Small-Amplitude Oscillatory Shear

Apply a sinusoidal shear strain

$$\gamma(t) = \gamma_0 \sin(\omega t) \tag{2-45}$$

The shear rate is therefore

$$\dot{\gamma}(t) = \gamma_0 \omega \cos(\omega t) = \dot{\gamma}_0 \cos(\omega t) \tag{2-46}$$

The stress is also sinusoidal with the same frequency, but leads the strain by **phase angle** δ.

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) \tag{2-47}$$

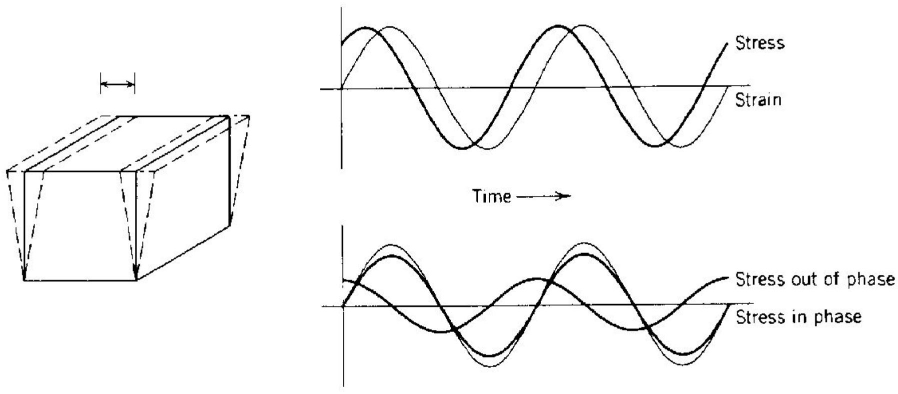

Figure 1: Oscillatory Shear. The stress leads the applied strain by phase angle δ.

Small-Amplitude Oscillatory Shear
BOLTZMANN SUPERPOSITION

Using the Boltzmann Superposition Principle

$$\sigma(t) = \int_{-\infty}^{t} G(t-t')\dot{\gamma}(t')dt' \qquad (2\text{-}8)$$

with $s \equiv t - t'$, $ds = -dt'$, $t' = t \Rightarrow s = 0$ and $t' = -\infty \Rightarrow s = \infty$

$$\sigma(t) = \int_{0}^{\infty} G(s)\gamma_0\omega\cos(\omega[t-s])ds$$

$$\sigma(t) = \gamma_0\left[\omega\int_0^\infty G(s)\sin(\omega s)ds\right]\sin(\omega t) + \gamma_0\left[\omega\int_0^\infty G(s)\cos(\omega s)ds\right]\cos(\omega t)$$

Define Storage Modulus

$$G'(\omega) \equiv \omega\int_0^\infty G(s)\sin(\omega s)ds \qquad (2\text{-}65)$$

and Loss Modulus

$$G''(\omega) \equiv \omega\int_0^\infty G(s)\cos(\omega s)ds \qquad (2\text{-}66)$$

Thus the stress is

$$\sigma(t) = \gamma_0\left[G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t)\right] \qquad (2\text{-}49)$$

Using the formula for the sine of a sum

$$\sigma(t) = \sigma_0\sin(\omega t + \delta) = \sigma_0\left[\cos(\delta)\sin(\omega t) + \sin(\delta)\cos(\omega t)\right]$$

Defining

$$G_d \equiv \frac{\sigma_0}{\gamma_0}$$

$$G' = G_d\cos(\delta) \qquad (2\text{-}50)$$

$$G'' = G_d\sin(\delta) \qquad (2\text{-}51)$$

The ratio

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

Small-Amplitude Oscillatory Shear
HOOKEAN SOLID

$$\text{Hooke's Law} \qquad \sigma = G\gamma \tag{2-52}$$

For oscillatory shear

$$\gamma(t) = \gamma_0 \sin(\omega t) \tag{2-45}$$

For the solid

$$\sigma(t) = \gamma_0 G \sin(\omega t) \tag{2-53}$$

Comparing with the general form

$$\sigma(t) = \gamma_0 \left[G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t)\right] \tag{2-49}$$

The solid has

$$G'(\omega) = G \qquad \text{and} \qquad G''(\omega) = 0$$

$$\delta = \tan^{-1}(G''/G') = 0$$

meaning that the stress is perfectly in phase with the strain.

