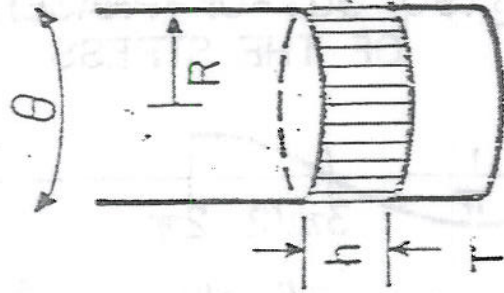


RHEOLOGY: THE STUDY OF THE DEFORMATION OF MATTER IN RESPONSE TO AN IMPOSED STRESS

TESTING OF POLYMERIC LIQUIDS

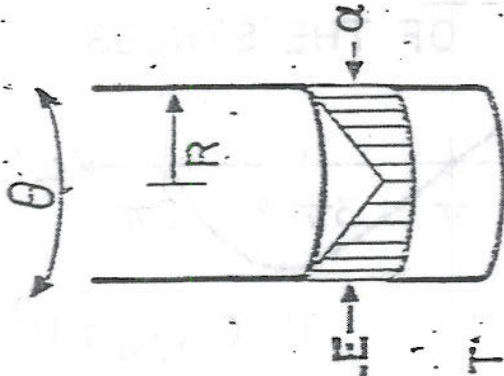
PARALLEL PLATE



$$\text{STRAIN } \gamma = \frac{R\theta}{h}$$

$$\text{STRESS } \sigma = \frac{2T}{\pi R^3}$$

