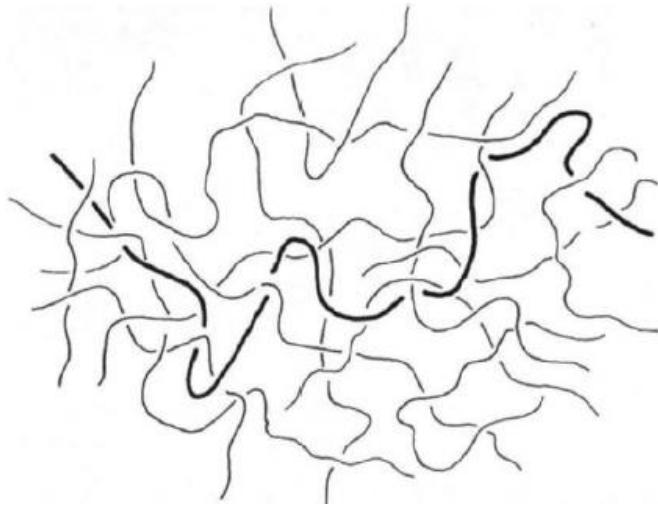
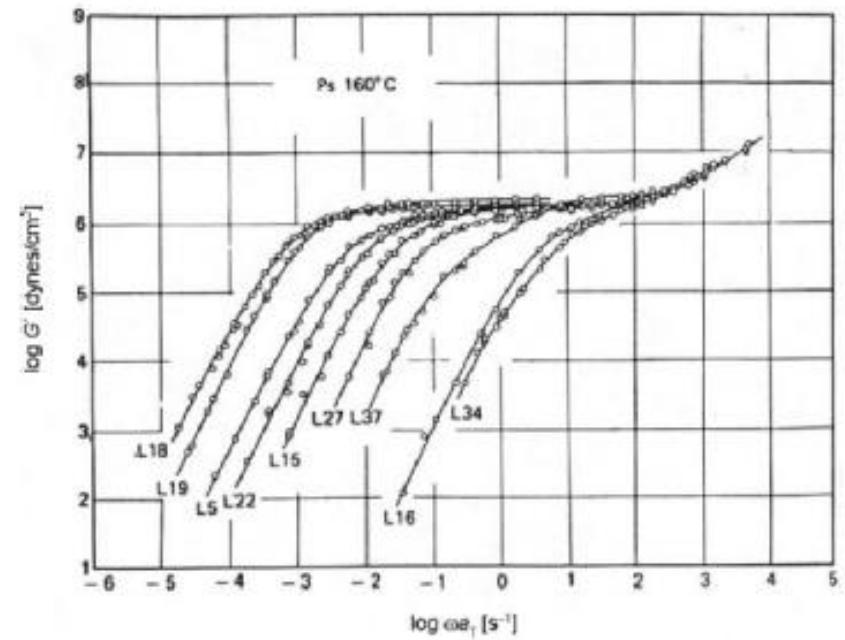
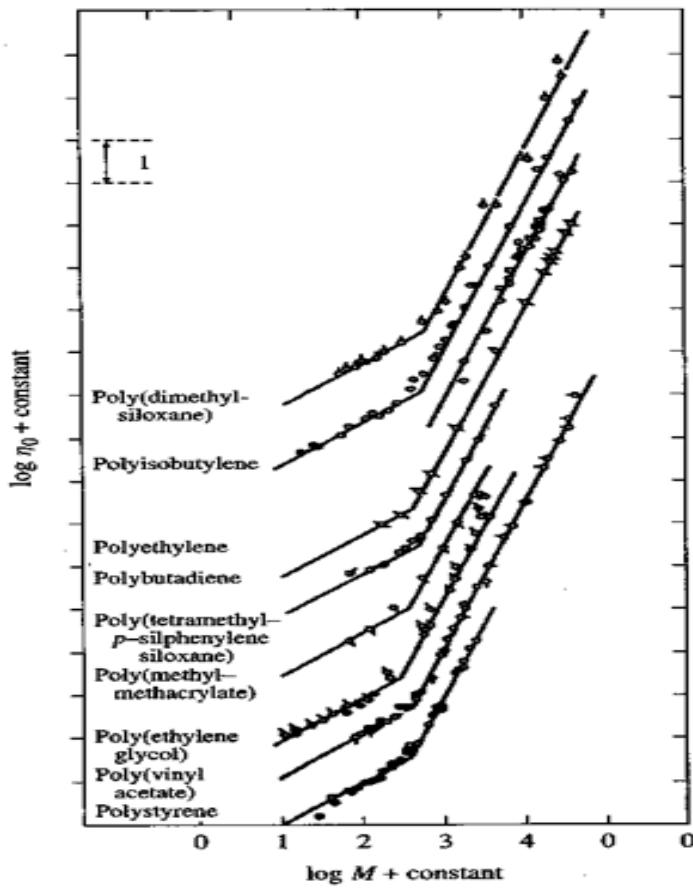