NEWTONIAN LIQUID

$$\text{Newton's Law } \sigma = \eta\dot{\gamma} \tag{2-54}$$

For oscillatory shear

$$\dot{\gamma}(t) = \gamma_0 \omega \cos(\omega t) \tag{2-46}$$

For the liquid

$$\sigma(t) = \eta\gamma_0\omega\cos(\omega t) \tag{2-55}$$

The liquid has

$$G'(\omega) = 0 \qquad \text{and} \qquad G''(\omega) = \eta\omega$$

$$\delta = \tan^{-1}(G''/G') = \pi/2$$

meaning that the stress is 90° out of phase with the strain (the stress is in phase with the rate of strain).

Small-Amplitude Oscillatory Shear BASIC PHYSICS - THE MAXWELL MODEL

$$G(t) = G_N^0 \exp(-t/\lambda)$$

Storage Modulus

$$G'(\omega) \equiv \omega \int_0^\infty G(t) \sin(\omega t) dt \tag{2-65}$$

$$G'(\omega) = \omega G_N^0 \int_0^\infty \exp(-t/\lambda) \sin(\omega t) dt = \frac{G_N^0 (\omega\lambda)^2}{1 + (\omega\lambda)^2}$$

and Loss Modulus

$$G''(\omega) \equiv \omega \int_0^\infty G(t) \cos(\omega t) dt \tag{2-66}$$

$$G''(\omega) = \omega G_N^0 \int_0^\infty \exp(-t/\lambda) \cos(\omega t) dt = \frac{G_N^0 \omega\lambda}{1 + (\omega\lambda)^2}$$

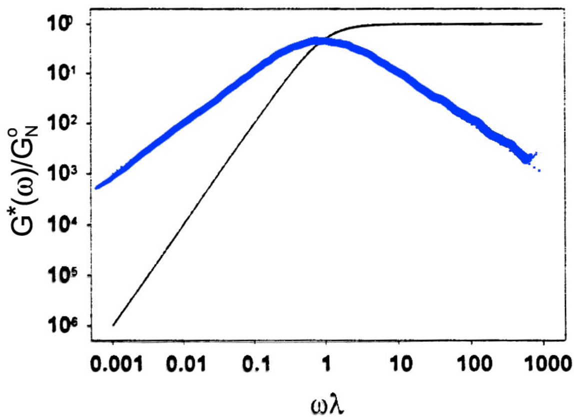

Figure 2: Storage and Loss Modulus for the Maxwell Model.

The real power of the oscillatory shear experiment is that we can probe the viscoelastic response on different time scales by applying different frequencies ω.

Small-Amplitude Oscillatory Shear COMPLEX MODULUS, VISCOSITY AND COMPLIANCE

COMPLEX MODULUS

$$G^*(\omega) \equiv G'(\omega) + iG''(\omega) \tag{2-58}$$

Magnitude

$$G_d \equiv \frac{\sigma_0}{\gamma_0} = |G^*| = \sqrt{(G')^2 + (G'')^2} \tag{2-59}$$

Phase

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

COMPLEX VISCOSITY

$$\eta^*(\omega) \equiv \frac{G^*(\omega)}{i\omega}$$

$$\eta^*(\omega) = \eta'(\omega) - i\eta''(\omega) \tag{2-63}$$

Magnitude

$$|\eta^*| = \sqrt{(\eta')^2 + (\eta'')^2} = \frac{|G^*(\omega)|}{\omega} \tag{2-64}$$