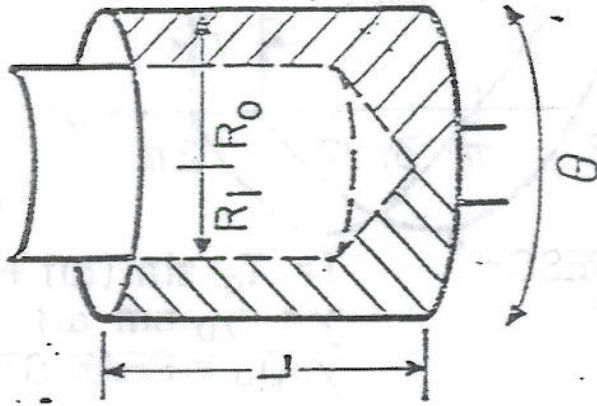
CONE AND PLATE



$$\gamma = \frac{\theta}{\alpha}$$

$$\sigma = \frac{3T}{2\pi R^3}$$

COUETTE

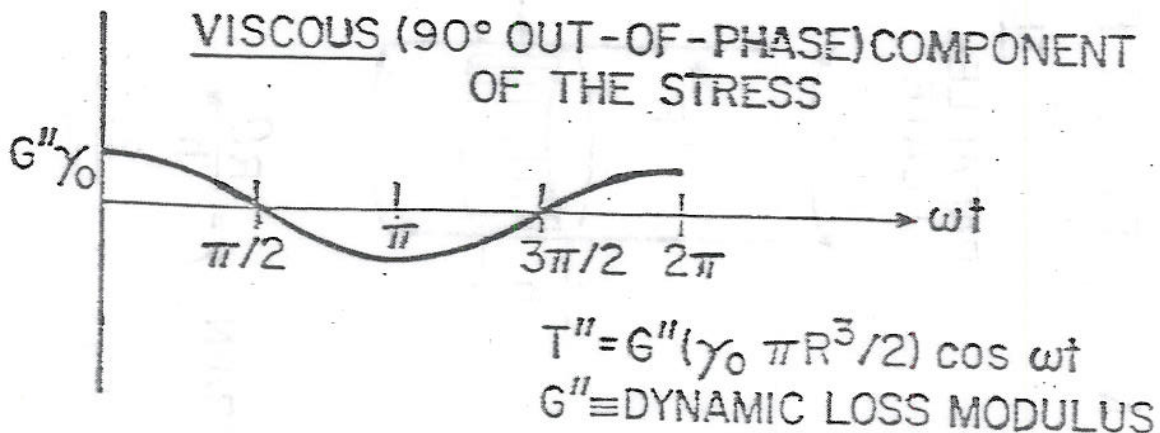
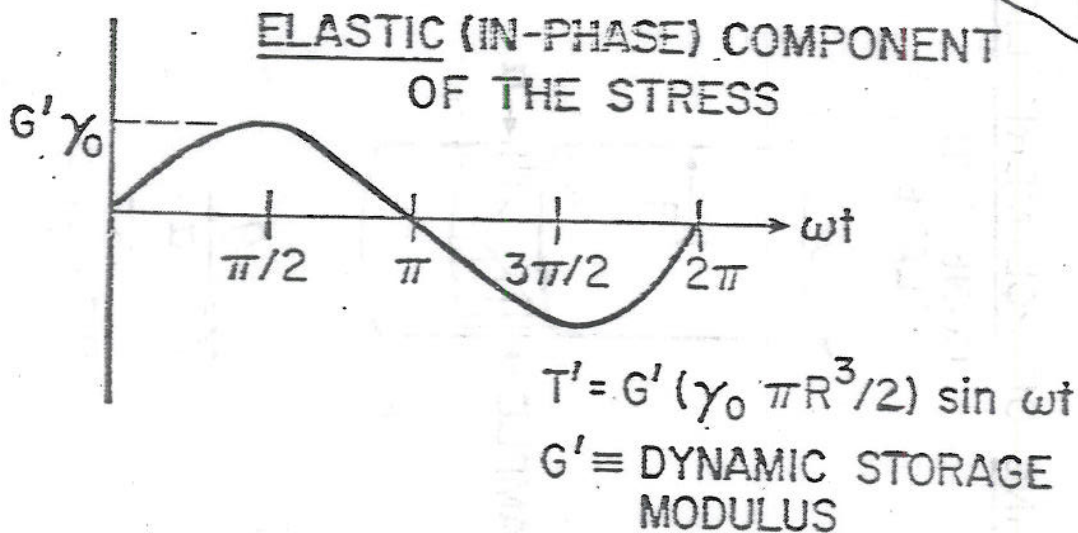
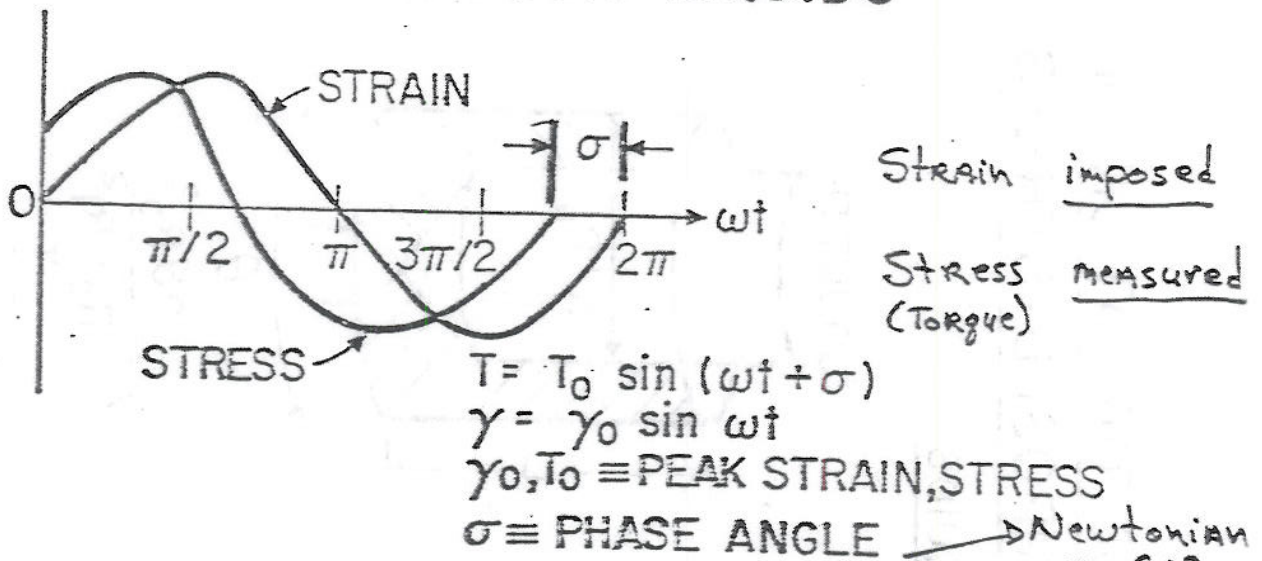


