# Introduction to Rheology of complex fluids
# Brief Lecture Notes

## Kinematics and material functions for shear flows



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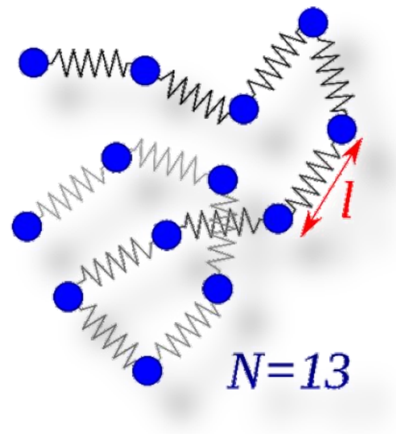
# Contents





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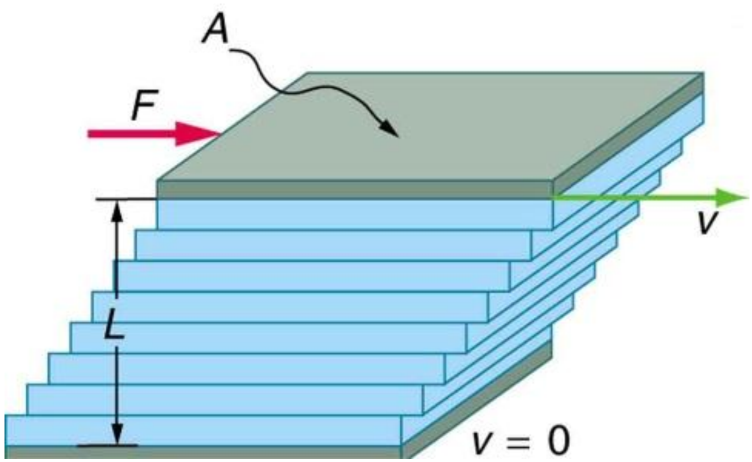
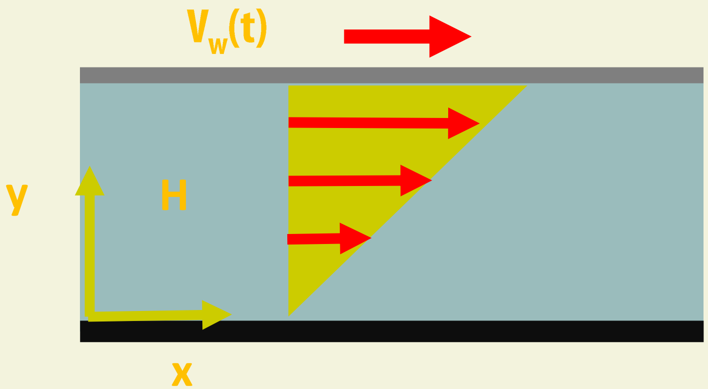



# Kinematics of Couette flow

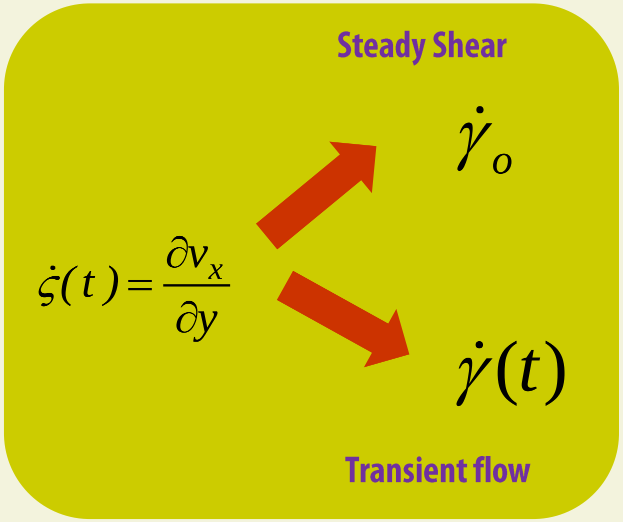
# Couette flow in parallel plates

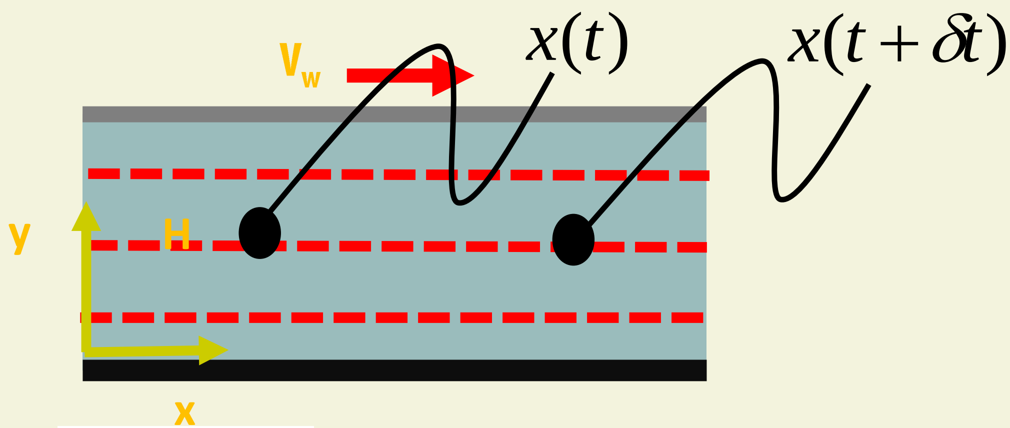



$$v_x(H)=V_w(t)=\dot{\gamma}(t)H$$

$$\underline{v}=\dot{\varsigma}(t)y\,\underline{e}_x$$

$\dot{\varsigma}(t)$ **Deformation rate**




**Path lines**

# Rate of deformation tensor for shear flow

Velocity Fields

$$\underline{v} = \dot{\varsigma}(t) y \underline{e}_x \qquad \dot{\varsigma}(t) = \frac{\partial v_x}{\partial y}$$

Rate of deformation tensor

$$\underline{\underline{\dot{\gamma}}} = \begin{pmatrix} 0 & \dot{\varsigma}(t) & 0 \\ \dot{\varsigma}(t) & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Rate of deformation magnitude

$$\dot{\gamma}(t) = \left|\underline{\underline{\dot{\gamma}}}\right| = \left|\nabla \underline{v} + (\nabla \underline{v})^T\right| = \frac{\sqrt{\underline{\underline{\dot{\gamma}}} : \underline{\underline{\dot{\gamma}}}}}{2} = \left|\dot{\varsigma}(t)\right|$$

Always positive

It can be positive or negative

**The rate of deformation may depend on time, but not in space.**

These flows are called homogeneous.



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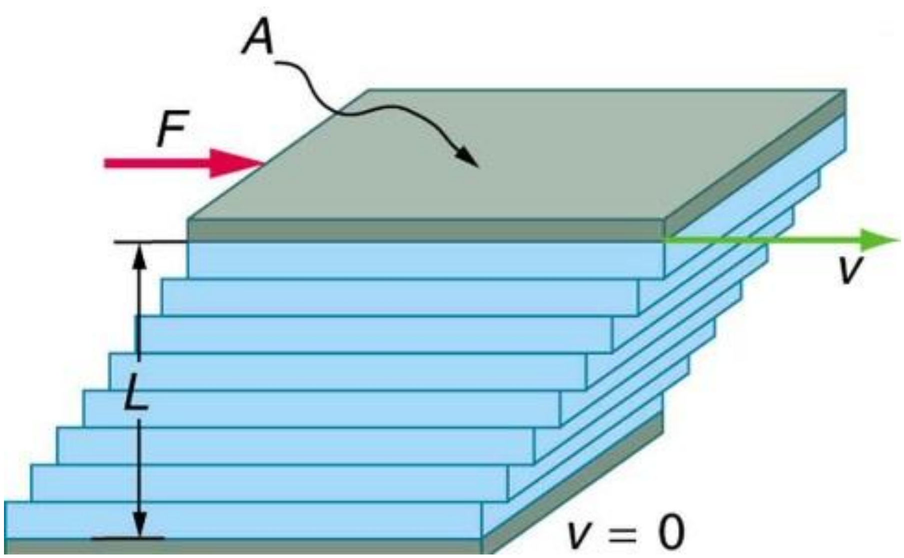
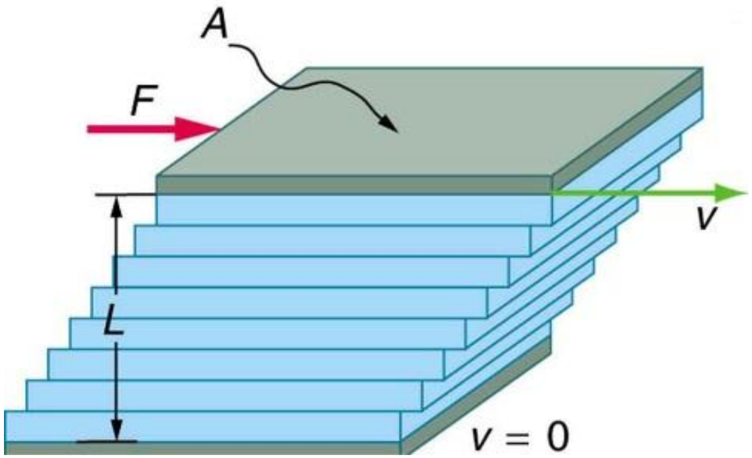
# Why shear-flow is a standard flow;

- It is the simplest flow field
- It represents various, more complex laminar flows
- The stress tensor has a simple form: 2x2 nonzero entries






# Shear Flows



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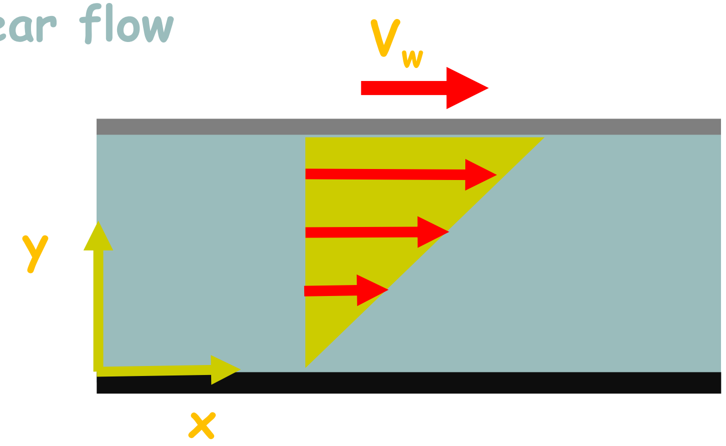
# All possible shear flows

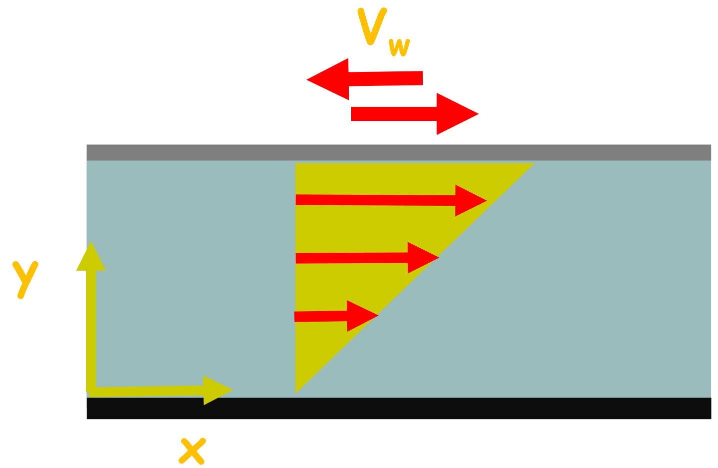
1. Steady shear flow




Velocity field

$$v_x = \dot{\gamma}_o\, y$$

2. Small amplitude oscillatory shear




$$v_x = \dot{\gamma}_o \cos(\omega t)\, y$$



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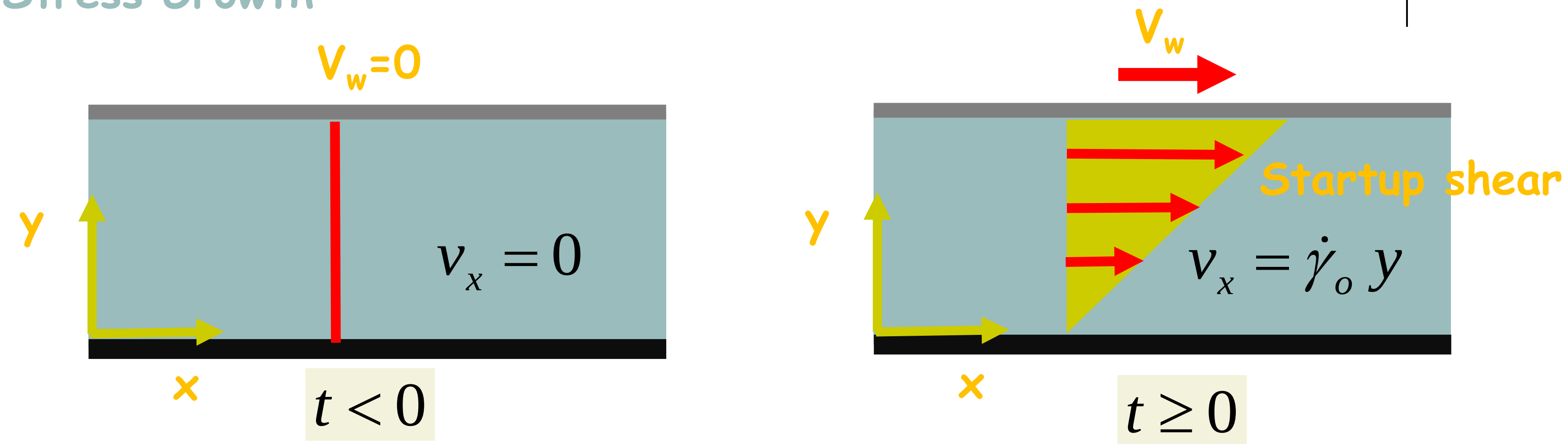
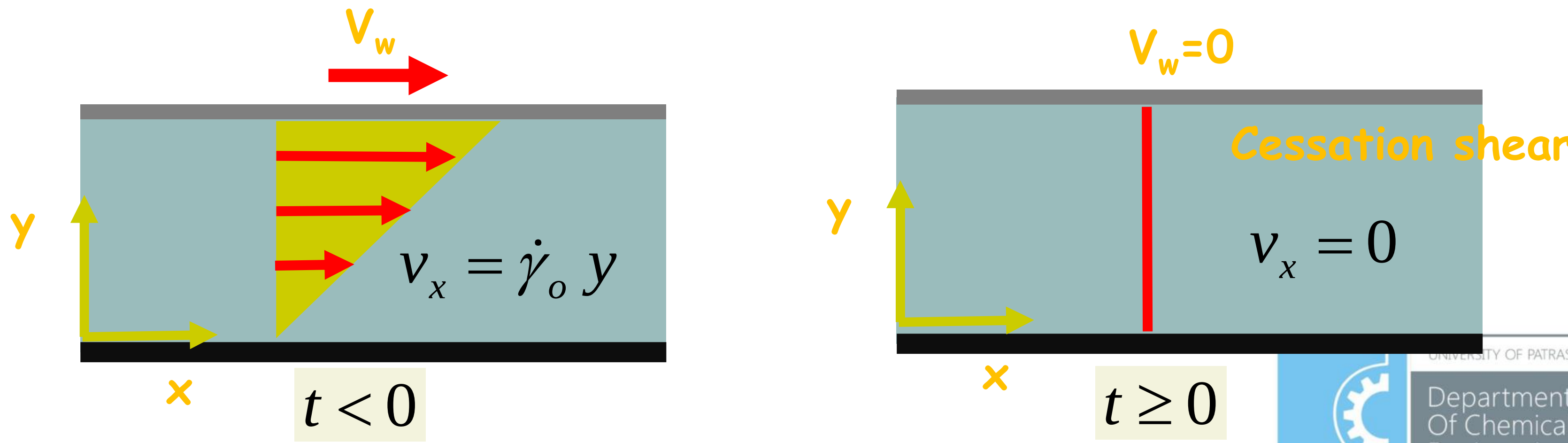
# All possible shear flows

## 3. Stress Growth

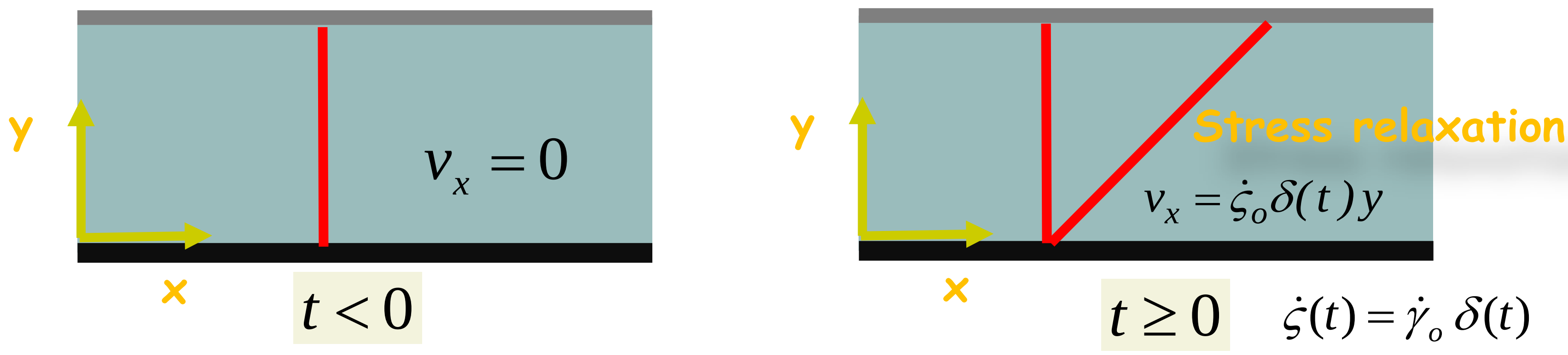



## 4. Stress relaxation

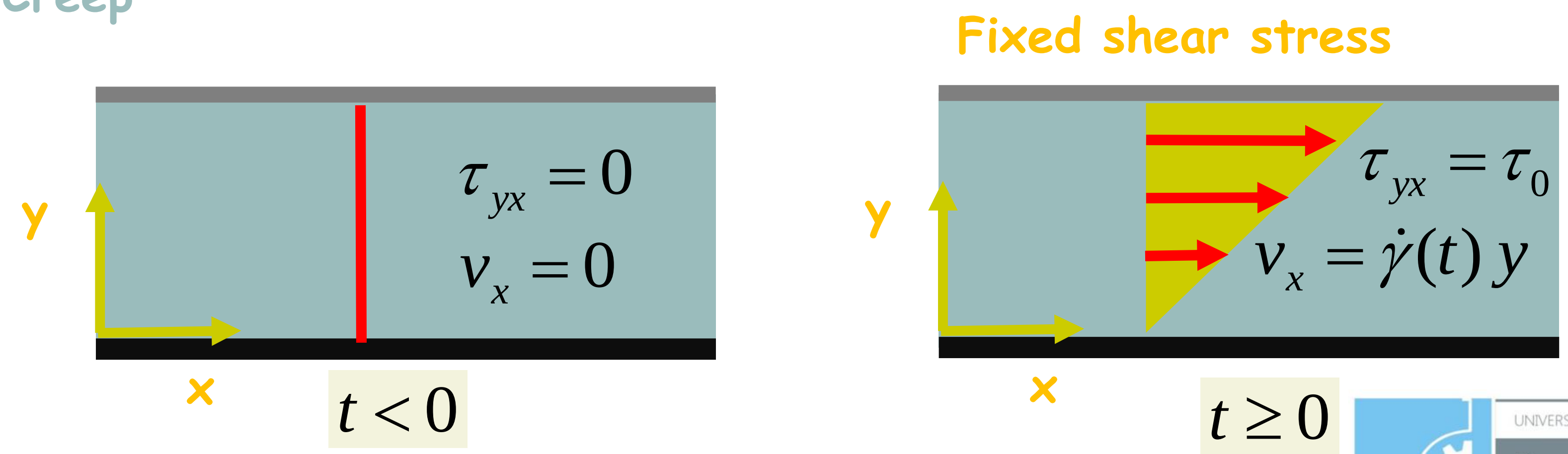


# All possible shear flows

## 5. Step strain




## 6. Creep

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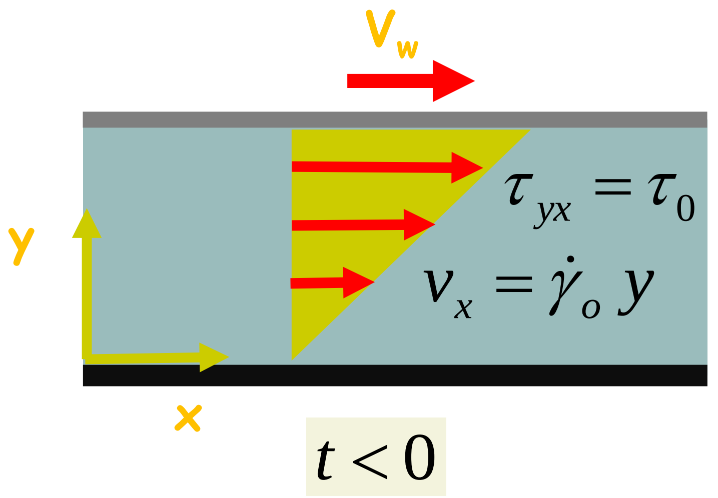
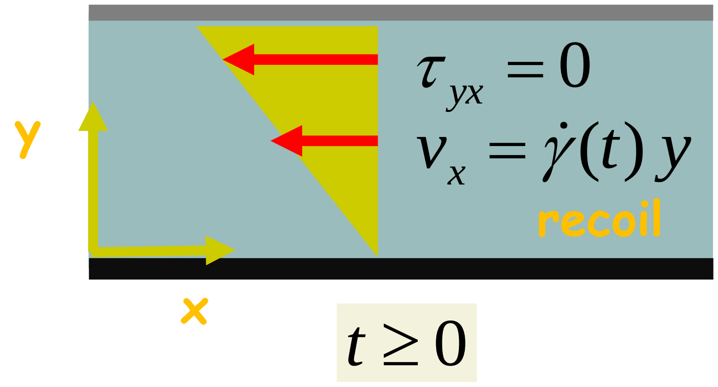
# All possible shear flows