$$\eta' = G''/\omega \tag{2-61}$$

$$\eta'' = G'/\omega \tag{2-62}$$

Phase

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

COMPLEX COMPLIANCE

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

Small-Amplitude Oscillatory Shear

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

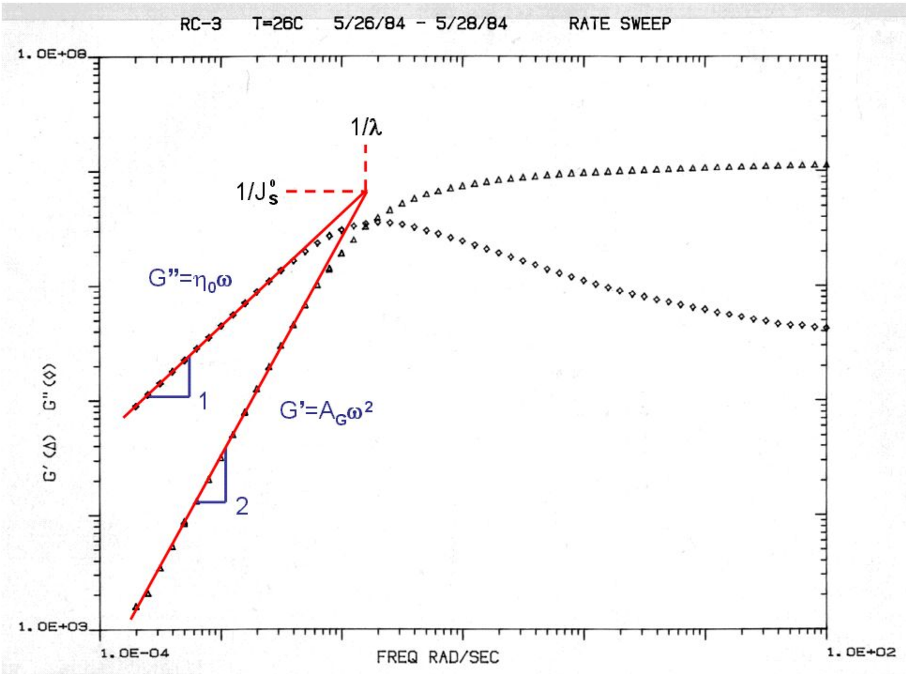

Figure 3: Storage and Loss Moduli of RC-3.

Time period for one cycle is $2\pi/\omega$.
For $\omega = 10^{-4}$ rad/sec, $2\pi/\omega \cong 1$ day.

Small-Amplitude Oscillatory Shear
VISCOSITY, PLATEAU MODULUS AND STEADY STATE COMPLIANCE

$$\eta_0 = \lim_{\omega \to 0} \left(\frac{G''(\omega)}{\omega} \right) = \lim_{\omega \to 0} \eta'(\omega) \tag{2-73}$$

$$\eta_0 = \frac{2}{\pi} \int_{-\infty}^{\infty} \frac{G'(\omega)}{\omega} d \ln \omega$$

$$G_N^0 = \frac{2}{\pi} \int_{-\infty}^{\infty} G''(\omega) d \ln \omega$$

$$A_G \equiv \lim_{\omega \to 0} \left(\frac{G'(\omega)}{\omega^2} \right) = \int_0^{\infty} G(s) s ds \tag{2-74}$$

Proof:

$$\lim_{\omega \to 0} \sin(\omega s) = \omega s$$

$$G'(\omega) \equiv \omega \int_0^{\infty} G(s) \sin(\omega s) ds \tag{2-65}$$

$$\lim_{\omega \to 0} \left(\frac{G'(\omega)}{\omega^2} \right) = \frac{1}{\omega} \int_0^{\infty} G(s) \omega s ds$$

Recall that

$$J_S^0 = \frac{1}{\eta_0^2} \int_0^{\infty} G(s) s ds \tag{2-33}$$

$$A_G = J_s^0 \eta_0^2 \tag{2-75}$$

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

INTERRELATIONS

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

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

Small-Amplitude Oscillatory Shear
INTEGRATION OF LOSS MODULUS TO GET THE PLATEAU MODULUS

