Part III. Polymer Dynamics – molecular models

I. Unentangled polymer dynamics

I.1 Diffusion of a small colloidal particle

I.2 Diffusion of an unentangled polymer chain

II. Entangled polymer dynamics

II.1. Introduction to Tube models

II.2. « Equilibrium state » in a polymer melt or in a concentrated solution:

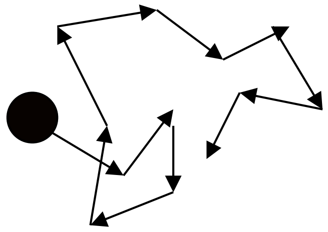
II.3. Relaxation processes in linear chains

Source: Polymer physics – Rubinstein,Colby

I. Unentangled polymer dynamics

I.1 Diffusion of a small colloidal particle:

random walk



Simple diffusive motion: Brownian motion

$$\left\langle \left[\vec{r}(t) - \vec{r}(0)\right]^2 \right\rangle = 6Dt$$

Diffusion coefficient

Friction coefficient:

A constant force applied to the particle leads to a constant velocity: $\vec{F} = \zeta \vec{v}$

Friction coefficient

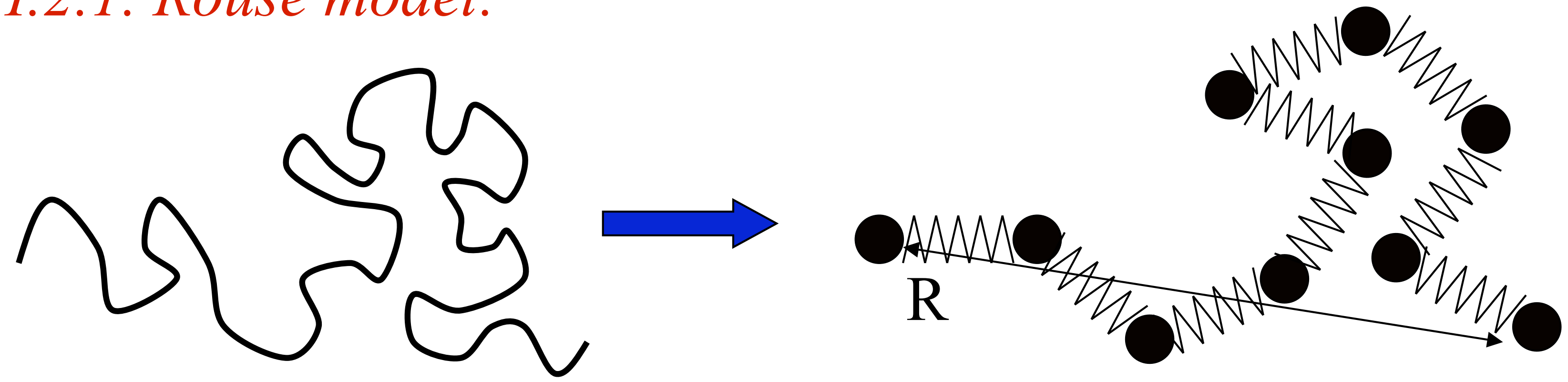
Einstein relationship: $D = \dfrac{kT}{\zeta}$

Stokes law: $\zeta = 6\pi\eta R$ (Sphere of radius R in a Newtonian liquid with a viscosity η)

Stokes-Einstein relation: $D = \dfrac{kT}{6\pi\eta R}$ ➡ Determination of $R_H = \dfrac{kT}{6\pi\eta D}$

I.2 Diffusion of an unentangled polymer chain:

I.2.1. Rouse model:



N beads of length b

- Each bead has its own friction ζ
- Total friction: $\zeta_R = N\zeta \quad \Longrightarrow \quad D_R = \dfrac{kT}{N\zeta}$
- Rouse time: $\tau_R \approx \dfrac{R^2}{D_R} \approx \dfrac{R^2}{kT/N\zeta} = \dfrac{\zeta}{kT} N R^2$

$t < \tau_{Rouse}$: *viscoelastic modes* $\qquad$ $t > \tau_{Rouse}$: *diffusive motion*

- Stokes law: $\zeta \approx \eta_s b$
- Kuhn monomer relaxation time: $\tau_0 \approx \dfrac{\zeta b^2}{kT} = \dfrac{\eta_s b^3}{kT} \quad \Longrightarrow \quad \tau_R \approx \tau_0 N^2$

Rouse relaxation modes:

The longest relaxation time: $\tau_R \approx \tau_0 N^2$

For relaxing a chain section of N/p monomers:

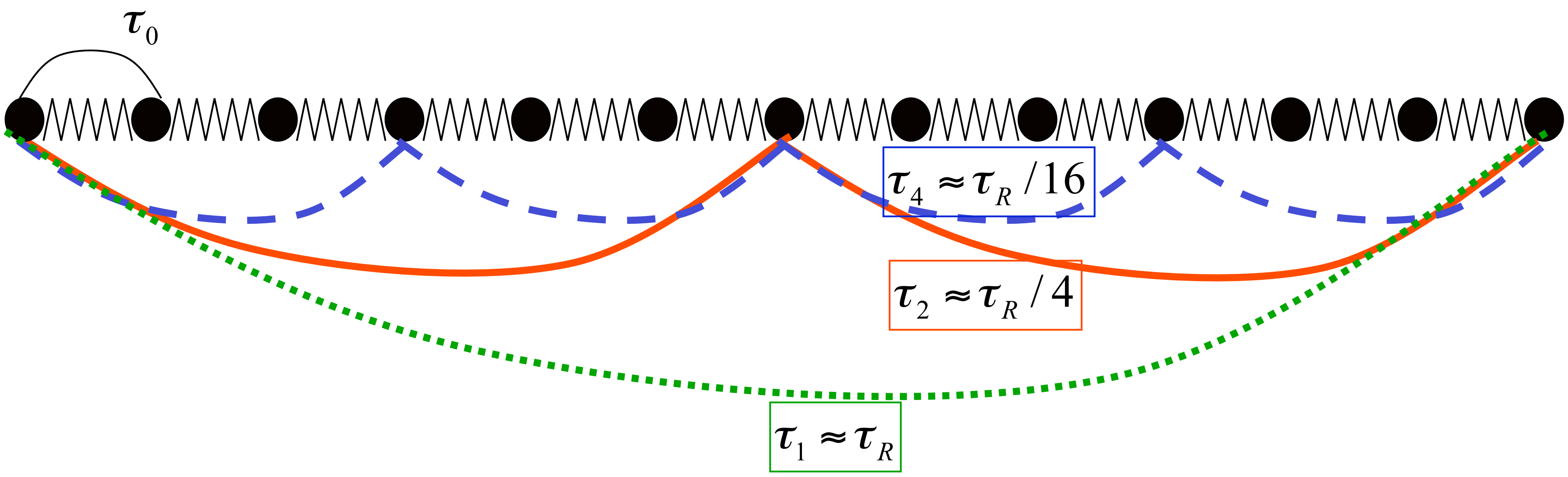
$$\boxed{\tau_p \approx \tau_0 \left(\frac{N}{p}\right)^2}$$

(p = 1,2,3,…,N)

N relaxation modes

$$\boxed{\tau_1 \approx \tau_R}$$

$$\boxed{\tau_i < \tau_{i-1}}$$



τ_0

$\tau_4 \approx \tau_R / 16$

$\tau_2 \approx \tau_R / 4$

$\tau_1 \approx \tau_R$

- At time t = τ_p, number of unrelaxed modes = p.