Melt theory



Entanglements



Rouse theory

$$G(t) = \frac{\rho RT}{M} \sum_{p=1}^N e^{-t/\tau_p}$$

$$\tau_p = \frac{b^2 N^2 \zeta}{6\pi^2 p^2 kT}$$

$$\tau_R = \frac{b^2 N^2 \zeta}{6\pi^2 kT} \sim M^2$$

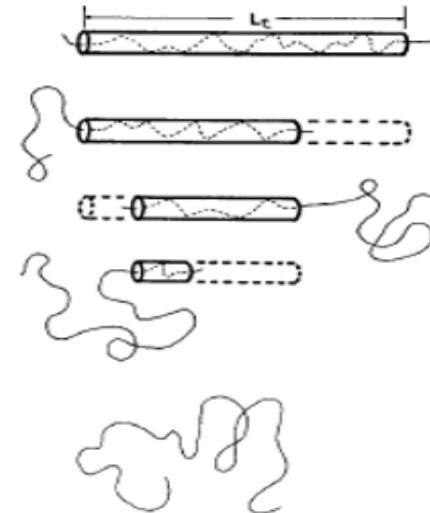
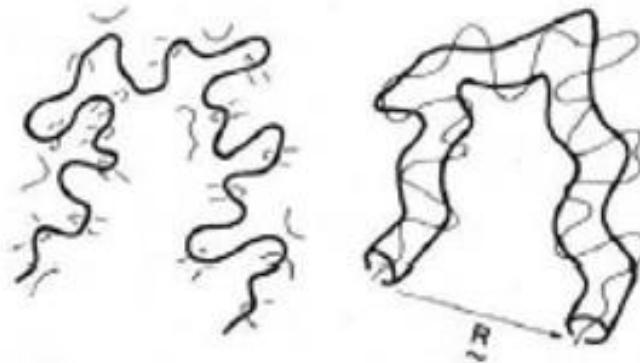
$$\tau_R = \frac{6\eta_o M}{\pi^2 \rho R T}$$

$$G'(\omega) = \frac{\rho RT}{M} \sum_{p=1}^N \frac{\omega^2 \tau_p^2}{1 + \omega^2 \tau_p^2}$$

$$G''(\omega) = \frac{\rho RT}{M} \sum_{p=1}^N \frac{\omega \tau_p}{1 + \omega^2 \tau_p^2}$$

