sigma(t) = \int_{-\infty}^t G_1(t-s) \dot{\gamma}(s) ds$$

$$\therefore t-s = s \rightarrow -ds = -ds$$

$$\sigma(t) = \int_0^\infty G_1(s) \left(\frac{d\gamma(t-s)}{ds} \right) ds$$

$$\gamma(t) = \gamma_0 \sin \omega t \quad \gamma(t-s) = \gamma_0 \sin(\omega(t-s))$$

$$\Rightarrow \frac{d\gamma(t-s)}{ds} = -\omega \gamma_0 \cos(\omega(t-s))$$

$$\sigma(t) = \int_0^\infty G_1(s) \omega \gamma_0 \cos(\omega(t-s)) ds$$

$$o(t) = r_0 w \int_0^\infty o_1(s) (\cos \omega t \cos \omega s + \sin \omega t \sin \omega s) ds$$

$$r(t) = r_0 w \left(\underbrace{\int_0^\infty o_1(s) \cos \omega s ds}_{\cos \omega t} \right) \cos \omega t + r_0 w \left(\underbrace{\int_0^\infty o_1(s) \sin \omega s ds}_{\sin \omega t} \right) \sin \omega t$$

$$\Rightarrow o'(t) = r_0 w \int_0^\infty o_1(s) \sin \omega s ds$$

$$\Rightarrow o'' = r_0 w \int_0^\infty o_1(s) \cos \omega s ds.$$

BSP :-

$$o(t) = \int_{-\infty}^t o_1(t-s) \overset{ds}{\underset{\text{ods}}{\overbrace{r}}} ds.$$

$$r(t) = \int_{-\infty}^t \overset{d}{\underset{\text{ds}}{\overbrace{r}}}(t-s) \overset{d\omega(s)}{\underset{\text{ods}}{\overbrace{o_1(s)}}} ds$$

$$r = r_0 \sin \omega t$$

$$-\cancel{\int_{-\infty}^t} = z, ds = -dz$$

$$-\int_{-\infty}^t o_1(z) \frac{dr(t-z)}{dz} dz \Rightarrow \int_{-\infty}^{\infty} o_1(z) \frac{dr(t-z)}{dz} dz$$

$$o(t) = - \int_{-\infty}^{\infty} o_1(z) \frac{dr(t-z)}{dz} dz$$

$$r = r_0 \sin \omega t$$

$$r(t-z) = r_0 \sin \omega (t-z)$$

$$\frac{dr(t-z)}{dz} = r_0 (\sin \omega t) \cos \omega z - (\cos \omega t) \sin \omega z$$

$$\frac{dr(t-z)}{dz} = -(r_0 \omega \sin \omega t \sin \omega z + r_0 \omega \cos \omega t \cos \omega z)$$

$$\Rightarrow r(t) = r_0 \int_0^\infty o_1(z) (\sin \omega z \sin \omega t + \cos \omega z \cos \omega t) dz$$

$$= r_0 \int_0^\infty o_1(z) \sin \omega z \sin \omega t dz + r_0 \int_0^\infty o_1(z) \cos \omega z \cos \omega t dz$$

$$o' = \frac{r_0}{r_0} = r_0 w \int_0^\infty o_1(z) \sin \omega z \sin \omega t dz = r_0 w \left(\int_0^\infty o_1(z) \sin \omega z dz \right) \sin \omega t$$

$$\Rightarrow r = r_0 \sin \omega t$$

$$o = r_0 \sin(\omega t + \delta) = r_0 \sin \omega t \cos \delta + r_0 \cos \omega t \sin \delta$$

$$o' = \frac{r_0 \cos \delta}{r_0} \quad o'' = \frac{r_0 \sin \delta}{r_0}$$

$$\alpha'(w) = w \left(\int_0^\infty g_1(z) \sin wz dz \right) \quad \alpha''(w) = \frac{1}{w} \left(\int_0^\infty g_1(z) \cos wz dz \right)$$

$$\frac{\dot{\gamma}(t)}{Y}$$

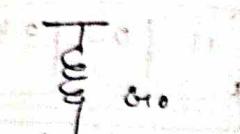
$$\frac{\eta_0 = \int_0^\infty g_1(z) dz}{\tau} \rightarrow \text{slow/sluggish relax?}$$

const. shear rate for finding viscosity:

$$\dot{\gamma}(t) = \int_{-\infty}^t \alpha(t-s) \dot{\gamma}(s) ds$$

BSP valid only for linear regime \rightarrow very small def.

disturbing the sample minimally



$$\alpha'(w) = w \int_0^\infty G_{10} e^{-z/\tau} \sin wz dz$$

$$= -w G_{10} e^{-z/\tau} \frac{\cos wz}{\tau} \Big|_0^\infty + \frac{1}{\tau} \int_0^\infty w G_{10} \cos wz dz$$

$$\alpha'(s) = G_{10} e^{-s/\tau}$$

$$\alpha' = w \int_0^\infty \alpha'(s) \sin ws ds$$

$$\underline{I.} = \frac{\alpha'}{G_{10} w} = \int_0^\infty e^{-s/\tau} \sin ws ds$$

12 | 09 | 23

$$\tau = \frac{\eta_0}{G_{10}}$$

$$\frac{\alpha'}{G_{10} w} = I = \frac{e^{-s/\tau} \cos ws}{\tau w} \Big|_0^\infty \left(-\frac{1}{\tau w} \right) \int_0^\infty e^{-s/\tau} \cos ws ds$$

$$I = \frac{1}{\tau w} - \frac{1}{\tau w} \int_0^\infty e^{-s/\tau} \cos(ws) ds$$

$$I_1 = \frac{e^{-s/\tau} \sin ws}{w} \Big|_0^\infty + \frac{1}{\tau w} \int_0^\infty \frac{e^{-s/\tau}}{w} \sin ws ds$$

$$I_2 = \frac{1}{\tau w} \int_0^\infty e^{-s/\tau} \sin ws ds$$

$$I_1 = \frac{I_2}{\tau w}$$

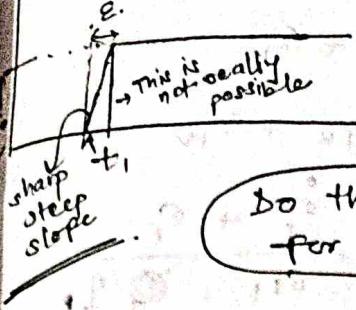
$$\textcircled{1}: I = \frac{1}{\tau w} - \frac{1}{\tau w} \times \frac{I_2}{\tau w} \Rightarrow I + \frac{I_2}{\tau^2 w^2} = \frac{1}{\tau w} \Rightarrow I \left(\frac{1 + \omega^2 \tau^2}{\tau^2 w^2} \right) = \frac{1}{\tau w}$$

$$\rightarrow I_2 = \omega \tau^2$$

$$\frac{G_1}{G_{10} w} = \frac{\omega \tau^2}{1 + \tau^2 w^2} \rightarrow G_1 = \frac{G_{10} \omega \tau^2}{1 + \tau^2 w^2}$$

Similarly we can find our α'' .

~~After doubt clearing.~~ We have applied strain we want to find out after general form of BSP:-



Do the same for KV model

$$\sigma(t) = \int_{-\infty}^t g_i(t-s) \frac{d\gamma}{ds} ds$$

$$= \int_{-\infty}^{t_1} g_i(t-s)(0) + \lim_{\epsilon \rightarrow 0} \int_{t_1}^{t_1+\epsilon} g_i(t-s) \frac{\gamma_0}{\epsilon}$$

$$+ \int_{t_1+\epsilon}^t () \gamma_0$$

$$= \lim_{\epsilon \rightarrow 0} \int_{t_1}^{t_1+\epsilon} g_i(t-s) \frac{\gamma_0}{\epsilon}$$

$$\sigma(t) = \lim_{\epsilon \rightarrow 0} \int_{t_1}^{t_1+\epsilon} g_i(t-s) \gamma_0 ds = \lim_{\epsilon \rightarrow 0} \gamma_0 g_i(t-t_1-\epsilon) = \gamma_0 g_i(t-t_1)$$

$$\sigma(t) = \gamma_0 g_i(t-t_1) = \gamma_0 g_{i_0} e^{(t-t_1)/\tau_i}$$

Multimaxwell Model Derivation :-

$$C_{10} = \int_0^\infty \sigma_i(s) ds = \sum g_{i_0} i e^{-s/\tau_i^0}$$

Zero shear μ

$$\Rightarrow \eta_0 = \int_0^\infty g_{i_0} i e^{-s/\tau_i^0} ds = \sum g_{i_0} i \tau_i^0 e^{-s/\tau_i^0} \Big|_0^\infty$$

$$= \sum g_{i_0} \tau_i^0 (1 - 0)$$

$$= \sum g_{i_0} \tau_i^0$$

Assignment 8s.