- Each unrelaxed mode contributes energy of order kT to the stress relaxation modulus:

$$\boxed{G(\tau_p) \approx \frac{kT}{b^3}\frac{\nu}{N}p}$$

(density of sections with N/p monomers: $\frac{\nu}{(N/p)b^3}$)

Volume fraction

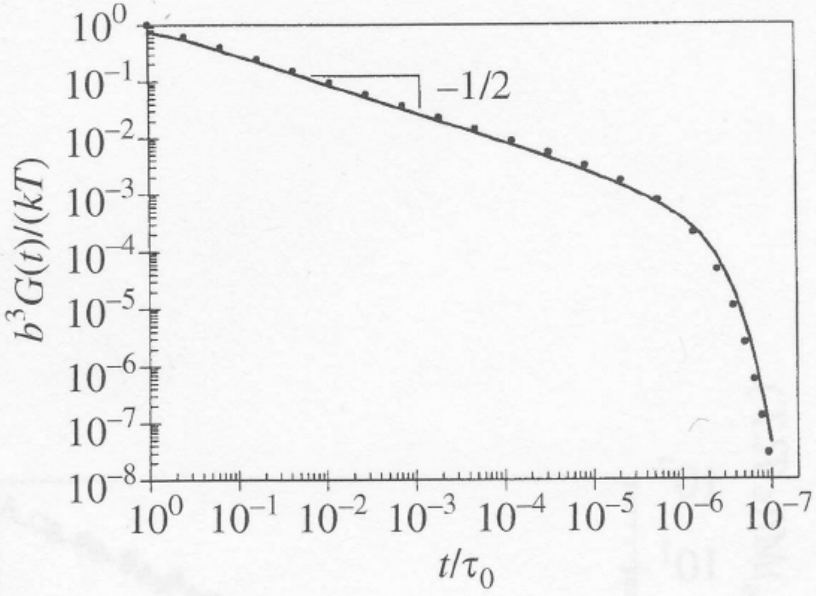
- Mode index at time t = τ_p: $p \approx \left(\frac{\tau_p}{\tau_0}\right)^{-1/2} N$

$$\Rightarrow \quad \boxed{G(t) \approx \frac{kT}{b^3}\nu\left(\frac{t}{\tau_0}\right)^{-1/2}}$$

, for $\tau_0 < t < \tau_R$

Approximation: $\boxed{G(t) \approx \frac{kT}{b^3}\nu\left(\frac{t}{\tau_0}\right)^{-1/2} \exp\left(\frac{-t}{\tau_R}\right)}$, for $t > \tau_0$

$$\boxed{G(t) \approx \frac{kT}{b^3} \nu \left(\frac{t}{\tau_0} \right)^{-1/2}}$$, for $\tau_0 < t < \tau_R$



Stress relaxation modulus predicted by the Rouse model for a melt of unentangled chains with $N = 10^3$. The solid curve is the exact Rouse result [Eq. (8.55)] and the dotted curve is the approximate Rouse result [Eq. (8.48)].

Viscosity of the Rouse model:

$$\eta = \int_0^\infty G(t)\,dt \approx \frac{kT}{b^3}\nu \int_0^\infty \left(\frac{t}{\tau_0}\right)^{-1/2} \exp\left(\frac{-t}{\tau_R}\right) dt$$

$$\approx \frac{kT}{b^3}\nu\sqrt{\tau_0\tau_R}\int_0^\infty x^{-1/2}\exp(-x)\,dx \approx \frac{kT}{b^3}\nu\sqrt{\tau_0\tau_R} \approx \frac{kT}{b^3}\nu\tau_0 N \approx \frac{\zeta}{b}N\nu$$

$$\Rightarrow \quad \boxed{\eta \approx \frac{\zeta}{b}N}$$

Or:

$$\left.\begin{array}{l} \tau_R \approx \tau_0 N^2 \\[2ex] G(\tau_R) \approx kT\dfrac{\nu}{Nb^3} \end{array}\right\} \Rightarrow \quad \boxed{\eta = \tau_R G(\tau_R) \approx \frac{\zeta}{b}N}$$

Exact solution of the Rouse model:

$$\boxed{G(t) = \frac{kT}{Nb^3}\nu \sum_{p=1}^{N} \exp\left(\frac{-t}{\tau_p}\right) \qquad \text{with} \qquad \tau_p = \frac{\zeta b^2 N^2}{6\pi^2 kTp^2}}$$

Each mode relaxes as a Maxwell element

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

The Rouse relaxation time is the half of the end-to-end correlation time.

Or:

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

The Rouse relaxation time is the end-to-end correlation time.

Rouse time determined from the free energy:

Free energy U of a Gaussian chain (see Part I):

$$\frac{U(\underline{R_0})}{kT} = cste + \frac{3}{2Nb^2}\left|\underline{R_0}\right|^2$$

Forces equilibrium after a displacement of ΔL:

$$\zeta \frac{d(\Delta L(t))}{dt} = -\frac{3kT}{Nb^2}\Delta L(t) \quad \Rightarrow \quad \Delta L(t) = \Delta L(0)\ \exp\left(\frac{-3kT}{Nb^2\zeta}t\right)$$

After the disorientation

“spring” force from the free energy

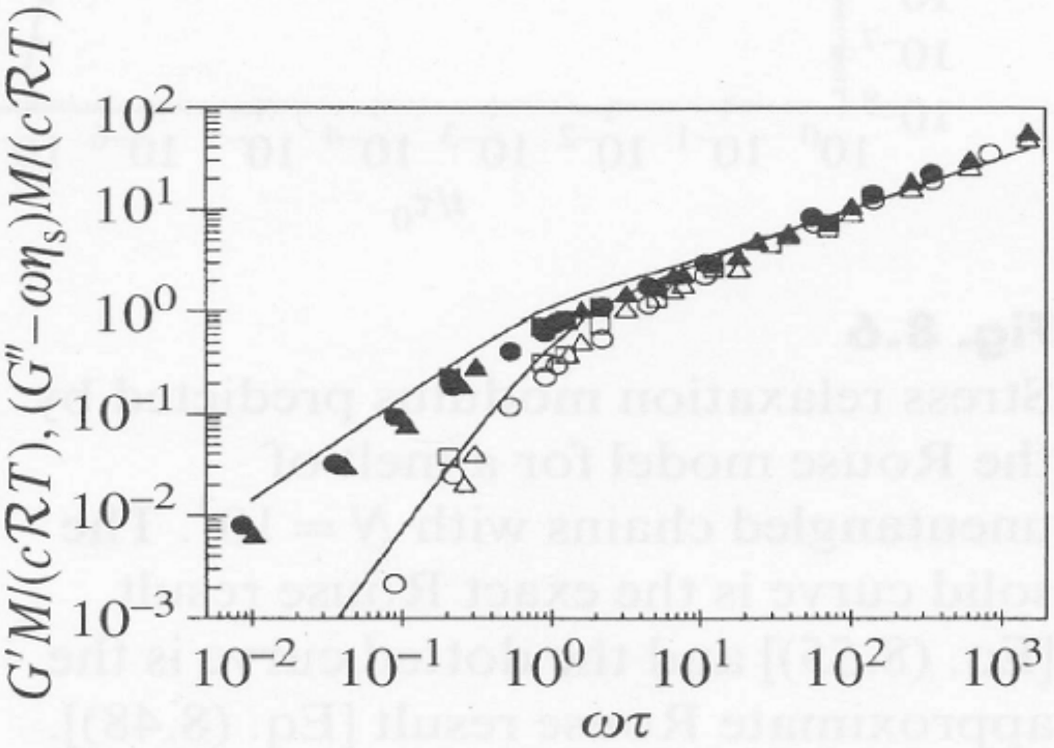
$$\boxed{\tau_R \approx \frac{\zeta b^2}{3kT} N^2}$$

