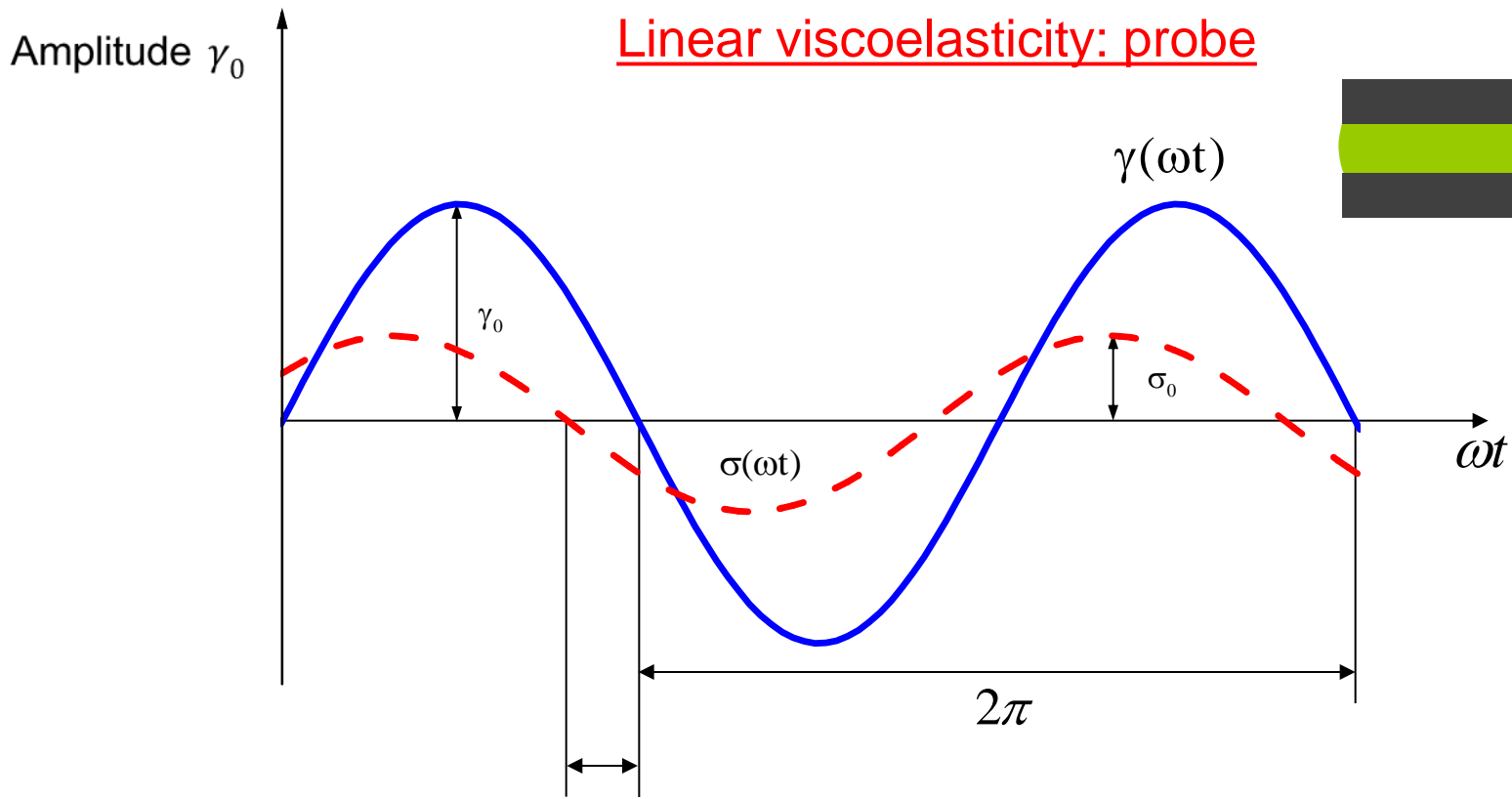


# Linear viscoelasticity: probe



**impose**

$$0 \leq \delta \leq \frac{\pi}{2}$$

$$\gamma(t) = \gamma_0 \cdot \sin(\omega t)$$

**probe**

Elastic response

Viscous response

$$\sigma(t) = \sigma_0 \cdot \sin(\omega t + \delta) = \gamma_0 \cdot \overbrace{G'(\omega) \cdot \sin(\omega t)}^{\text{Elastic response}} + \gamma_0 \cdot \overbrace{G''(\omega) \cdot \cos(\omega t)}^{\text{Viscous response}}$$

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

$$D = \frac{kT}{\zeta}$$

# Mesoscopic modeling: bead-spring models

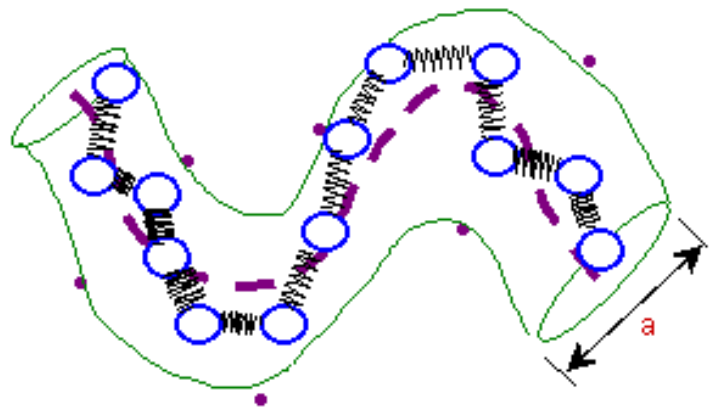
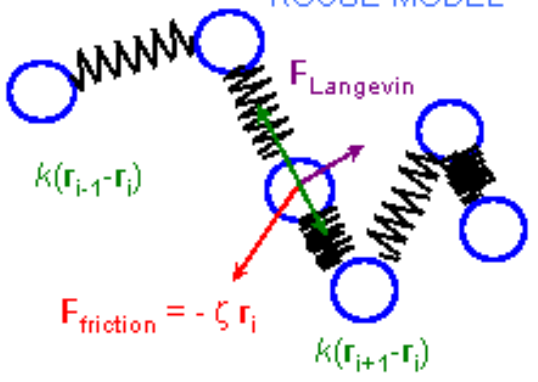
short chains  
(unentangled)

long chains (entangled)



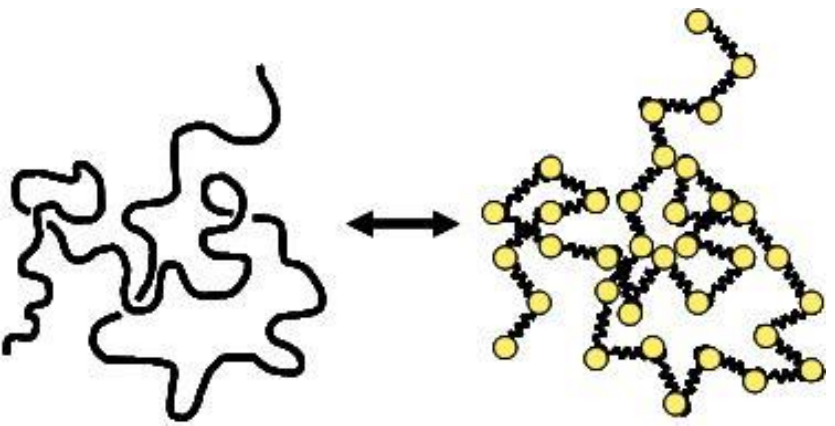
ROUSE MODEL

REPTATION MODEL



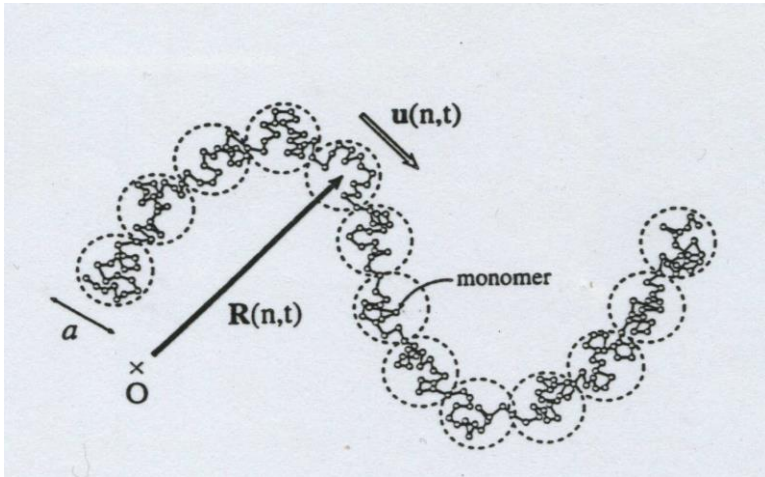
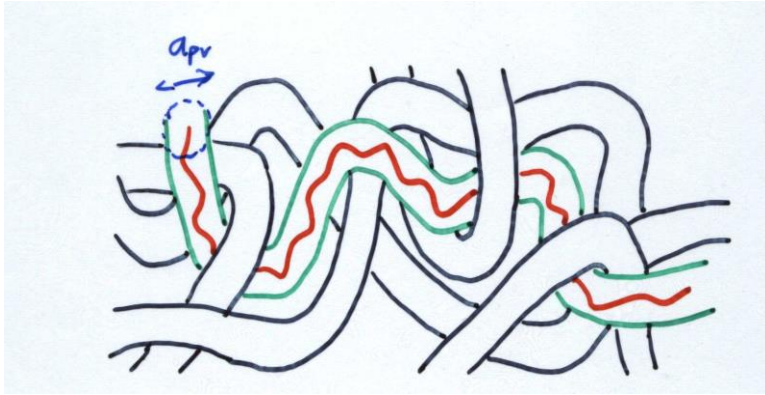
Parameters  $k=3k_B T/b^2$ ,  $\zeta$