Assignment 2.

$$(3) Relax modulus :- \sigma_i(t) = g_{i_1} e^{-t/\tau_1} + g_{i_2} e^{-t/\tau_2}$$

$$\sigma(t) = \int_{-\infty}^t g_i(t-s) \frac{d\gamma}{ds} ds$$

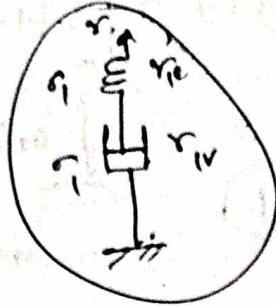
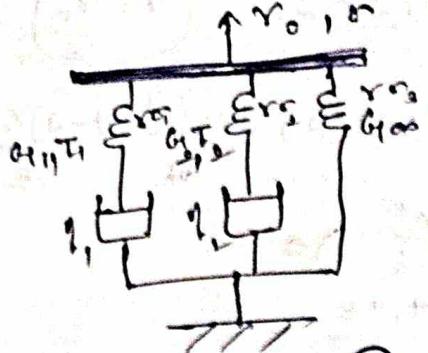
$$= \int_0^{t_1} \left(g_{i_1} e^{-(t-s)/\tau_1} + g_{i_2} e^{-(t-s)/\tau_2} \right) K ds - \int_{t_1}^{\infty} \left(g_{i_1} e^{-(t-s)/\tau_1} + g_{i_2} e^{-(t-s)/\tau_2} \right) K ds$$

$$= K \left(\tau_1 g_{i_1} e^{-(t-t_1)/\tau_1} \Big|_0^{t_1} + \tau_2 g_{i_2} e^{-(t-t_1)/\tau_2} \Big|_0^{t_1} \right)$$

$$= K \left(\tau_1 g_{i_1} e^{-(t-t_1)/\tau_1} \Big|_{t_1}^{\infty} + \tau_2 g_{i_2} \exp \left(-\frac{(t-t_1)}{\tau_2} \right) \Big|_{t_1}^{\infty} \right)$$

*Assignment :-

$$① \sigma(t) = G_1 e^{-t/\tau_1} + G_2 e^{-t/\tau_2} + G_{\infty}$$



$$V_B = V_1 e^{-t/\tau_1}$$

$$\dot{V}_B = V_1 e^{-t/\tau_1}$$

$$① \dot{\sigma} = \frac{\dot{\sigma}_1}{G_1} + \frac{\dot{\sigma}_2}{G_2}$$

$$② \dot{\sigma}_B = \frac{\dot{\sigma}_1}{G_1} + \frac{\dot{\sigma}_2}{G_2} \quad ③ \dot{\sigma}_B = \frac{\dot{\sigma}}{G_{\infty}}$$

$$\Rightarrow \dot{\sigma}_B = \frac{\dot{\sigma}}{G_{\infty}}$$

$$\sigma_1 + \sigma_2 + \sigma_3 = \sigma$$

$$\Rightarrow \sigma_1 + \sigma_2 + \sigma_{\infty} = \sigma$$

$$④ \Rightarrow \frac{\sigma_1 + \sigma_2}{\sigma} = \frac{\sigma - \sigma_{\infty}}{\sigma}$$

$$\sigma_1 + \sigma_2 + \sigma_3 = \sigma \Rightarrow (\dot{\sigma}_1 + \dot{\sigma}_2 + \dot{\sigma}_{\infty}) = (\dot{\sigma} - \dot{\sigma}_{\infty}) \quad ⑤$$

\Rightarrow

$$\dot{\sigma} = \frac{\dot{\sigma} - \dot{\sigma}_{\infty}}{G_1} + \frac{\dot{\sigma}_2}{G_2} + \frac{\dot{\sigma}_{\infty}}{G_{\infty}}$$

$$\Rightarrow \left(\dot{\sigma} - \frac{\dot{\sigma}_{\infty}}{G_2} \right) G_2 = ⑥ \dot{\sigma}_2$$

$$\Rightarrow \dot{\sigma}_2 = \frac{\dot{\sigma} - \dot{\sigma}_{\infty}}{G_1} - \frac{\dot{\sigma} G_2 - \dot{\sigma}_{\infty} G_1}{G_1 G_2} + \frac{\dot{\sigma}_{\infty} G_1}{G_1}$$

$$eqn ④/G_1 + eqn ⑤/G_1$$

$$\frac{\sigma_1}{G_1} + \frac{\sigma_2}{G_1} = \left(\frac{\sigma_1}{G_1} + \frac{\sigma_2}{G_1} \right) + \frac{\sigma_2}{G_1} + \frac{\sigma_2}{G_1} + \frac{\dot{\sigma}_{\infty} G_1}{G_1} + \frac{\dot{\sigma}_{\infty} G_1}{G_1}$$

$$\Rightarrow \frac{\sigma_1}{G_1} + \frac{\sigma_2}{G_1} = \dot{\sigma} + \left(\frac{\sigma_1}{G_1} + \frac{\sigma_2}{G_1} \right) + \frac{\dot{\sigma}_{\infty} G_1}{G_1} + \frac{\dot{\sigma}_{\infty} G_1}{G_1} \quad ⑦$$

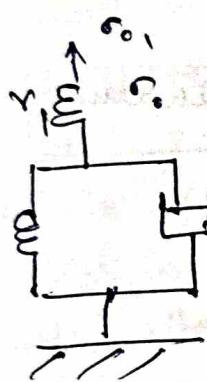
$$\Rightarrow \underbrace{\frac{r_1 + \dot{r}_1}{\eta_1} + \left(\frac{r_2 + \eta_1 r_{1\infty}}{\eta_1} + \frac{r_2 \eta_{1\infty}}{\eta_1} \right)}_{P = \frac{r_1}{\eta_1} + \frac{\dot{r}_1}{\eta_1}} = \frac{r_2}{\eta_2} + \frac{\dot{r}_2}{\eta_2}$$

$$\Rightarrow \textcircled{7} \times \eta_1 - \textcircled{2} \times \eta_2$$

$$\Rightarrow \eta_1 P + \eta_2 \dot{r} = \frac{\eta_1 r_2}{\eta_1} + \cancel{\dot{r}_2} - \cancel{\dot{r}_2} - \frac{\eta_2 r_2}{\eta_2}$$

$$\Rightarrow \dot{r}_2 = \frac{P \eta_1 - \dot{r}_2 \eta_2}{\frac{\eta_1}{\eta_2} - \frac{\eta_2}{\eta_2}}$$

~~see pgf~~



$$r = r_1 + r_2$$

$$r = \eta_1 r_1 + \eta_2 r_2 \quad \text{or} \quad r_0 = \eta_2 r_2 + \eta_1 r_2$$

$$\frac{dr_2}{dt} + \frac{\eta_1 r_2}{\eta_2} = \frac{r_0}{\eta_2}$$

$$\boxed{\begin{aligned} r_2 &= \frac{r_0}{\eta_2} + r_2^0 \\ r(t) &= \frac{r_0}{\eta_2} + r_2(t) \end{aligned}}$$

$$r_2^0 \exp\left(\frac{\eta_1 t}{\eta_2}\right) \Big|_0^+ = \frac{r_0}{\eta_2} \exp\left(\frac{\eta_1 t}{\eta_2}\right) \Big|_0^+$$

$$\Rightarrow r_2^0 \exp\left(\frac{\eta_1 t}{\eta_2}\right) - r_2^0 (t=0)$$

$$= \frac{r_0}{\eta_2} \frac{r_2^0 \exp\left(\frac{\eta_1 t}{\eta_2}\right)}{\exp\left(\frac{\eta_1 t}{\eta_2}\right) - 1} \Big|_0^+$$

$$= \frac{r_0}{\eta_2} \left(\exp\left(\frac{\eta_1 t}{\eta_2}\right) - 1 \right)^{-1} \Big|_0^+$$

$$\Rightarrow r_2^0 \exp\left(\frac{\eta_1 t}{\eta_2}\right) - 0 = \frac{r_0}{\eta_2} \left(\exp\left(\frac{\eta_1 t}{\eta_2}\right) - 1 \right)$$

$\therefore \text{at } t=0, r = r_1 = \frac{r_0}{\eta_1}$

$$r(t) = \frac{r_0}{\eta_2} + K \nu \text{part} = \frac{r_0}{\eta_1} + \frac{r_0}{\eta_2} \left(1 - \exp\left(-\frac{\eta_1 t}{\eta_2}\right) \right)$$