Example: Frequency sweep test:

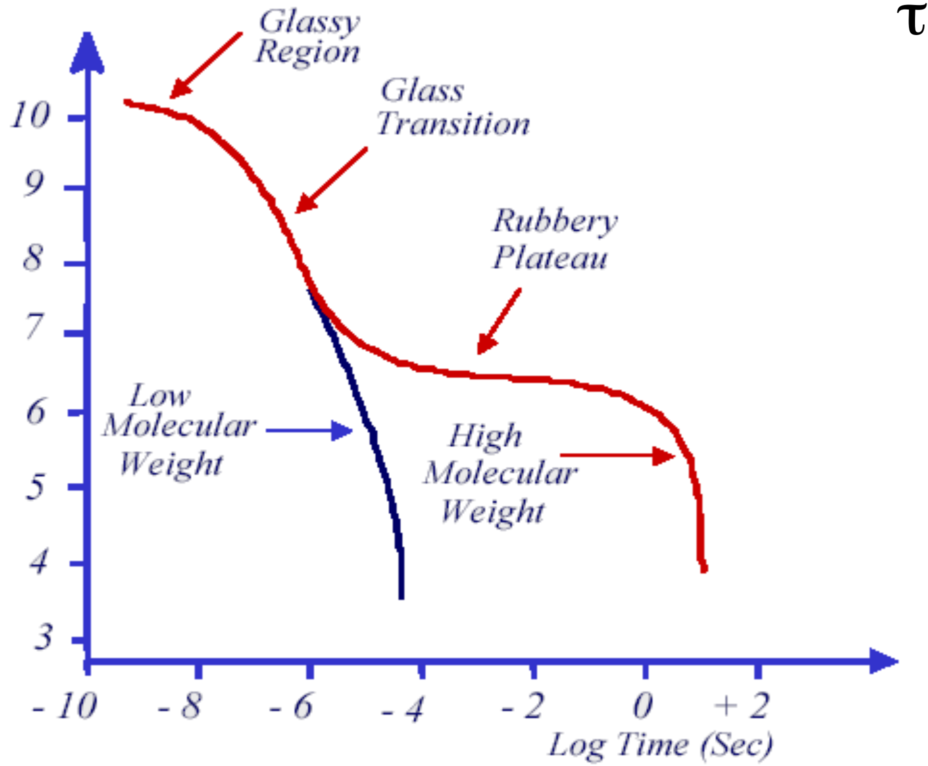
$$G'(\omega) \simeq G''(\omega) \sim \omega^{1/2}$$ For $1/\tau_R < \omega < 1/\tau_0$

$$\begin{cases} G'(\omega) \sim \omega \\ G''(\omega) \sim \omega^2 \end{cases}$$ For $\omega < 1/\tau_R$

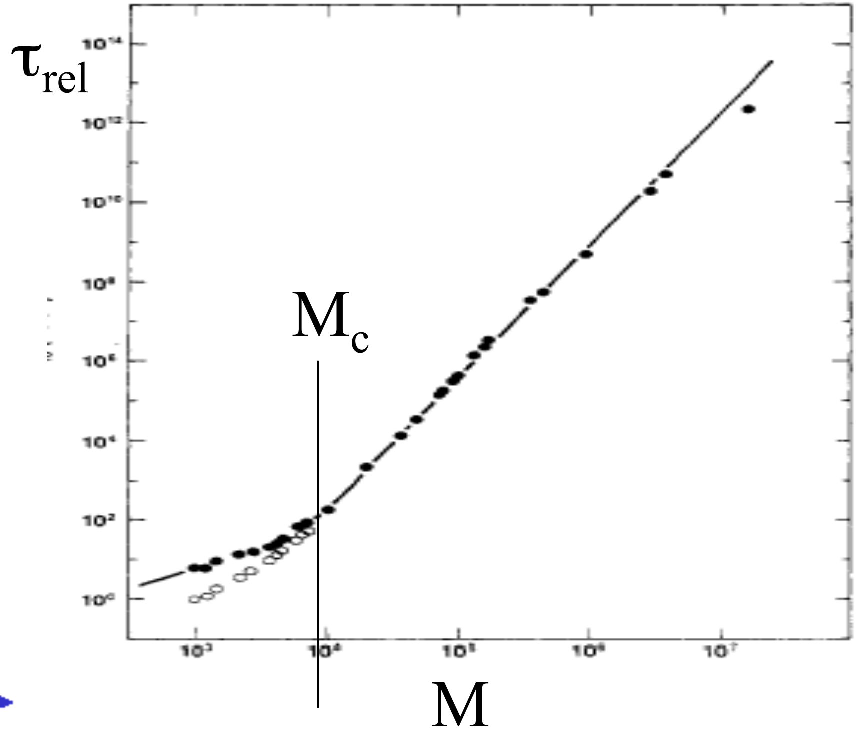
Oscillatory shear data for solutions of poly(2-vinyl pyridine) in 0.0023 M HCl in water. Open symbols are the storage modulus G' and filled symbols are the loss modulus G''. Squares have $c = 0.5\ \mathrm{g\ L^{-1}}$, triangles have $c = 1.0\ \mathrm{g\ L^{-1}}$, and circles have $c = 2.0\ \mathrm{g\ L^{-1}}$. The curves are the predictions of the Rouse model [Eqs (8.49) and (8.50)]. Data from D. F. Hodgson and E. J. Amis, *J. Chem. Phys.* **94**, 4581 (1991).



Rouse model: also valid for unentangled chains in polymer melts:



Relaxation times



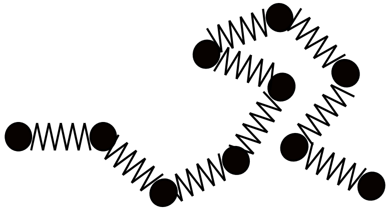
For $M < M_c$: $\tau_{rel} \propto M^2$

For $M > M_c$: $\tau_{rel} \propto M^{3.2 \rightarrow 3.4}$

I.2.2. Zimm model:

Viscous resistance from the solvent: the particle must drag some of the surrounding solvent with it.

