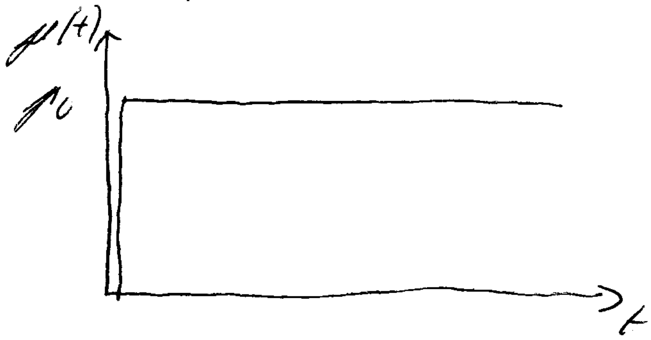
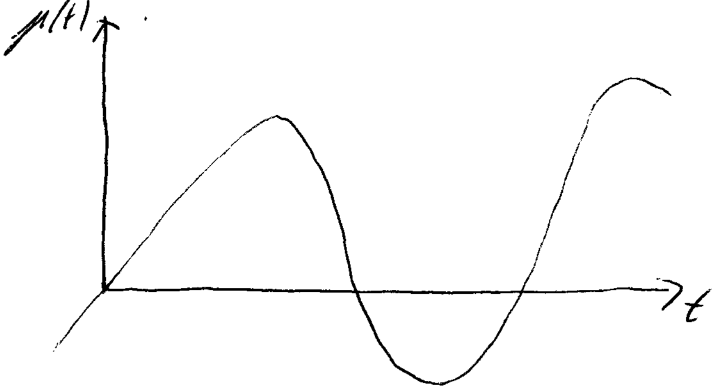
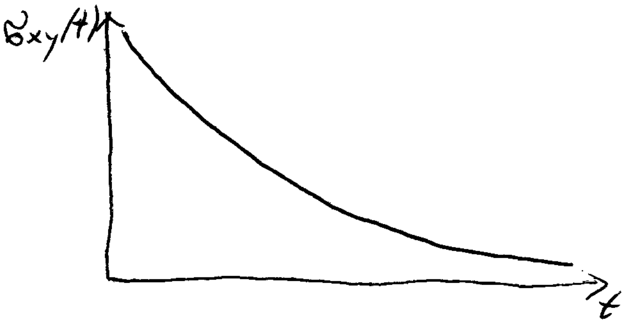
Viscoelasticity of Semiflexible Filaments

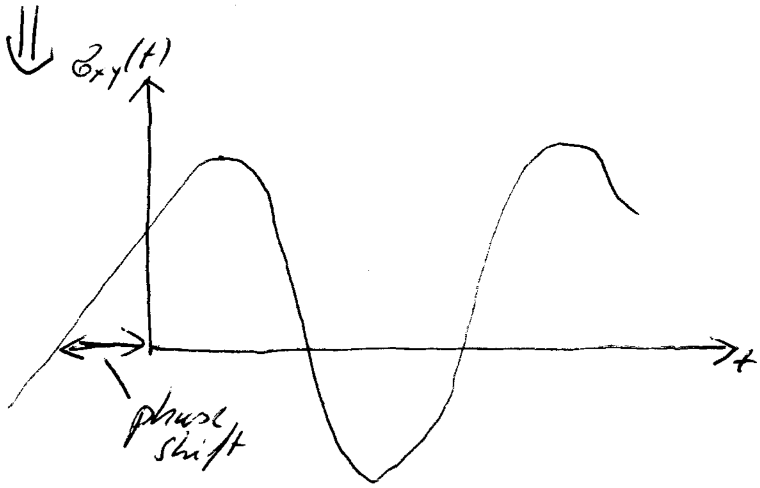
stepwise shear strain



oscillating shear strain







$$\gamma(t) = \begin{cases} 0 & \text{for } t<0 \\ \gamma_0 & \text{for } t>0 \end{cases}$$