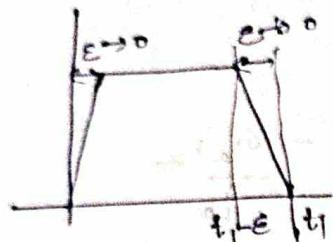
For $t=0 \rightarrow \underline{\text{initial will be } r_1}$

$$\frac{r(t)}{G_{10}} = \frac{1}{G_{11}} + \frac{1}{G_{12}} \left(1 - e^{-\tau_p \left(-\frac{t-t_0}{\tau_p} \right)} \right)$$

Assignment (2)

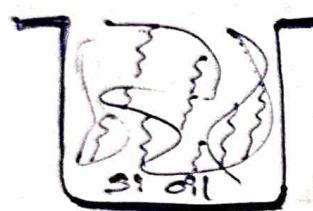
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$$(8) G_1(t) = G_{10} e^{-H/T}$$



$$\sigma(t) = \int_{t=0}^t G_{10} e^{-(t-s)/\tau} ds = \frac{G_{10}}{\tau} \int_{t=0}^t e^{-(t-s)/\tau} ds = \frac{G_{10}}{\tau} \left[1 - e^{-(t-t_0)/\tau} \right]$$

$$\begin{aligned} \sigma(t) &= \gamma_0 \left(\int_{t=0}^t G_1(t-s) ds - \int_{t=t_0}^t G_1(t-s) ds \right) \\ &= \gamma_0 [G_1(t) - G_1(t-t_0)] \\ &= \gamma_0 G_{10} \left[e^{-t/\tau} - e^{-(t-t_0)/\tau} \right] \end{aligned}$$



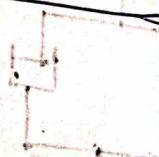
$$10:1 \\ V/V$$

(Cross linker)

$$u_g \rightarrow u_{gel}$$

Annealing dependence

chemical gel	\rightarrow	soft crosslinked
physical gel (clay)	\rightarrow	no crosslinking



TEM \rightarrow Transmission Electron Microscope.

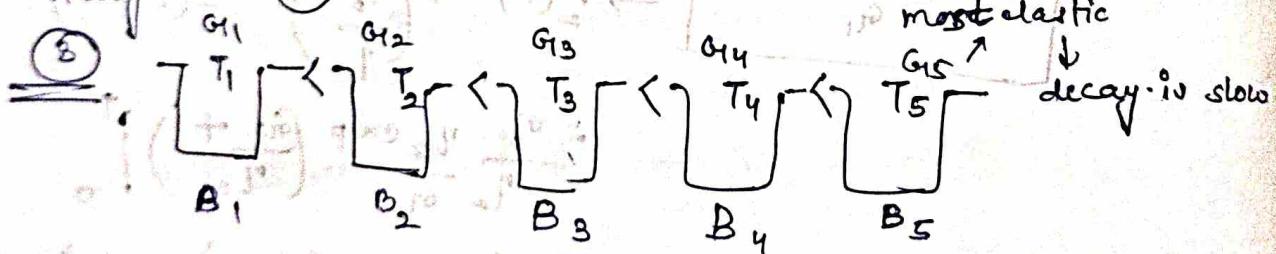
$$KE = eV_{app.}$$

(particle nature) \rightarrow De Broglie

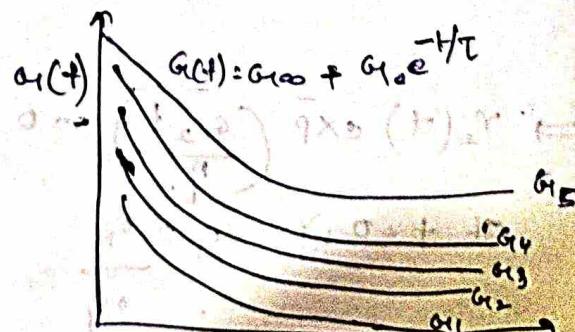
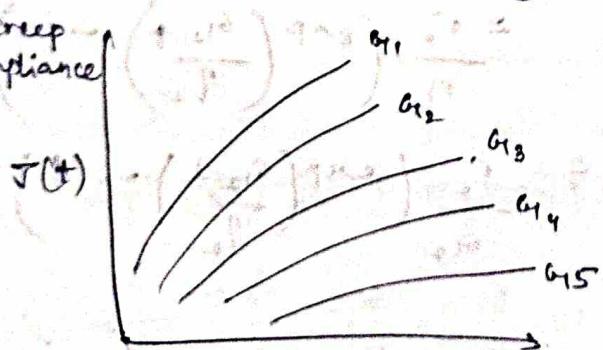
+ wave nature

$$P = \frac{h}{\lambda} \quad k = \frac{h}{\sqrt{2m eV_{app.}}}$$

Assignment (3)

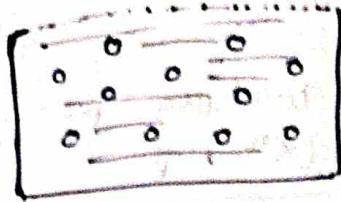


creep compliance

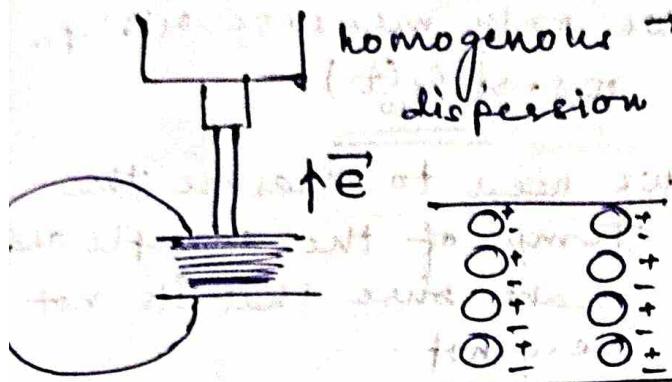


Slower \rightarrow more elasticity.
higher \rightarrow time scale

Project 1 → Electro - Rheology (ER)
(ER fluids)



- Dipolar dielectric particles in oil → stir it dispersion obtained.
- No settling because of increased viscosity



homogeneous → dielectric particles become dipole in the presence of electric field. (polarized)

→ formation of chains

Like toothpaste, there is a certain threshold of strain that needs to be crossed for the particles to flow. Chain of microstructures with elastic character. particles align in chain like fashion and the material becomes solid like. (on applicn of \vec{E}) (μ)

Transition of liq. like to solid like on applicn of \vec{E}

$\boxed{\text{Yield stress after } \vec{E} > \text{yield stress before } \vec{E}}$

Using \vec{E} , we can tune the flowability of a material (how much they can flow)

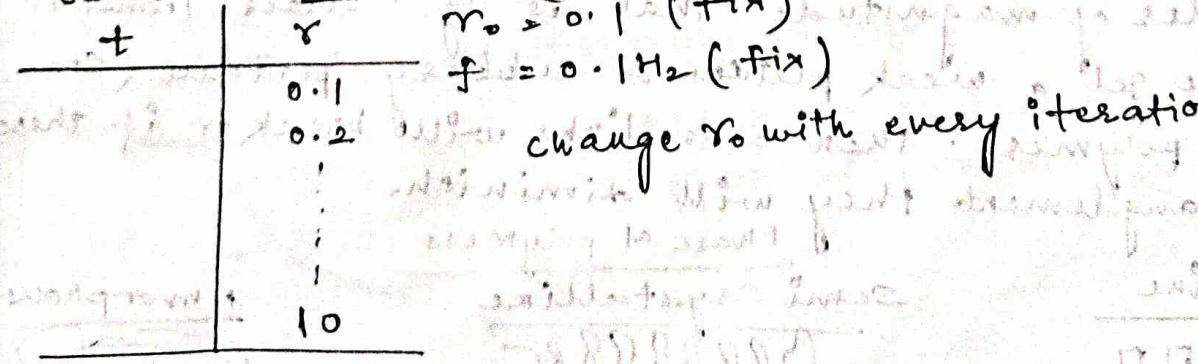
Project 2 → Sinooidal strain profile to be put in practical sense.

input $\rightarrow r_0 \sin(2\pi ft)$

+ $r = r_0 + 0.1 \text{ (fix)}$

$f = 0.1 \text{ Hz (fix)}$

change r_0 with every iteration (new idea)



WAVEFORM

values of

disperse and shear

disperse and shear

WAVE

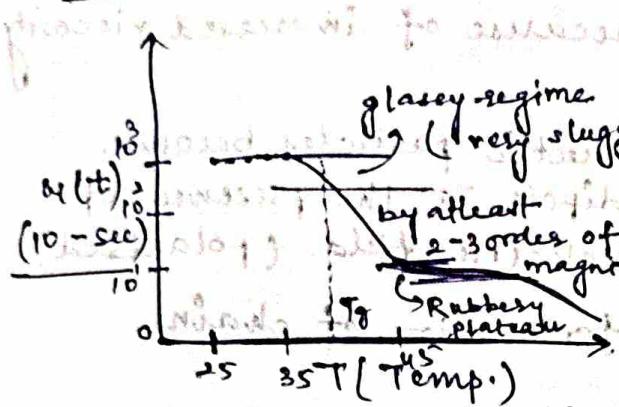
higher index of refraction after applying shear at operating strain

Polymers Rheology

21/10/23

What is a polymer? → collection of monomers connected with each other.