Hydrodynamic interaction: *long-range force acting on solvent (and other particles) that arises from motion of one particle.*



When one bead moves: interaction force on the other beads (Rouse: only through the springs)

→ The chain moves as a solid object: $\boxed{\zeta_Z \approx \eta_s R}$

$$\boxed{D_Z = \frac{kT}{\zeta_Z} \approx \frac{kT}{\eta_s R}}$$

→ Zimm time:

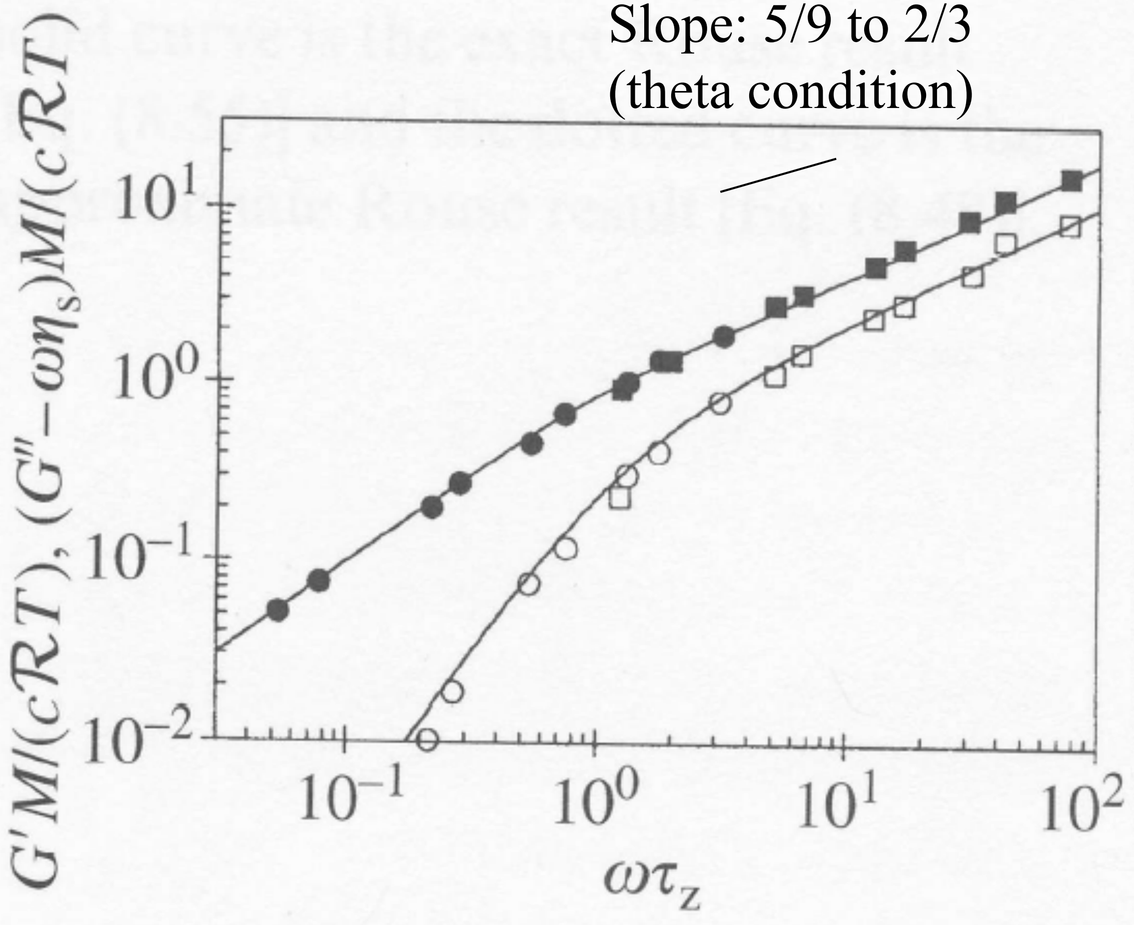
$$\tau_Z \approx \frac{R^2}{D_Z} \approx \frac{\eta_s}{kT} R^3 \approx \frac{\eta_s b^3}{kT} N^{3/2} \approx \tau_0 N^{3/2} \quad \text{(In a theta solvent)}$$

Rouse time versus Zimm time:

$$\tau_R \approx \frac{R^2}{D_R} \approx \frac{R^2}{kT / N\zeta} \approx \frac{R^2}{kT / N\eta_s b} \approx \frac{\eta_s b^3}{kT} N^2$$

$$\tau_Z \approx \frac{R^2}{D_Z} \approx \frac{R^2}{kT / \zeta_Z} \approx \frac{R^2}{kT / \eta_s R} \approx \frac{\eta_s b^3}{kT} N^{3/2} \approx \tau_0 N^{3/2}$$

- τ_{Zimm} has a weaker M-dependence than τ_{Rouse}.
- $\tau_{\mathrm{Zimm}} < \tau_{\mathrm{Rouse}}$ in dilute solution
- real case: often a combination of both



Slope: 5/9 to 2/3
(theta condition)

Oscillatory shear data on dilute solutions of polystyrene with $M = 860\,000$ g mol^{-1} in two θ-solvents (circles are in decalin at 16 °C and squares are in di-2-ethylhexyl phthalate at 22 °C). Open symbols are the dimensionless storage modulus and filled symbols are the dimensionless loss modulus, both extrapolated to zero concentration. The curves are the predictions of the Zimm model [Eqs (8.67) and (8.68)]. Data from R. M. Johnson *et al., Polym. J.* **1**, 742 (1970).

Dilute PS in Θ-solvent
Zimm model

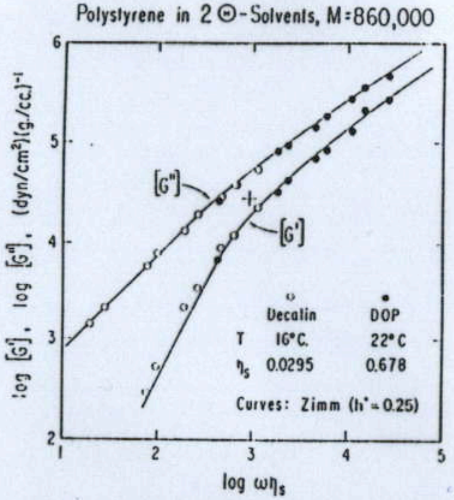


Fig. 5.1. Intrinsic moduli for narrow distribution polystyrene ($M = 860000$) in two theta solvents (*114*). This comparison with theory is equivalent to that of reduced moduli described in the text. [Reproduced from Polymer J. 1, 747 (1970).]