Tube model

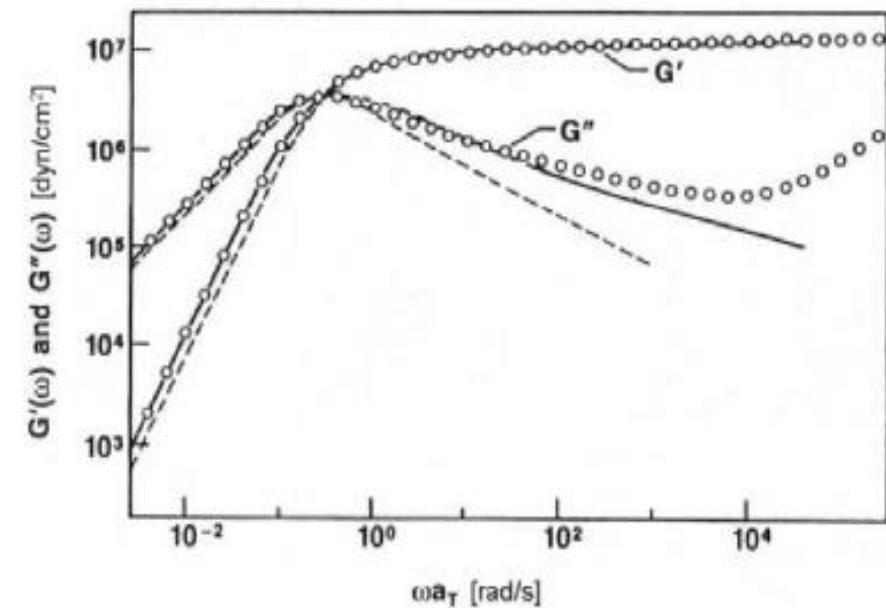
1. Reptation



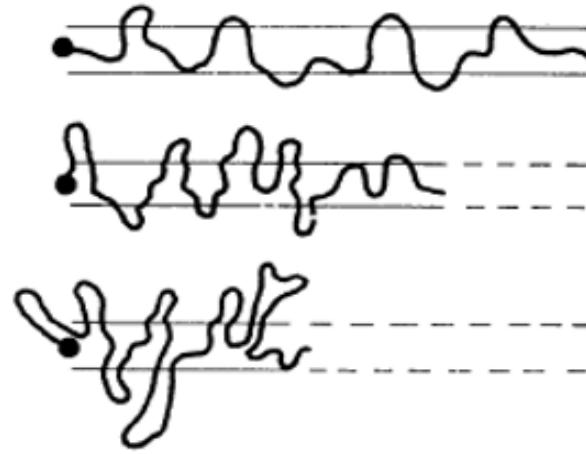
$$G(t) = \sum_{i,odd} G_i e^{-t/\tau_i}$$