Time-Temperature Superposition:



$T_g \rightarrow$ glass transition Temp.

We are not looking for complete relaxn,

We only measure $\alpha(t)$ for $10^{-5} \rightarrow 10^{-1}$ s $\rightarrow G(t)$.

We need to measure the Temp. of the sample and make sure that it's not very hot.

usually, the T is set to be 25°C .

We apply strain (const.) for sometime and then remove the step strain. We measure the relaxn modulus.

when we go to another T we ignore that again apply step strain for like 10^{-5} and measure the relaxn modulus.

The graph is log-log scale.

Big polymer molecules — many connected monomers. At the start of the experiment, due to application of T .

vibrational & translational energy \uparrow . Thus, as a result entanglement \downarrow . beyond a certain T , the molecules can flow freely. Initially the decrease in entanglement is very slow but at some point there is jump by like 1-3 orders of magnitude. That is $T_g \rightarrow$ Glass Transition T .

Then we get a weak plateau or rubbery plateau (cross-linked polymers). Then cross links will break or if there are entanglements they will diminish.

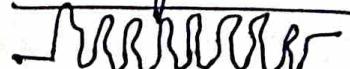
crystalline



proper shape and order

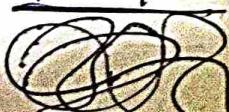
More force reqd. to make polymers crystalline or semi-crystalline

Phase of polymers
Semi Crystalline



order but no proper shape.

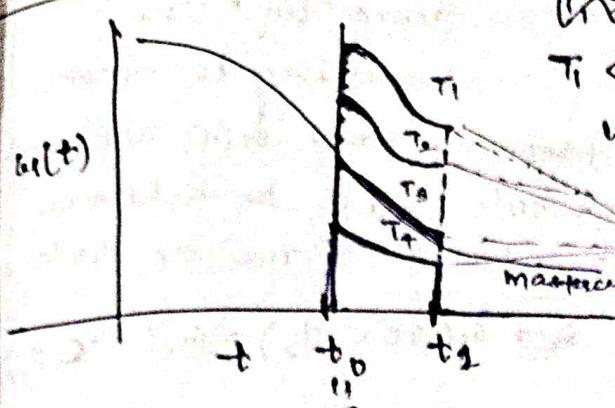
Amorphous



no order

When there are crystals — proper shape & order is there.

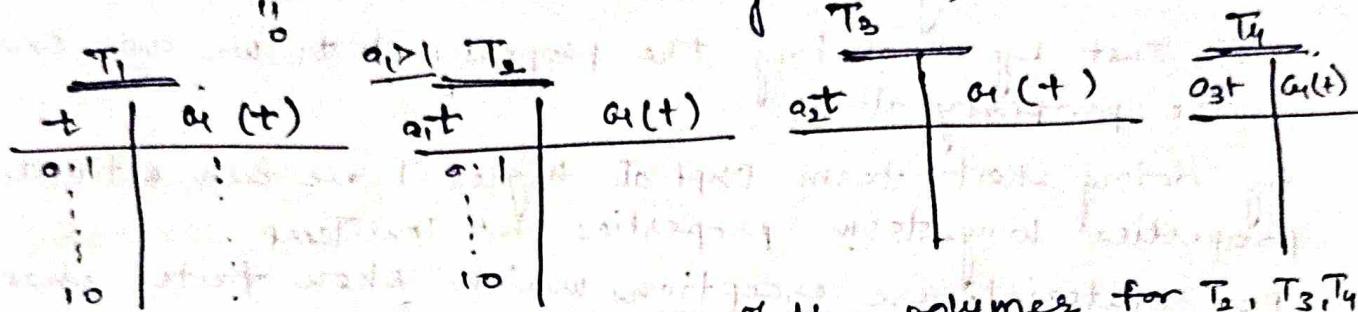
Temperature Superposition:



$$T_4 > T_3 > T_2 > T_1$$

$$T_1 < T_2 < T_3 < T_4$$

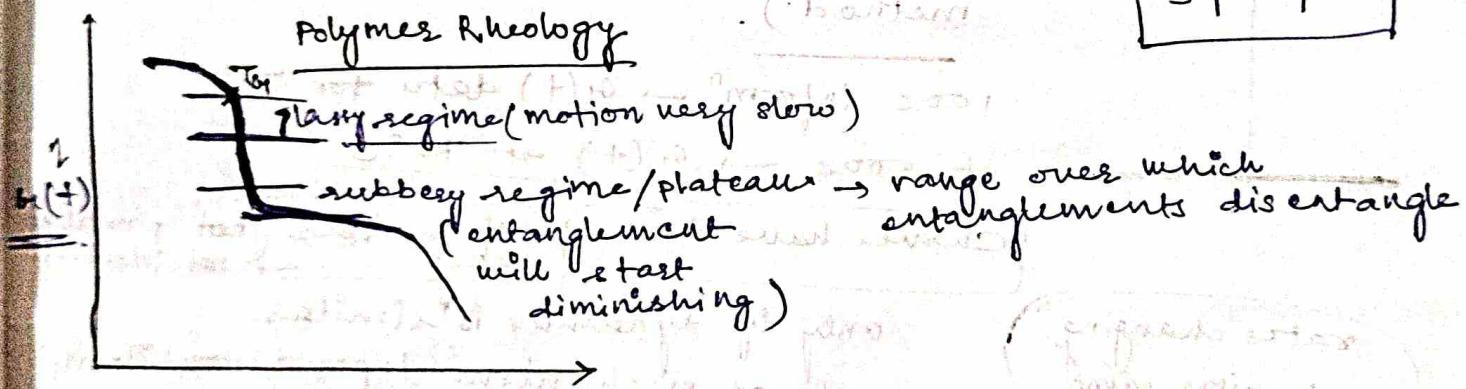
We took a sample, applied σ_{step} for t , time and after making sure that the Temp. has ~~massively~~ reached T_i for all molecules we stop (after removing strain for enough time).



By finding out the response of the polymer for T_2, T_3, T_4 we can find the long term response of the polymer at T_1 . At lower T , the phenomena which is going to happen we can shift it before.