Additional parameter  $a$



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

# Reptation model in a tube (de Gennes): How to treat topological interactions



Ideal chain: Random walk  $R = bN^{1/2}$   
(Kuhn, 1945)

Tube: topological constraints

Chain in a tube:  $\alpha = bN_e^{1/2}$  (tube diameter)  
**Random walk of  $N_e$  entanglement segments**

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

Curvilinear Diffusion (1-D along tube):

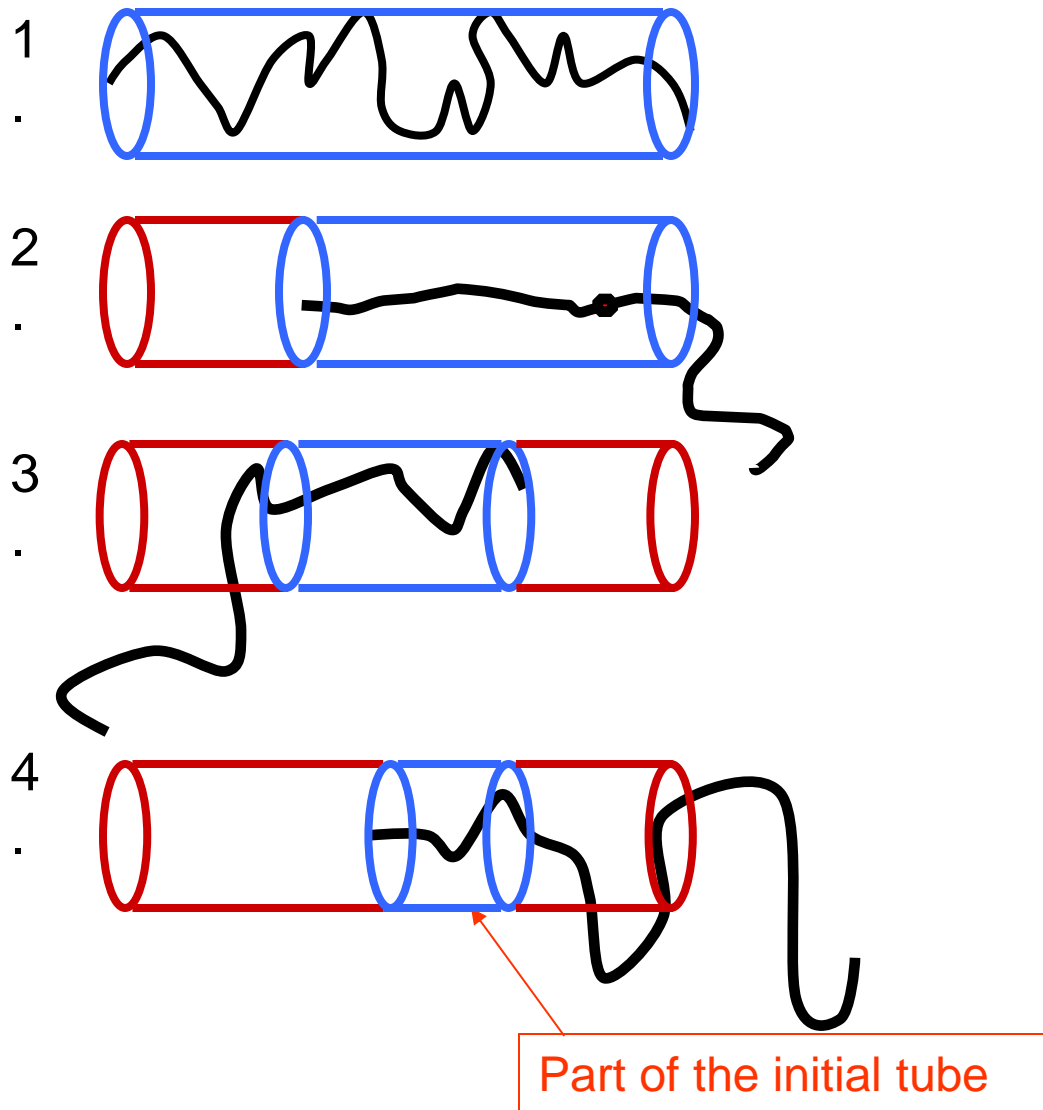
$$D = \frac{kT}{\zeta_p} = \frac{kT}{N\zeta} \sim N^{-1}$$

$$\tau = \frac{l^2}{D} \sim N^3 \quad \eta = G\tau \sim N^3$$

**stronger N-dependence !  
(compared to Rouse)**

# Reptation

## Doi-Edwards model



$$G(t) = G_N^0 P(t)$$

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

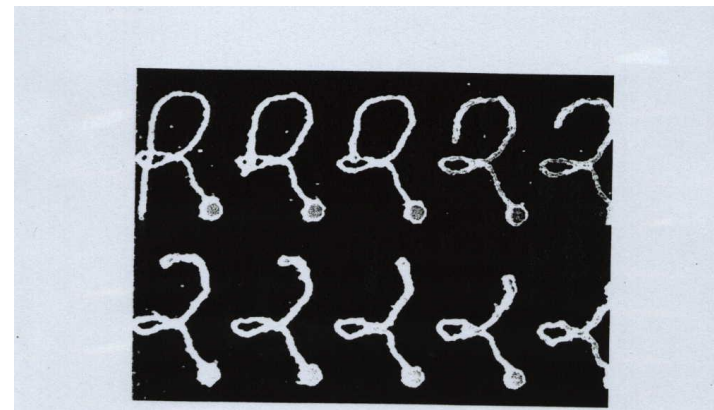
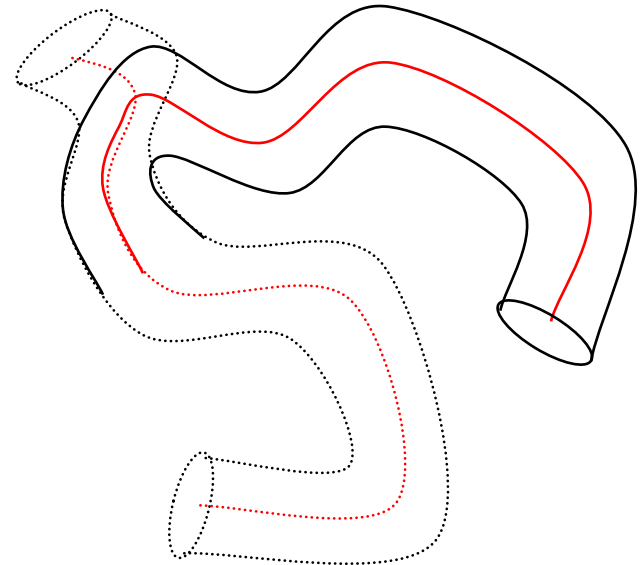
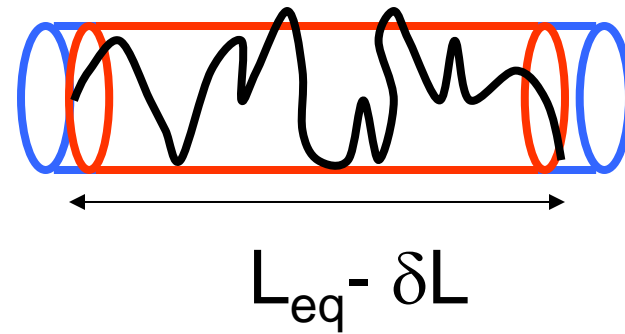
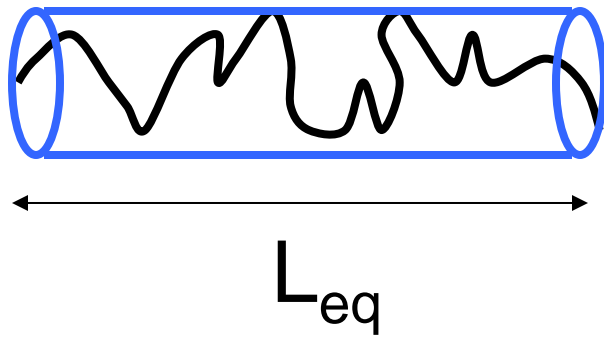


Figure 3.4 Time sequence of images showing retraction of one end of a fluorescent 60- $\mu\text{m}$ -long DNA molecule entangled in a solution of other, non-fluorescing DNA molecules. The fluorescing molecule was attached at one end to a small sphere that was pulled through the solution using a laser-optical trap, to form the letter R. The free end then retracts through a "tube-like" region formed by the surrounding mesh of other, invisible DNA chains. (Reprinted with permission from the cover of *Science*, May 6, 1994; Copyright 1994, American Association for the Advancement of Science.)