$$G_i = \frac{8}{\pi^2} \frac{G_N^o}{i^2}, \quad \tau_i = \frac{\tau_d}{i^2}$$

$$\tau_d = \frac{\zeta N^3 b^4}{\pi^2 k T a^2}$$

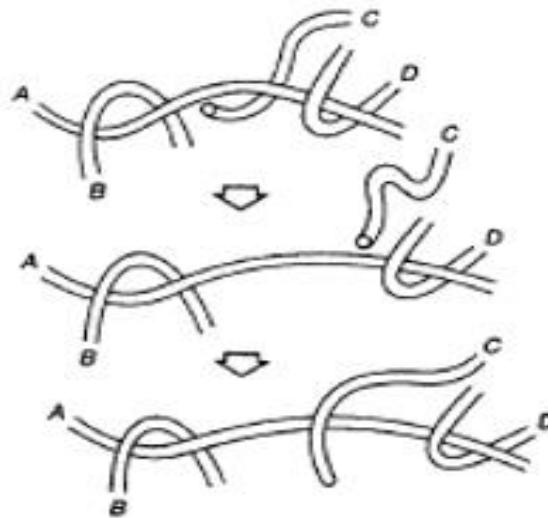


2. Primitive path fluctuation



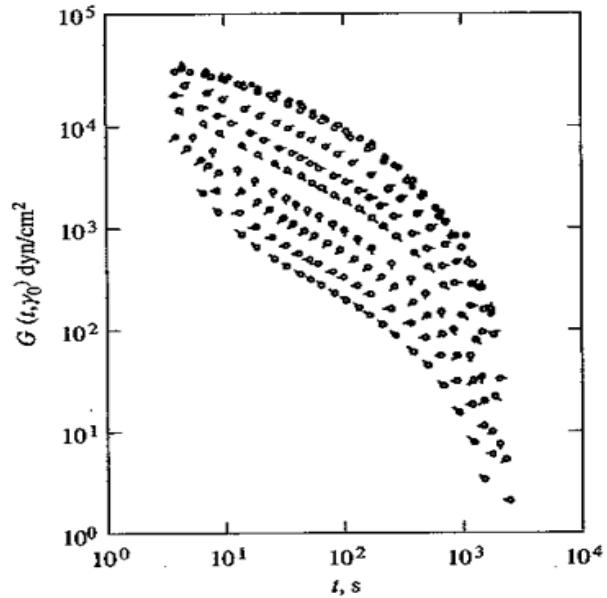
$$\tau_1 = \tau_d (1 - XZ^{-1/2})^3 \quad \eta_o = \eta_{o,NF} (1 - XZ^{-1/2})^3 \sim M^{3.4}$$

3. Constraint release



4. Chain retraction

$$\tau_s = 2\tau_R = \frac{\zeta N^2 b^2}{3\pi^2 kT} \sim M^2$$



5. Convective constraint release

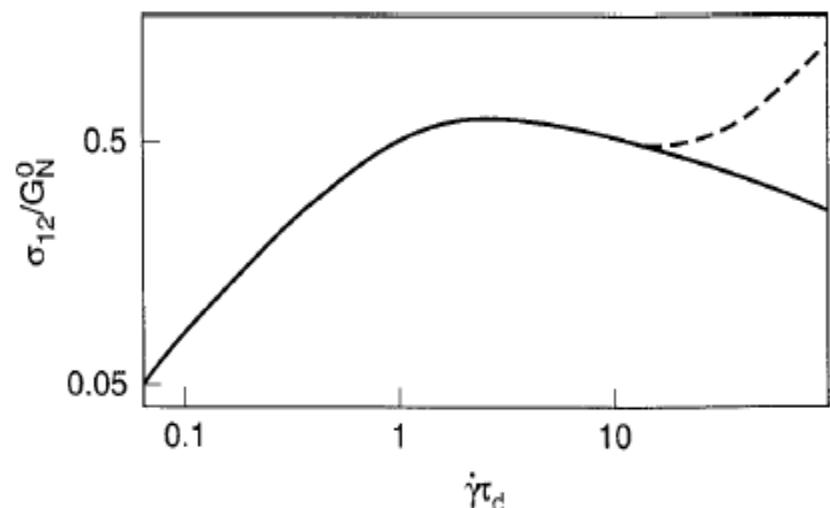
Doi-Edwards (DE) model

$$\boldsymbol{\sigma} = \int_{-\infty}^t dt' m(t-t') \mathbf{Q}[\mathbf{E}(t,t')] \quad m(t-t') = \sum_{i=1,odd}^{\infty} \frac{G_i}{\tau_i} \exp[-(t-t')/\tau_i]$$

$$\boldsymbol{\sigma} = G_N^o \int_{-\infty}^t \frac{dt'}{\tau_d} \exp[-(t-t')/\tau_d] \mathbf{Q}[\mathbf{E}(t,t')]$$

$$\mathbf{Q} \simeq \left(\frac{5}{J-1} \right) \mathbf{B} - \left[\frac{5}{(J-1)(I_2 + 13/4)^{1/2}} \right] \mathbf{C}$$

$$J = I_1 + 2(I_2 + 13/4)^{1/2} \quad I_1 = \text{tr}(\mathbf{B}), \quad I_2 = \text{tr}(\mathbf{C})$$