5/10/23

Polymer Rheology

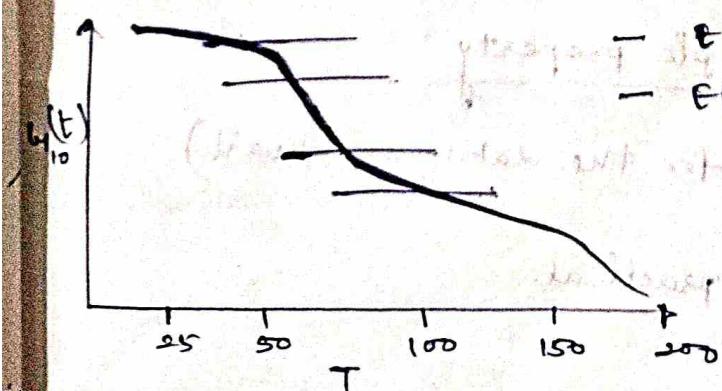


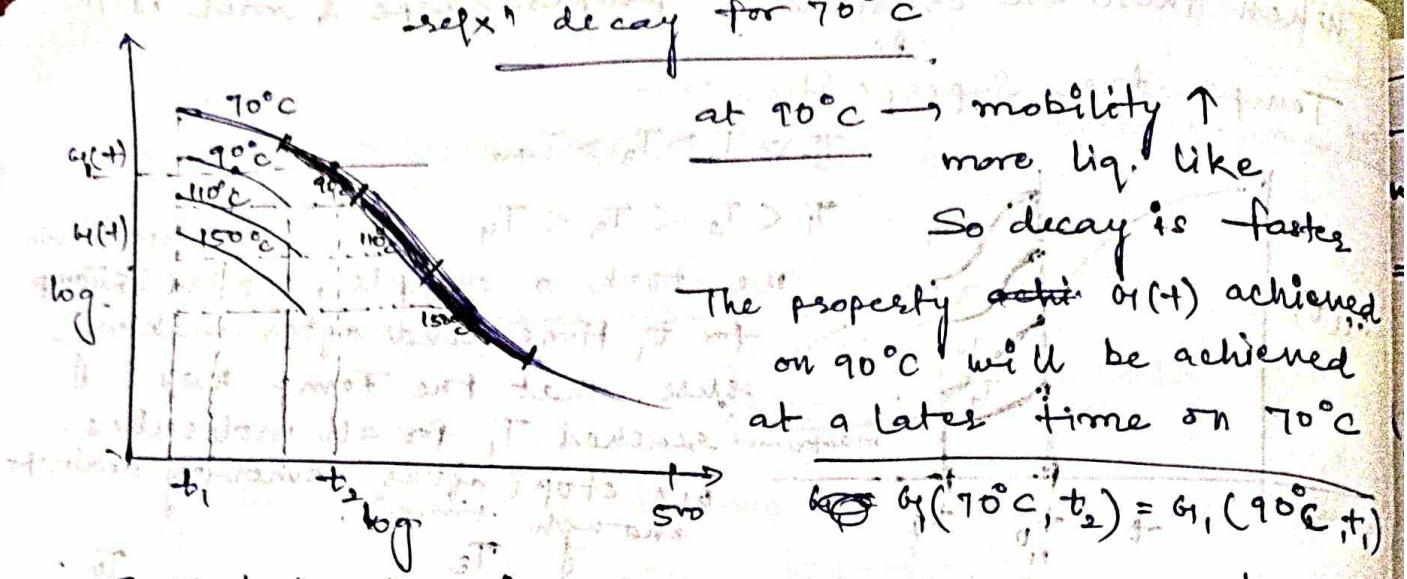
* In case of cross linked polymer \rightarrow cross link will break down (v Temp. Specific)

\rightarrow 2 variables $\rightarrow T, G(t)$

\rightarrow we perform the expt. discretely on different T's.

- Effect of Molecular Wt.
- Effect of crosslinking density





So just by knowing the property at t_1 we can know the property at t_2 .

By doing short-term Expt at higher T we can estimate the properties long-term properties at low Temp.

Few materials are exceptions which show faster change in lower Temp.

* Horizontal Shifting of higher Temp. curve to lower temperature by multiplying with a factor (found by hit & trial method).

<u>t</u>	<u>$G(t)$</u>

100s $\rightarrow G(t)$ data for 70°C

at 500s $\rightarrow G(t)$ at 70°C

Curves have to be self-similar (not parallel, not identical)

only if dynamics is similar

only rate of mechanism depends on Temp.

The mechanism ~~is~~ is independent of Temp.

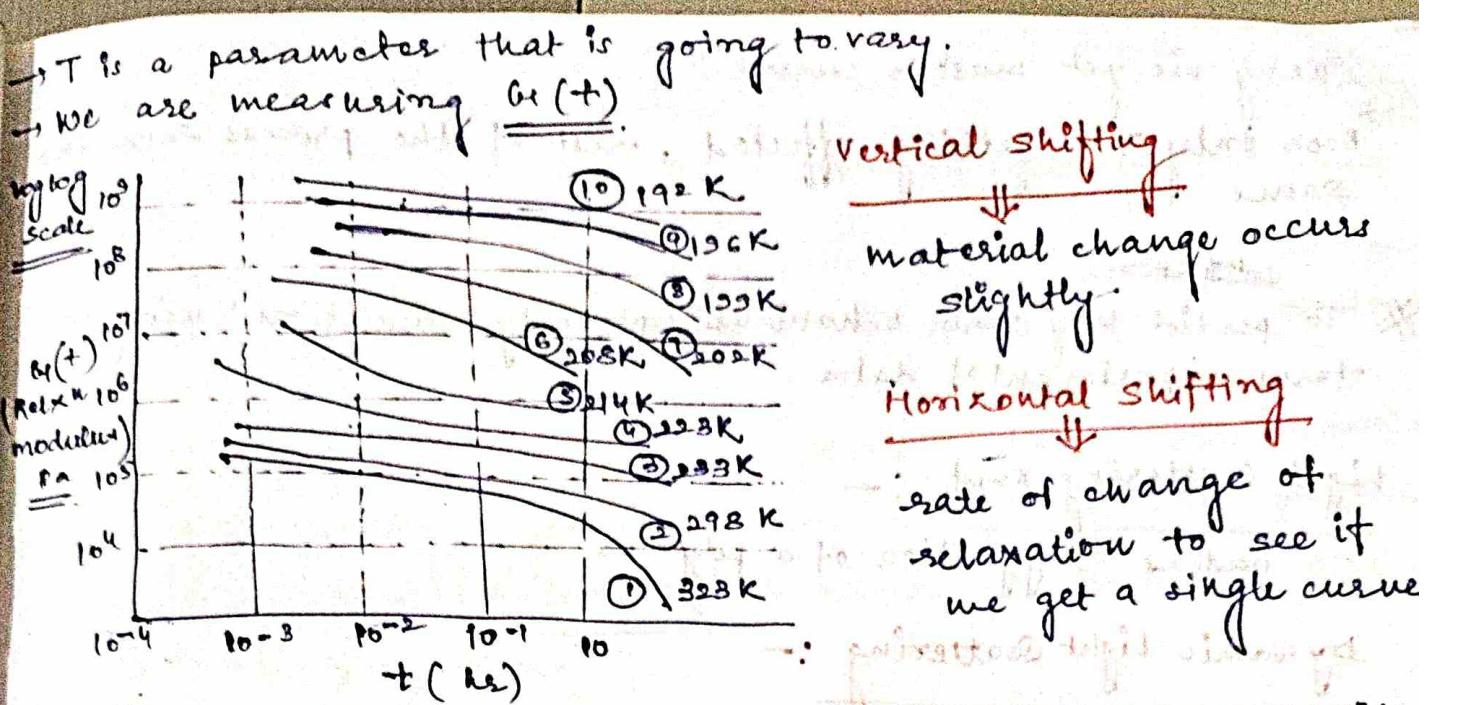
Linear chain polymer

10 - 10 - 2023

\rightarrow our objective is to get macroscopic property

\rightarrow All the T's higher than T_{g} . (for the data see mail)

* Endsem is going to be purely practical.



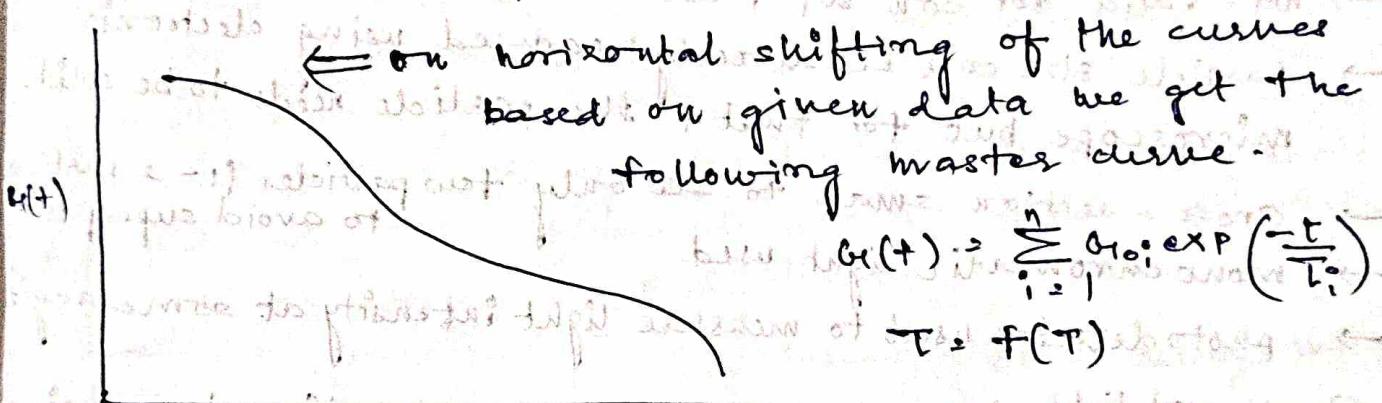
Vertical shifting

↓
material change occurs slightly.