# Non-reptative modes: Contour length fluctuations

Doi (1984):



$$\tau_{reptf}(Z) \cong \tau_{rept}(Z) \left( 1 - \frac{2C_1}{\sqrt{Z}} + \frac{C_2}{Z} + \dots \right)$$

Z: number of tube segments

$$G_f(Z) = G_N^0 \left( 1 - \frac{C_3}{\sqrt{Z}} + \dots \right)$$

Reptation occurs on along a smaller tube length

# Non-reptative modes: Contour length fluctuations

$$\tau_{reptf}(Z) \cong \tau_{rept}(Z) \left( 1 - \frac{2C_1}{\sqrt{Z}} + \frac{C_2}{Z} + \dots \right)$$

**CLF:** affect more the smaller chains

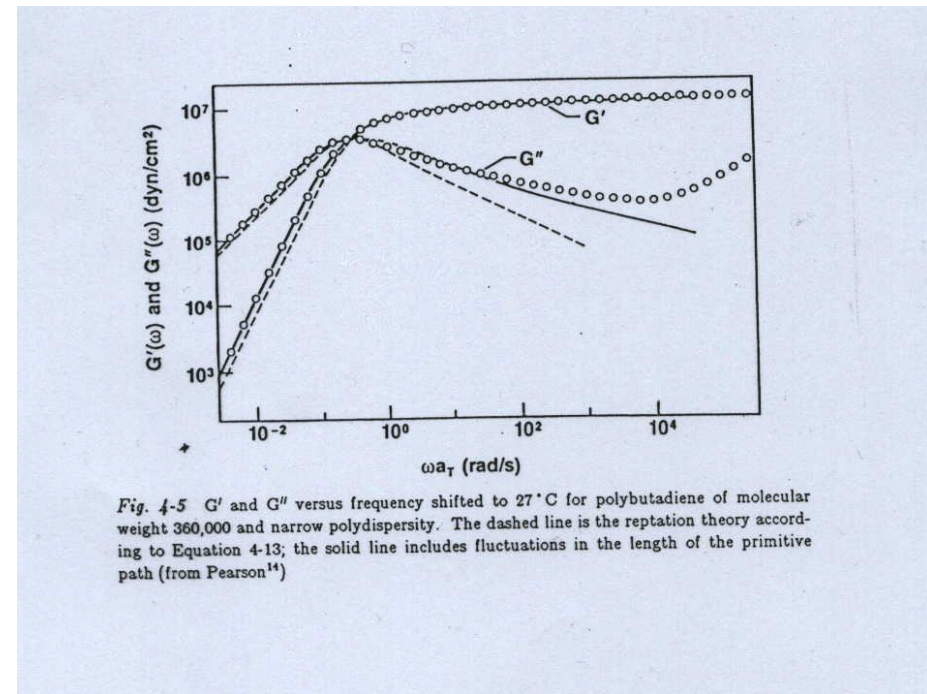
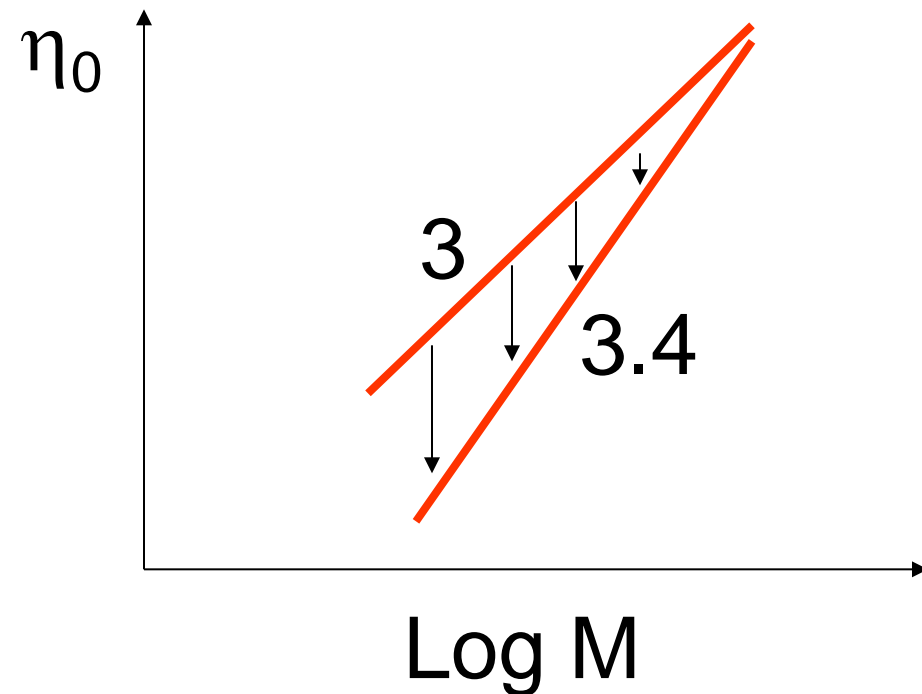
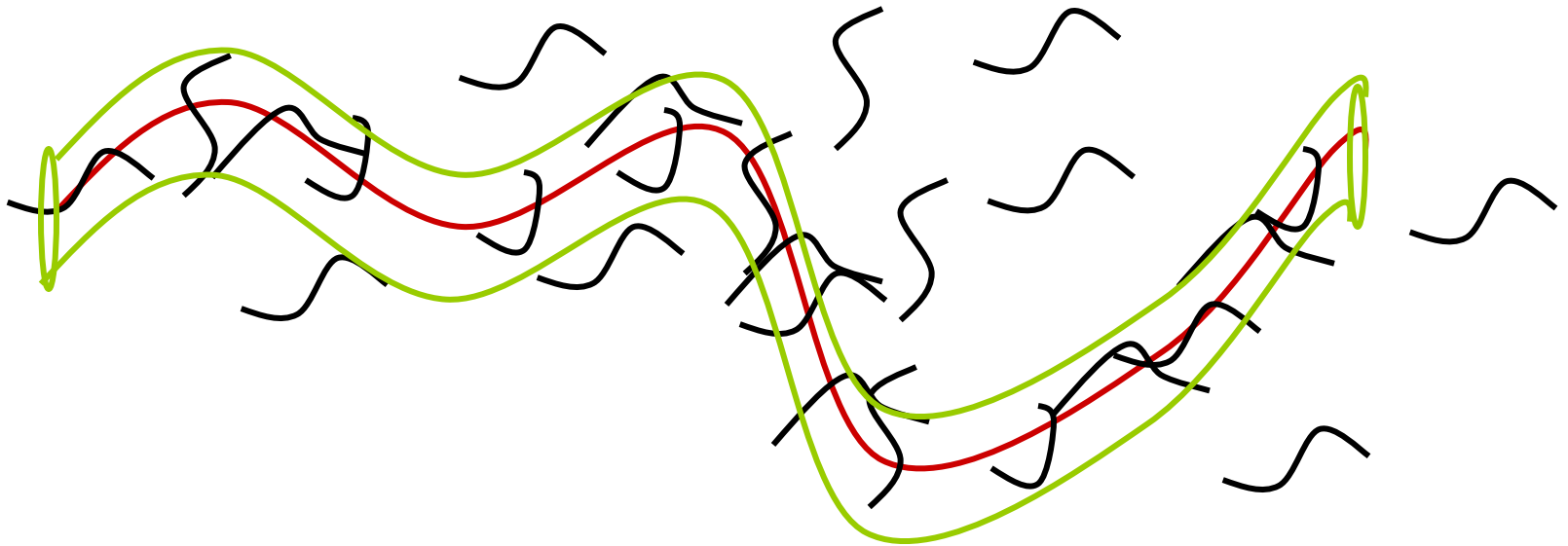


