impose
\[ \gamma(t) = \gamma_0 \cdot \sin(\omega t) \]

probe
\[ \sigma(t) = \sigma_0 \cdot \sin(\omega t + \delta) = \gamma_0 \cdot G'(\omega) \cdot \sin(\omega t) + \gamma_0 \cdot G''(\omega) \cdot \cos(\omega t) \]

\[ \sigma = \eta \dot{\gamma} = \eta \frac{\gamma}{\lambda} = G\gamma \Rightarrow \eta = G\lambda \]

\[ D = \frac{kT}{\zeta} \]
Mesoscopic modeling: bead-spring models

Spring (constant $k \rightarrow G$): elastic element
Bead (friction $\zeta \rightarrow \eta$): viscous element

short chains (unentangled)

ROUSE MODEL

$F_{\text{Langevin}}$

$F_{\text{friction}} = -\zeta r_i$

Parameters $k = 3k_B T/b^2$, $\zeta$

long chains (entangled)

REPTATION MODEL

Additional parameter $a$
Reptation model in a tube (de Gennes): How to treat topological interactions

Ideal chain: Random walk \[ R = bN^{1/2} \]

(Tube diameter) (Kuhn, 1945)

Tube: topological constraints

Chain in a tube: \[ \alpha = bN_e^{1/2} \]

Random walk of \(N_e\) entanglement segments

Primitive path: \[ l = \frac{N}{N_e} \alpha \sim N \]

Curvilinear Diffusion (1-D along tube):

\[ D = \frac{kT}{\zeta_p} = \frac{kT}{N \zeta} \sim N^{-1} \]

\[ \tau = \frac{l^2}{D} \sim N^3 \]

\[ \eta = G \tau \sim N^3 \]

stronger N-dependence!

(compared to Rouse)

De Gennes, Polymer concepts in polymer physics 1979

Doi, Edwards, The theory of polymer dynamics 1986
Reptation
Doi-Edwards model

\[ G(t) = G_N^0 P(t) \]

\[ P(t) = \sum_{i, \text{odd}} \frac{8}{\pi^2 i^2} \exp\left[-i^2 t / \tau\right] \]

Doi, Edwards, The theory of polymer dynamics 1986
Non-reptative modes: Contour length fluctuations

Doi (1984):

\[ \tau_{\text{reptf}}(Z) \approx \tau_{\text{rept}}(Z) \left( 1 - \frac{2C_1}{\sqrt{Z}} + \frac{C_2}{Z} + \ldots \right) \]

\[ G_f(Z) = G_N^0 \left( 1 - \frac{C_3}{\sqrt{Z}} + \ldots \right) \]

Z: number of tube segments

Reptation occurs on along a smaller tube length
Non-reptative modes: Contour length fluctuations

\[ \tau_{reptf}(Z) \approx \tau_{rept}(Z) \left( 1 - \frac{2C_1}{\sqrt{Z}} + \frac{C_2}{Z} + \ldots \right) \]

CLF: affect more the smaller chains

\[ \eta_0 \]

Log M

3

3.4

Fig. 4-5  \( G' \) and \( G'' \) versus frequency shifted to 27 °C for polybutadiene of molecular weight 360,000 and narrow polydispersity. The dashed line is the reptation theory according to Equation 4-13; the solid line includes fluctuations in the length of the primitive path (from Pearson°)}
Question:

How does this long chain relax in the presence of shorter chains?

Constraint Release (CR) – dynamic tube dilation (DTD)
Constraint Release
Figure 2. Experimental (---) and predicted (—) dynamic moduli using the Doi and Edwards kernel (eq 2) and double reptation (eqs 1 and 5) for (a) PS1, (b) PS9, (c) PS12, and (d) PS13.

<table>
<thead>
<tr>
<th>Polydispersity</th>
<th>$M_w$ (g/mol)</th>
<th>$M_n$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS1</td>
<td>1.02</td>
<td>355 500</td>
</tr>
<tr>
<td>PS2</td>
<td>1.02</td>
<td>191 300</td>
</tr>
<tr>
<td>PS3</td>
<td>1.09</td>
<td>886 900</td>
</tr>
<tr>
<td>PS4</td>
<td>1.04</td>
<td>176 700</td>
</tr>
<tr>
<td>PS5</td>
<td>1.03</td>
<td>60 400</td>
</tr>
<tr>
<td>PS6</td>
<td>1.03</td>
<td>58 400</td>
</tr>
<tr>
<td>PS7</td>
<td>1.02</td>
<td>146 400</td>
</tr>
<tr>
<td>PS8</td>
<td>1.04</td>
<td>676 000</td>
</tr>
</tbody>
</table>