Horizontal shifting

↓
rate of change of relaxation to see if we get a single curve

→ If we have to find out if "Time - Temp. superpos" is valid
 We do look at the Temp. range



→ Higher is the T, faster is the "relax" process. So T is a decreasing $\frac{1}{t}$ of Temp.

→ What accounts for change in T? → Shift factors are manifestation of change in T.

$$G_{T_1}(t) = G_0 \exp\left(-\frac{t}{T_1}\right) \quad (\text{at temp. } T_1)$$

$$G_{T_2}(t) = G_0 \exp\left(-\frac{t}{T_2}\right) \quad (\text{at temp. } T_2)$$

$$T_2 = a T_1 \quad \Rightarrow \quad G_{T_2}(t) = G_0 \exp\left(-\frac{t}{a T_1}\right)$$

some no.

Fundamental parameter for us is "relax" time scale

$$\begin{array}{c} T \rightarrow a_T \text{ (shift factor)} \\ \downarrow \\ f(T) \end{array} \quad \begin{array}{c} \text{if} \\ \downarrow \\ \text{"relax" time scale} \end{array}$$

Why we get master curve?

Because only τ is getting affected, rest of the process remains same.

- * To predict long term behaviour (property estimation) using short term experimental data.

Light scattering Expt.:-

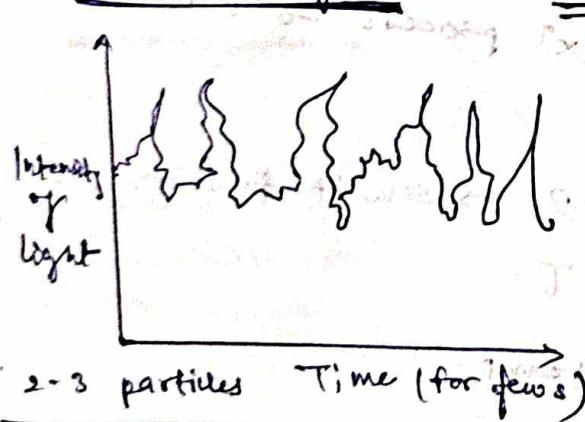
radius of gyration of a polymer

Dynamic Light Scattering :-

Effective particle size depends on the solvent the particle is dissolved in.

- not valid for conc soln, use dil. soln
- particle size can be directly measured using electronic microscope but for that, the particle needs to be solid.
- cross-section small to see only few particles (1 - 2 particles)
- monochromatic light used. to avoid superposn
- photodetector used to measure light intensity at some angle

Scattered light :-



⇒ Photodetector takes time to give one intensity values after that time only, we get one data point

⇒ The particle goes away after some time, so intensity memory will fade with time, correl b/w

particles dies out after sometime

⇒ Mobility is hindered in case of more no. of particles (or \uparrow conc) so memory of correl may remain for some time. (for \downarrow conc, mobility \uparrow , memory fading \uparrow)

⇒ correl b/w intensity pts. decay.

⇒ In case of bigger particles, relax is slower as mobility \downarrow for smaller particles, mobility \uparrow , so correl "memory" decays faster (relax faster).

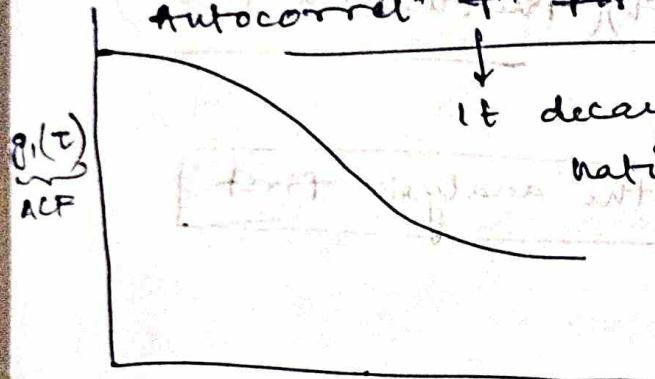
Autocorrelⁿ fn is a type of method which can be used to explain a lot of things.

Using this, we get an idea → size of particles through mobility correlⁿ.
↳ from here, we get to know if the polymer likes the solvent (more soluble & radius of gyration ↑) or does not (rad↓)

generic use of autocorrelⁿ fn → [Checking how much brownian motion is getting affected] & the [correlⁿ b/w the particles & solvent] and [before-after condⁿ of particles for a duration of time].
correlate 2 data pts. → take the reference & multiply it.

any data changing with time is time series.

autocorrelⁿ fn for intensity data in our case



it decays due to the electromagnetic nature of waves (smaller particles → decay faster)

Any intensity data decays with time for a fixed point

$$ACF = 1 + \beta \exp(-\frac{\tau}{T})$$

If we have monodispersed particles, then → this is valid.

Not valid for polydispersed particles.

T → related to particle properties → ∇q^2
↓
diffusivity

$$q = \frac{4\pi}{\lambda} \sin\theta$$

$$\beta = \frac{kT}{c\pi\mu R}$$

ACF will die out.

We can estimate particle size using Intensity data fitting.

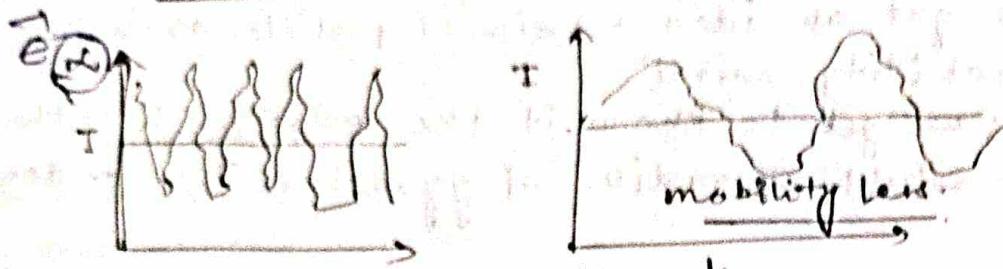
2 process -

- ① Hydrodynamic force.
- ② Thermodynamic force.

Dynamic Light Scattering

12/10/20

Bruce J. Bass
and
Robert Pecora



interaction b/w molecules electron cloud & electric field of electromagnetic wave (light)

* Whenever you correlate ACF of intensity fluctuation

$$\frac{\langle I(t), I(t+\tau) \rangle}{\langle I(t) \rangle} g^2(\tau) = 1 + A \exp(-\tau/\tau) \underbrace{e^{i\vec{e}(t)\vec{e}(t+\tau)}}_{g'(\tau)} \underbrace{\delta''(\tau)}_{\text{due to the } \vec{e} \text{ of the particle}} (\text{fluctuation in } \vec{e})$$

Multipponential decay

$\eta_2 \rightarrow$ polydispersity index.

* Polymers grafted Nanoparticle

Explain the analysis first

We consider effect

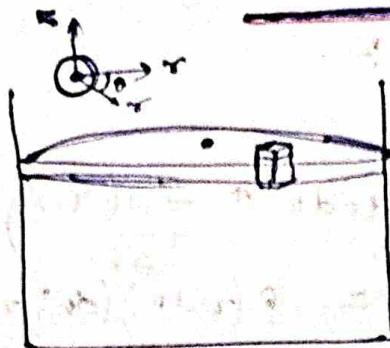
Step 1:- force balance \rightarrow stress \times area = force

normal shear

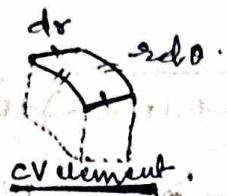
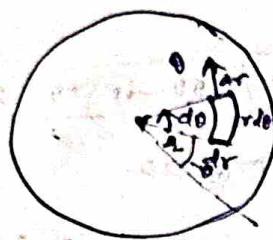
Weissenberg Effect

→ vortex form
→ rod climbing effect.