Excessive shear thinning

$$N_2 = -\frac{2}{7} N_1$$

Doi-Edwards-Marrucci-Grauzutti (DEM) model

$$\mathbf{S} = \int_{-\infty}^t \frac{dt'}{\tau_d} \exp[-(t-t')/\tau_d] \mathbf{Q}[\mathbf{E}(t,t')]$$

$$\dot{\lambda} = \lambda \mathbf{k} : \mathbf{S} - \frac{k_s(\lambda)}{\tau_s} (\lambda - 1)$$

$$\boldsymbol{\sigma} = G_N^o k_s(\lambda) \lambda^2 \mathbf{S}$$

$$k_s(\lambda) = \frac{(3\lambda_{\max}^2 - \lambda^2)(\lambda_{\max}^2 - \lambda^2)}{(3\lambda_{\max}^2 - 1)(\lambda_{\max}^2 - 1)}$$

Predicts stress overshoot
extension thickening
excessive shear thinning

Mead-Larson-Doi (MLD) model

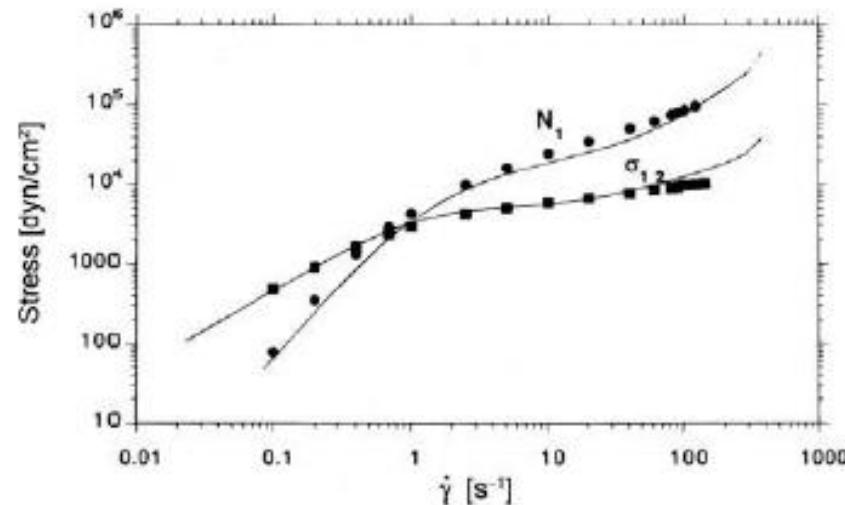
Reptation, chain stretch, primitive path fluctuation, convective constraint release

$$\frac{1}{\tau} = \frac{1}{\lambda^2 \tau_d} + f(\lambda)(\kappa : \mathbf{S} - \frac{\dot{\lambda}}{\lambda})$$

$$\mathbf{S} = \int_{-\infty}^t \frac{dt'}{\tau(t')} \exp\left[-\int_{t'}^t \frac{dt''}{\tau(t'')}\right] \mathbf{Q}[\mathbf{E}(t, t')]$$

$$\dot{\lambda} = \lambda \kappa : \mathbf{S} - \frac{k_s(\lambda)}{\tau_s} (\lambda - 1) - \frac{1}{2} (\lambda - 1) (\kappa : \mathbf{S} - \frac{\dot{\lambda}}{\lambda})$$

$$\boldsymbol{\sigma} = G_N^o k_s(\lambda) \lambda^2 \mathbf{S}$$



Differential models

Doi-Edwards (DE) model

$$\mathbf{S}_{(1)} + \frac{2}{3} \boldsymbol{\kappa} : \mathbf{S} \mathbf{S} + \frac{1}{\tau_d} (\mathbf{S} - \boldsymbol{\delta}) = \mathbf{0}, \quad \boldsymbol{\sigma} = G_N^o \mathbf{S} \quad N_2 = 0$$

Likhtman-Graham-McLeish (LGM) model

Reptation, convective constraint release

$$\boldsymbol{\sigma}_{(1)} + \frac{2}{3G_N^o} \boldsymbol{\kappa} : \boldsymbol{\sigma} \left[\boldsymbol{\sigma} + \beta (\boldsymbol{\sigma} - G_N^o \boldsymbol{\delta}) \right] + \frac{1}{\tau_d} (\boldsymbol{\sigma} - G_N^o \boldsymbol{\delta}) = \mathbf{0}$$