$$\gamma = \frac{2\theta R_0^2}{R_0^2 - R_1^2}$$

$$\sigma = \frac{T}{2\pi L R_0^2}$$

Steady Shear: replace θ with ωt to get $\dot{\gamma}$.
 $\dot{\gamma}$ is steady rotation velocity

DYNAMIC MECHANICAL TESTING OF VISCOELASTIC LIQUIDS



Rheological Functions

Dynamic Oscillatory Testing:

$$G^* = G' + iG'' \quad \text{Complex modulus}$$

$$G' = (\sigma/\gamma)_0 \cos \delta \quad \text{Elastic (storage) Modulus}$$

$$G'' = (\sigma/\gamma)_0 \sin \delta \quad \text{Viscous (loss) Modulus}$$

$$G''/G' = \tan \delta \quad \delta = \text{phase angle}$$

$$J^* = 1/G^* \quad \text{Complex Compliance}$$

$$\eta^* = \eta' - i\eta'' = (\eta'^2 + \eta''^2)^{1/2} \quad \text{Complex Viscosity}$$
$$= \frac{(G'^2 + G''^2)^{1/2}}{\omega}$$

$$\eta' = G''/\omega \quad \text{dynamic Viscosity}$$

Steady Shear Testing

$$\eta = \sigma_{12}/\dot{\gamma} \quad \text{steady shear viscosity}$$

$$\eta_0 = \lim_{\dot{\gamma} \rightarrow 0} \eta(\dot{\gamma}) \quad \text{zero-shear viscosity}$$

$$N_1 = \sigma_{11} - \sigma_{22} \quad 1^{\text{st}} \text{ Normal Stress Difference}$$

$$\Psi_1 = \frac{(\sigma_{11} - \sigma_{22})}{\dot{\gamma}^2} \quad 1^{\text{st}} \text{ Normal Stress Coefficient}$$

$$\Psi_2 = \frac{(\sigma_{22} - \sigma_{33})}{\dot{\gamma}^2} \quad 2^{\text{nd}} \text{ Normal Stress Coefficient}$$

Constitutive Equation for Linear Viscoelasticity in Simple Shear

stress tensor: Simple Shear flow (SSF)

$$\sigma_{ij} = \begin{pmatrix} 0 & \sigma_{12} & 0 \\ \sigma_{21} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

strain tensor:

$$\gamma_{ij} = \begin{pmatrix} 0 & \gamma_{12} & 0 \\ \gamma_{21} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \gamma_{12} = \gamma_{21} = \frac{\partial u_1}{\partial x_2}$$

Stress and strain are time dependent and are connected by the constitutive equation for linear viscoelasticity (LVE), which for Simple Shear is based on the concept that the effects of sequential changes in strain are ADDITIVE.

$$\sigma_{21}(t) = \int_{-\infty}^t G(t-t') \dot{\gamma}_{21}(t') dt'$$

where $\dot{\gamma}_{21} = \partial \gamma_{21} / \partial t = \nabla$ Shear rate

$G(t-t') \Rightarrow$ relaxation modulus

where integration is carried out over all past times (t') up to the current time, (t).