## 7. Constrained Recoil after steady Shear Flow



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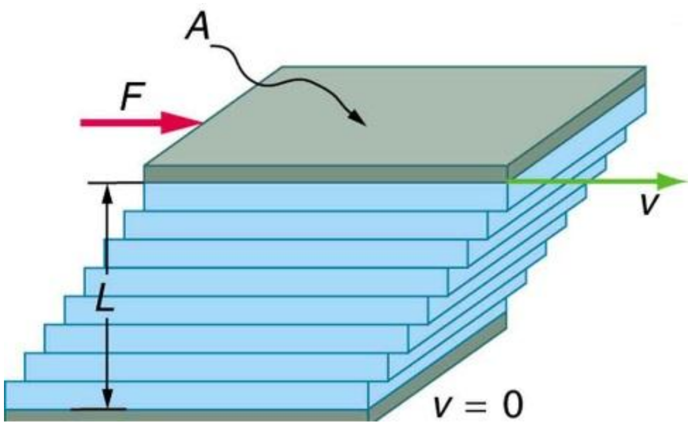


# Steady Shear Flow



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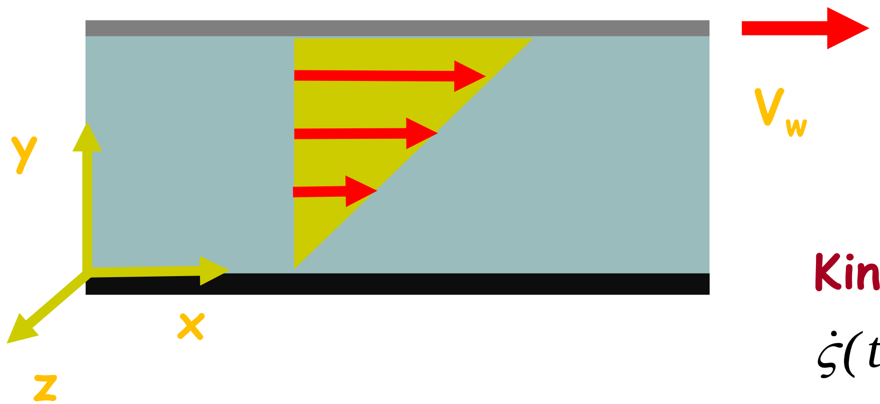
# Steady shear flow

Velocity Field

$$v_x(x,y,z) = \dot{\gamma}_o\, y$$

$$v_y(x,y,z) = 0$$

$$v_z(x,y,z) = 0$$




Notation

1,2,3 ⟷ x,y,z

Kinematics

$$\dot{\varsigma}(t) = \dot{\gamma}_o$$

Material properties

Viscosity

$$\eta = \frac{\tau_{xy}}{\dot{\gamma}}$$

$$\eta = \eta(\dot{\gamma})$$

Coefficient of 1st normal stress difference

$$\psi_1 = \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}^2}$$

$$\psi_1 = \psi_1(\dot{\gamma})$$

Coefficient of 2nd normal stress difference

$$\psi_2 = \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}^2}$$

$$\psi_2 = \psi_2(\dot{\gamma})$$



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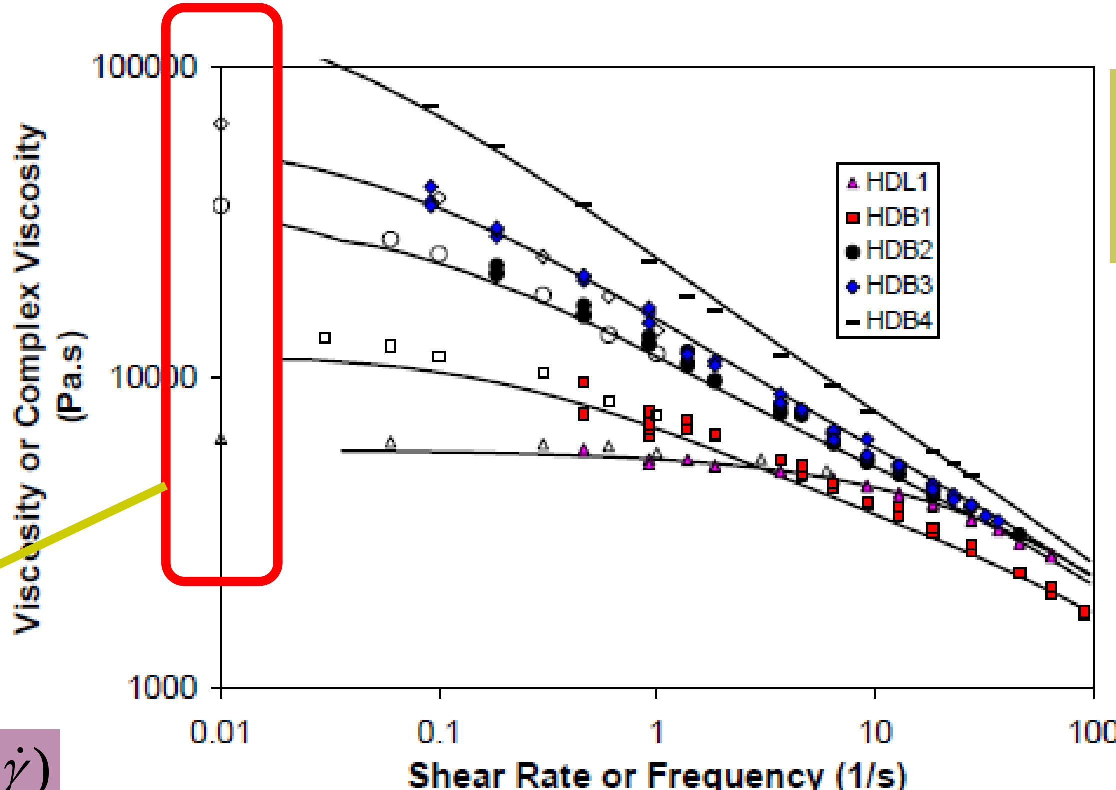
# Material properties: shear viscosity

$$\eta = \frac{\tau_{xy}}{\dot{\gamma}}$$




A typical polymeric fluid

$\eta_o$

$$\eta_o = \lim_{\dot{\gamma} \to 0} \eta(\dot{\gamma})$$

**At low shear rates the viscosity is independent of the shear rate. It is called zero shear rate viscosity $\eta_o$.**



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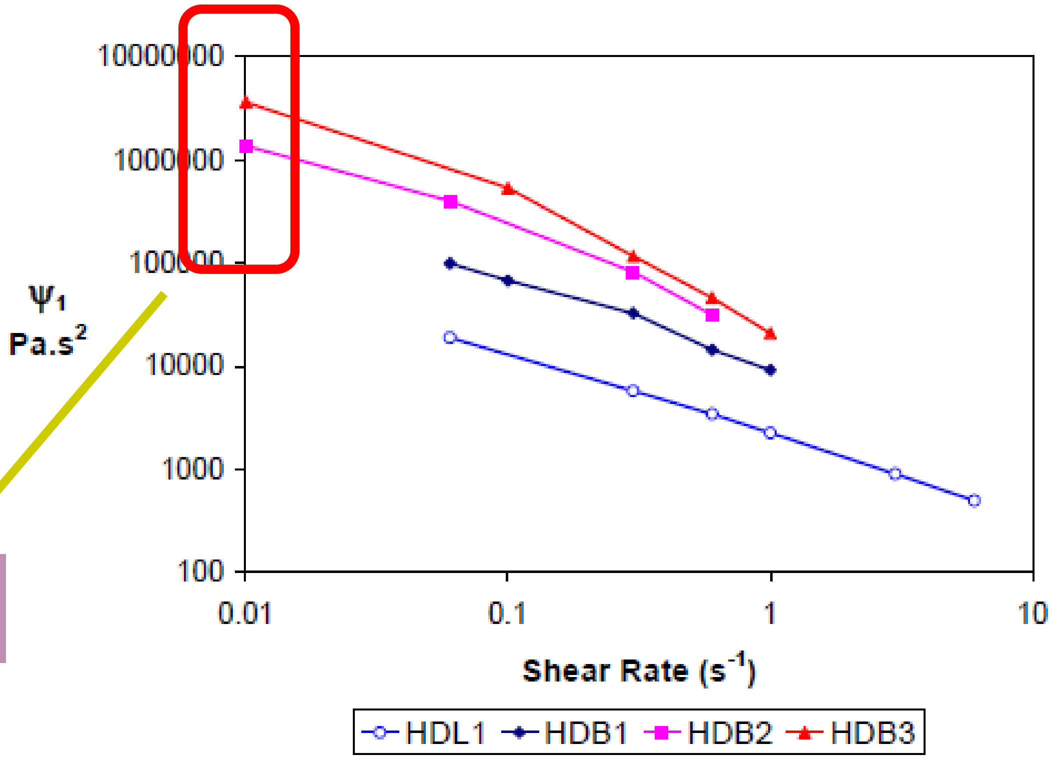
# Material properties: $\Psi_1$

A typical polymeric fluid

$$\psi_1 = \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}^2}$$




$$\psi_{1,o} = \lim_{\dot{\gamma}\to 0} \psi_1(\dot{\gamma})$$

**For Newtonian Fluids** $\psi_1 = \psi_2 = 0$



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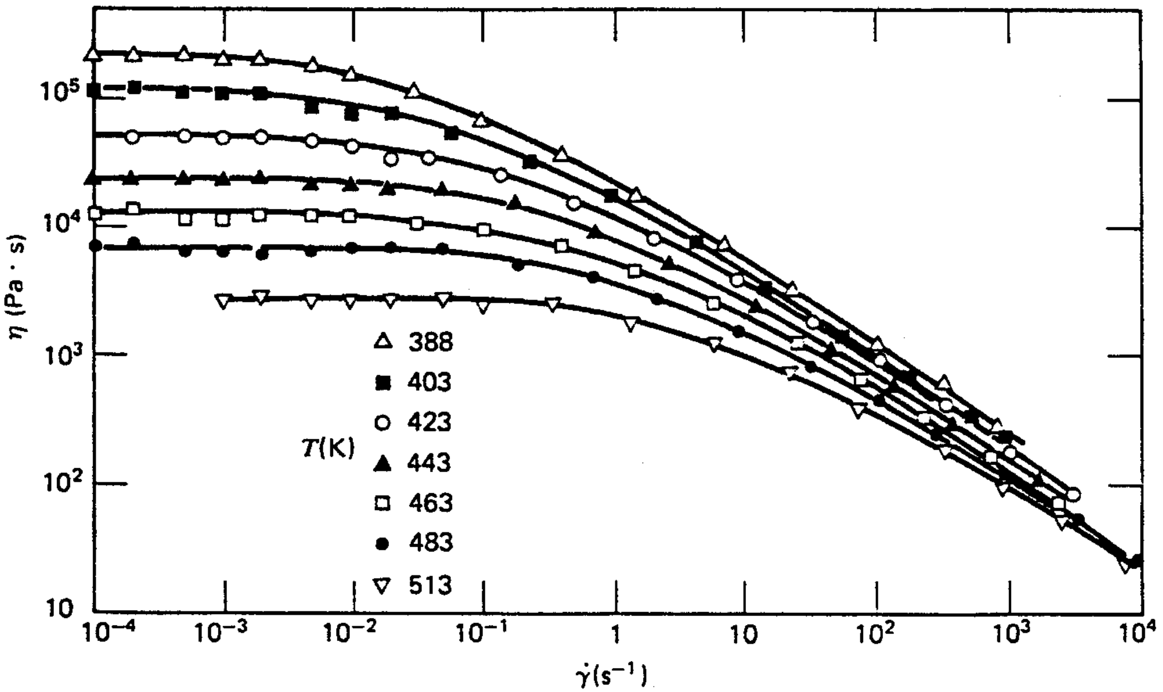
# Material properties: shear viscosity for melts

$$\eta = \frac{\tau_{xy}}{\dot{\gamma}}$$




Polymer melts

Viscosity of LDPE melts at various temperatures



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# Material properties: shear viscosity for solutions

Polymer Solution

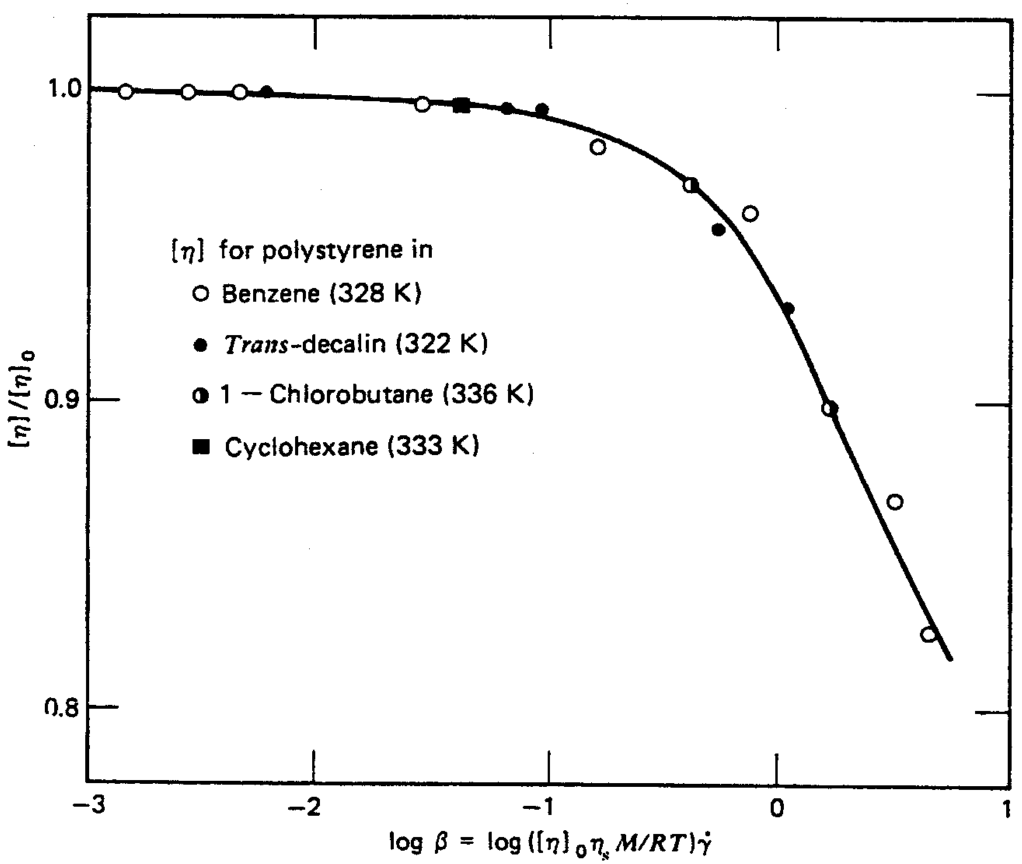
Intrinsic viscosity:

$$[\eta] \equiv \lim_{c \to 0} \left( \frac{\eta - \eta_s}{c \eta_s} \right)$$

c: polymer concentration

Higgins Law:

$$\eta_r = \frac{\eta}{\eta_s} = 1 + [\eta]c + k'[\eta]^2 c^2 + \cdots$$




The intrinsic viscosity **[η]** of polystyrene in various solvents, as a function of a normalized rate of deformation, ***β***.
$[\eta]_o$: zero shear value, $\eta_s$ solvent viscosity.