Fig. 4-5  $G'$  and  $G''$  versus frequency shifted to 27°C for polybutadiene of molecular weight 360,000 and narrow polydispersity. The dashed line is the reptation theory according to Equation 4-13; the solid line includes fluctuations in the length of the primitive path (from Pearson<sup>14</sup>)

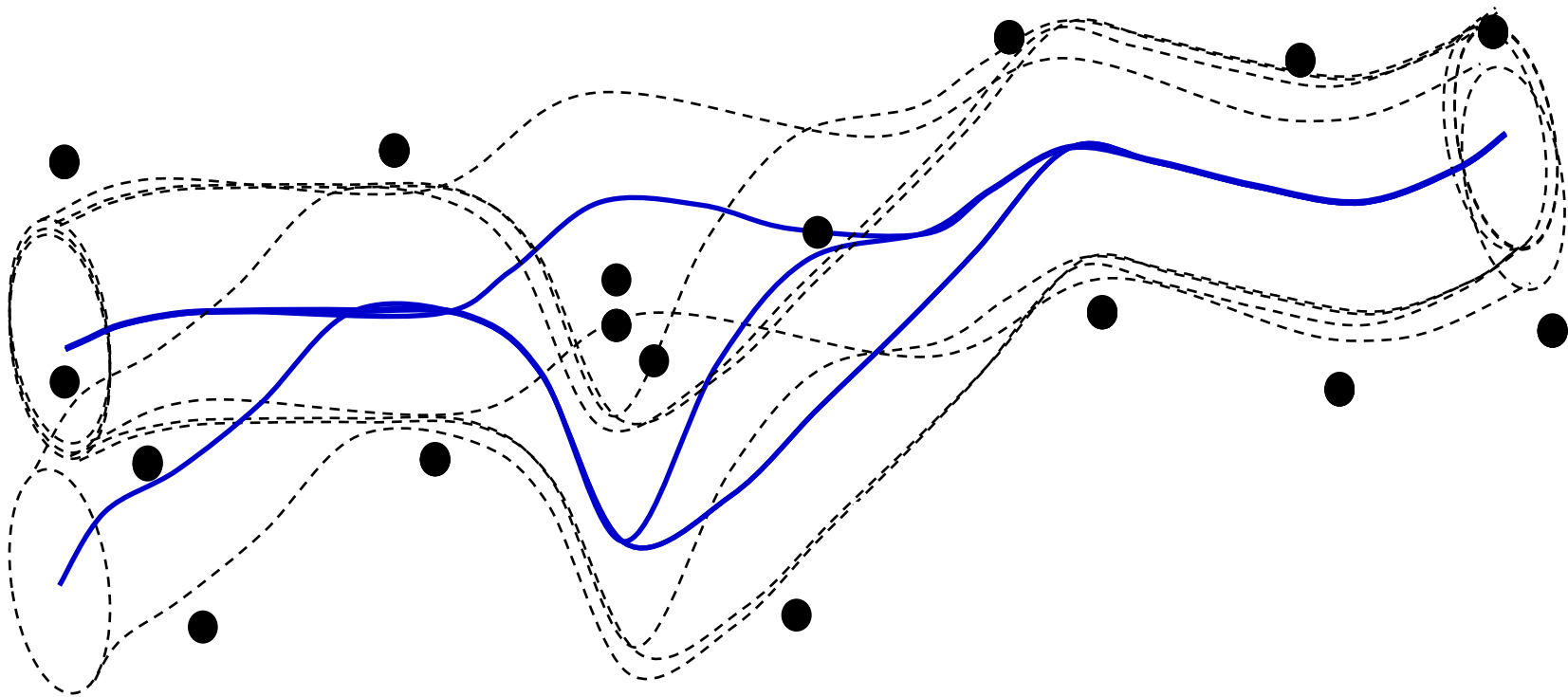
Question:

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

Constraint Release (CR) – dynamic tube dilation (DTD)