Undiluted short PS
Rouse model

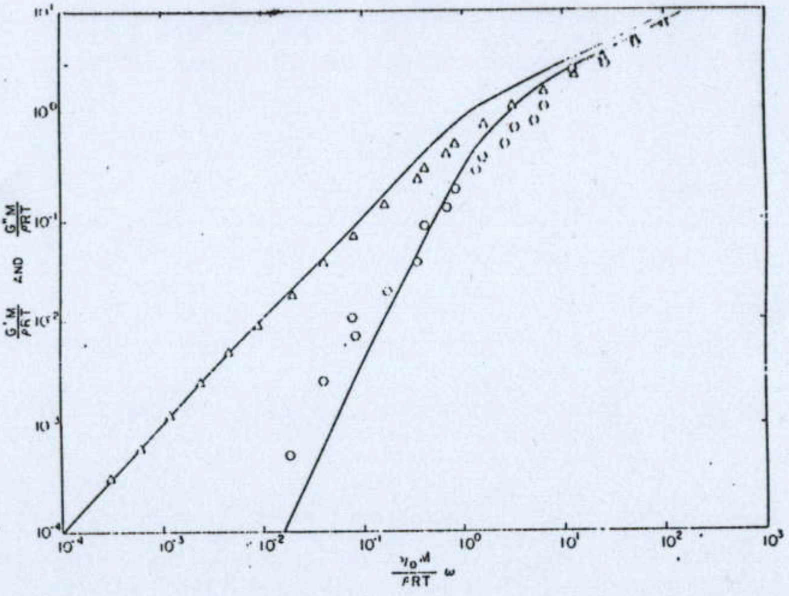
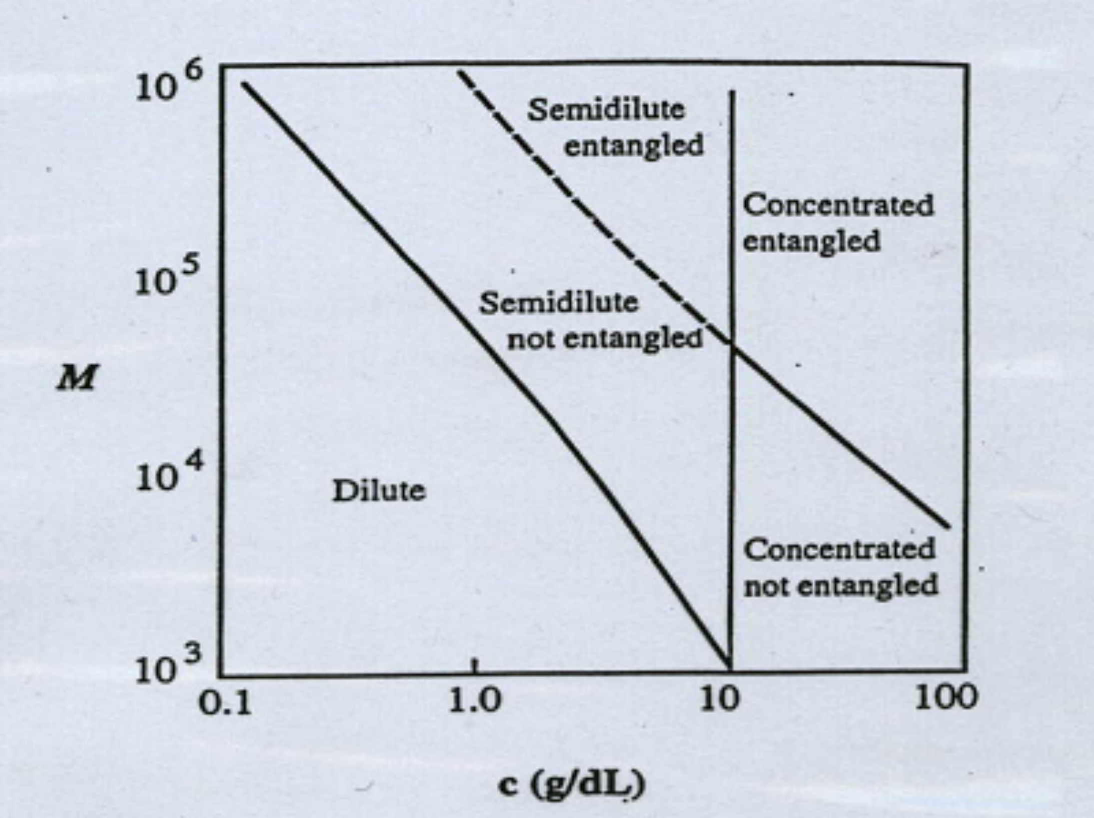


Fig. 5.2. Reduced dynamic moduli for undiluted narrow distribution polystyrene of low molecular weight. Data for a sample of $\bar{M}_w = 28900$ were reduced to 160 °C, for which $\varrho = 1.0$ gm/ml and $\eta_0 = 54500$ poise (*124*). The solid lines were calculated from the Rouse theory

$M_w = 28900$ g/mol
$M_e \simeq 13300$

Rheological Regimes:

(Graessley, 1980)



Dilute solutions: Zimm model – H.I. – no entanglement

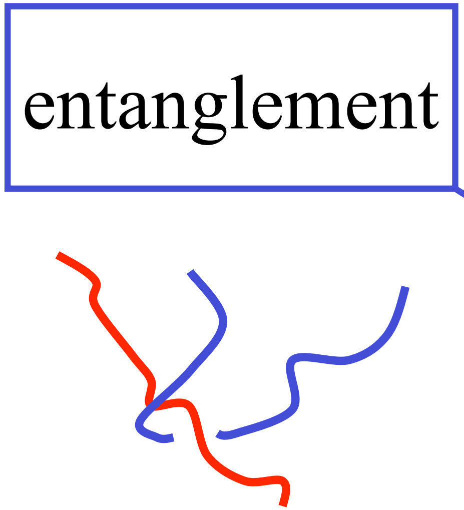
Unentangled chains (Non diluted): Rouse model – no H.I. – no entanglement