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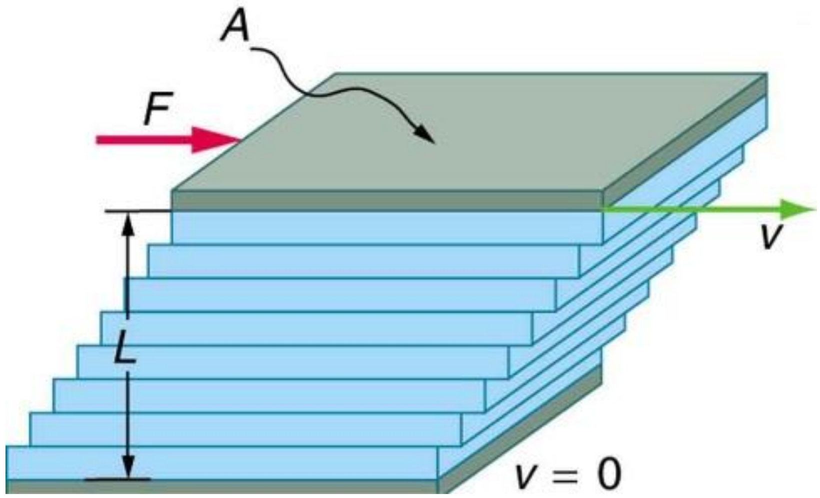


# Startup of Steady Shear Flow

## or Stress Growth



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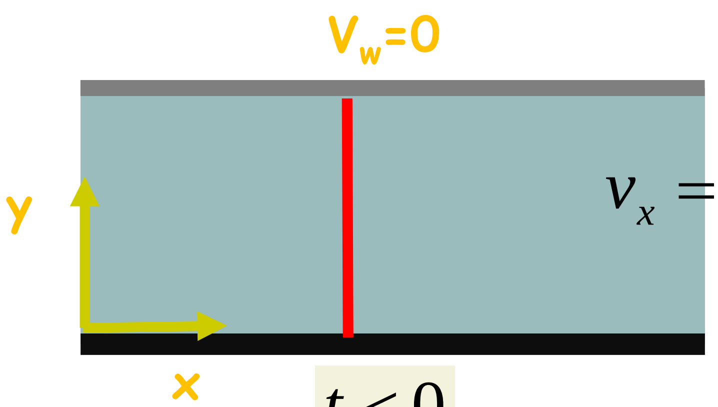
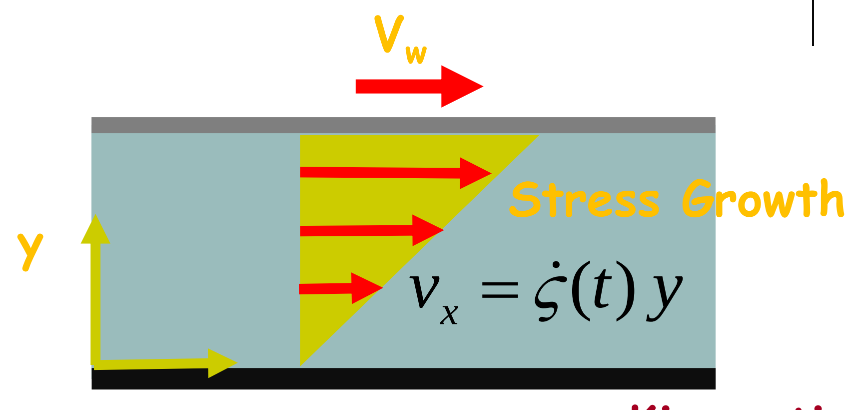
# Steady Shear Flow Startup




$$v_x = 0$$

$$t < 0$$




$$v_x = \dot{\varsigma}(t)\, y$$

$$t \geq 0$$

**Kinematics**

$$\dot{\varsigma}(t) = \begin{cases} 0 & t < 0 \\ \dot{\gamma}_0 & t \geq 0 \end{cases}$$

## Material properties

**Startup Viscosity**

$$\eta^+ = \frac{\tau_{xy}}{\dot{\gamma}}$$

**Coefficient of 1st normal stress difference**

$$\psi_1^+ = \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}^2}$$

**Coefficient of 2nd normal stress difference**

$$\psi_2^+ = \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}^2}$$



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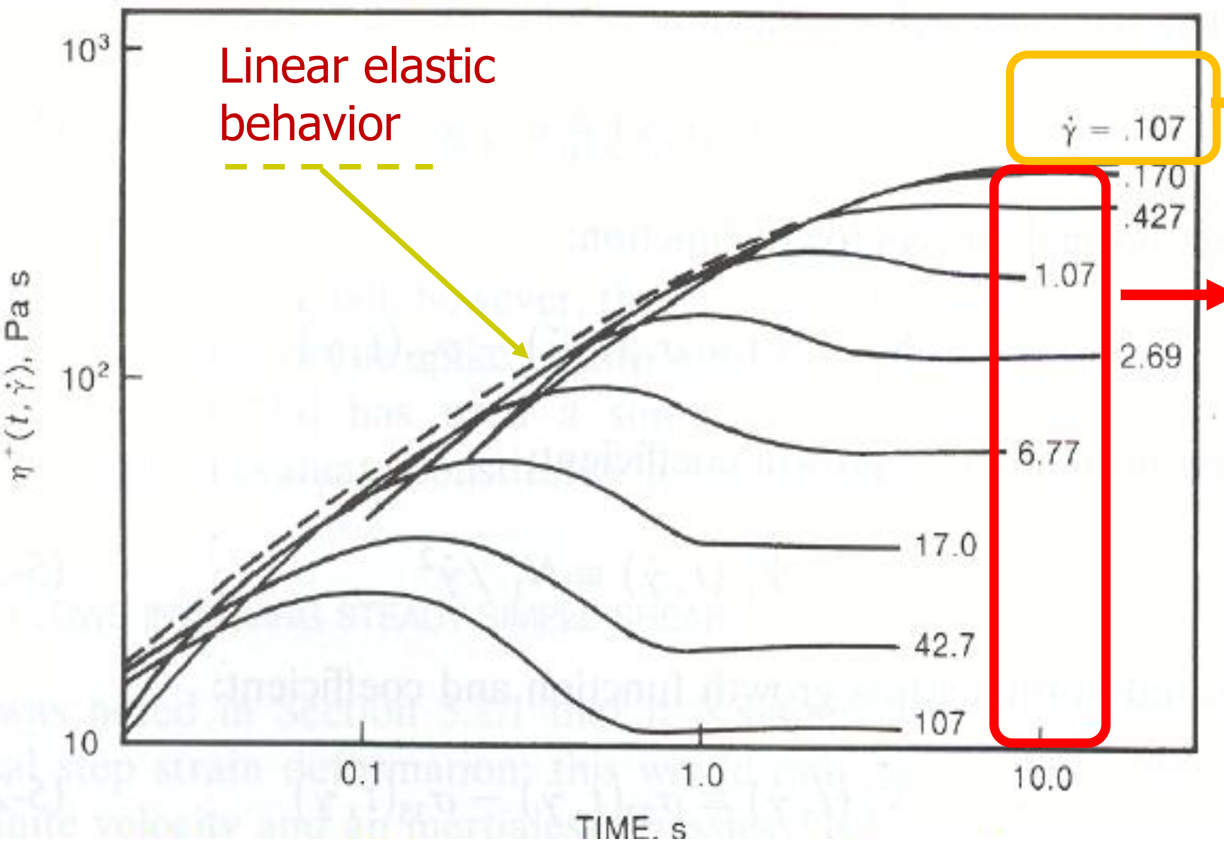
# Material properties: Startup shear viscosity

## Initially entangled chains, later disentangled

$$\eta^+(t) = \frac{\tau_{xy}}{\dot{\gamma}}$$




$$\eta_o = \lim_{\dot{\gamma}_o \to 0} \eta(\dot{\gamma}_o)$$

$$\eta(\dot{\gamma}_o) = \lim_{t \to \infty} \eta^+(t; \dot{\gamma}_o)$$

Polystyrene solution

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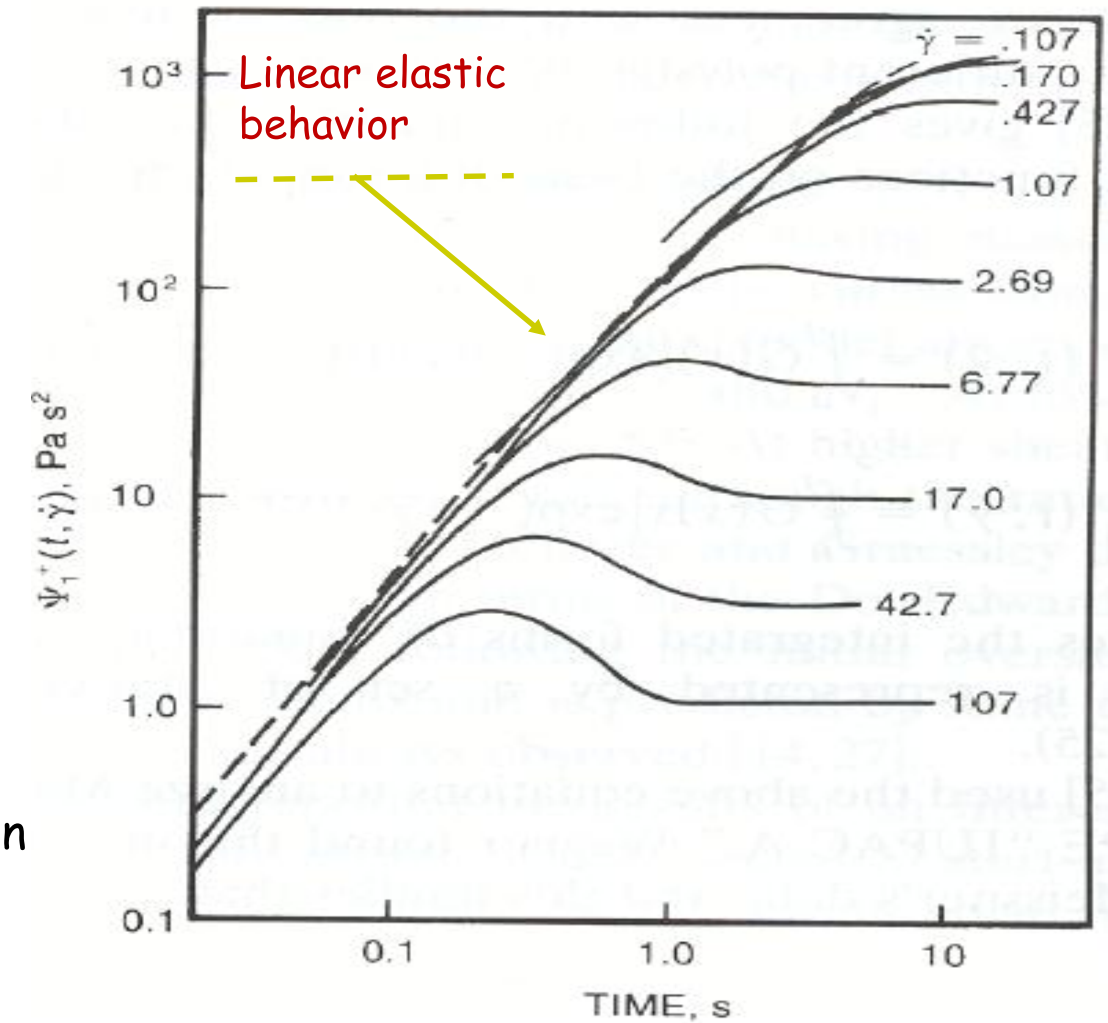
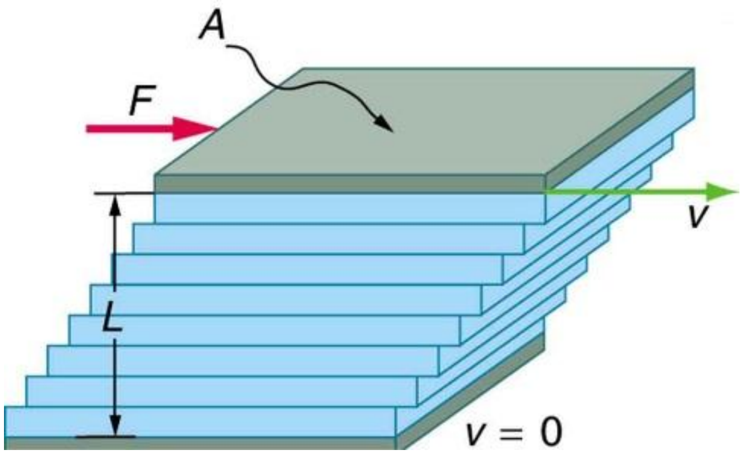
# Material properties: Startup $\Psi_1^+$

$$\psi_1^+(t) = \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}^2}$$




Polystyrene solution




# Cessation of a Steady Shear Flow

## or Stress Relaxation



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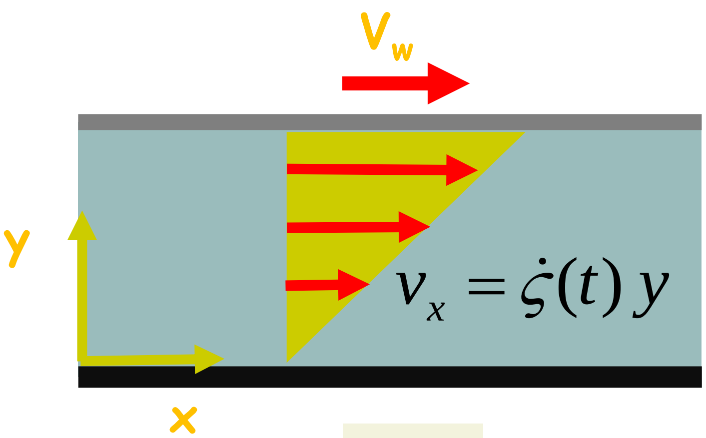
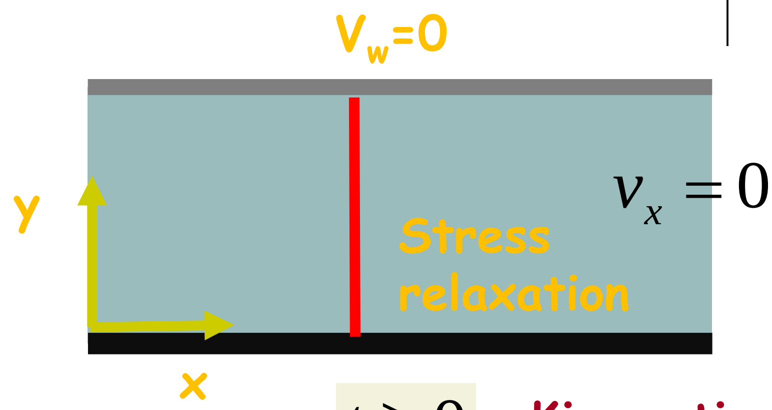
# Cessation of shear flow




$t < 0$




$t \geq 0$

**Kinematics**

$$\dot{\varsigma}(t) = \begin{cases} \dot{\gamma}_0 & t < 0 \\ 0 & t \geq 0 \end{cases}$$

**Material properties**

Cessation Viscosity

$$\eta^{-} = \frac{\tau_{xy}}{\dot{\gamma}}$$

Coefficient of 1st normal stress difference

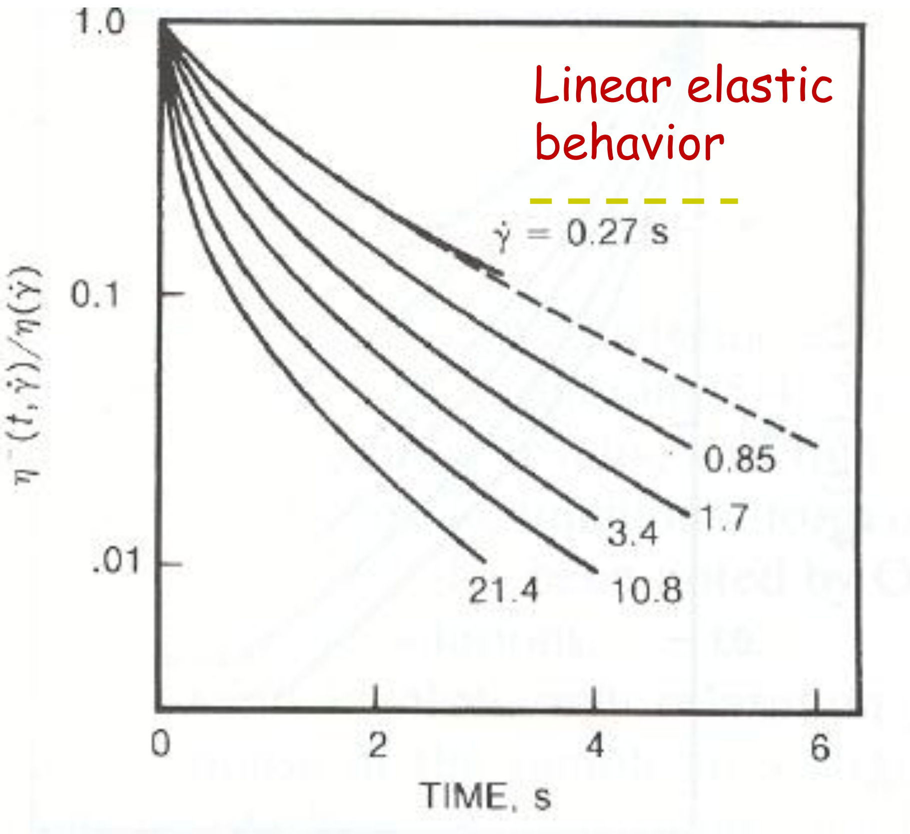
$$\psi_1^{-} = \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}^2}$$

Coefficient of 2nd normal stress difference

$$\psi_2^{-} = \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}^2}$$

# Material properties: Cessation shear viscosity

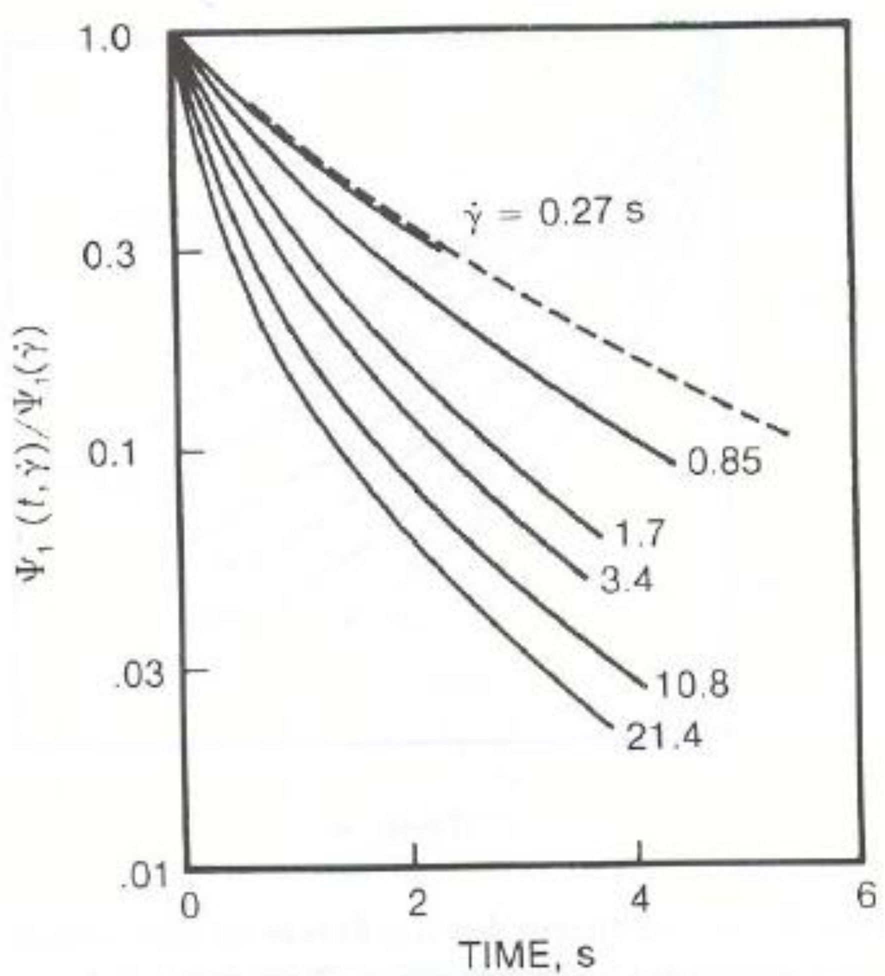
$$\eta^{-}(t) = \frac{\tau_{xy}}{\dot{\gamma}}$$




Polyisobutylene solution

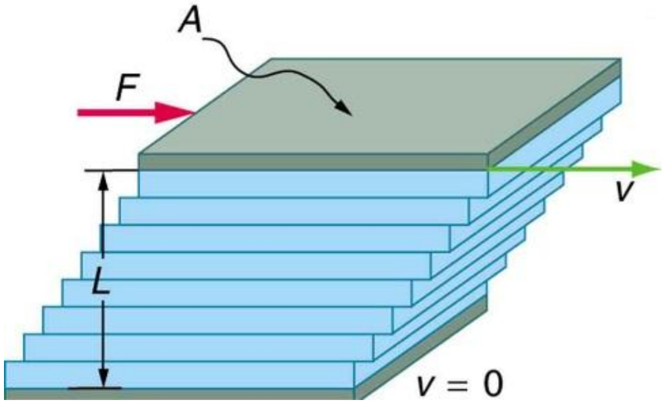
# Material properties: Cessation $\Psi_1^-$

$$\psi_1^-(t) = \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}^2}$$




Linear elastic behavior

Polyisobutylene solution




# Small Amplitude Oscillatory Shear: SAOS



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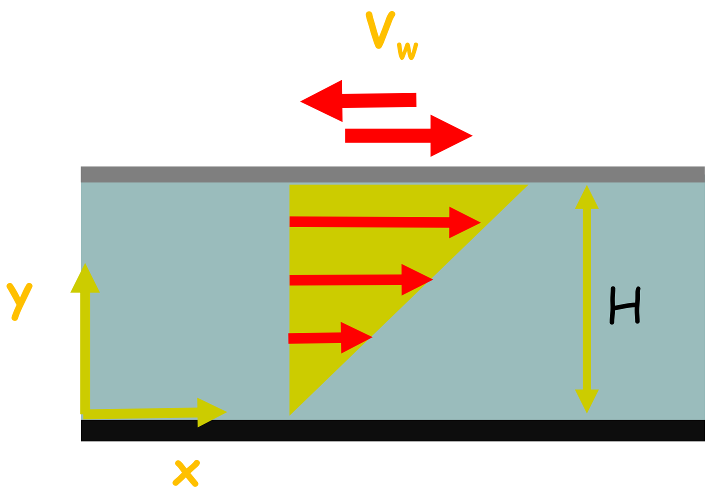
# Small Amplitude Oscillatory Shear (SAOS)




$$\gamma_{yx}(t) = \gamma_o \sin(\omega t)$$

$$\dot{\gamma}_{yx}(t) = \omega\gamma_o \cos(\omega t)$$

$$\dot{\gamma}_o = \omega\gamma_o$$

$$v_x = \dot{\gamma}_o \cos(\omega t)\, y$$

Location of a wall-point under steady shear

$$l(t) = V_w t = H\dot{\gamma}_o t$$

Location of a wall-point under oscillatory shear

$$l(t) = H\gamma_o \sin(\omega t) = \frac{H}{\omega}\dot{\gamma}_o \sin(\omega t)$$