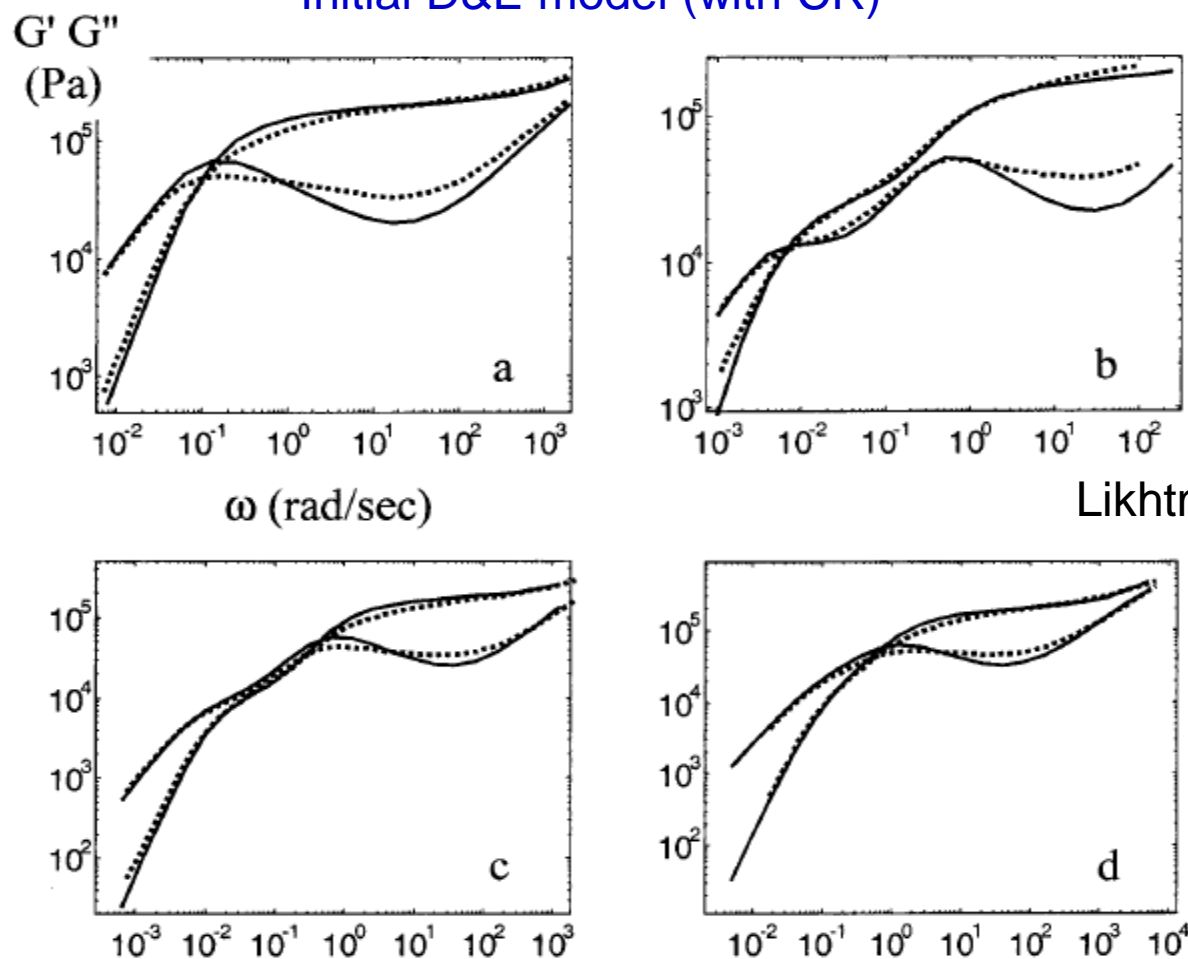


# Constraint Release





## Initial D&amp;E model (with CR)



Lichtman-McLeish 2002

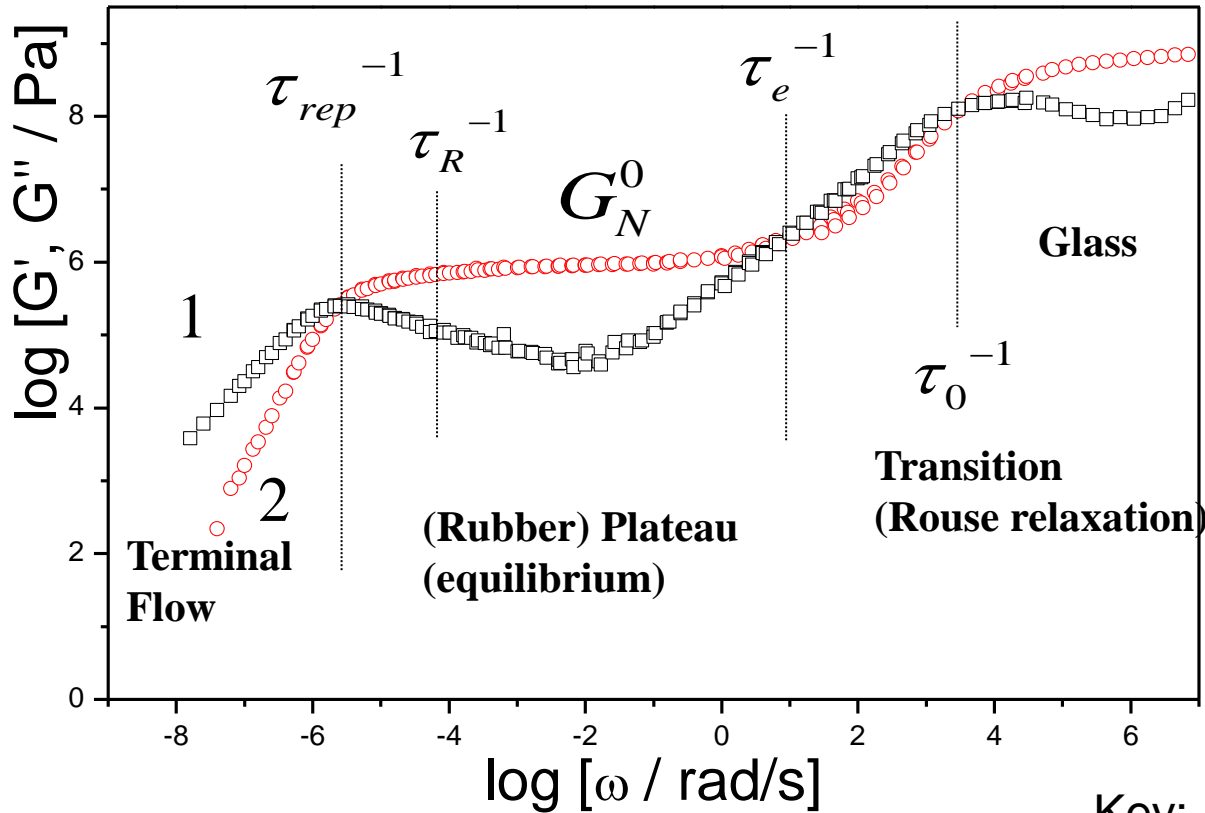
**Figure 2.** Experimental (···) and predicted (—) dynamic moduli using the Doi and Edwards kernel (eq 2) and double reptation (eqs 1 and 5) for (a) PS1, (b) PS9, (c) PS12, and (d) PS13.

	polydispersity	$M_w$ (g/mol)	$M_n$ (g/mol)
PS1	1.02	355 500	346 200
PS2	1.02	191 300	187 600
PS3	1.09	886 900	813 500
PS4	1.04	176 700	169 900
PS5	1.03	60 400	58 600
PS6	1.03	58 400	56 900
PS7	1.02	146 400	143 300
PS8	1.04	676 000	650 900

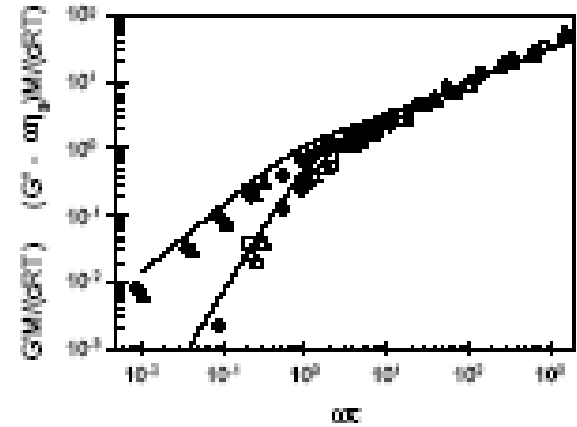
(b) Bi- or Tridisperse	
composition	
PS9	50% PS2, 50% PS3
PS10	20% PS4, 80% PS5
PS11	80% PS4, 20% PS5
PS12	65% PS2, 35% PS8
PS13	30% PS7, 30% PS2, 40% PS1

# Mechanical spectroscopy (linear viscoelasticity)

$M > M_e$



$M < M_e$



Terminal region:

$$G' \sim \omega^2 \quad G'' \sim \omega$$

Key:

Each experimental frequency corresponds to an inverse characteristic time of the polymer