17-10-23



- differential volume.
- Fluid rotation \rightarrow clockwise dirⁿ.
- dirⁿ of flow \rightarrow a disk.
- vel. gradient in or disk:
max. at the centre
min (or zero) at the tip (edge)



σ_{xx} \rightarrow acting on the plane exactly 1^r to a disk

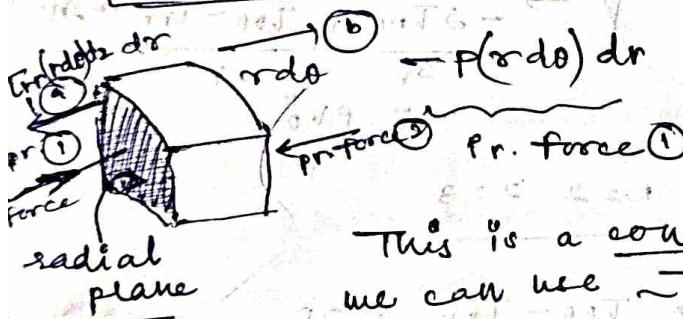
We are only considering normal stresses
force balance in radial dirⁿ! —

Eqn of motion in circular disk
all the forces = centripetal force ($\frac{mv^2}{r}$)

$\sigma_{rr} = \text{normal stress} + \text{deviatoric stress}$

$$\sigma_{rr} = -\frac{p}{(pr)} + \tau_{rr} \quad (\text{change in vol.})$$

p can change τ can only change shape
 τ both are opp. in nature
 p tries to compress vol
 τ tries \uparrow the vol.
(try finding more differences b/w the 2)

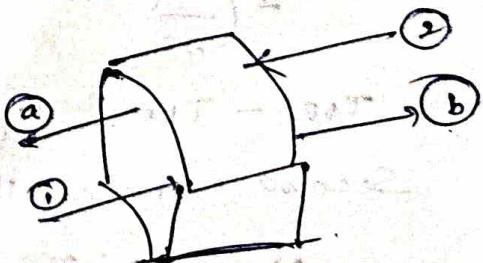


This is a continuum means we can use ~Taylor Series. All the f's are continuous and differentiable f's (smooth f's)

continuum approximⁿ is generally valid till you

Kinematic approximⁿ \rightarrow continuous or not.

$$① p(r do).dr + \left(\frac{\partial (pr \partial \theta dr)}{\partial r} \right) dr$$



$$② (T_{rr})r do$$

$$③ (T_{rr})r do + \left(\frac{\partial (T_{rr} r do)}{\partial r} \right) dr$$

$P_1 = P_2 = 0$ \rightarrow plane balance!

$$P_{xx} = -P + T_{xx}$$

$$-P dr dz + (T_{xx}) dr dz + \frac{\partial(r T_{xx})}{\partial r} dr dz + \frac{\partial(r dr dz)}{\partial r} = .P(dr dz)(dr) \frac{v^2}{2r}$$

$$(P_{xx} dr dz)(dr dz) = T_{xx} dr dz$$

$$- \frac{\partial}{\partial r} (T_{xx} dr dz) dr dz$$

$$\rightarrow -P + T_{xx} - \frac{\partial(r T_{xx})}{\partial r} + \frac{\partial(P_{xx})}{\partial r} = P v^2$$

30/10/23

$$f = P r d\theta dz$$

$$\rightarrow T_{xx} = r dT_{rr} - T_{rr}$$

$$+ \frac{\partial P}{\partial r} - P v^2$$

$$\rightarrow -\frac{\partial T_{rr}}{\partial r} + \frac{T_{xx} - T_{rr} + \partial P}{r} = \frac{P v^2}{r}$$

$$\rightarrow \sigma = \frac{1}{r} r = 2 \quad 2 = 3$$

$$-\frac{\partial T_{rr}}{\partial r} + \frac{T_{xx} - T_{rr} + \partial P}{r} = \frac{P v^2}{r}$$

$$+\frac{\partial T_{22}}{\partial r} - \frac{\partial T_{22}}{\partial r}$$

$$\rightarrow \sigma = \left(\frac{\partial}{\partial r} (T_{rr} - T_{22}) \right) + \left(\frac{\partial}{\partial r} (T_{22} - P) \right) + \left(\frac{T_{xx} - T_{rr}}{r} \right) = \frac{(\bar{\sigma}) P v^2}{r}$$

for polymer melt

$$T_{xx} - T_{rr} = N_1 = \text{first Normal stress difference}$$

$$\text{Second Normal stress difference } T_{rr} - T_{22} = N_2$$

$$-\frac{\partial N_2}{\partial r} + \frac{\partial(T_{22} - P)}{\partial r} = \frac{N_1 - P v^2}{r}$$

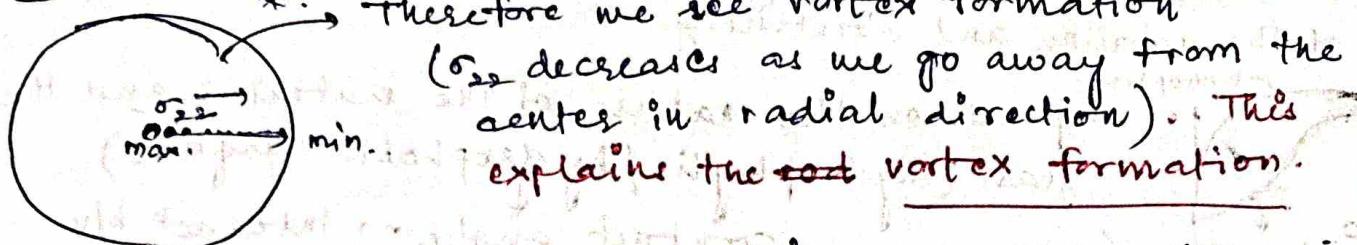
$N_2 \ll N_1$ $\Rightarrow \frac{\partial(T_{22} - P)}{\partial r} = \frac{N_1 - P v^2}{r}$

$$\rightarrow \frac{\partial T_{22}}{\partial r} = \frac{N_1 - P v^2}{r}$$

(Newtonian fluid) $\Rightarrow N \approx 0$. $\frac{d\sigma_{22}}{dr} = \frac{\rho v_0^2}{r}$

This

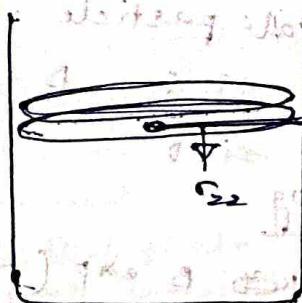
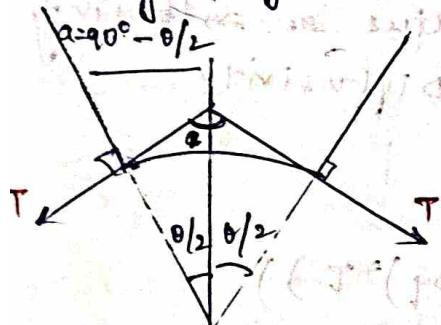
force is max. near the centre and lowest near the periphery
Therefore we see vortex formation



(σ_{22} decreases as we go away from the center in radial direction). This explains the ~~vortex~~ vortex formation.

* if for some fluid $N_1 \gg \rho v_0^2 \rightarrow$ Then σ_{22} will be an $\uparrow f^n$ of $r \rightarrow$ So fluid will be pushed most at the periphery (pulled most at the center) This explains the rod climbing effect (N_1 is large) $\rightarrow N_1 = T_{00} - Trn$

Long polymer solution.



occurs in non-linear regime



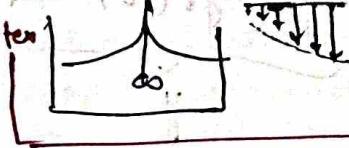
$$N_1 = T_{00} - Trn \text{ conc}$$

long polymer chain solution
 N_1 is large

For dilute solution :-

particle dispersion $N_1 = \Theta$

Why the rise & drop ("form" of a vortex up or down)?



$$T \cos(90^\circ - \frac{\theta}{2}) = T \sin \frac{\theta}{2}$$

θ is very small $\rightarrow T(\frac{\theta}{2})$

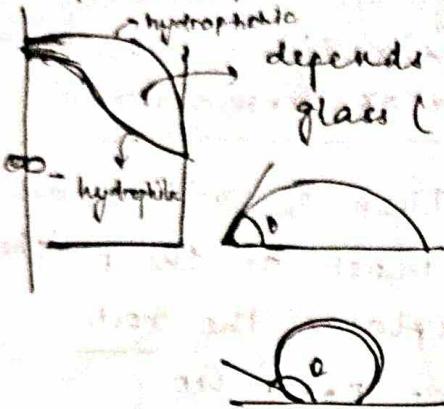
$$T \text{ Both sides} \Rightarrow \text{Total } T = T(\frac{\theta}{2}) \times 2 = T\theta$$

So, Total force \rightarrow radially inward when the beaker is rotated vigorously.

* must have the property to get stretched (the long polymers chain being rotated). rotation \rightarrow vigorously to stretch the polymer chains

In particle dispersion, rod climbing effect cannot be observed because they cannot be stretched.

- Impaction
- Tension in polymer chain \rightarrow originated due to the alignment of polymer chain along the flow.
- Because of T_{rr} , T_{tt} get generated \rightarrow these generate only because of the rotation and stretching.