# Small Amplitude Oscillatory Shear (SAOS)

displacement $$\gamma_{yx} = \frac{\dot{\gamma}_o}{\omega}\sin(\omega t) = \gamma_o \sin(\omega t)$$

δ: phase difference

stress $$\tau_{yx} = \tau_o \sin(\omega t + \delta)$$

$$= \left(\tau_o \cos(\delta)\right)\sin(\omega t) + \left(\tau_o \sin(\delta)\right)\cos(\omega t)$$

Solid
δ=0

"In phase" with the applied displacement

"Out of phase" with the applied displacement

Fluid
δ=90

# SAOS

## Viscous fluid

$$\tau_{yx} = \dot{\gamma}_o \eta'' \cos(\omega t)$$

**Viscous behavior, completely "out of phase" with deformation**

## Elastic solid

$$\tau_{yx} = \gamma_o G \sin(\omega t)$$

**Elastic behavior, completely "in phase" with deformation**

# Complex shear modulus $G^*$

$$\tau_{yx} = \gamma_o G' \sin(\omega t) + \gamma_o G'' \cos(\omega t)$$

**Storage modulus** $$G' \equiv \frac{\tau_o}{\gamma_o}\cos(\delta)$$ Elastic behavior, in phase with deformation

**Loss modulus** $$G'' \equiv \frac{\tau_o}{\gamma_o}\sin(\delta)$$ Viscous behavior, out of phase with deformation

**Complex shear modulus**

$$G^*(\omega) \equiv G'(\omega) + iG''(\omega)$$

# Complex viscosity $\eta^*$

$$\tau_{yx} = \dot{\gamma}_o \eta' \sin(\omega t) + \dot{\gamma}_o \eta'' \cos(\omega t)$$

$$\eta' \equiv \frac{\tau_o}{\dot{\gamma}_o} \sin(\delta) = \frac{G''}{\omega} \qquad \eta'' \equiv \frac{\tau_o}{\dot{\gamma}_o} \cos(\delta) = \frac{G'}{\omega}$$

Complex viscosity

$$\eta^*(\omega) \equiv \eta'(\omega) - i\,\eta''(\omega)$$

# Material functions for SAOS

| | |
|---|---|
| Magnitude of shear modulus | $\left\|G^*\right\| = \sqrt{G'^2 + G''^2}$ |
| Loss angle | $\tan(\delta) = \dfrac{G''}{G'}$ |
| Dynamic viscosity | $\eta' = \dfrac{G''}{\omega}$ |
| Out of phase component of $\eta^*$ | $\eta'' = \dfrac{G'}{\omega}$ |
| Magnitude of complex viscosity | $\left\|\eta^*\right\| = \sqrt{\eta'^2 + \eta''^2}$ |
| Magnitude of complex compliance | $\left\|J^*\right\| = \dfrac{1}{\left\|G^*\right\|}$ |
| Storage compliance | $J' = \dfrac{1/G'}{1+\tan^2(\delta)}$ |
| Loss compliance | $J'' = \dfrac{1/G''}{1+\tan^{-2}(\delta)}$ |



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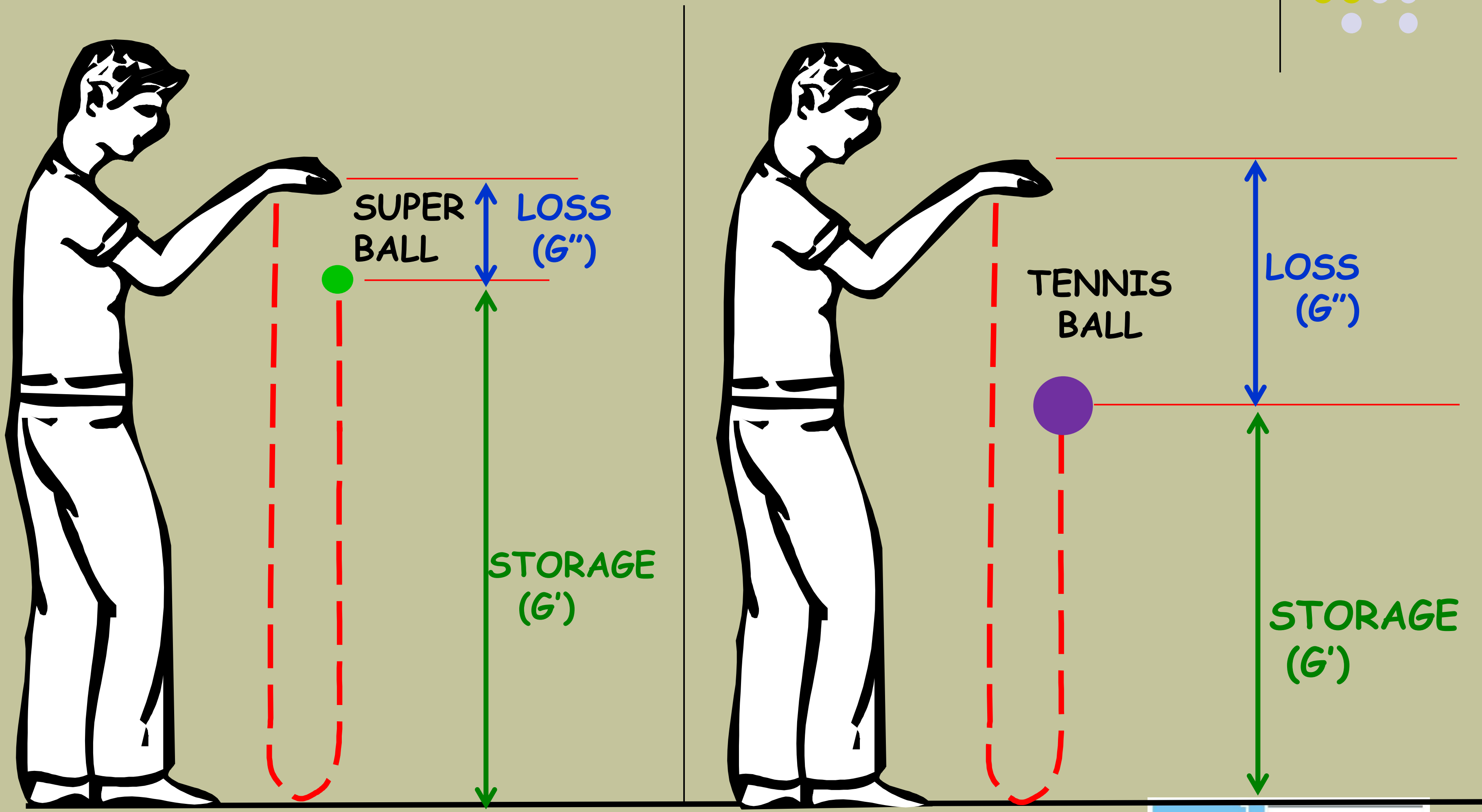
# Storage and loss moduli



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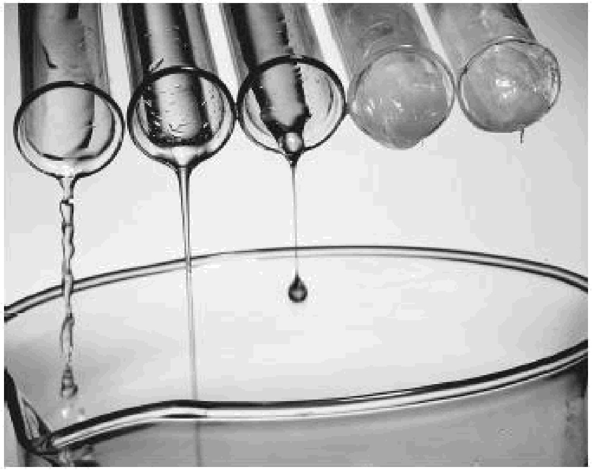
# How strongly viscoelastic is a material?

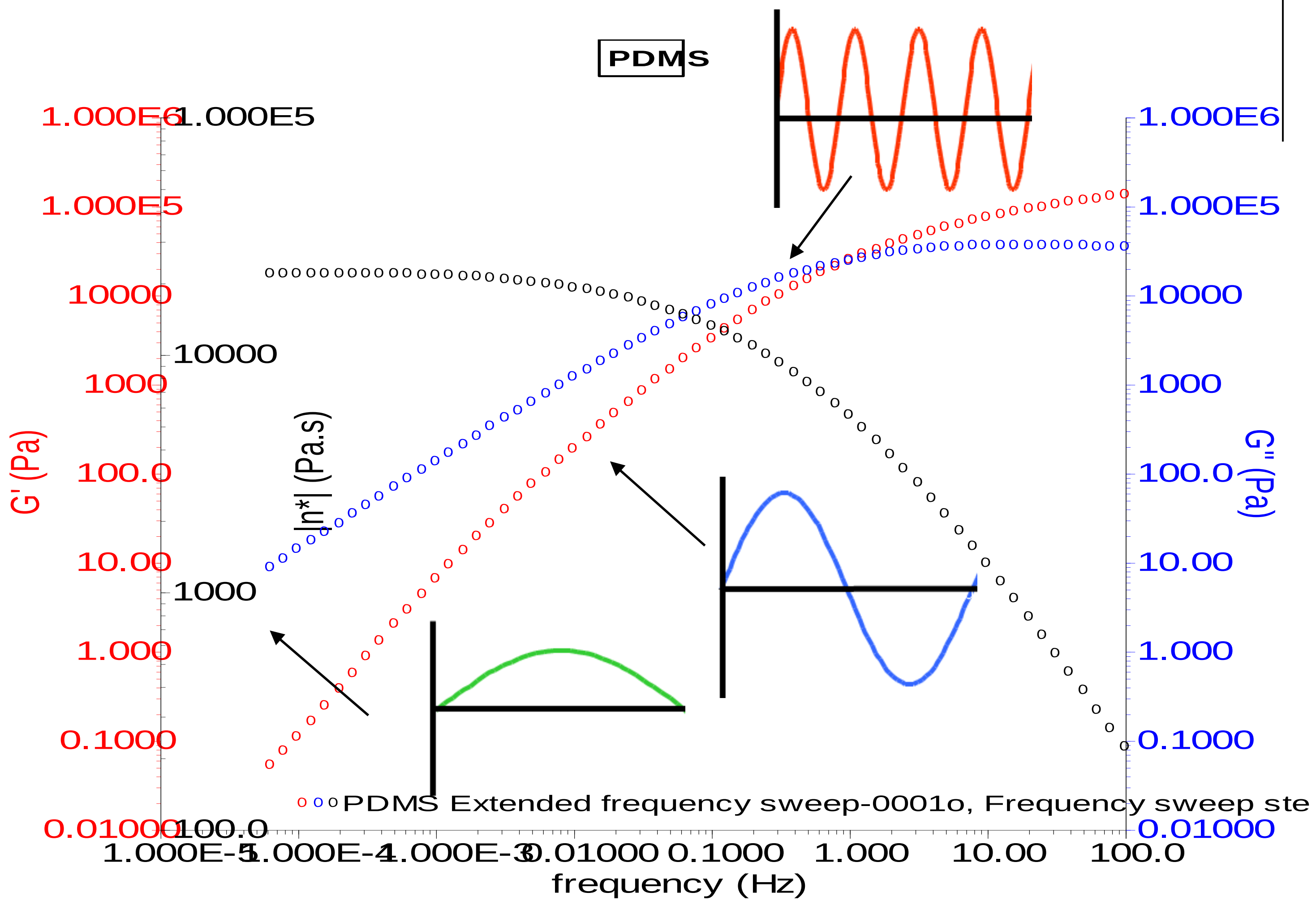


viscous ← viscoelastic → elastic

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

| | | | | |
|---|---|---|---|---|
| G'' >> G' | G'' > G' | G'' = G' | G' > G'' | G' >> G'' |
| Viscous behavior | | Viscoelastic behavior | Elastic behavior | |
| $\tan\delta >> 1$<br>$\rightarrow \infty$ | $\tan\delta > 1$ | $\tan\delta = 1$ | $\tan\delta < 1$ | $\tan\delta << 1$<br>$\rightarrow 0$ |

# G' & G'' vs. applied frequency




**The amplitude of deformation can be chosen arbitrarily, but it should be small enough.**



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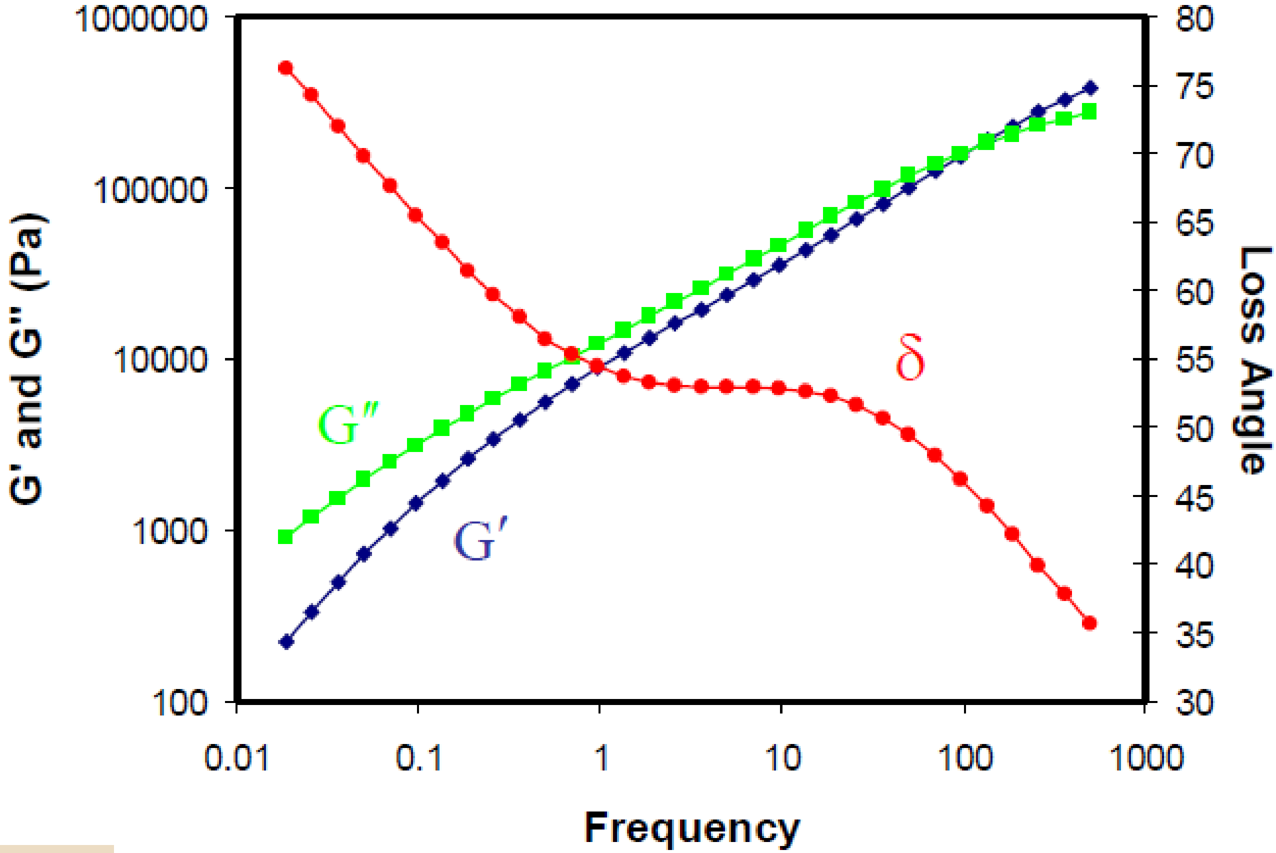
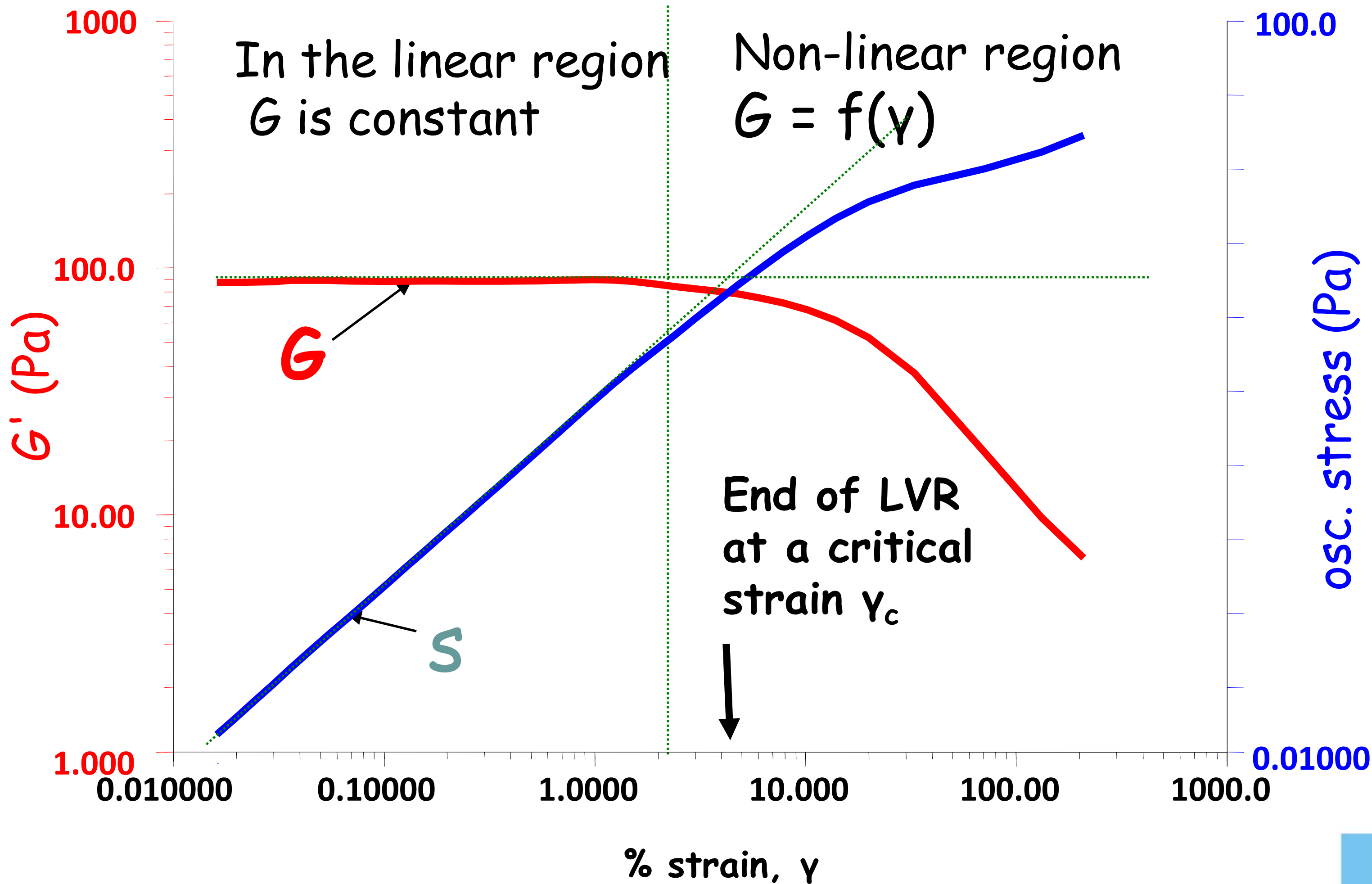
# Loss Angle




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

It is a function of temperature, frequency and polymer structure

# Linear Viscoelastic Region (LVR)



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# Linear Viscoelastic Region (LVR)