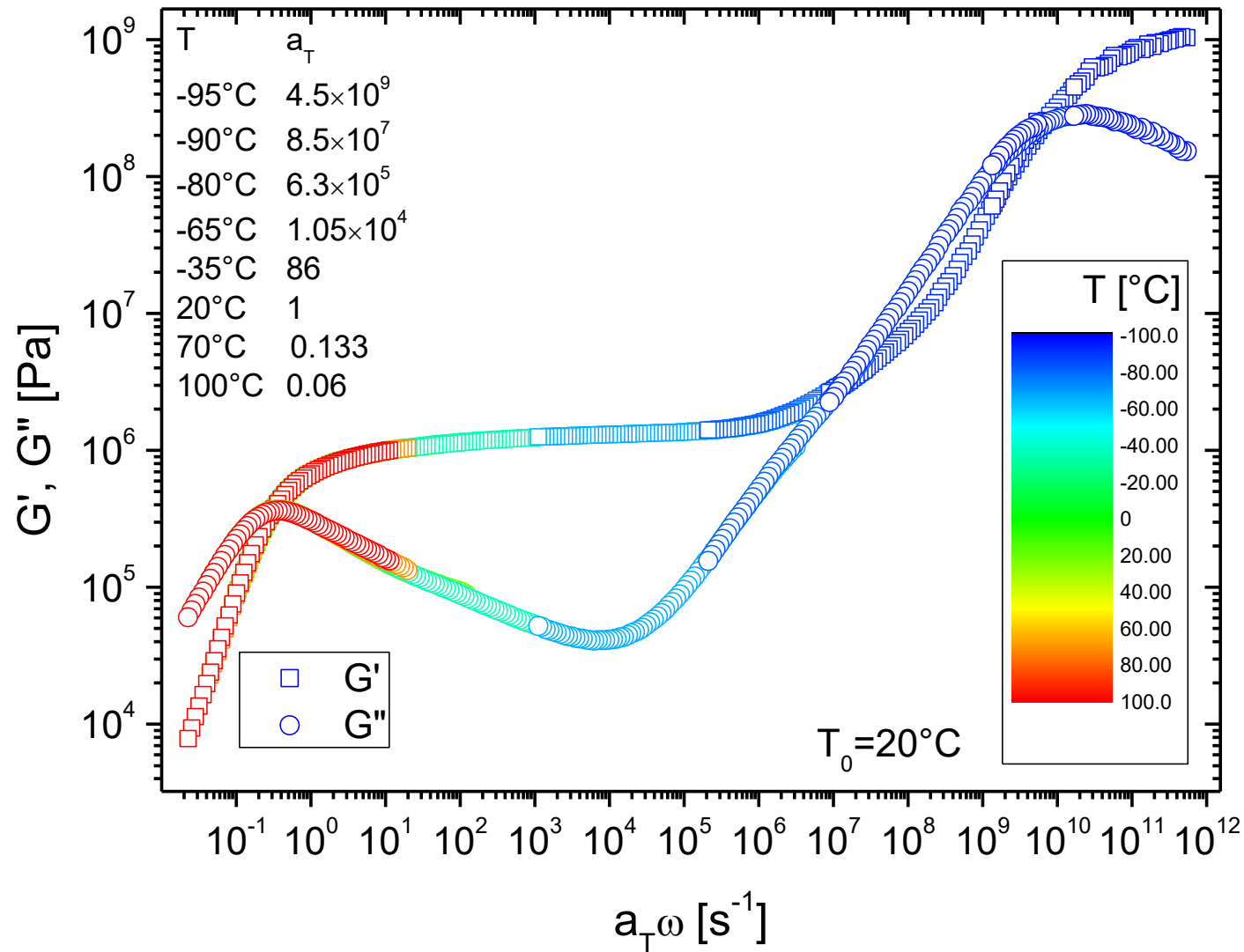
High frequencies: segmental time

Low frequencies: time for motion of the whole macromolecule

# Complete master curve of PBd 430kg/mol (~220 Me)

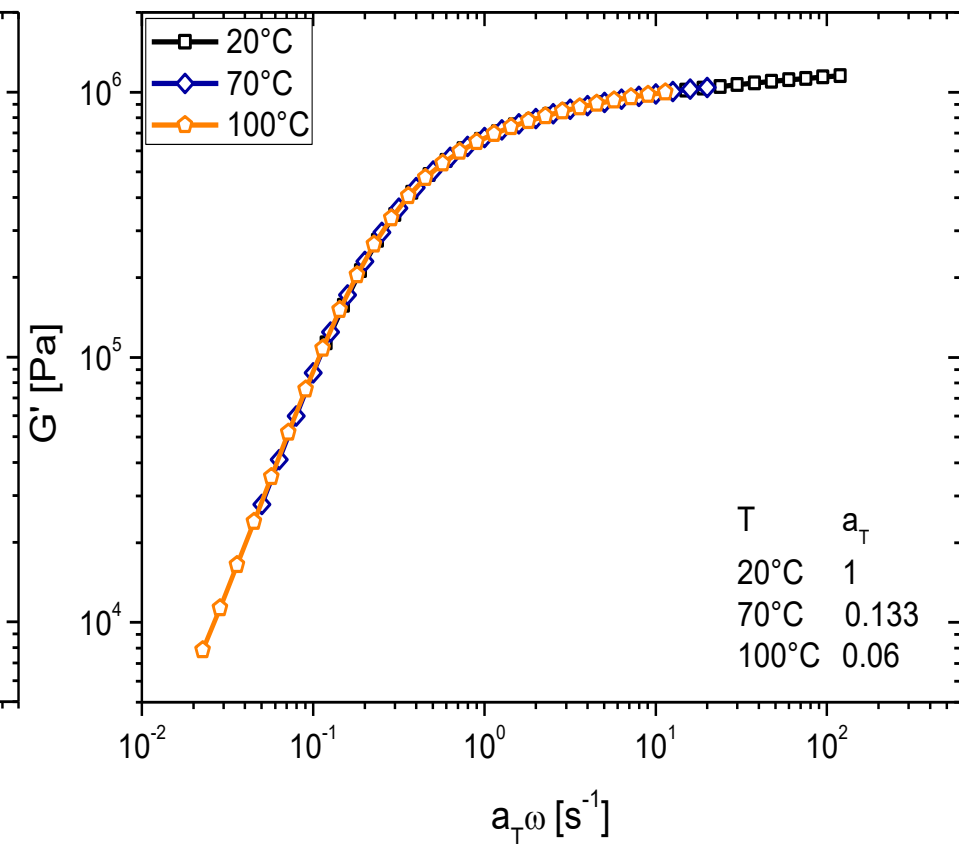
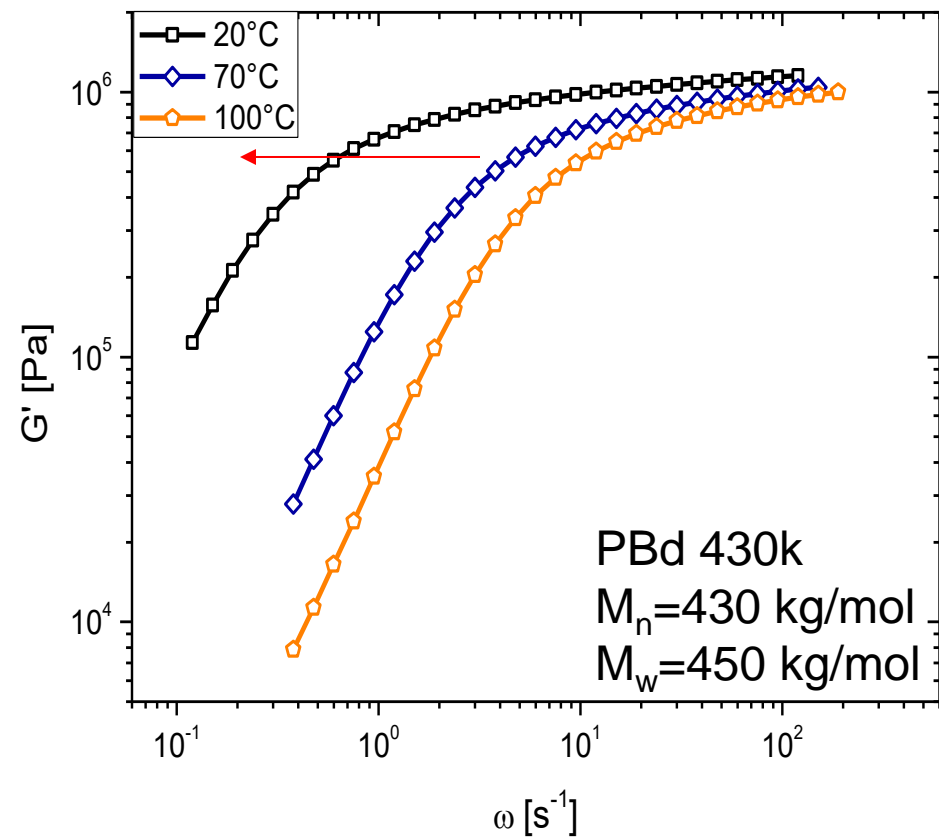
Entanglements  
(physical) network

## Time Temperature Superposition (TTS)



Data: F. Stadler, E. vanRuymbeke

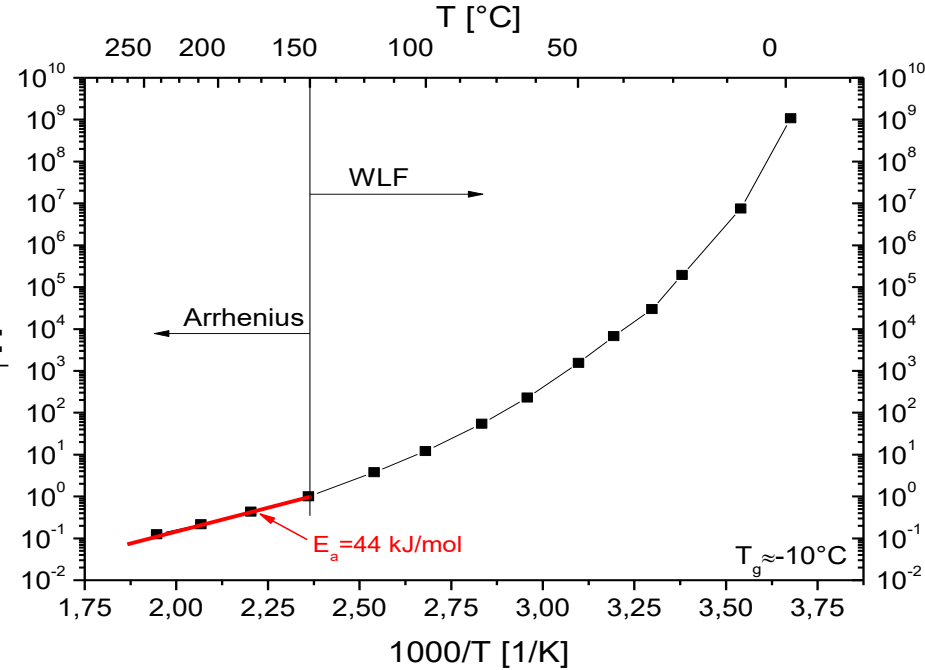
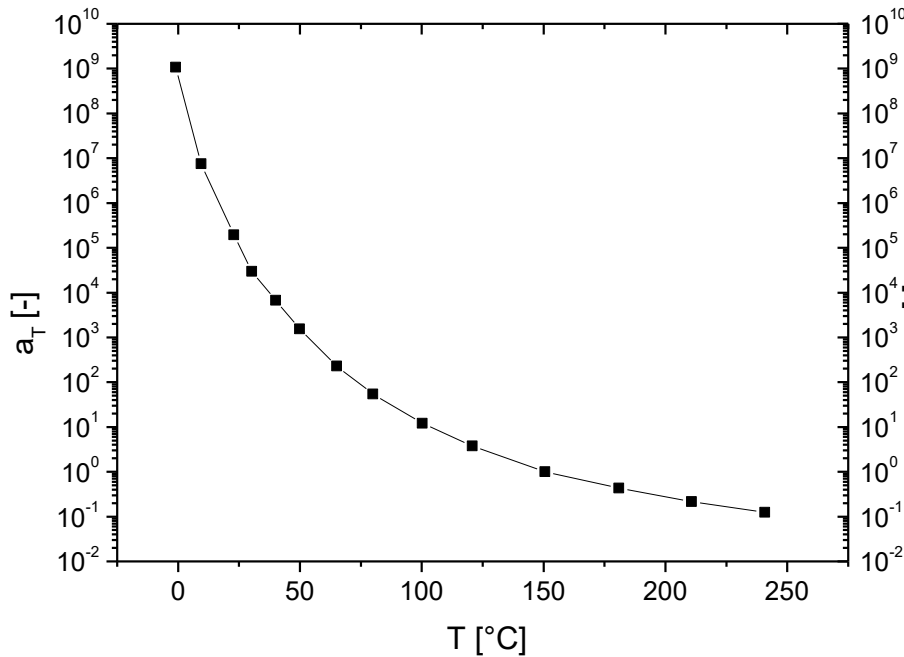
# Shifted storage modulus $G'(w)$ at different temperatures (horizontal)



# WLF- and Arrhenius dependencies of the shift factors

$$T_0 = T_{ref}$$

Horizontal Shift factors:



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

(Williams-Landel-Ferry equation: WLF)