Entangled chains: Reptation model – no H.I. – entanglement

II. Entangled polymer dynamics

II.1. Introduction to Tube models

The test chain is entangled
with its neighbouring
polymers

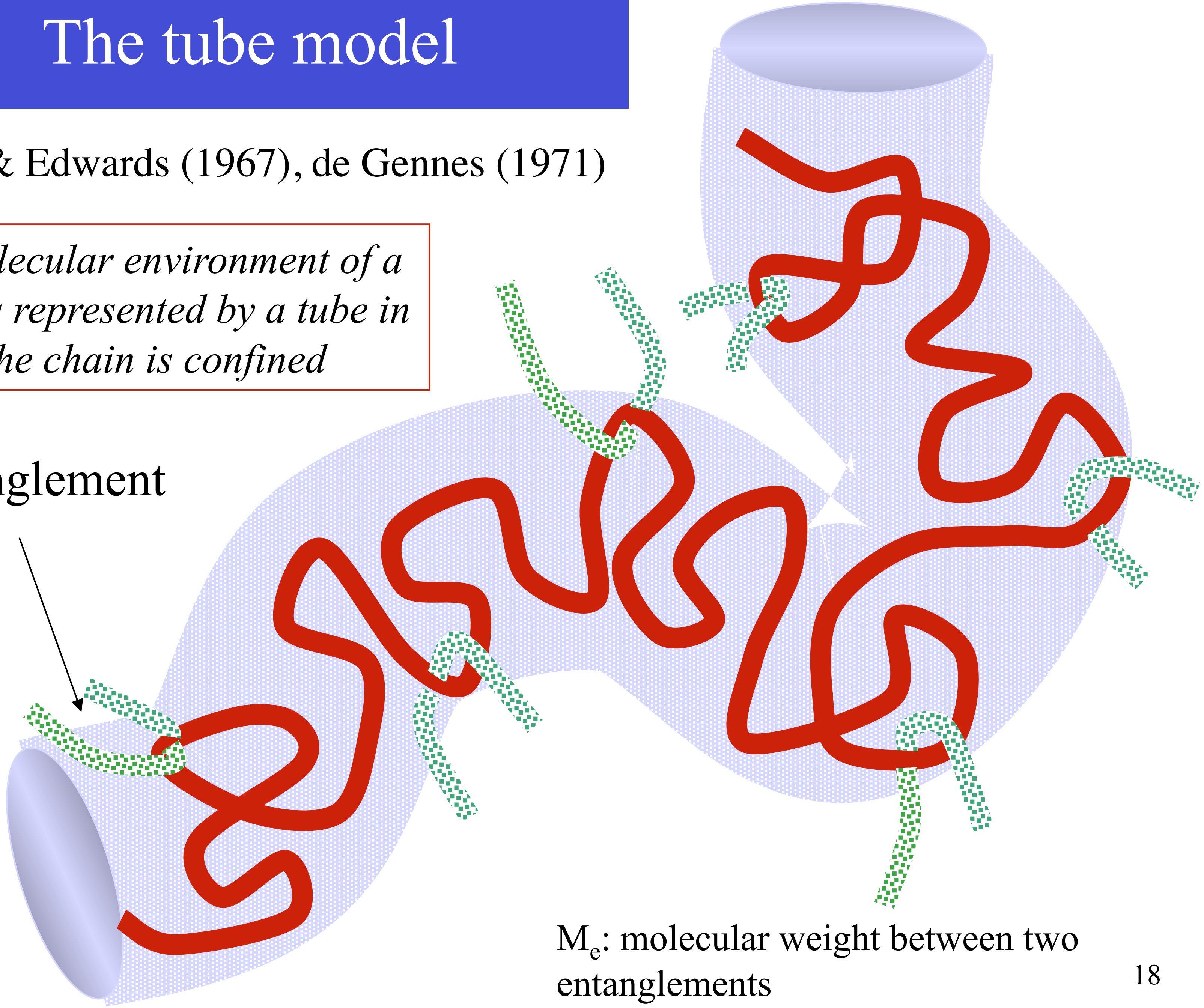


Molecules cannot cross
each other

The tube model

Doi & Edwards (1967), de Gennes (1971)

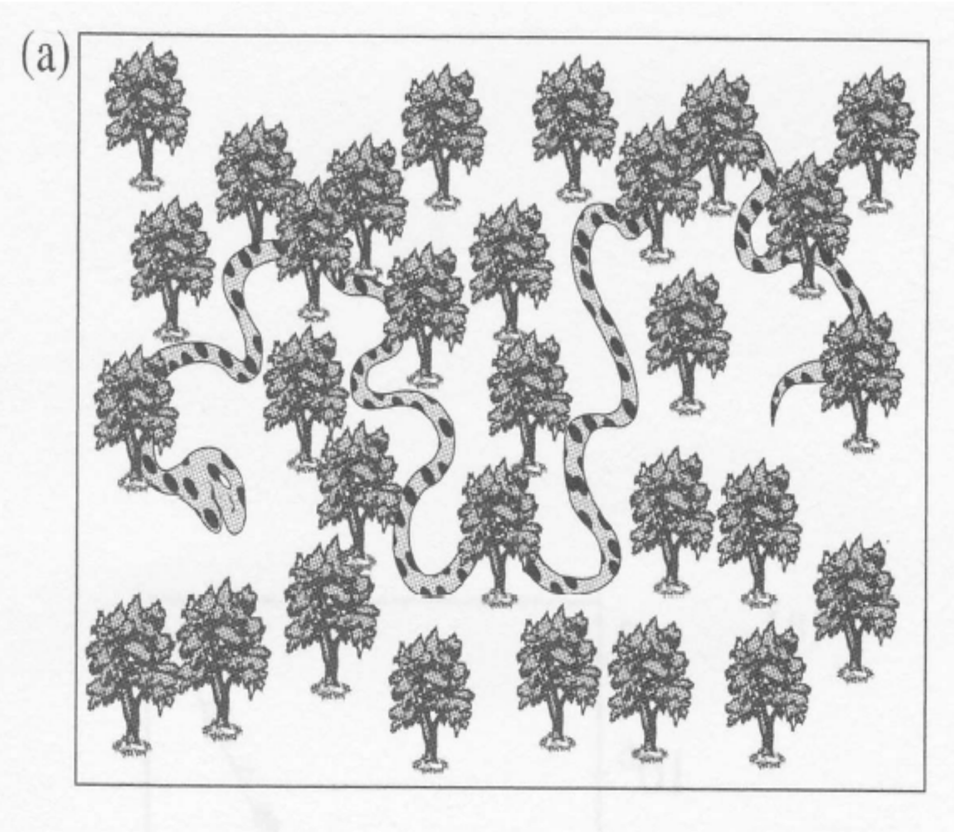
The molecular environment of a chain is represented by a tube in which the chain is confined