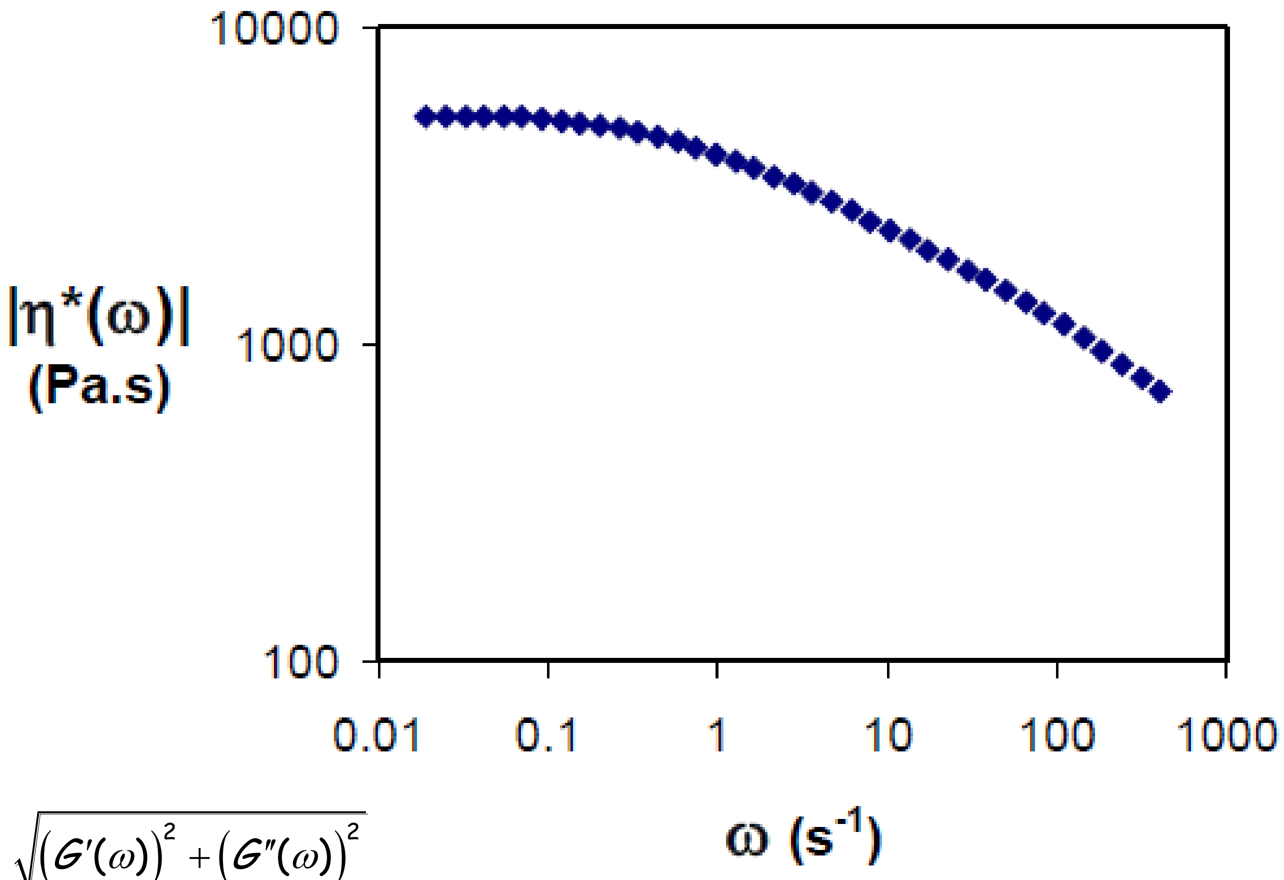
Concept of Linear Viscoelastic Region

"If the deformation is small, or applied sufficiently slowly, the molecular arrangements are never far from equilibrium. The mechanical response is then just a reflection of dynamic processes at the molecular level which continue constantly, even for a system at equilibrium. This is the domain of LINEAR VISCOELASTICITY. ***The magnitudes of stress and strain are related linearly***, and the behavior for any liquid is completely described by a single function of time." (Bill Graessley, Princeton University)

Reference:

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

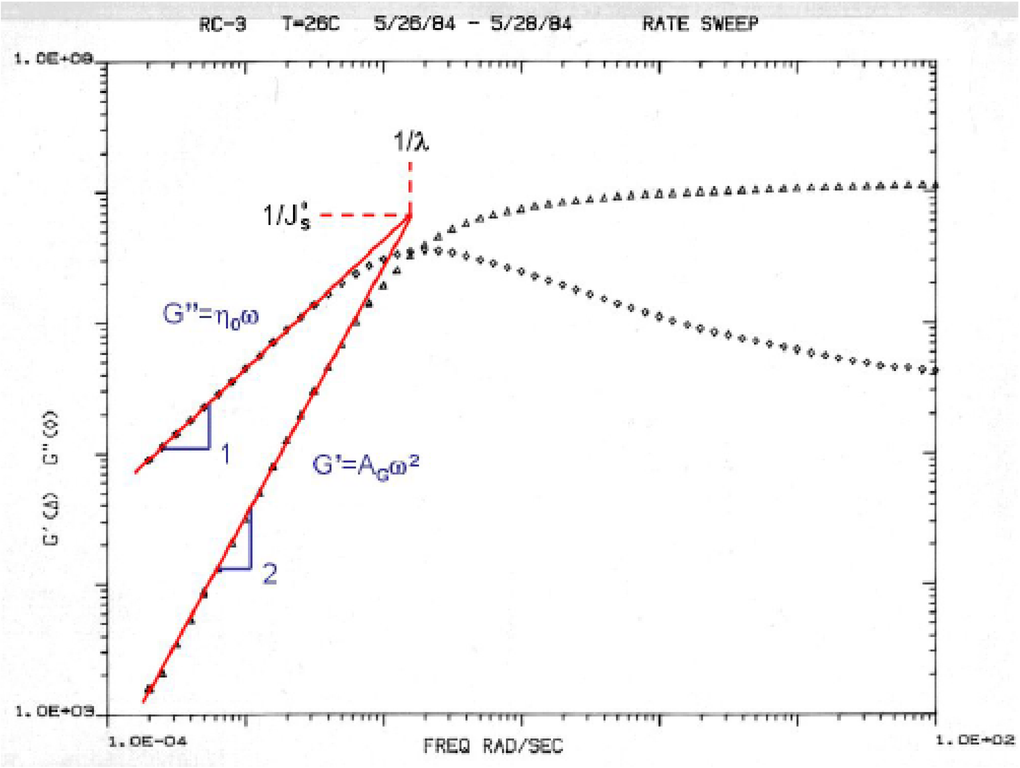
# Magnitude of complex viscosity




$$\left|\eta^*(\omega)\right| = \frac{\sqrt{\left(G'(\omega)\right)^2 + \left(G''(\omega)\right)^2}}{\omega}$$

# Calculation of λ, $\eta_0$, $J^s_0$ from SAOS

**RC-3 polybutylene $M_w$=940,000 $M_w$/ $M_n$<1.1, $T_g$=-99°C**




$$\eta_o = \lim_{\omega \to 0}\left(\frac{G''(\omega)}{\omega}\right) = \lim_{\omega \to 0}\left(\eta'(\omega)\right)$$

$$J_s^o = \lim_{\omega \to 0}\left(\frac{G'(\omega)}{G''^2(\omega)}\right)$$

$$A_G = J_s^o \eta_o^2$$

**For a cycle the period is given by** $2\pi / \omega$

**For** $\omega = 10^{-4} rad / \sec, 2\pi / \omega \cong 1 day$



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# Cox-Merz's rule

At the limit of low frequencies $\omega \to 0$

$$\eta(\dot{\gamma}) = \left|\eta^*(\omega)\right|_{\omega=\dot{\gamma}} = \sqrt{[(G'/\omega)^2 + (G''/\omega)^2]}_{\omega=\dot{\gamma}}$$

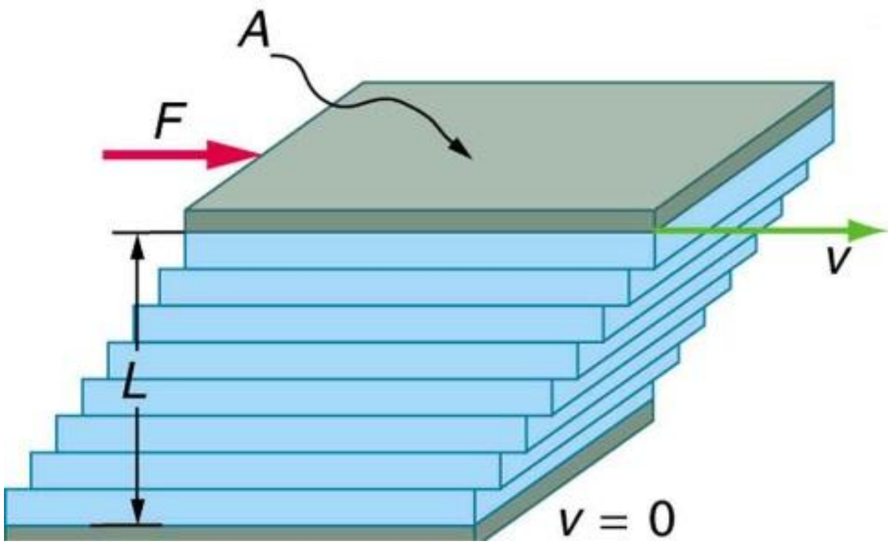
At low frequencies the elastic behavior is weak

$$\eta(\dot{\gamma}) = \left|\eta'(\omega)\right|_{\omega=\dot{\gamma}}$$

# Laun's rule

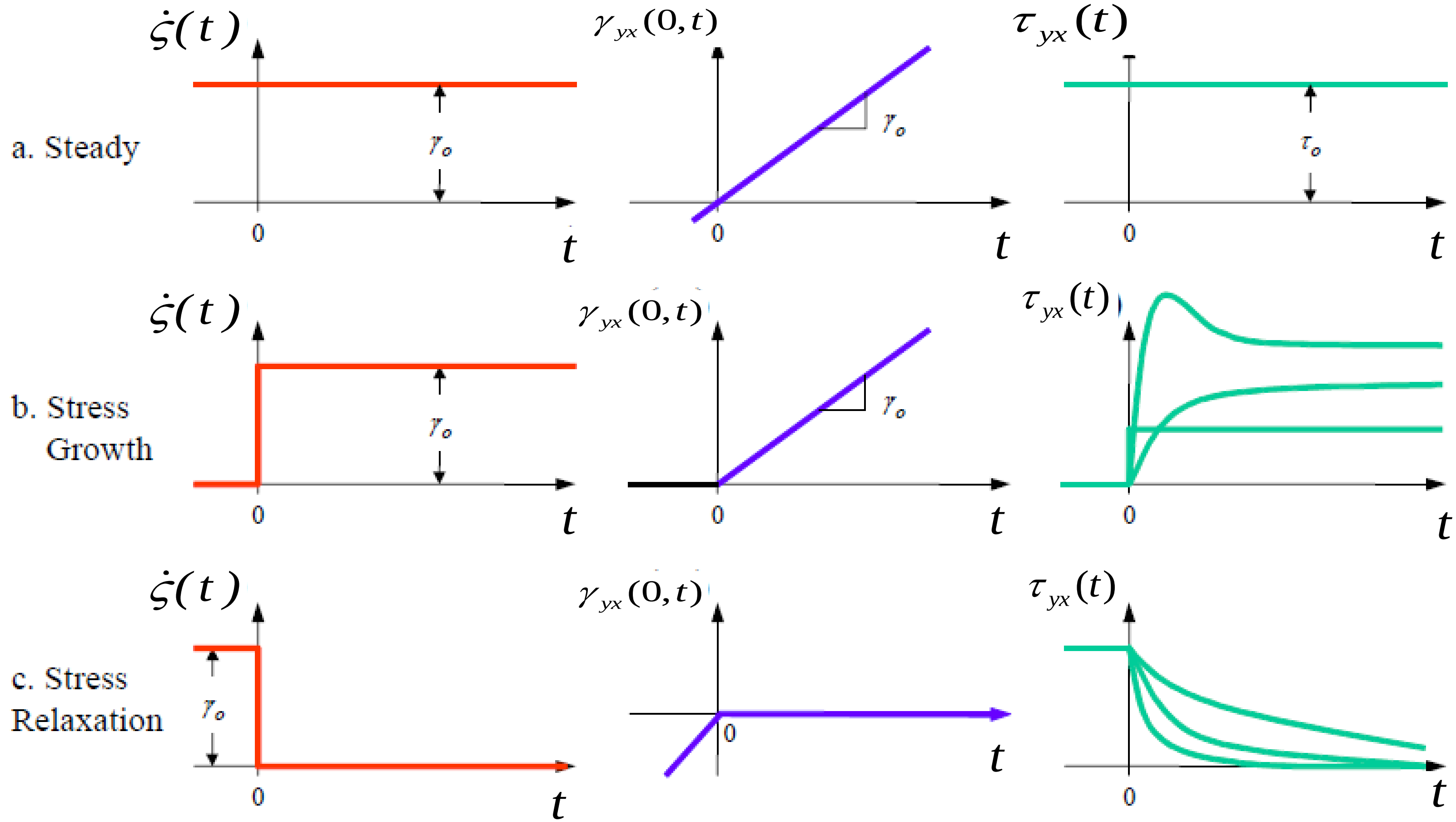
At the limit of low frequencies $\omega \to 0$

$$\Psi_1(\dot{\gamma}) = 2\left(\frac{G'(\omega)}{\omega^2}\right)\left\{1+\left(\frac{G'(\omega)}{G''(\omega)}\right)^2\right\}^{0.7}\Bigg|_{\omega=\dot{\gamma}}$$

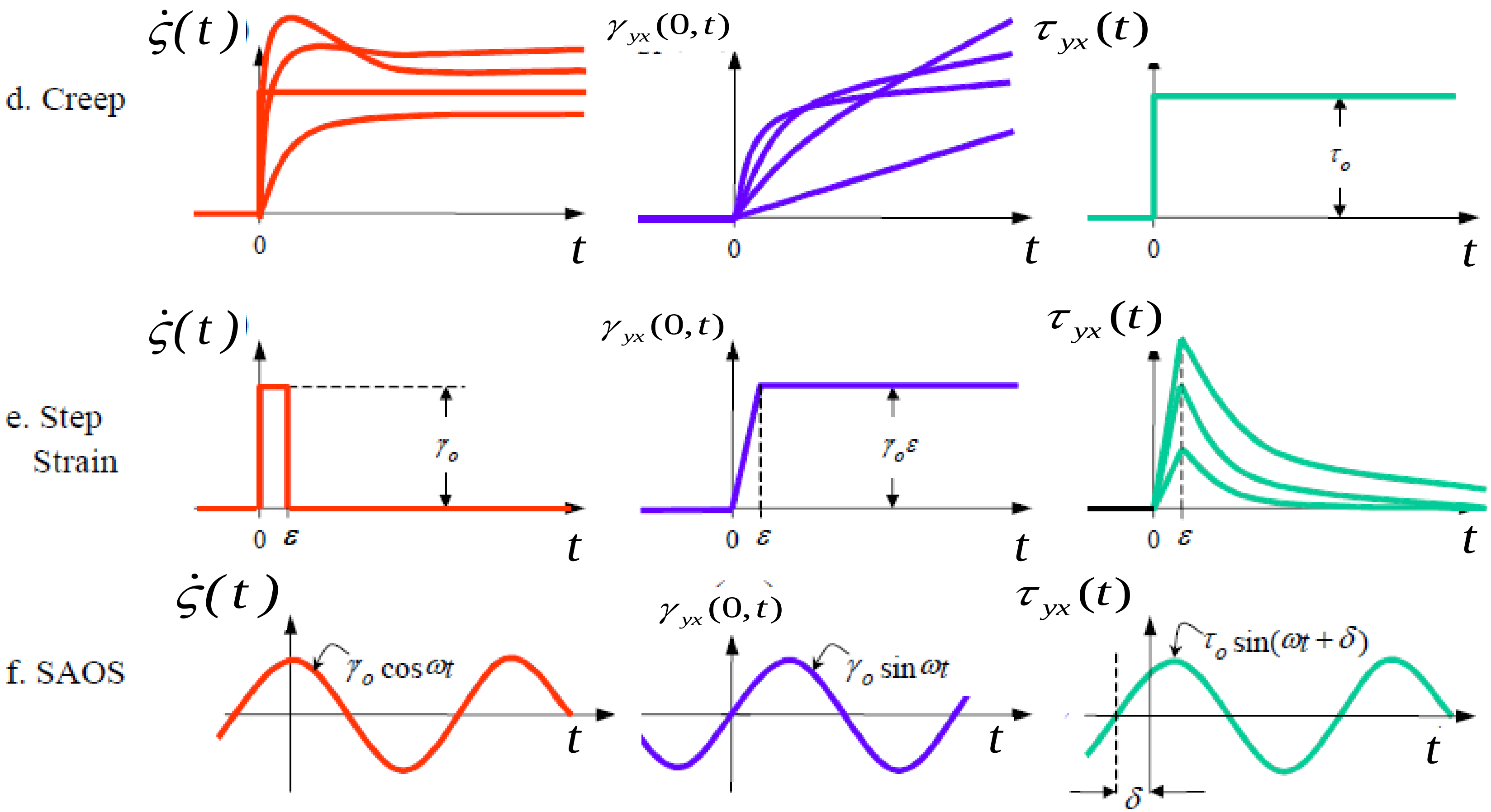



# A summary of standard shear flows, deformations and stresses

# Flow Deformation stress



# Flow Deformation stress



# Summary of flows and Material Properties

| Flow | | Material Function |
|---|---|---|
| Steady shear flow | $\dot{\gamma}_{yx} = \dot{\gamma} = constant$ | $\eta(\dot{\gamma}),\ \Psi_1(\dot{\gamma}),\ \Psi_2(\dot{\gamma})$ |
| Small-amplitude oscillatory shear | $\dot{\gamma} = \dot{\gamma}_0 \cos \omega t$ | $\eta'(\omega),\ \eta''(\omega)$<br>$G'(\omega) = \eta''\omega,\ G''(\omega) = \eta'\omega$ |
| stress growth upon inception of steady shear flow | $\dot{\gamma} = 0\ \ t < 0,\ \ \dot{\gamma} = \dot{\gamma}_o\ \ t \geq 0$ | $\eta^+(t,\dot{\gamma}_0),\ \Psi_1^+(t,\dot{\gamma}_0),\ \Psi_2^+(t,\dot{\gamma}_0)$ |
| Stress relaxation after cessation of steady shear flow | $\dot{\gamma}_{yx} = \dot{\gamma}_o\ \ t < 0,\ \ \dot{\gamma}_{yx} = 0\ \ t \geq 0$ | $\eta^-(t,\dot{\gamma}_0), \Psi_1^-(t,\dot{\gamma}_0), \Psi_2^-(t,\dot{\gamma}_0)$ |
| Stress relaxation after a sudden shearing displacement | $\dot{\gamma}_{yx} = \dot{\gamma}_o \delta(t)$ | $G(t,\gamma_0),\ G_{\Psi_1}(t,\gamma_0)$ |
| Creep | $\tau_{yx} = 0\ \ t < 0,\ \ \tau_{yx} = \tau_o\ \ t \geq 0$ | $J(t,\gamma_0)$ |
| Constrained recoil after steady shear flow | $\tau_{yx} = \tau_o\ \ t < 0,\ \ \tau_{yx} = 0\ \ t \geq 0$ | $\gamma_r(0,t,\tau_0),\ \gamma_\infty(\tau_0),\ J_e^0(\tau_0)$ |