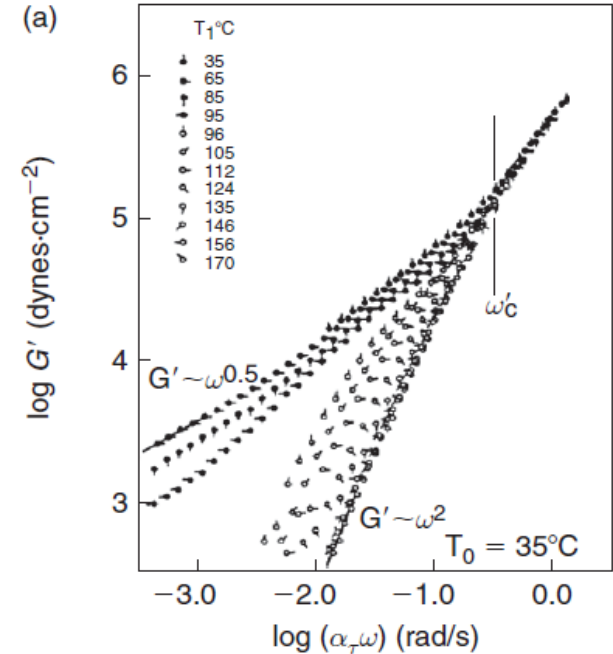
- $c_1, c_2$ : depends on the nature of the polymer melts (not on the structure)
- Thermo-rheologically simple

## Why does it work:

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

$$\lambda(T) \sim \sum \lambda_i(T) \sim \sum \zeta_i(T)$$

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



Rosedale + Bates, *Macromolecules* 1984

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)

Kremer, Schöenhals, *Broadband dielectric spectroscopy* 2003

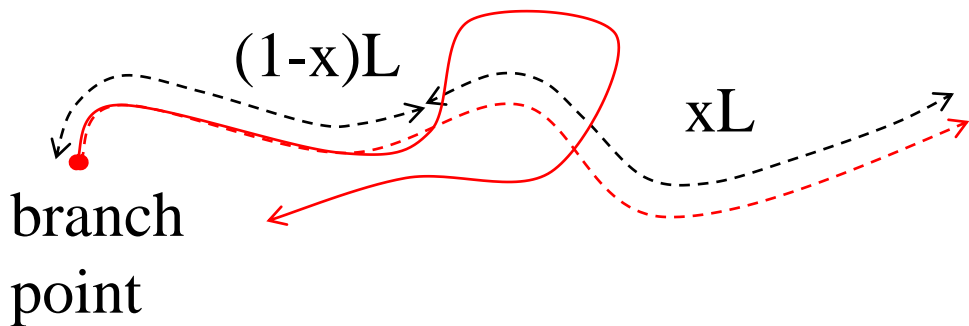
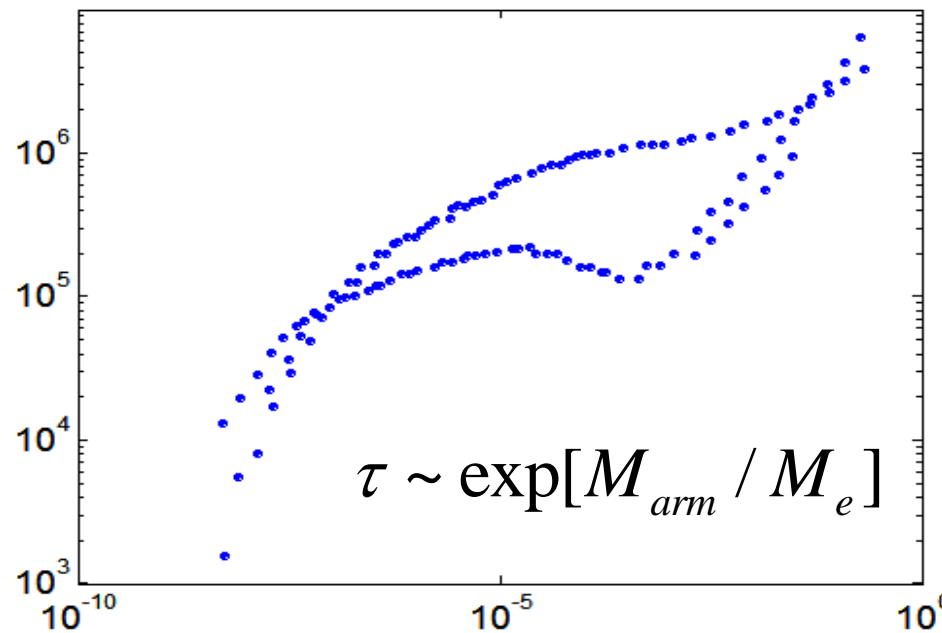
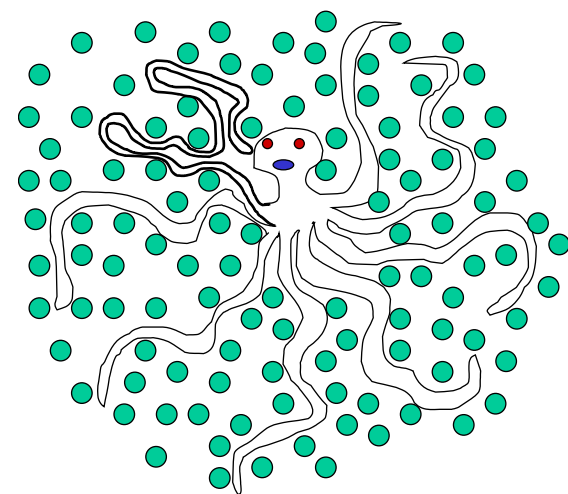
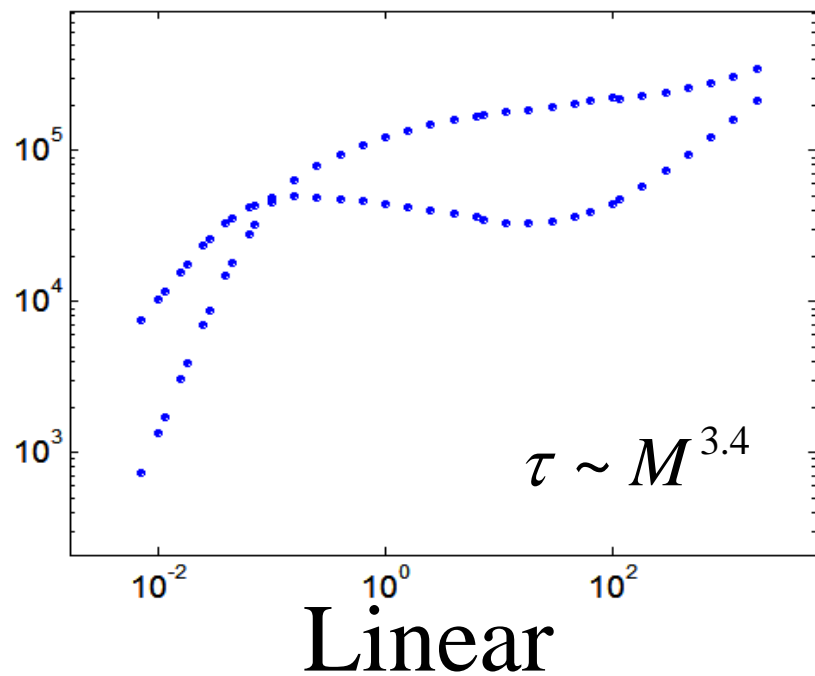
Ferry, *Viscoelastic properties of polymers* 1980