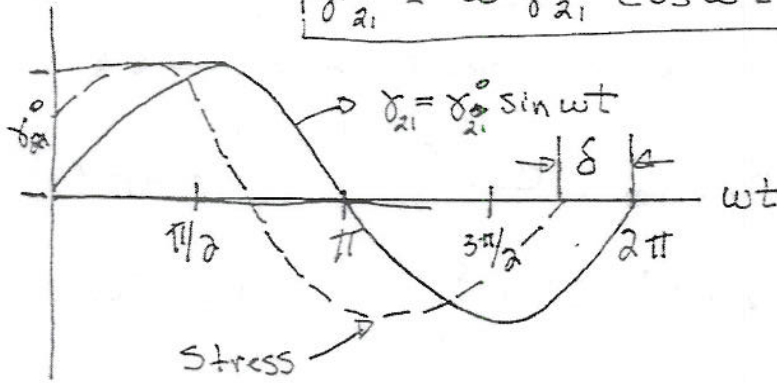
Dynamic Oscillatory Shear.

Strain (imposed):

$$\gamma_{21} = \gamma_{21}^0 \sin \omega t$$

γ_{21}^0 = peak strain ω = frequency.

$$\dot{\gamma}_{21} = \omega \gamma_{21}^0 \cos \omega t \Rightarrow \text{shear rate}$$



δ = phase angle

$\delta = 90^\circ$ (viscous)

$\delta = 0^\circ$ (Elastic)

Substituting into LVE Simple Shear Constitutive Eq.

with $(t-t') = s$

$$\sigma_{21}(t) = \int_0^\infty G(s) \omega \gamma_{21}^0 \cos[\omega(t-s)] ds$$

$$= \gamma_{21}^0 \left[\omega \int_0^\infty G(s) \sin \omega s ds \right] \sin \omega t + \gamma_{21}^0 \left[\omega \int_0^\infty G(s) \cos \omega s ds \right] \cos \omega t$$

\therefore $\sin \omega t$ term "in-phase" with γ_{21}

$\cos \omega t$ term "out-of-phase by 90° " with γ_{21}

• Stress (σ_{21}) \Rightarrow ① periodic in ω

② out-of-phase with γ_{21}

$$\sigma_{21} = \gamma_{21}^0 (G' \sin \omega t + G'' \cos \omega t)$$

defining G' = "in-phase" with γ_{21}

G'' = "out-of-phase" with γ_{21}

Dynamic Oscillatory Shear (continued)

An alternative form for the stress (σ_{21}) uses the Amplitude of the stress (σ_{21}°) and the phase angle (δ)

$$\sigma_{21} = \sigma_{21}^{\circ} (\sin \omega t + \delta) = \sigma_{21}^{\circ} \cos \delta \sin \omega t + \sigma_{21}^{\circ} \sin \delta \cos \omega t$$

Comparison with the previous equation gives:

$$G' = (\sigma_{21}^{\circ} / \gamma_{21}^{\circ}) \cos \delta \quad \text{storage (elastic) modulus}$$

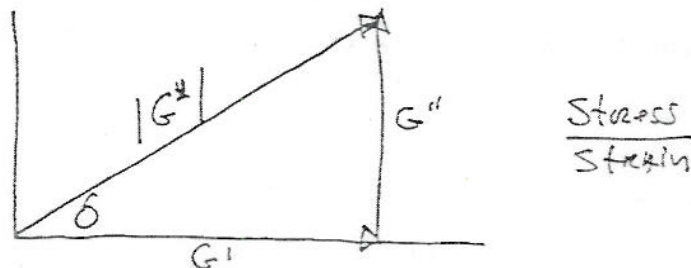
$$G'' = (\sigma_{21}^{\circ} / \gamma_{21}^{\circ}) \sin \delta \quad \text{loss (viscous) modulus}$$

$$G''/G' = \tan \delta \quad \text{loss tangent}$$

It can be shown (with some work) that the sinusoidally varying stress can be expressed as a complex quantity: The modulus is also complex, given by:

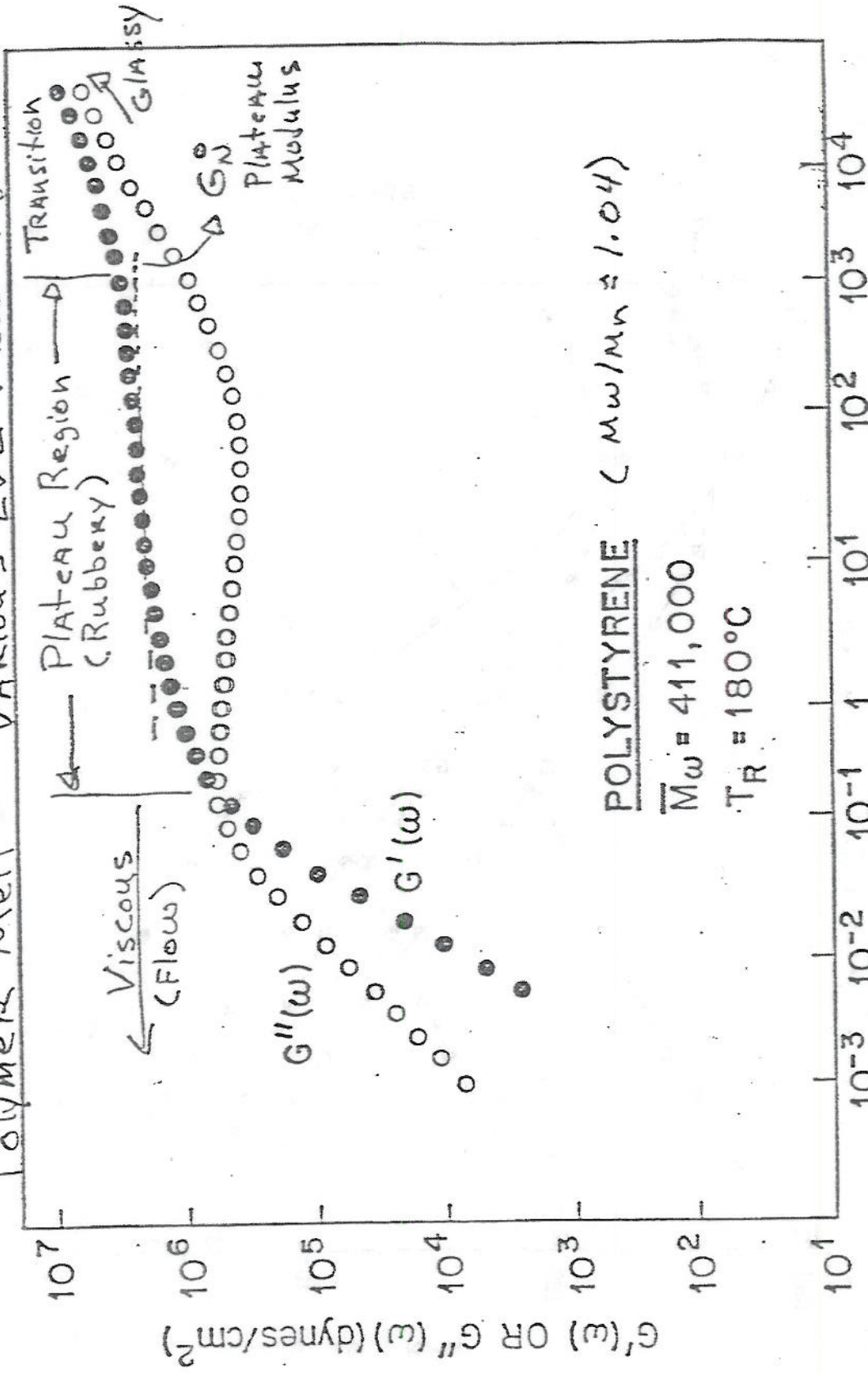
$$\sigma_{21}^* / \gamma_{21}^{\circ} = G^* = G' + iG''$$

$$|G^*| = \sigma_{21}^{\circ} / \gamma_{21}^{\circ} = (G'^2 + G''^2)^{1/2} \quad \leftarrow$$



$$\begin{aligned} G' &= |G^*| \cos \delta \\ G'' &= |G^*| \sin \delta \end{aligned} \quad \leftarrow$$

Polymer Melt - Various LVE Flow Regimes



POLYSTYRENE ($M_w/M_n \approx 1.04$)

$\bar{M}_w = 411,000$

$T_R = 180^\circ\text{C}$

ω in rad/sec