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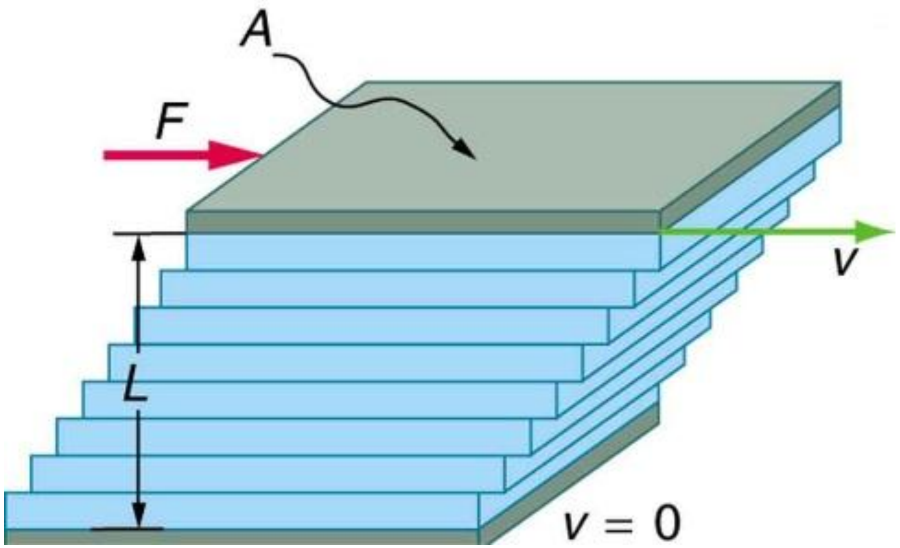
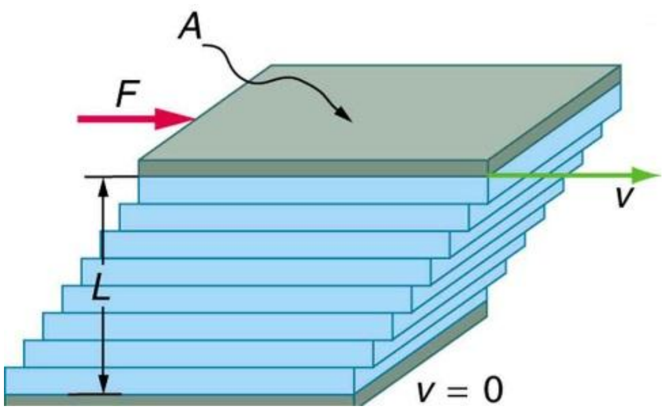



# End of lecture




# Creep and recoil



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# Complex compliance $J^*$

$$J^*(\omega) \equiv \frac{1}{G^*(\omega)} = J'(\omega) - iJ''(\omega)$$

where

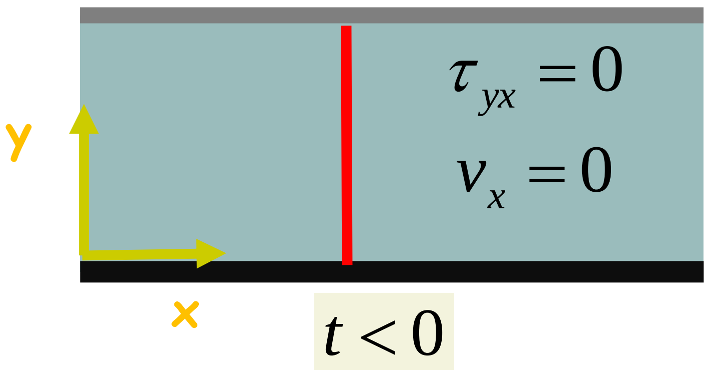
$$G' = \frac{J'}{(J')^2 + (J'')^2}$$

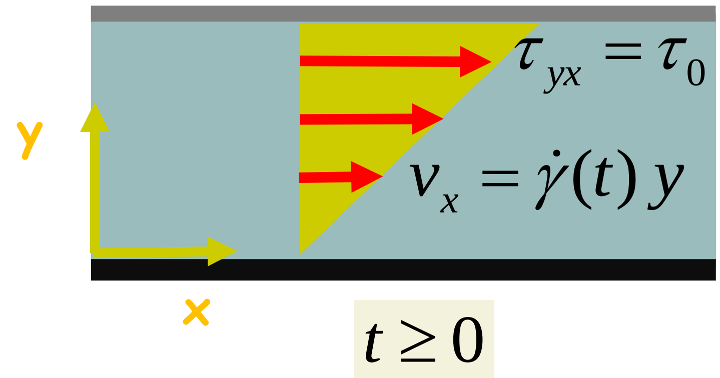
$$G'' = \frac{J''}{(J')^2 + (J'')^2}$$

# Shear creep and recoil

## 6. Creep

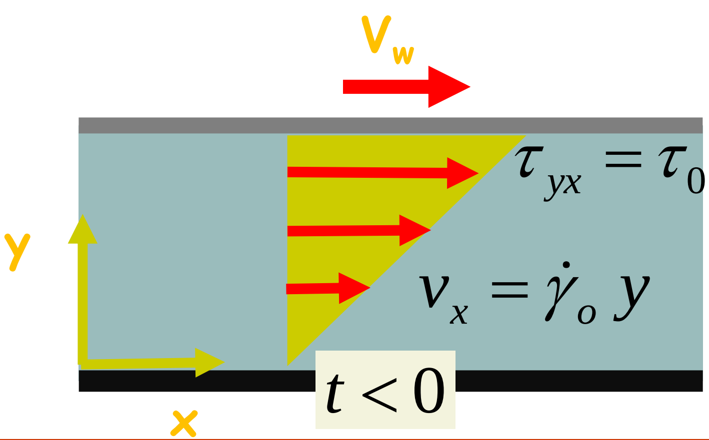
Application of constant shear stress

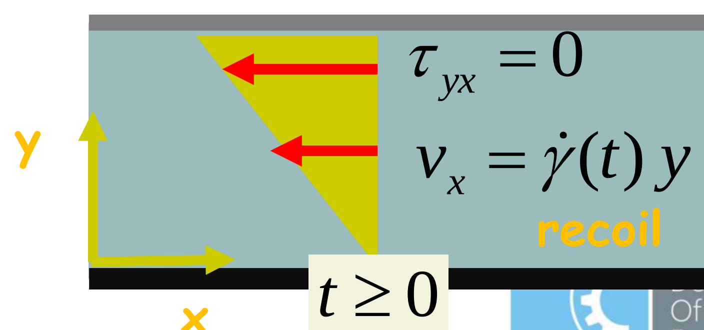


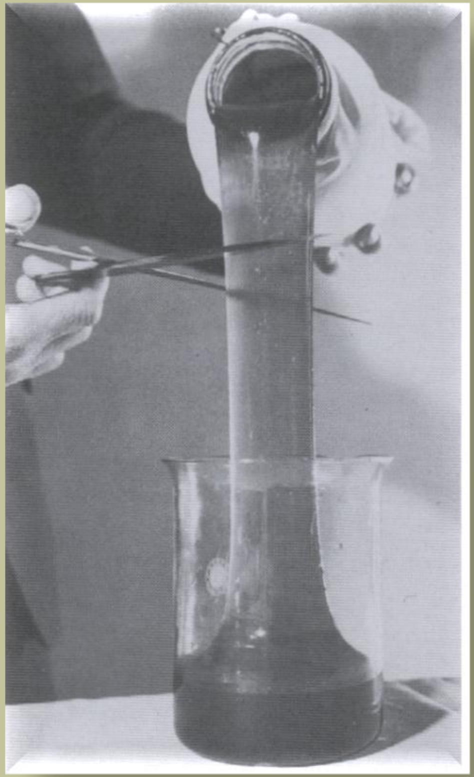

## 7. Constrained Recoil after steady Shear Flow

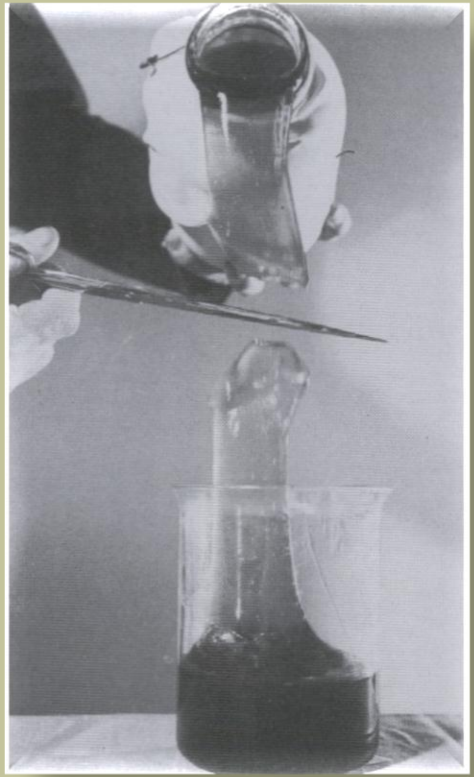
Zeroing of applied shear stress

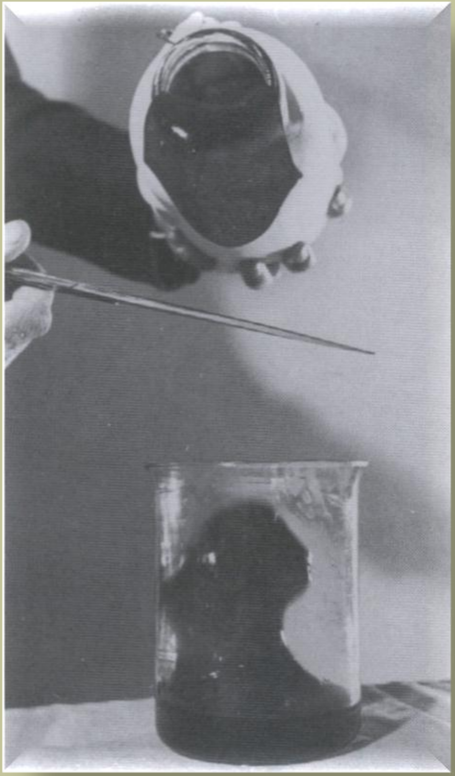


# Viscoelastic recoil







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# Shear Creep

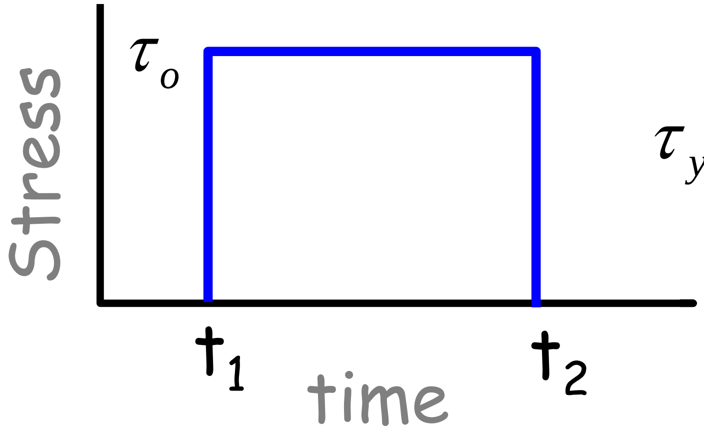
The shear stress is imposed and we measure the deformation

$$\tau_{yx}(t)=\begin{cases}0, & t<0\\ \tau_o, & t\geq 0\end{cases}$$

- At steady state, both shear stress and shear rate are constant.
- Thus at steady state (e.g. viscosity curve), the results are the same whether one imposes the shear rate or the shear stress.
- However, the transient behaviors are described by different material functions.

# Shear creep and recoil

- Shear creep: A stress starts to be applied at $t_1$. The deformation γ(t) is plotted as function of time
- Recoil: Stress is zeroed at $t_2$, and deformation γ(t) is measured as function of time.




$$\tau_{yx}(t) = \begin{cases} 0, & t < t_1 \\ \tau_o, & t_2 \geq t \geq t_1 \end{cases}$$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# Creep kinematic and Material Functions

**kinematic**

$$\underline{v} \equiv \dot{\gamma}_{yx}(t) y \underline{e}_x$$

$$\tau_{yx}(t) = \begin{cases} 0, & t < 0 \\ \tau_o, & t \geq 0 \end{cases}$$

**Material functions**

$$J(t, \tau_o) \equiv \frac{\gamma_{yx}(0,t)}{\tau_o}$$

Shear compliance

$$J_r(t', \tau_o) \equiv \frac{\gamma_r(t')}{\tau_o}$$

Recoverable compliance

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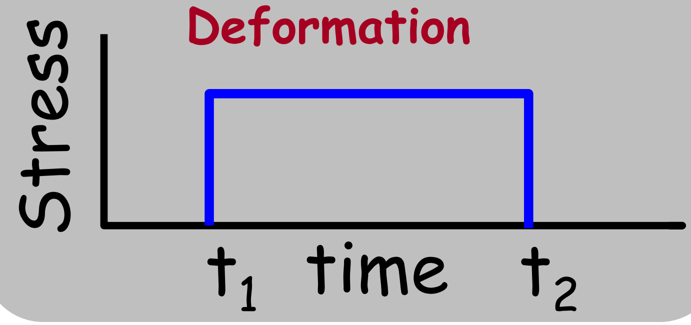
# Shear creep and recoil:

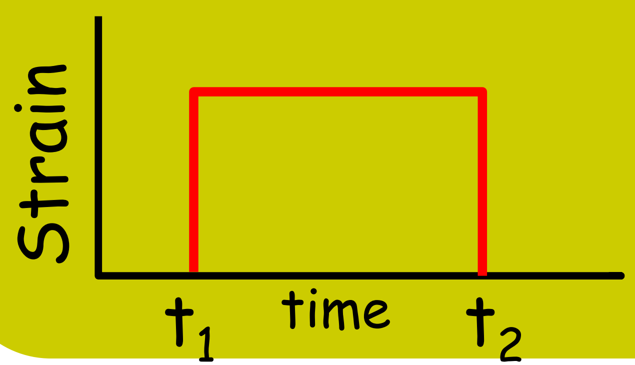
## Elastic and Viscous Materials

### Deformation



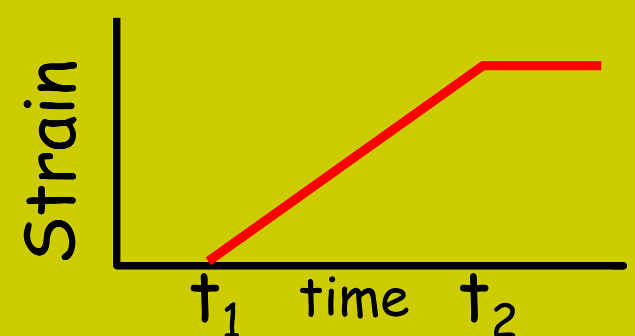

### Elastic Material

- For $t>t_1$ the deformation is constant
- For $t>t_2$ the deformation is zero

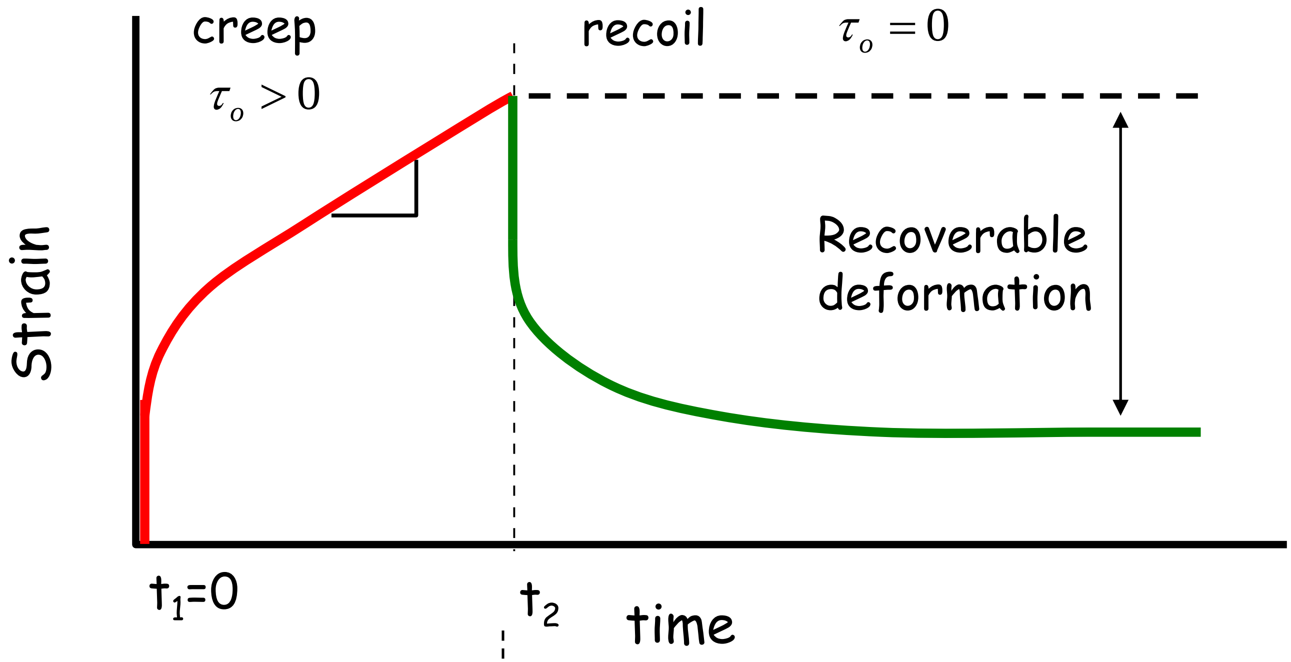



### Viscous Material

- For $t>t_1$ the rate of deformation is constant
- For $t>t_1$ the deformation increases in time
- For $t>t_2$ the rate of deformation is 0



# Shear creep and recoil: Viscoelastic Material




**Rate of deformation reduces up to a constant value.**

**Viscoelastic fluid recoils, and reaches at a steady state, having a permanent deformation.**



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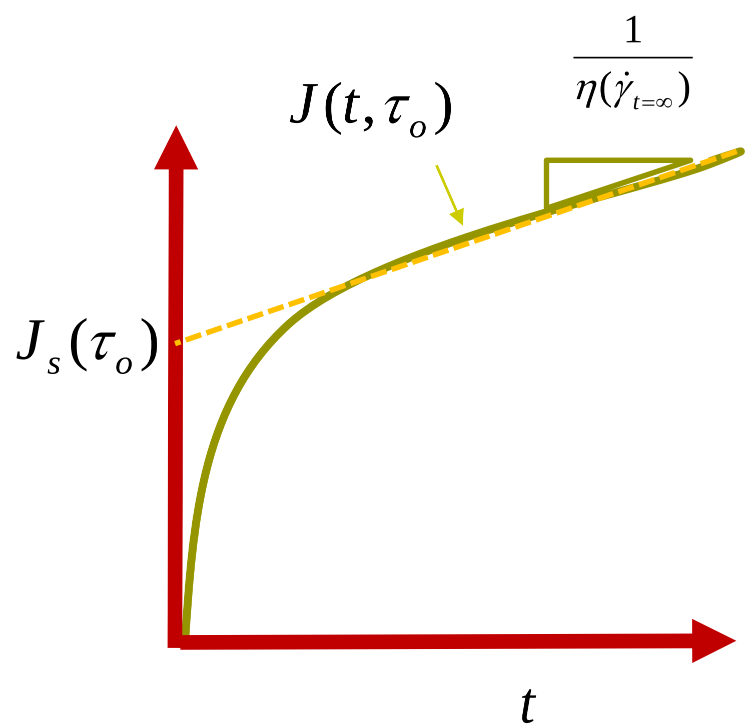
# Creep compliance

**Compliance**

$$J(t,\tau_o) \equiv \frac{\gamma_{yx}(0,t)}{\tau_o}$$

**the flow ability of a material as a response of an applied stress (~ 1/ (shear rate) )**




**At steady state**

$$J(t,\tau_o) \equiv J_s(\tau_o) + \frac{t}{\eta(\dot{\gamma}_{t=\infty})}$$

Steady state compliance

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# Creep compliance at steady state

At large times, the compliance exhibits a linear variation

$$\left.\frac{dJ(t,\tau_o)}{dt}\right|_{steadystate} \equiv \frac{d\gamma_{yx}(0,t)}{dt}\frac{1}{\tau_o} = \frac{\dot{\gamma}_\infty}{\tau_o} = \frac{1}{\eta(\dot{\gamma}_\infty)}$$