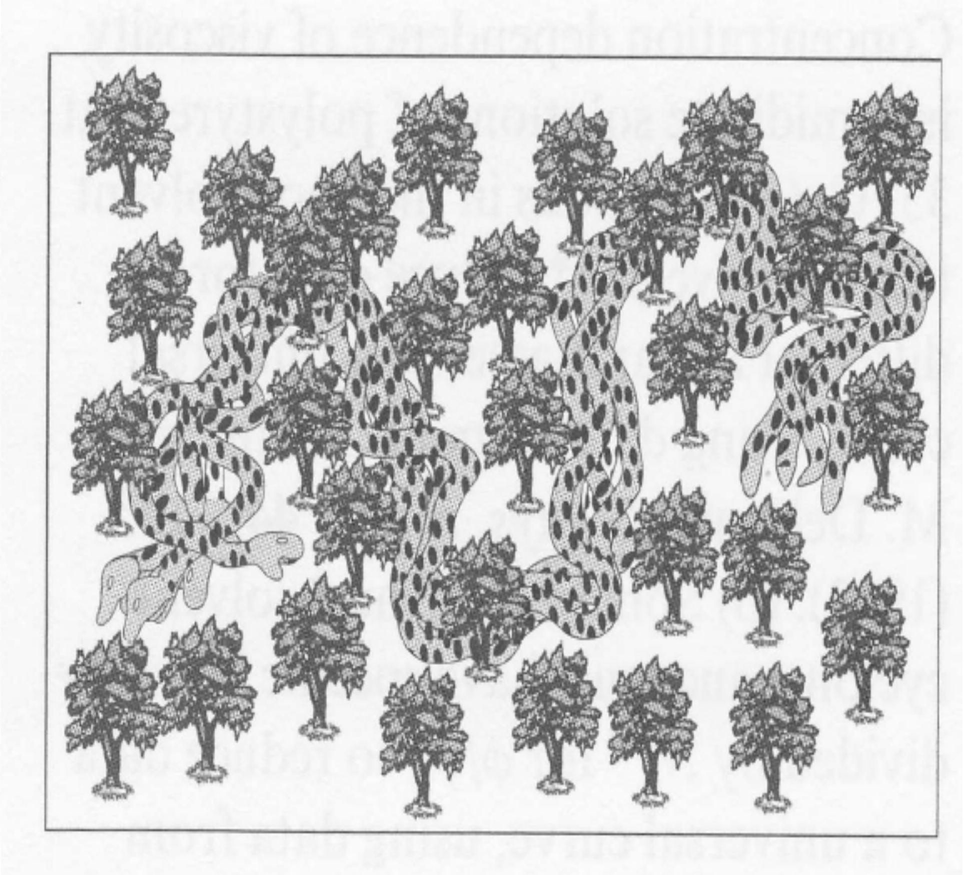


entanglement

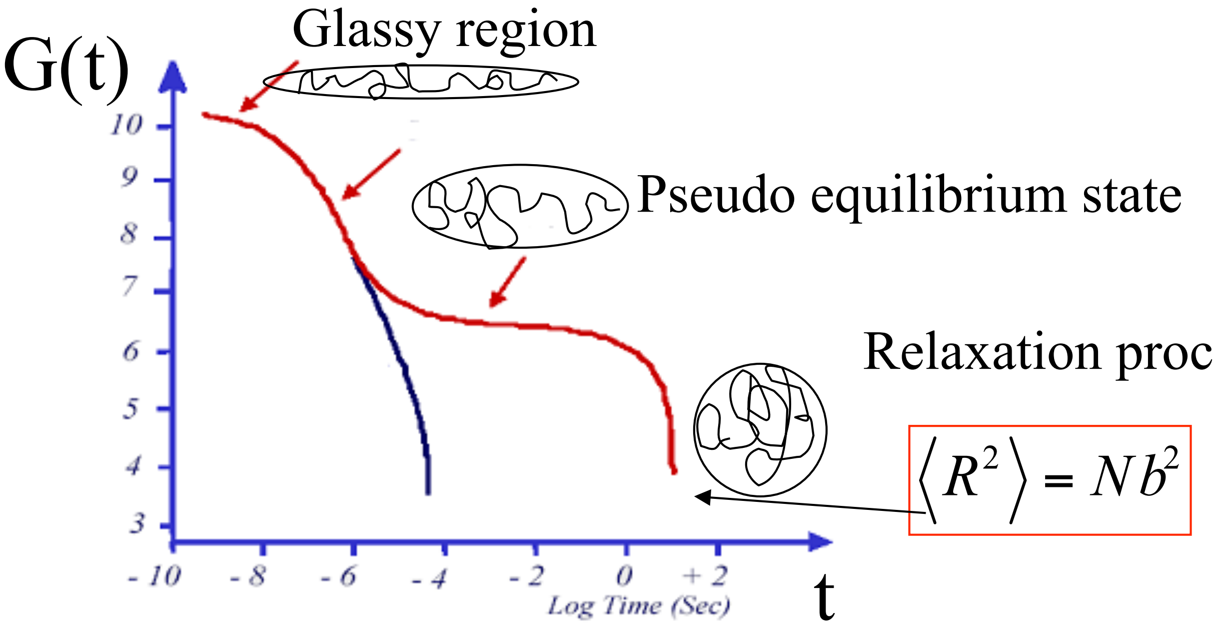
M_e: molecular weight between two entanglements

Tube model and entanglements:

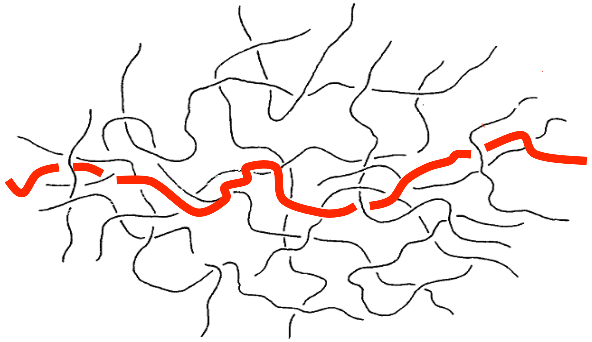




Concentrated solutions or polymer melts:



$$\langle R^2 \rangle = Nb^2$$

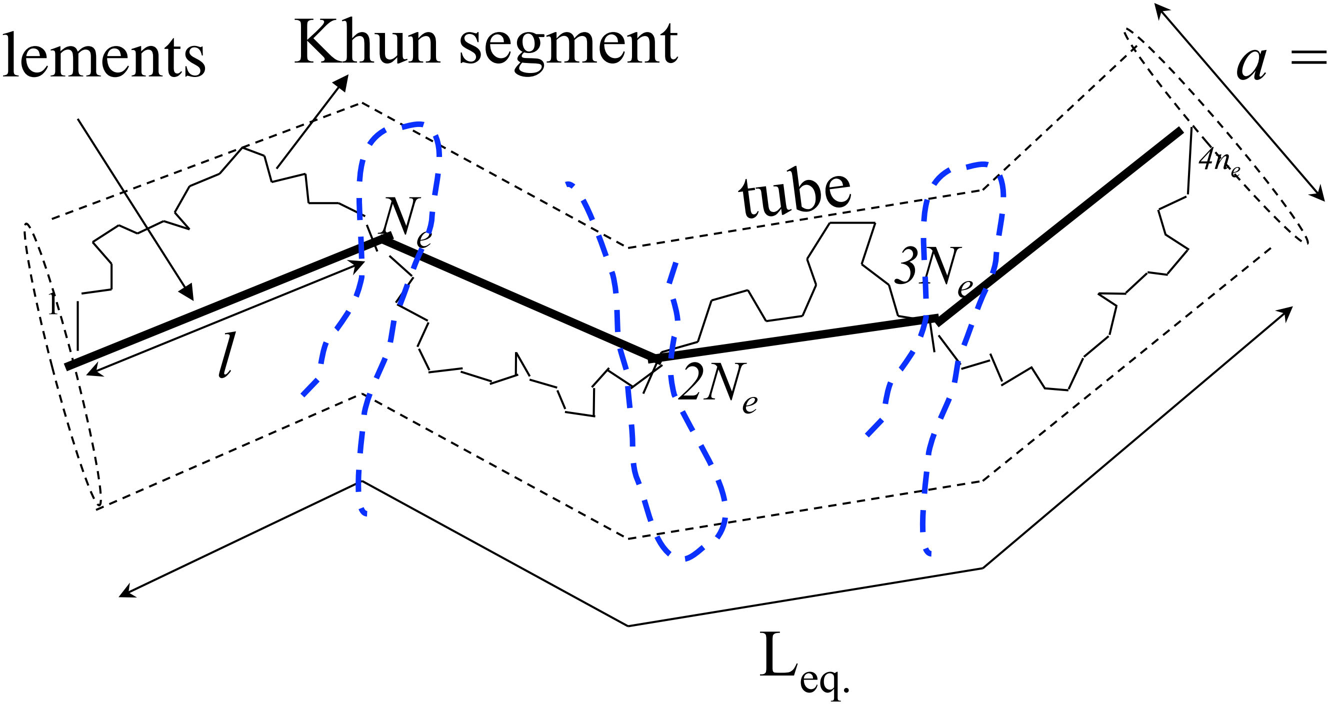


Pseudo equilibrium state:

The chains are not in their stable shape. The other chains prevent their relaxation. The tube picture becomes active.