Plazek, *J. Rheol.* 2000

McKenna, *J. Rheol.* 2010

# Compare linear and star polymers:

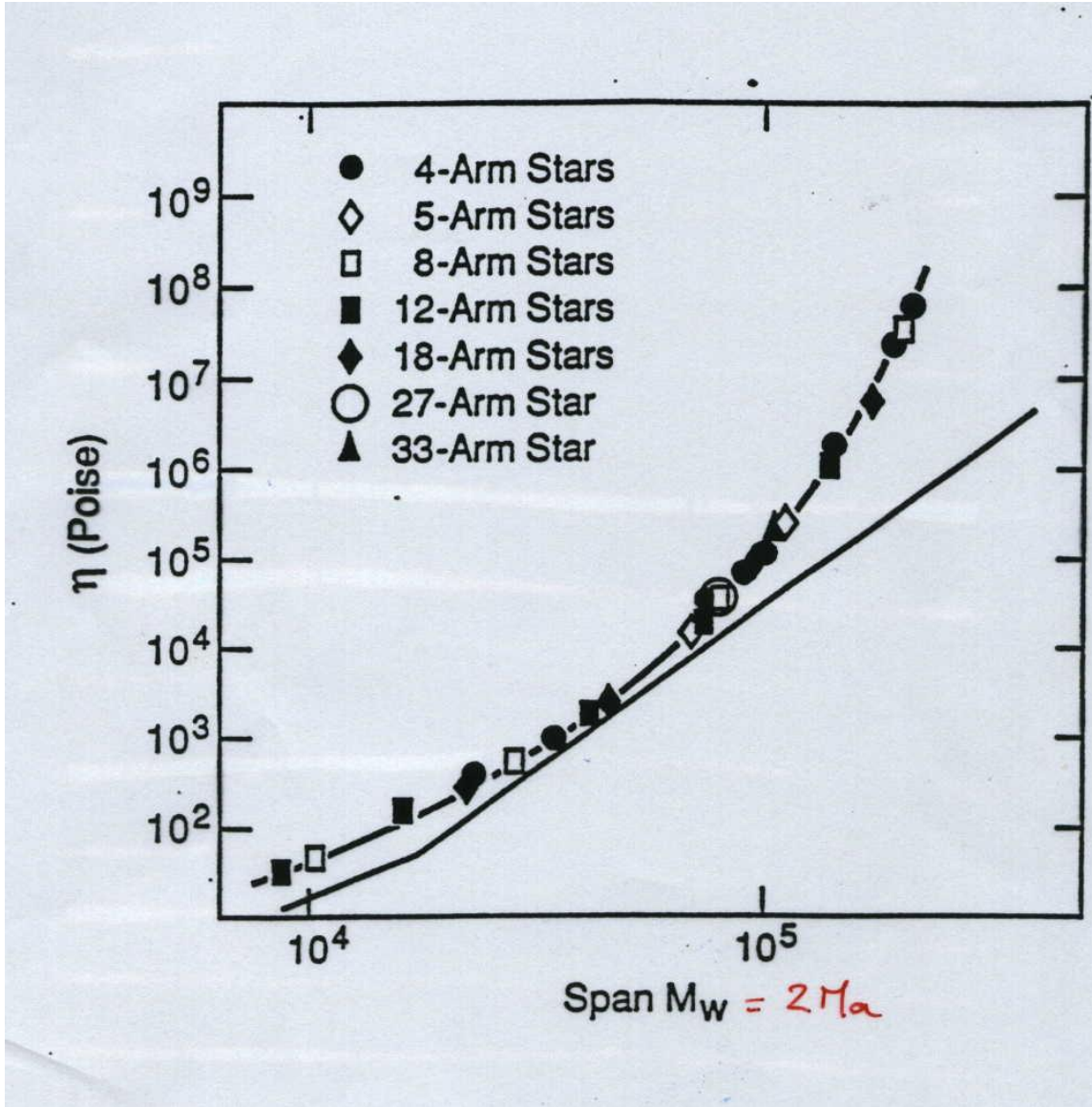
reptation - power law vs. retraction – exponential



Star (no reptation)

Consequence 1:

Star has larger viscosity which does not depend on number of arms!

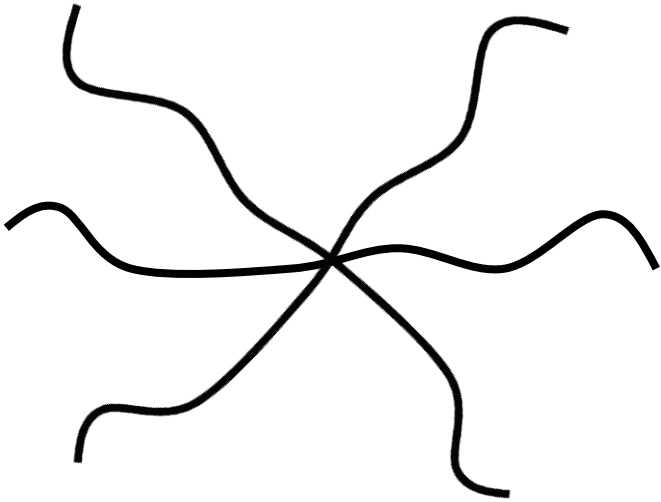


Not true for  
 $f > 36$  roughly



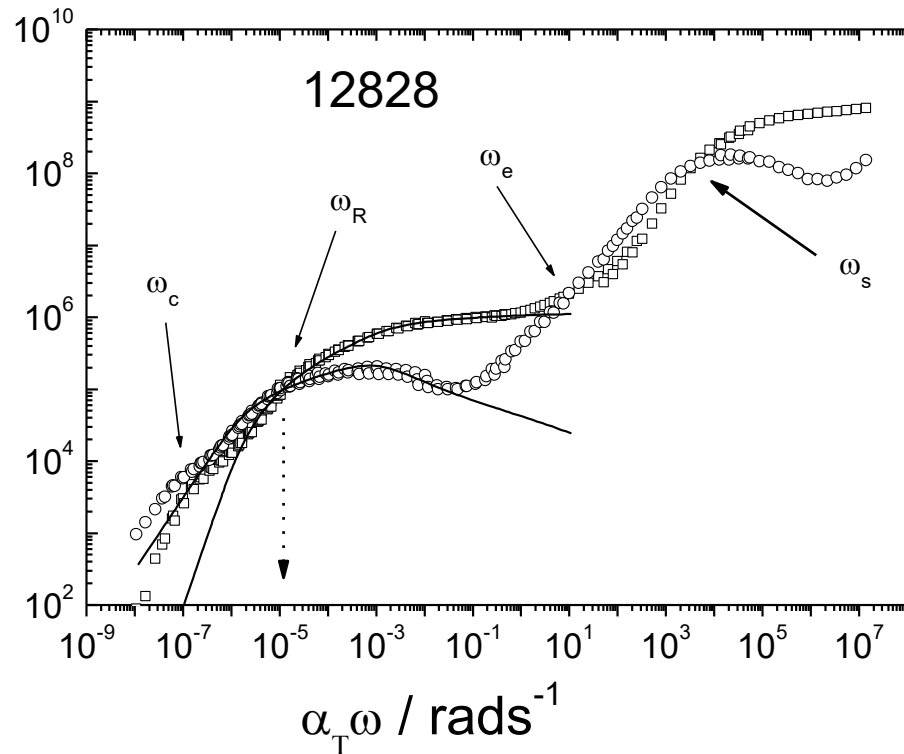
## Consequence 2:

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

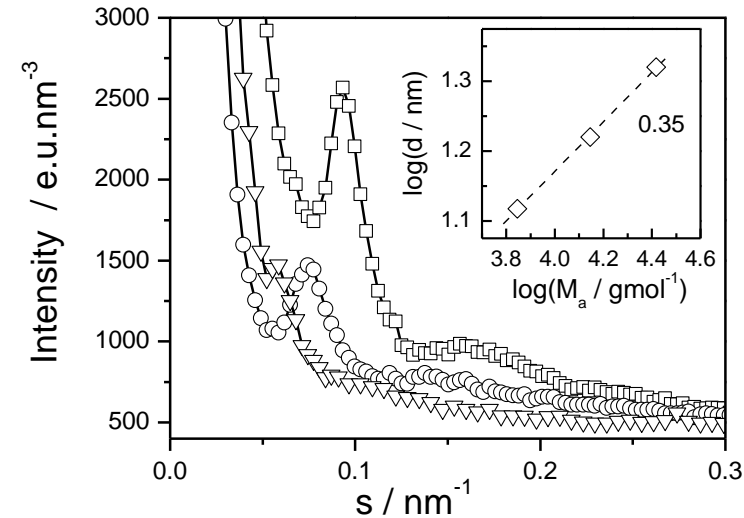
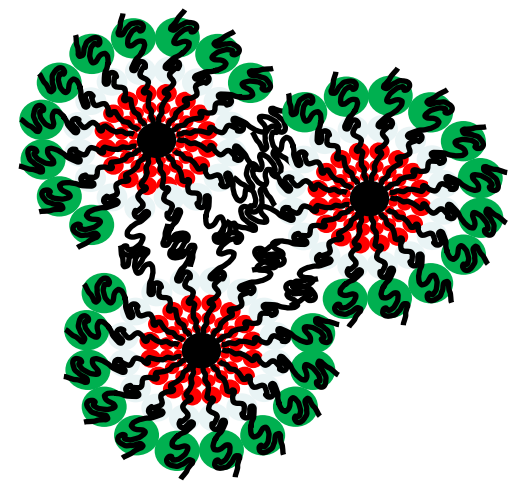


Fast polymeric mode (star like)

Slow colloidal mode:

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

- Roovers et al. *Macromolecules* 1993
- Pakula, *Comput. Theor. Polym. Sci.* 1998,
- Macromolecules* 1998 ; Kapnistos et al. *JCP* 1999
- M. Daoud, J. P. Cotton, *J. Phys. (Paris)* 1982
- 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:  $\eta = G\lambda$