**The slope**

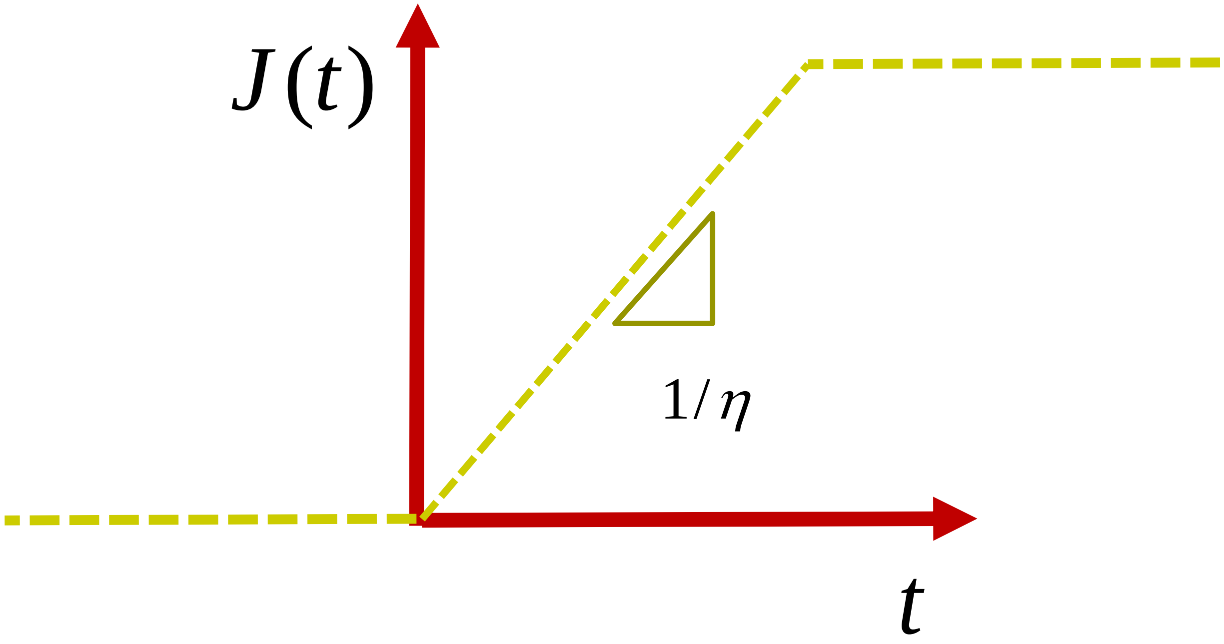
If we integrate it in time, we get:

$$\left.\frac{dJ(t,\tau_o)}{dt}\right|_{steadystate} = \frac{1}{\eta(\dot{\gamma}_\infty)} \Rightarrow J(t,\tau_o)\Big|_{steadystate} = \frac{1}{\eta(\dot{\gamma}_\infty)}t + C$$

$J_s(\tau_o)$

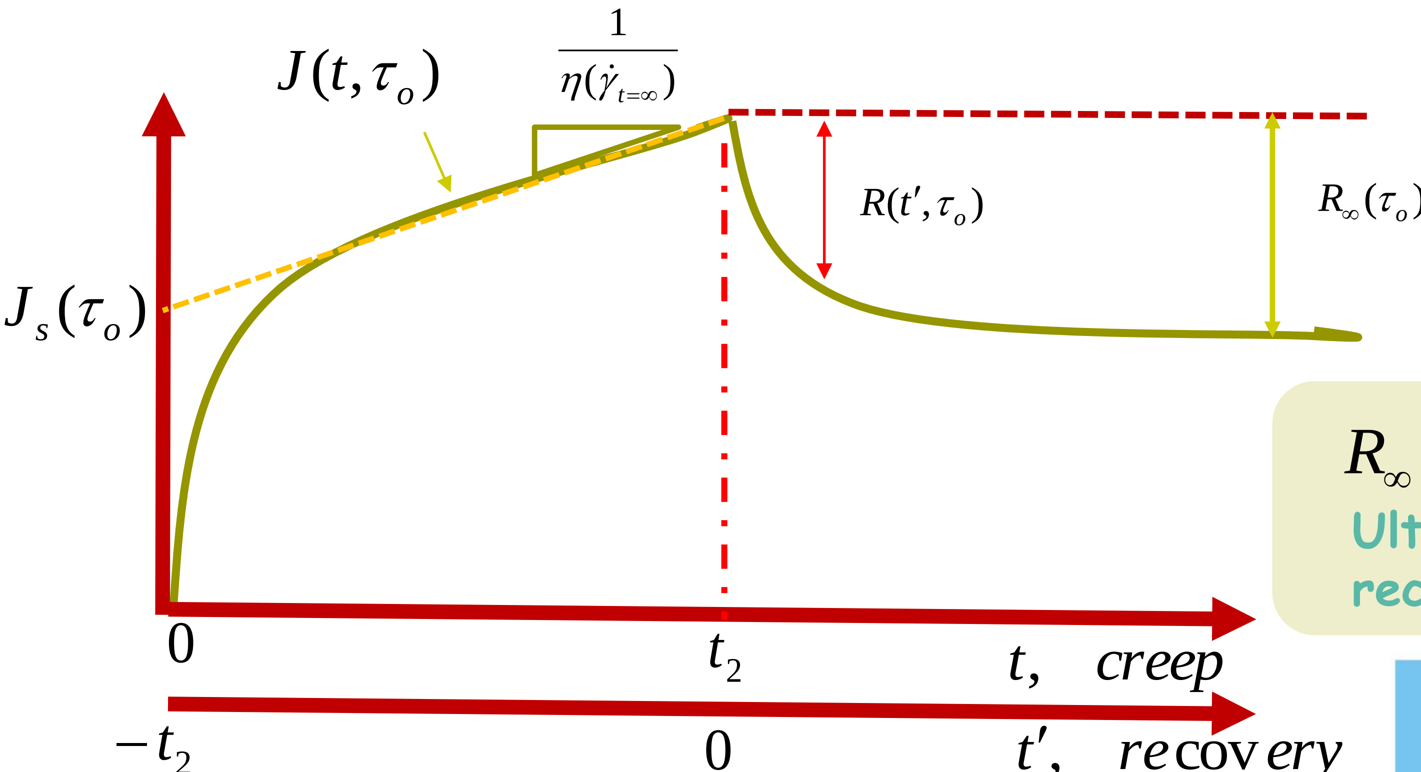
**Compliance at steady state**

# Compliance of a Newtonian Fluid



# Creep recovery

- After the imposition of creep, the applied stress is zeroed
- Elastic and viscoelastic materials will recoil in the opposite direction of the creep




$R_\infty(\tau_o)$
Ultimate recoil function



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# Kinematic and Material Functions

Deformation recovery in recoil

$$\gamma_r \equiv \gamma_{21}(0,t_2) - \gamma_{21}(0,t)$$

As function of t

$$\gamma_r(t) \equiv -\int_{t_2}^{t} \gamma(t'')dt''$$

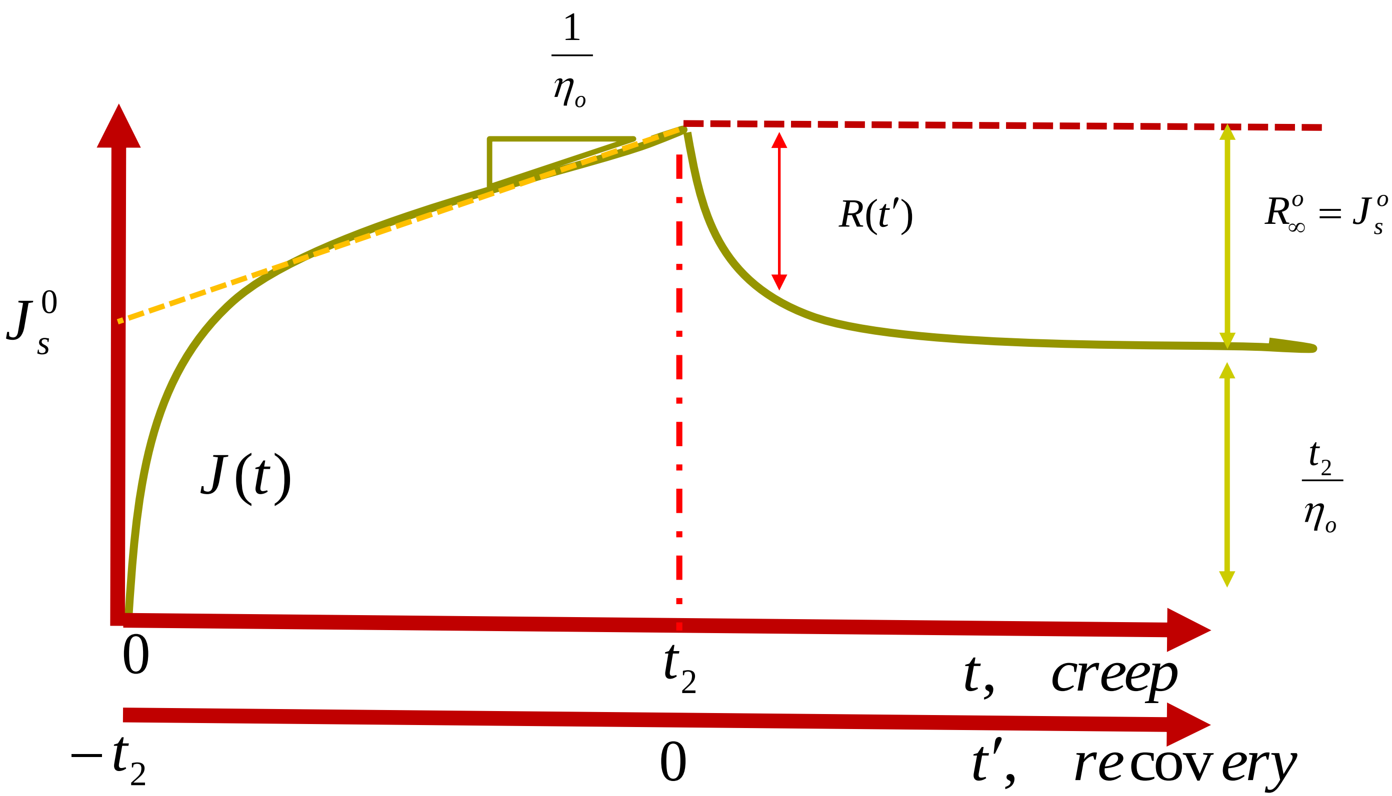
As function of t'

$$\gamma_r(t') \equiv -\int_{0}^{t'} \gamma(t'')dt''$$

Recoverable compliance or recoil function:

$$J_r(t',\tau_o) = R(t',\tau_o) \equiv \frac{\gamma_r(t)}{\tau_o}$$

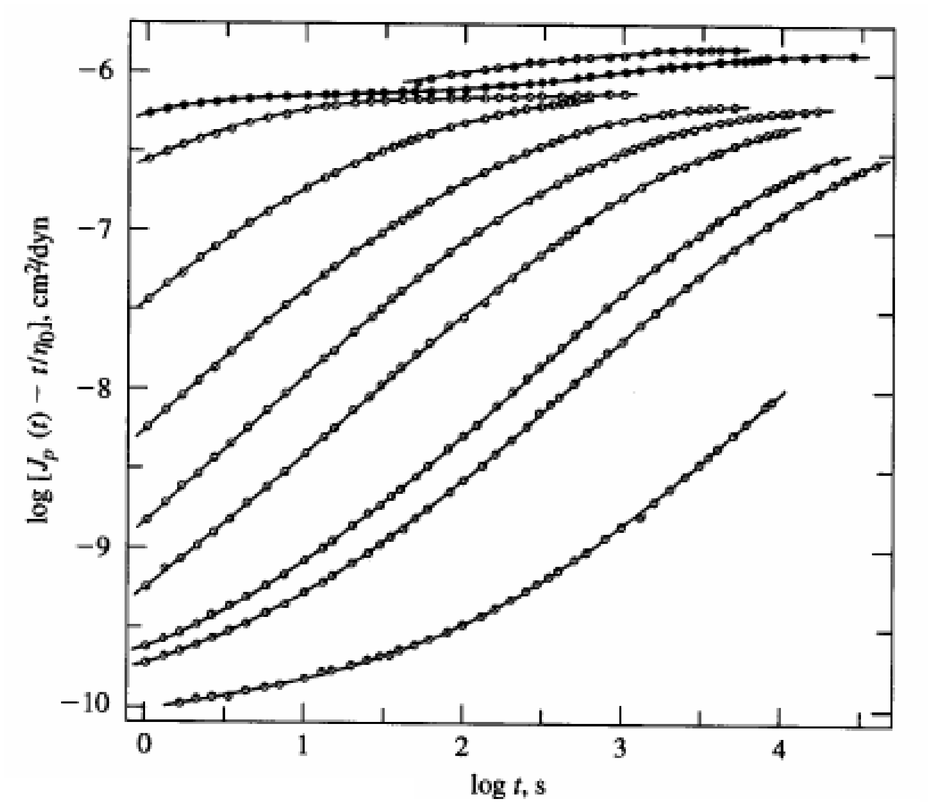
# Recovery functions




$$J(t)\Big|_{steadystate} \equiv J_s^o + \frac{t}{\eta_o}$$

$$J(t) \equiv R(t) + \frac{t}{\eta_o}$$

# Shear recoil

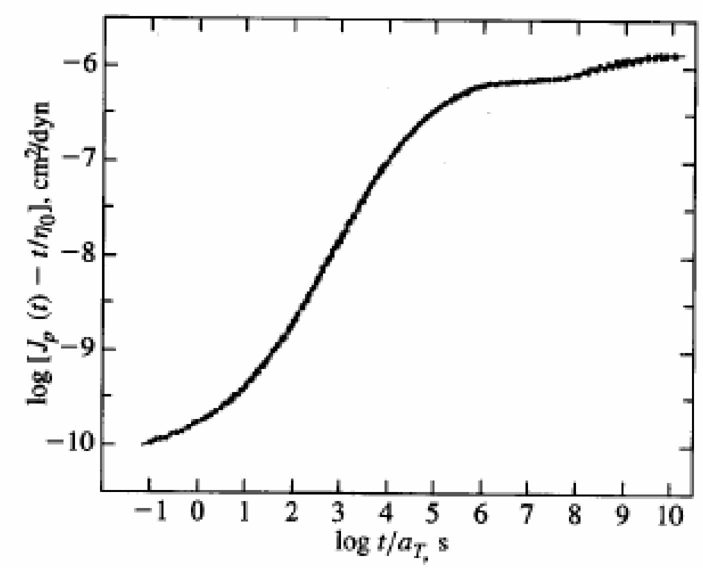



recoverable strain

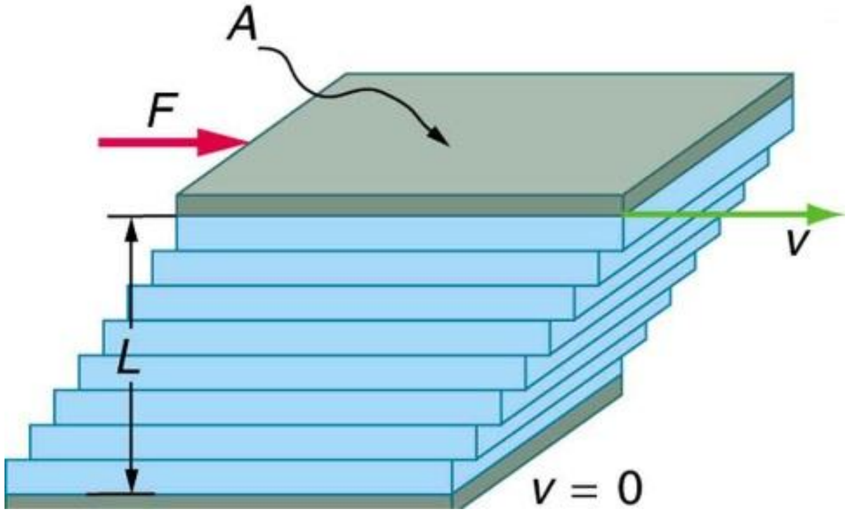
$$\underbrace{\gamma(t)}_{\text{total strain}} = \overbrace{\gamma_r(t)}^{\text{recoverable strain}} + \underbrace{t\dot{\gamma}_\infty}_{\text{non-recoverable strain}}$$

total strain

non-recoverable strain




**PS melt**




# Step stain in shear



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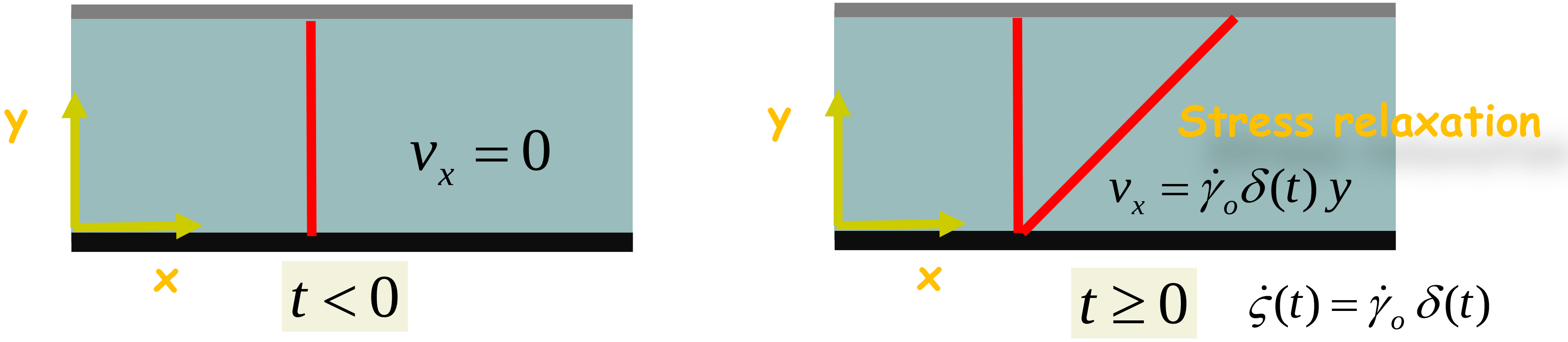
# Step strain in shear

## 5. Step strain in shear



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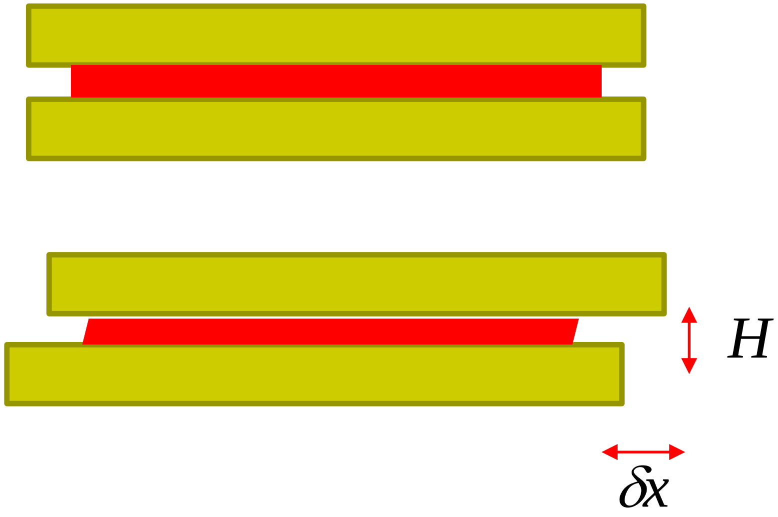
# Step strain for elastic materials

- Deformation is not a flow, unless the material is viscoelastic.
- If we impose an elastic solid in such a deformation, we can calculate the shear modulus as G.