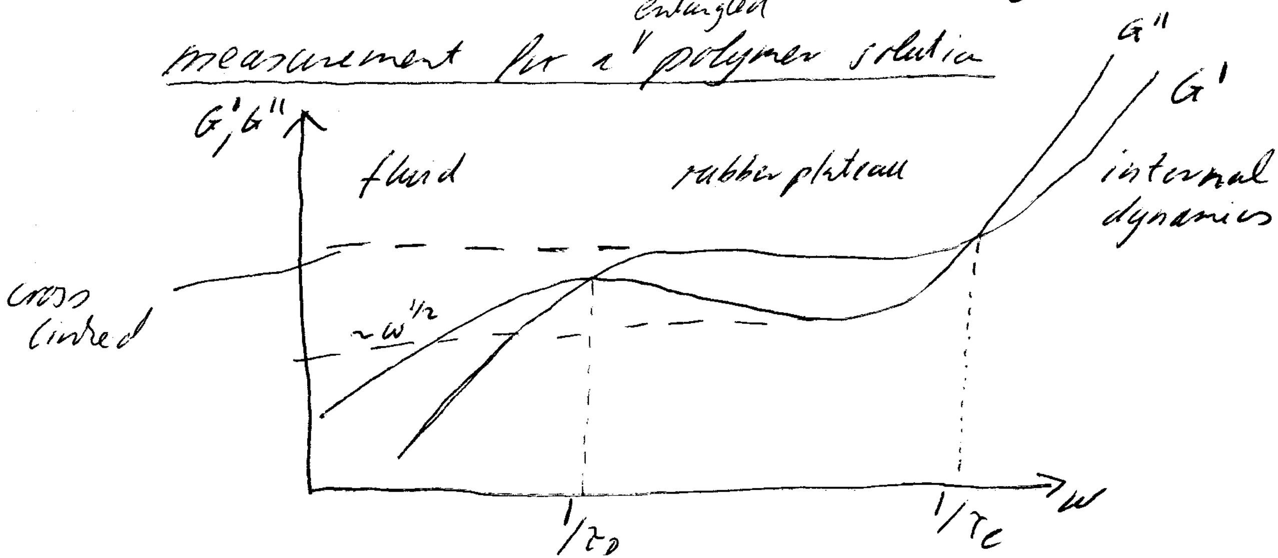
$$\gamma(t) = \gamma_0 \cos\omega t$$

$$\sigma_{xy}(t) = G(t)\,\gamma_0$$

(linear elasticity!)

$$\sigma_{xy}(t) = [\underbrace{G'(\omega)}_{\text{storage modulus} \Rightarrow \text{elastic}} \cos\omega t - \underbrace{G''(\omega)}_{\text{loss modulus} \Rightarrow \text{viscous}} \sin\omega t]\,\gamma_0$$

measurement for a entangled polymer solution



<u>fluid:</u> deformation is slow enough that solution behaves fluid

<u>rubber plateau:</u> deformation is fast enough that polymers cannot follow motion, the solution reacts elastic

<u>internal dynamics:</u> deformation is so fast that the shear stress cannot propagate along polymer chain

<u>reptation, τ_d:</u>

L: length of polymer chain

tube formed by surrounding polymers

Brownian motion $\Rightarrow$ diffusion along the tube $D_{\parallel}$ diffusion coefficient parallel to tube

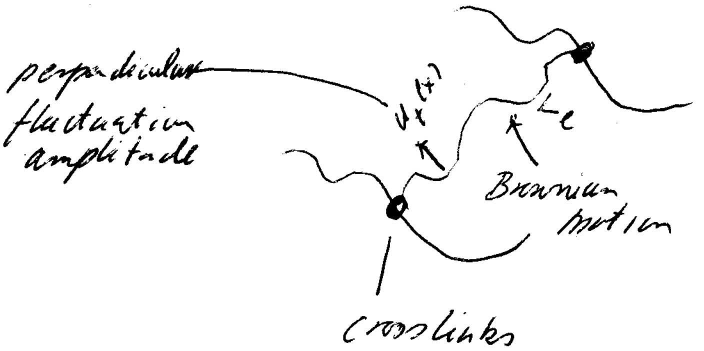
$\Rightarrow$ reptation time:

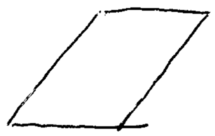
$$\tau_D \simeq \frac{L^2}{D_{\parallel}}$$

$$D_{\parallel} = \frac{k_B T}{2\pi \eta L \ln L/b} \approx \frac{k_B T}{\eta L}$$

$$\Rightarrow \boxed{\tau_D \sim \frac{\eta L^3}{k_B T}}$$

Elastic behavior of a crosslinked semiflexible polymer network:





L_e: ~~mesh size~~ length of polymer chain between two entanglements

ξ: mesh size of polymer network

$\Rightarrow$ shear pulls on crosslinks and causes entropic tension τ:

distance between crosslinks

relaxed ℓ_0

stretched ℓ

energy per unit length: $$H = \underbrace{\tfrac{1}{2} K_c (\nabla^2 u_t)^2}_{\text{bending}} + \underbrace{\tfrac{1}{2} \tau (\nabla u_t)^2}_{\text{entropic tension}}$$

$$L_e - \ell \approx \frac{1}{2} \int dx \, (\nabla u_t)^2$$

$$u_t(x) = \sum_q u_q \sin qx \qquad q = \frac{\pi}{\ell}, \frac{2\pi}{\ell}, \ldots$$

$\Rightarrow$ equipartition theorem provides $\langle u_q^2 \rangle$

$$\Rightarrow \quad L_e - \ell \approx k_B T \sum_q \frac{1}{K q^2 + \tau}$$

to linear order: $$L_e - \ell \approx + \frac{k_B T \ell^2}{6 K_c} - \frac{k_B T \ell^4}{90 K_c^2} \tau$$

$$\ell \approx \underbrace{L_e - \frac{k_B T \ell^2}{6 K_c}}_{= \ell_0} + \frac{k_B T \ell^4}{90 K_c^2} \tau$$

$$\Rightarrow \quad \underbrace{\ell - \ell_0}_{= \delta\ell} = \frac{k_B T \ell^4}{90 K_c^2} \tau$$

$$\Rightarrow \quad \boxed{\tau \sim \frac{K_c^2}{k_B T \ell^4} \delta \ell}$$

γ : strain, relative deformation

for small deformations: $\delta L \sim L_e \gamma \Rightarrow \gamma \sim \frac{\delta L}{L_e}$

$\Rightarrow$ elastic storage modulus G': $\ell \approx L_e$
(along a plane parallel to the shear, there are $\frac{1}{\xi^2}$ chains per unit area)

stress $\sigma \sim \frac{1}{\xi^2} \tau \, \delta L$

$$\sim \frac{1}{\xi^2} \frac{\kappa_c^2}{k_B T L_e^4} L_e \gamma$$

$$\sigma \sim \underbrace{\frac{\kappa_c^2}{k_B T \xi^2 L_e^3}}_{= G'} \gamma$$

for tightly entangled: $\xi \sim L_e$

$$\xi \sim \frac{1}{\sqrt{a c_{filament}}}$$

$$\Rightarrow G' \sim \frac{\kappa_c^2}{k_B T} (a c_{filament})^{5/2}$$

for entangled semiflexible polymer networks:

entropic tension caused by tube deformation causes elastic behavior (→Tony Maggs, David Morse)

$$G' = \frac{7 k_B T \, c_{Filament}}{5 L_e} + \frac{3 k_B T \, c_{Filament}}{5 e}$$