(b) Bi- or Tridisperse composition

<table>
<thead>
<tr>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS9</td>
</tr>
<tr>
<td>PS10</td>
</tr>
<tr>
<td>PS11</td>
</tr>
<tr>
<td>PS12</td>
</tr>
<tr>
<td>PS13</td>
</tr>
</tbody>
</table>
Mechanical spectroscopy (linear viscoelasticity)

Terminal region:

\[ G' \sim \omega^2 \quad G'' \sim \omega \]

Data: Pakula et al., Macromolecules 1998

Key:
Each experimental frequency corresponds to an inverse characteristic time of the polymer
High frequencies: segmental time
Low frequencies: time for motion of the whole macromolecule
Complete master curve of PBd 430kg/mol (~220 Me)

Time Temperature Superposition (TTS)

Data: F. Stadler, E. vanRuymbeke
Shifted storage modulus $G'(\omega)$ at different temperatures (horizontal)

PBd 430k
$M_n=430$ kg/mol
$M_w=450$ kg/mol

Data: F. Stadler, E. vanRuymbeke
WLF- and Arrhenius dependencies of the shift factors

Horizontal Shift factors:

\[
\log a = \frac{-c_1 \cdot (T - T_0)}{c_2 + (T - T_0)}
\]

(Williams-Landel-Ferry equation: WLF)

- \(c_1, c_2\): depends on the nature of the polymer melts (not on the structure)

- Thermo-rheologically simple

J. D. Ferry, *Viscoelastic properties of polymers*, Wiley, 1980
Why does it work:

\[ \lambda_i(T) = \frac{R^2}{D} = \frac{R^2}{k_B T} \zeta_i(T) \]

\[ \lambda(T) \sim \sum \lambda_i(T) \sim \sum \zeta_i(T) \]

**Key:** homogeneous distribution of friction with same T-dependence

(works with systems of same single microscopic friction, e.g. homopolymers -- but there are issues near the glass transition)

Rosedale + Bates, Macromolecules 1984

Exceptions: Determine transitions (e.g., block copolymers)

Kremer, Schoenhals, Broadband dielectric spectroscopy 2003
Ferry, Viscoelastic properties of polymers 1980
Plazek, J. Rheol. 2000
McKenna, J. Rheol. 2010
Compare linear and star polymers:

reptation - power law vs. retraction – exponential

\[ \tau \sim M^{3.4} \]

\[ \tau \sim \exp\left[ \frac{M_{\text{arm}}}{M_e} \right] \]

Linear

Star (no reptation)
Consequence 1:
Star has larger viscosity which does not depend on number of arms!

Not true for \( f > 36 \) roughly

Pakula et al. Macromolecules 1998
Consequence 2:
Star with same total molar mass as linear, but several arms (>3) may have smaller viscosity!

Wider application to hyperbranched polymers: viscosity “control”
Multiarm Star Melts: between polymers and colloids

Fast polymeric mode (star like)
Slow colloidal mode:

\[ \tau \sim \tau_0 \alpha^{-1/3} f^{11/9} N^{26/9} N_e^{-1} \exp \left( \frac{C_1}{\alpha} \frac{f^{5/3}}{N^{1/3}} + C_2 \alpha^2 \frac{N^{11/3}}{N_e f^{4/3}} \right) \]

Roovers et al. Macromolecules 1993
Macromolecules 1998 ; Kapnistos et al. JCP 1999
Likos et al. PRL 1998
Das et al., J. Rheol. 2006  Read et al., Science 2011

Analogy:
- solvent-free colloids (NOHMs)
- nanoparticle organic hybrid materials

Agarwal et al., PRL 2011 ; Nano Lett. 2010
Chremos et al., JCP 2012
Chremos + Panagiotopoulos, PRL 2011
Questions:

Which are the key differences between polymers and colloids? (length, time, energy, interactions)

We discussed De, Wi, Pe. How do they compare?

Are there rheological (and other) differences between polymeric and colloidal glasses?

What is the analogy of entanglement-response of polymers to colloidal response?
Summary (polymers & colloids):

Synthesis: \( N, b \)

Size: \( R = N^{1/2}b \)

Distribution: \( P(R) \propto \exp\left(\frac{-3R^2}{2Nb^2}\right) \)

Modulus: \( G = \nu kT = kT/\xi^3 \)

Diffusion: \( D = \frac{kT}{\zeta} = \frac{R^2}{\tau} \)

Hooke: \( F = kx \)

Newton: \( \eta \equiv \frac{\sigma}{\dot{\gamma}} \)

Viscoelasticity: \( \eta = G\lambda \)