**Step strain**

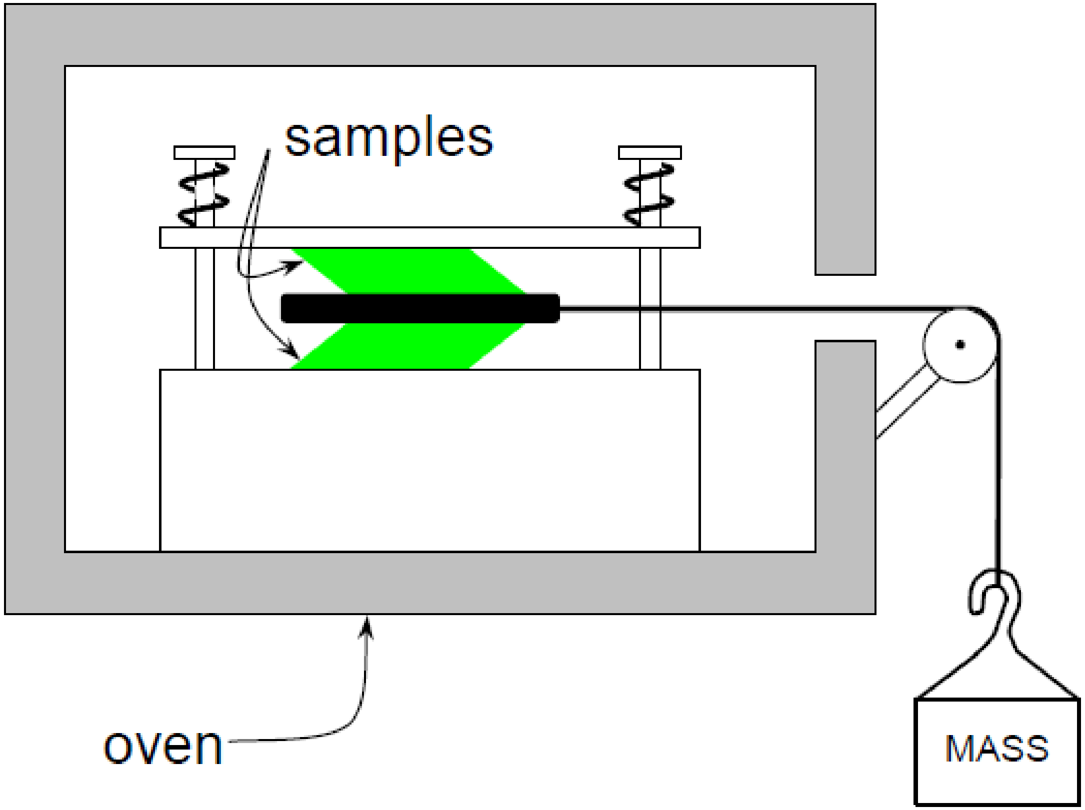



**Shear modulus**

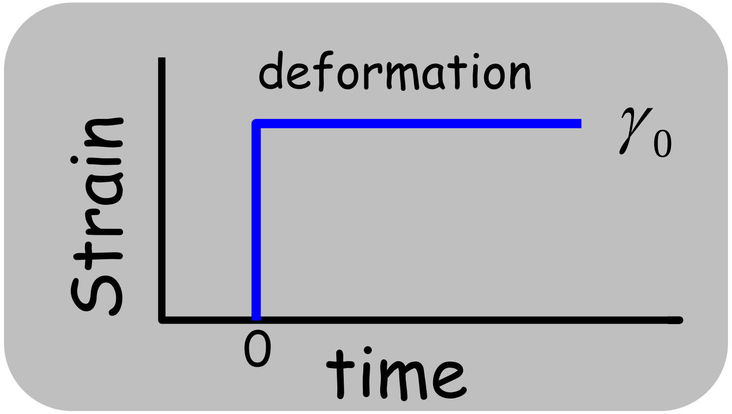
$$G = \frac{\tau_{xy}}{\gamma_o}$$

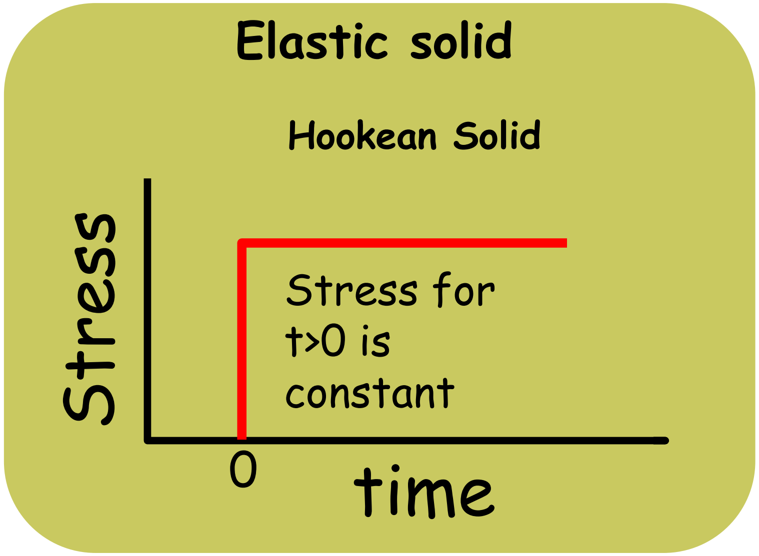
$$\gamma_o = \frac{\delta x}{H}$$

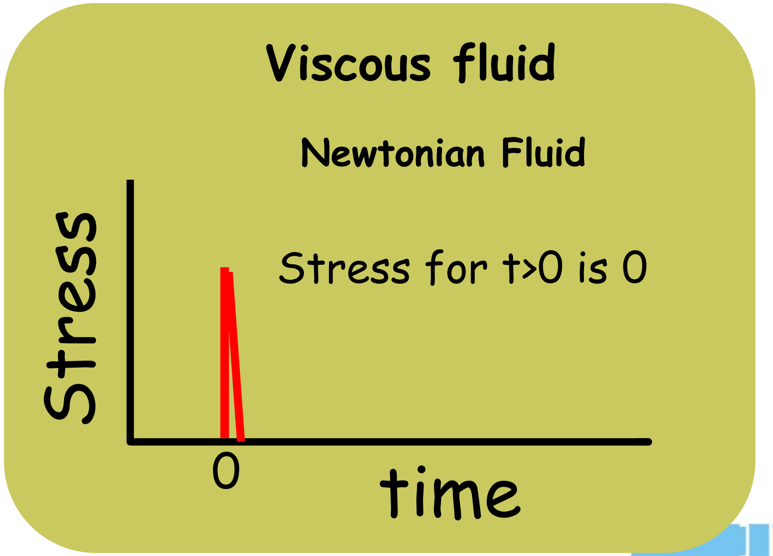
# Relaxation experiment for an elastic material



# Stress relaxation experiment



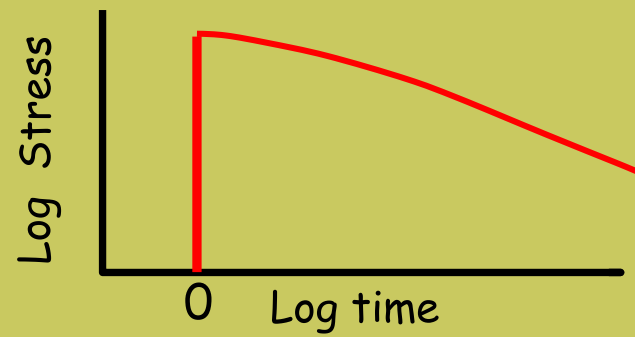



# Relaxation experiment for a viscoelastic material

- Shear stress is decreasing function of time.
- In small deformations (in LVE), the ratio stress to deformation is only function of time.
- It is called shear modulus G(t):

$$G(t) = \tau_{yx}(t)/\gamma_o$$



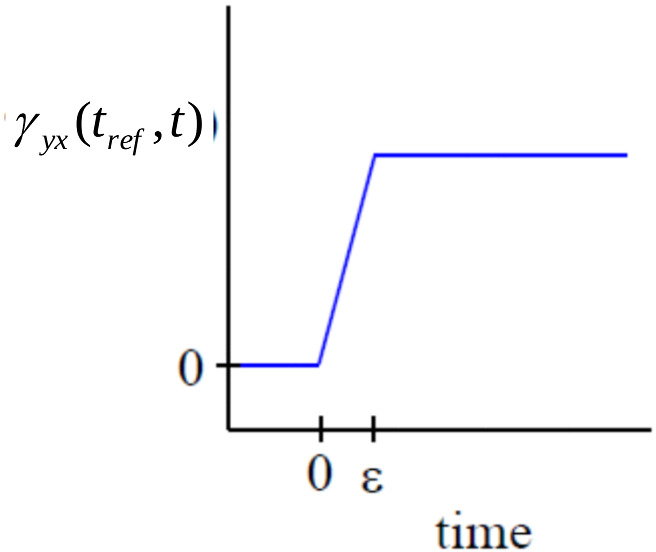

**Shear deformation $\gamma_o$ can be imposed via the application of a large deformation rate in a short time step**

$$\gamma_o = \dot{\gamma}_o \delta t$$

# Step strain in shear

**Kinematic for step strain in shear**

$$\dot{\gamma}(t) = \lim_{\varepsilon \to 0} \begin{cases} 0 & t < 0 \\ \dot{\gamma}_o & 0 \le t < \varepsilon \\ 0 & t \ge \varepsilon \end{cases}$$




**Relation between deformation and rate of deformation in shear flow:**

$$\frac{d\gamma_{yx}(t_{ref}, t)}{dt} = \dot{\gamma}_{yx} \qquad \gamma_{yx}(-\infty, t) = \dot{\gamma}_0 \varepsilon \equiv \gamma_0$$

# Material functions for step strain

Relaxation modulus

$$G(t,\gamma_o) \equiv \frac{\tau_{yx}(t,\gamma_o)}{\gamma_o}$$

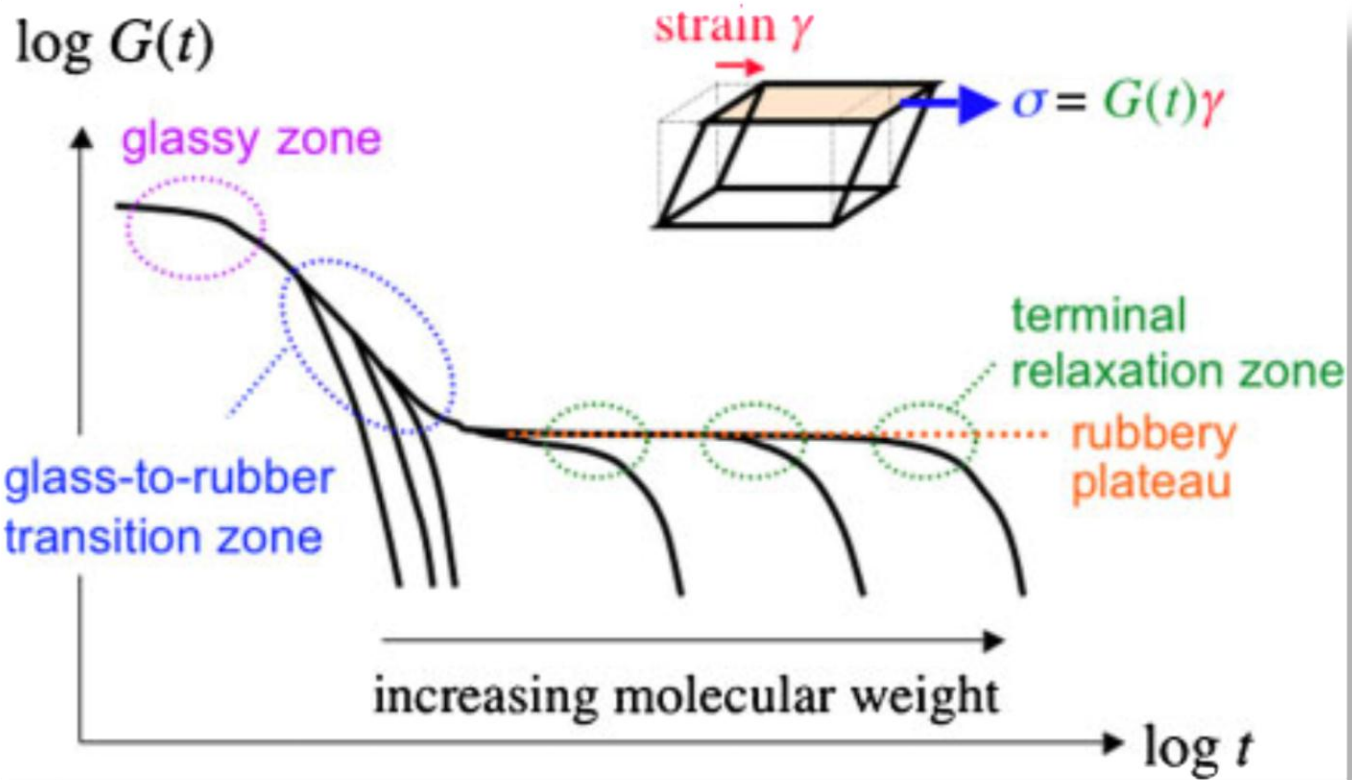
Relaxation modulus for the 1st normal stress difference

$$G_{\psi_1}(t,\gamma_o) \equiv \frac{\tau_{xx} - \tau_{yy}}{\gamma_o}$$

Relaxation modulus for the 2nd normal stress difference

$$G_{\psi_2}(t,\gamma_o) \equiv \frac{\tau_{yy} - \tau_{zz}}{\gamma_o}$$

# Linear Viscoelasticity

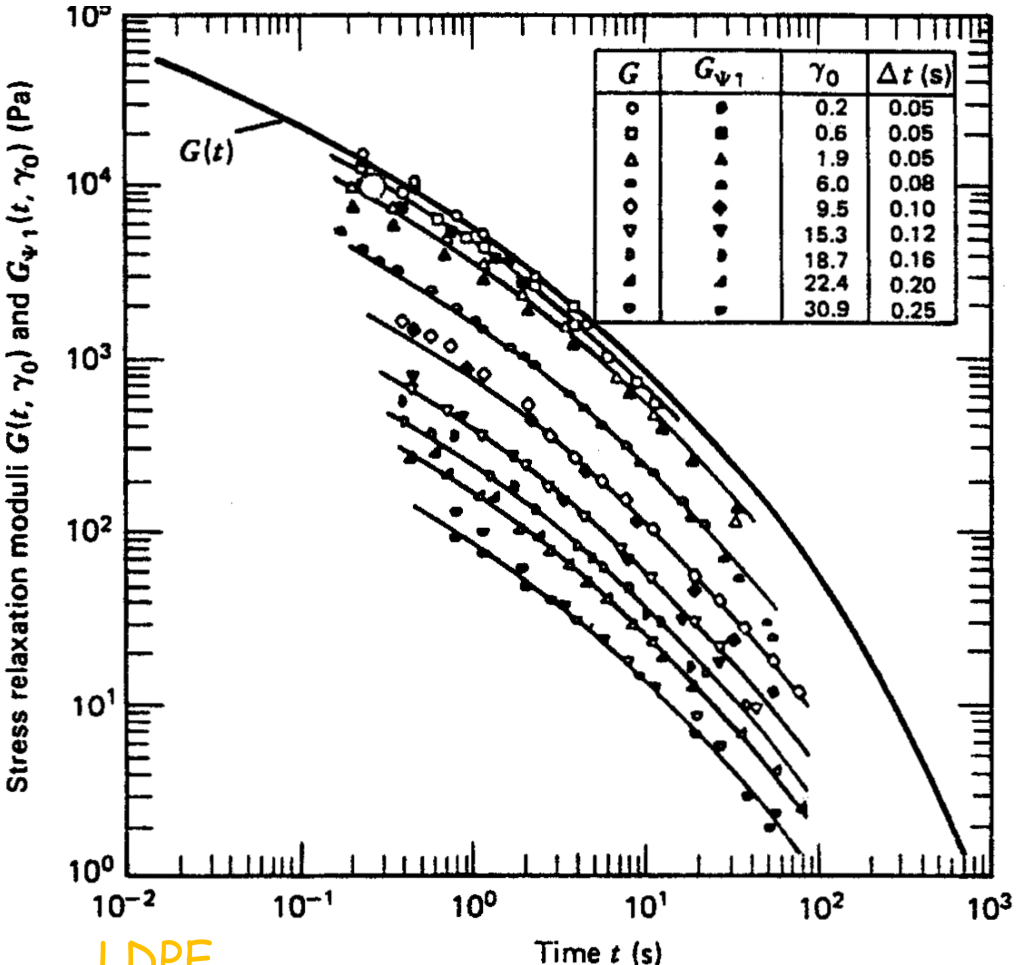



$$G(t) = \lim_{\gamma \to 0} \frac{\tau_{yx}(t)}{\gamma}$$

***Viscoelastic relaxation modulus of flexible linear polymers.***

***Polym J*. 2009, 41(11), 929.**

# Experimental observations




LDPE

Relaxation Modulus:*

$$G(t,\gamma_o) \equiv \frac{\tau_{yx}(t,\gamma_o)}{\gamma_o}$$

For small deformations

$$\lim_{\gamma_0 \to 0} G(t,\gamma_0) = G(t)$$

Lodge-Meissner's rule:

$$\frac{G(t,\gamma_0)}{G_{\Psi_1}(t,\gamma_0)} = 1$$



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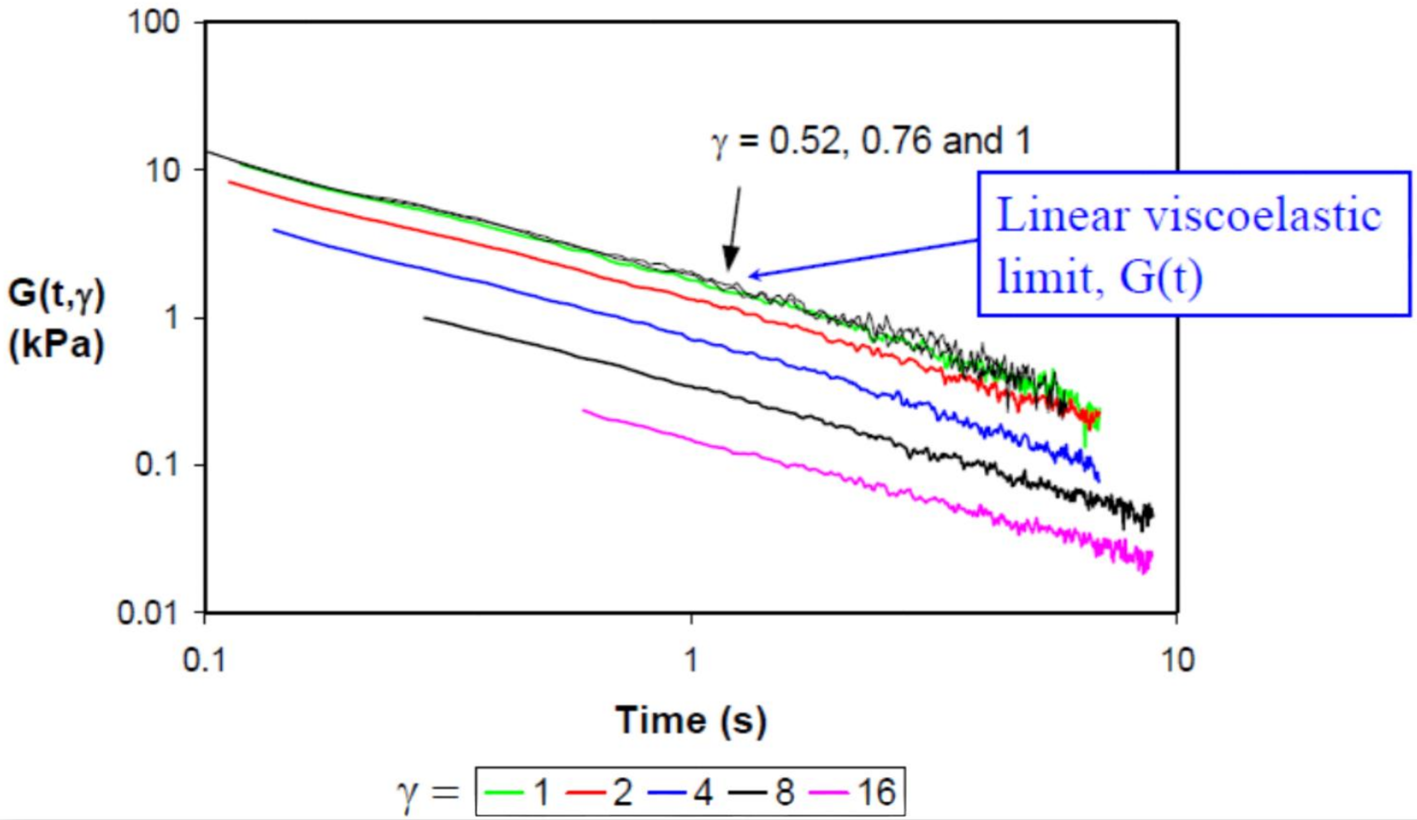
# Experimental observations



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# Gleissle's rule

Bird, Armstrong, Hassager (1987); Dealy & Wissbrun (1990)

$$\eta^{+}(t) \approx \eta(\dot{\gamma})\Big|_{t=1/\dot{\gamma}}$$

$$\Psi^{+}(t) \approx \Psi_1(\dot{\gamma})\Big|_{t=k/\dot{\gamma}}$$

$$\Psi_1(\dot{\gamma}) \approx -2\int_{\dot{\gamma}/k}^{\infty} x^{-1}\left[\frac{\partial \eta(x)}{\partial x}\right]dx$$

They are valid in the linear elastic region

$\eta \leftarrow \eta^{+}$

$\Psi_1 \leftarrow \Psi^{+}$

$\Psi_1 \leftarrow \eta$

k varies between 2<k<3, and can be calculated with a fitting procedure