$$G_N^0 = \frac{2}{\pi}\int_{-\infty}^{\infty} G''(\omega)\, d\ln\omega$$

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

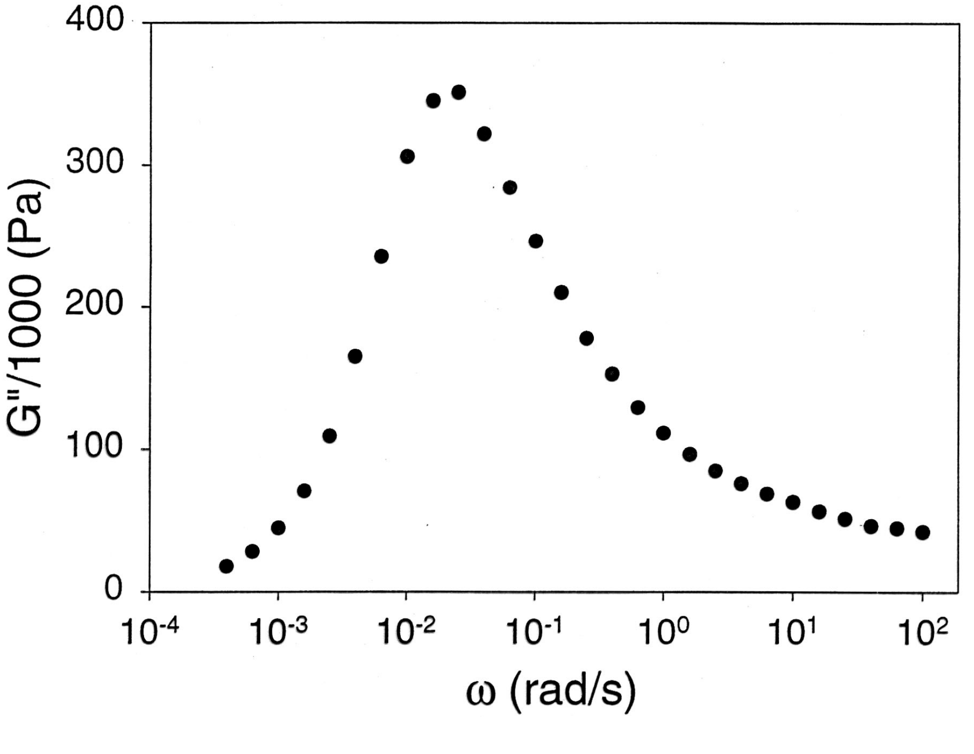

Figure 4: Loss Modulus of RC3 at 26°C.

Small-Amplitude Oscillatory Shear
DISSIPATED ENERGY PER CYCLE

Dissipated Energy (WORK) per unit volume

$$\underline{W} = \int \sigma \dot{\gamma} dt \tag{2-56}$$

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) \tag{2-47}$$

$$\dot{\gamma}(t) = \gamma_0 \omega \cos(\omega t) \tag{2-46}$$

$$\underline{W} = \int_0^{2\pi/\omega} \sigma_0 \gamma_0 \omega \sin(\omega t + \delta) \cos(\omega t) dt$$

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

$$\underline{W} = \int_0^{2\pi/\omega} \sigma_0 \gamma_0 \omega \left[\cos(\delta) \sin(\omega t) \cos(\omega t) + \sin(\delta) \cos^2(\omega t)\right] dt$$

$$\underline{W} = \sigma_0 \gamma_0 \omega \left[-\cos(\delta) \frac{\cos(2\omega t)}{4\omega} + \sin(\delta) \left(\frac{t}{2} + \frac{\sin(2\omega t)}{4\omega} \right) \right]_0^{2\pi/\omega}$$

$\cos(0) = \cos(4\pi) = 1, \qquad \sin(0) = \sin(4\pi) = 0$

$$\underline{W} = \sigma_0 \gamma_0 \omega \left[-\cos(\delta) \frac{1-1}{4\omega} + \sin(\delta) \left(\frac{2\pi/\omega}{2} + \frac{0-0}{4\omega} \right) \right]$$

$$\underline{W} = \pi \sigma_0 \gamma_0 \sin(\delta)$$

Recall $$G'' = G_d \sin(\delta) = \frac{\sigma_0}{\gamma_0} \sin(\delta) \tag{2-51}$$

$$\underline{W} = \pi \gamma_0^2 G'' \tag{2-57}$$

The loss modulus is proportional to the dissipated energy.