(depends on the nature of the material and the glass (hydrophytic/hydrophobic surface))
contact angle \rightarrow interaction b/w material and glass (surface free)

$+$	$Arc \ g_2(\tau)$
\vdash	\vdash

You are given auto correlation function

$$g_2(\tau) = A + B \exp(-(\frac{D}{q})\tau)$$

cal. particle radius or diffusivity

$$q = \frac{4\pi r}{3} \quad D = \text{diffusivity}$$

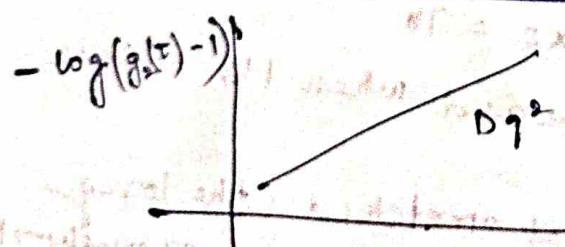
Sir ka favourite \rightarrow Log

$$\log(g_2(\tau)) = \log(A + B \exp(-(\frac{D}{q})^2 \tau))$$

$$\rightarrow \log(g_2(\tau) - 1) = \log B + -(\frac{D}{q})^2 \tau$$

$$\rightarrow -\log(g_2(\tau) - 1) = -B + (\frac{D}{q})^2 \tau$$

$$y = mx + c$$

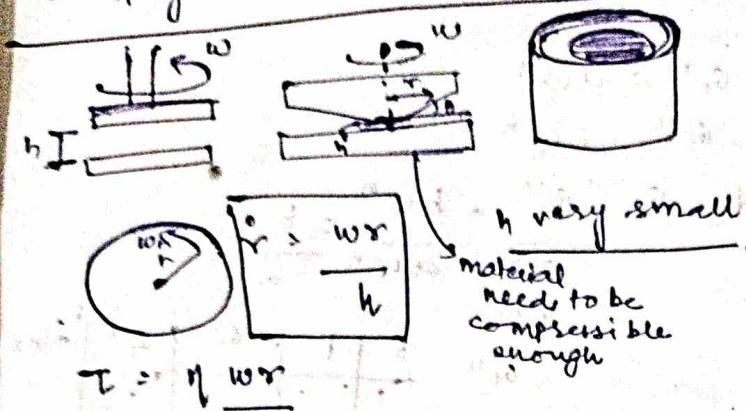


Theory depends on the assumption that all the particles are following Brownian motion

concept of DL's can be used

- Time Temp Superpos
- Other types of Superpos \rightarrow When mechanism is not changing only rate is changing
- Purpose of Superpos (self-similar curves)

- Is it always guaranteed that on horizontal displacement we get a single master curve? → Entanglement mechanism should be same otherwise no.
- Time conc superpos"
 - Any parameter that can slow down the relax"



No way to apply const. stress bcoz at each pt. stress is different (Torque can't be const.)

$$T \text{ (Torque)} = \vec{\tau} \times \vec{F}$$

$$dF = \tau (r d\theta) dr$$

stress × area

problem with parallel plate rheometers → can't get const. shear rate (different tangential velocities)

$$\tau \text{ (Torque)} = Th (r d\theta) dr \times r \times \sin\left(\frac{\pi}{2}\right)$$

$dM = \int r dF \cdot r = \int \tau r^2 d\theta dr$

all the torques in axial dir^h (Dir same) → So we can simply integrate.

$$M = \int_0^R \eta w r^3 dr (2\pi)$$

$$M = \left(\frac{1}{6} \eta \pi R^4 \right)$$

Stress derivation is not really possible.

tanθ = $\frac{r}{y} \rightarrow y = \frac{r}{\tan\theta}$

$v = wr$

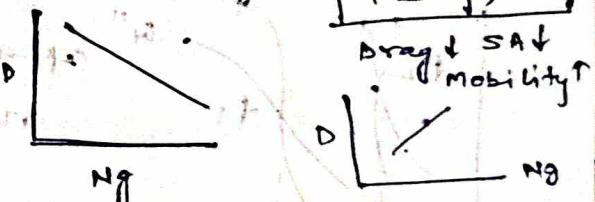
$\dot{y} = wr + wr \cdot \frac{1}{\tan\theta} = wr + w \cdot \tan\theta$

We can maintain a const. shear rate & shear stress in this case.

1 bead = 4C chain
Polymer grafted Nanoparticle
 N_g (no. of polymers)
 N (no. of beads)
covalent bond b/w polymers & NP grafting density.

N_g is high
Brush config
Steric repulsion
(Polymers chains cannot fold)
mobility low
stokes

N_g is low
Mushroom config
(polymers chains fold within themselves)
decay faster bcoz mobility higher (OLS Theory)

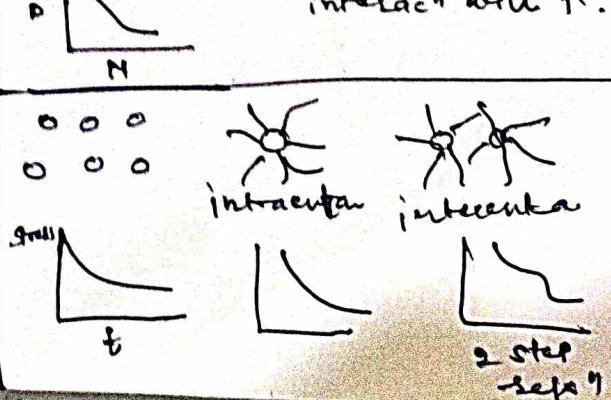


If high conc resin → interentanglement diffusivity ↑ as we graft more nanoparticles. (grafting density↑)
Beyond a certain grafting density the repulsion is much stronger b/w chains.

mean sq. displacement v/s time
dist. 2 min / 5 min / 10 min → P64N
 $D = \frac{1}{2} \langle \Delta r^2 \rangle$ on avg is diffusivity

Track the trajectory
Mean disp. → (square of it)/Time
Then get diffusivity.

Chain length ↑ → interentanglement
intermolecular interaction with T.



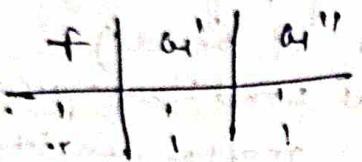
$$\text{written} \quad g_0(\tau) = A + B \exp(-\tau^2 D \tau)$$

$$\text{get} \quad -\ln(g_0(\tau) - 1) = -B_1 + (\tau^2 D) \tau$$

$$\frac{\tau}{10^{-6}} \quad \frac{g_0(\tau) - 1}{}$$

Cyclic frequency Sweep

$$v = v_0 \sin(2\pi f t)$$

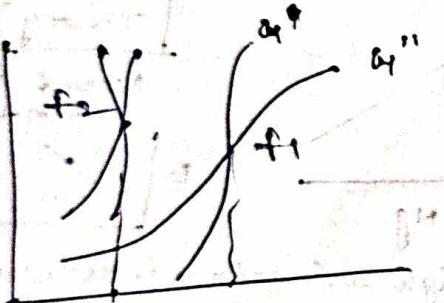
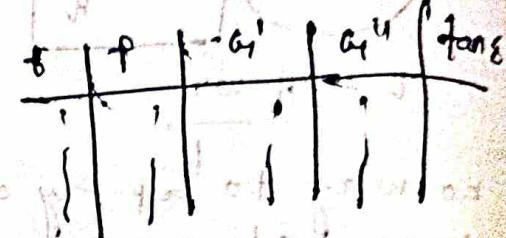


for gel :-

$$a' = aw^n$$

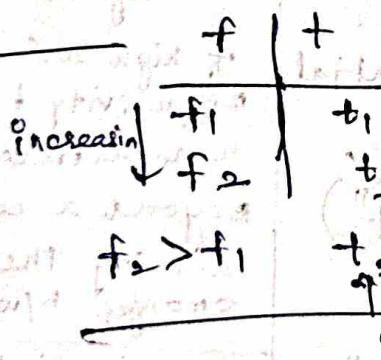
$$a'' = bw^n$$

$$\tan S = \frac{a''}{a'} = \frac{bw^n}{aw^n} = \frac{b}{a}$$



$$\text{apparent } t_{\alpha} = \text{gel(pt.)} \quad \tau = 3.75$$

our freq. should not change our gel pt



Method should be independent of frequency
Both a' and a'' show identical exponent
(only const. associated is different)

The t where $\tan S$ is identical for all the pts. (all the frequencies same), is known as the true gel pt.

$$(P_A)(N) = N$$

where P_A is polarization