M_e: M_w of the longest sub-chain relaxed by a Rouse process

II.2. « Equilibrium state » in a polymer melt or in a concentrated solution:



Z = segments number =4

Segment between two entanglements

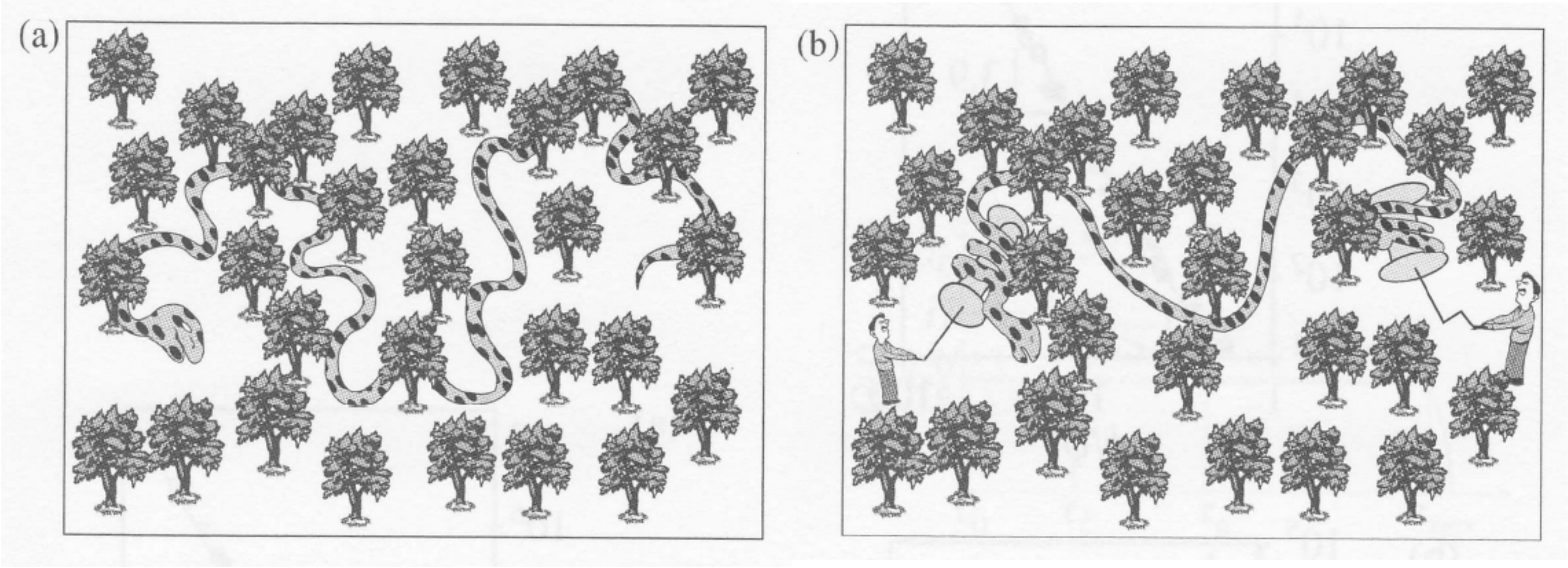
Khun segment

a = tube diam.

- Each segment between two entanglements is relaxed by the Rouse process

- The primitive path of the chain is defined by its segments between the entanglements. Its length = $L_{eq.}$ → Coarse grained model

Primitive path

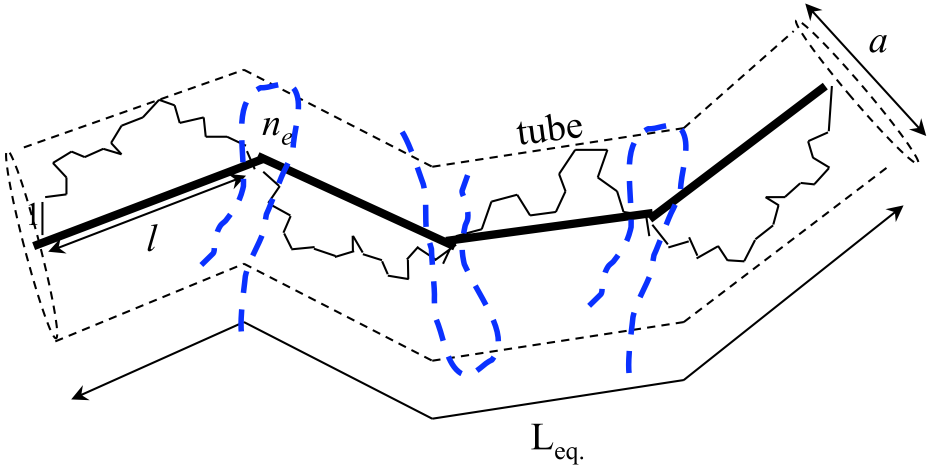


- Simpler description of the chain

- Coarse grained model: subchains of mass M_e are considered as a segment of length l

- relaxation time of subchain M_e: Rouse relaxation

Equilibrium state in a polymer melt: parameters



L_{eq} = length of the primitive path

Z = number of segments between two ent.

l = length of a segment between two ent.

a = tube diameter

b = length of a Khun segment

N_e = number of Khun segments between two entanglements

N = total number of Khun segments in the chain

$$Z = \frac{M}{M_e}$$

Gaussian chain in solution: *the end-to-end distance* $R_0^2 = Nb^2$

Gaussian chain in a melt or concentrated solution:

$$\boxed{l^2 \approx N_e b^2}$$

$$\boxed{L_{eq} = Z \cdot l = \frac{N}{N_e} \cdot l}$$

Constitutive equation of a polymer melt

For a Rouse chain (unentangled chain):

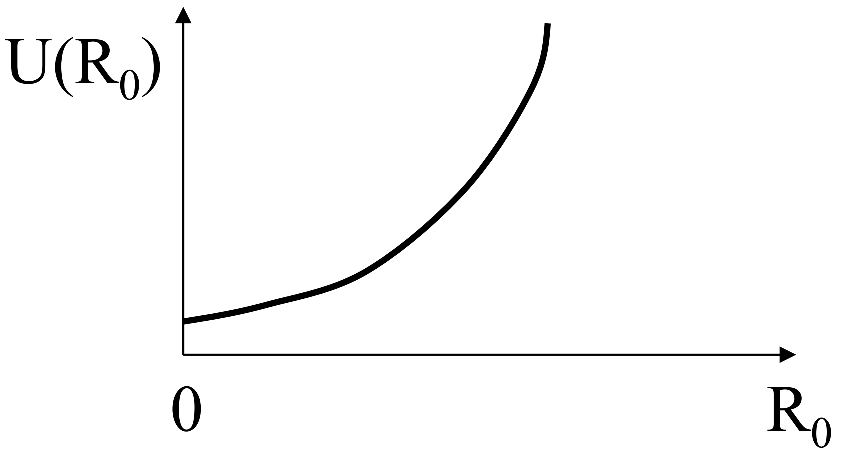
Entropic material:

In a fixed direction:

$U = -TS$ (free energy) $\qquad S = k \ln P$

$$\Rightarrow P(\underline{R_0} = \underline{R}) \propto \exp\left(\frac{-3|\underline{R}|^2}{2Nb^2}\right) \text{ (Gaussian)}$$

$$\Rightarrow \frac{U(\underline{R_0})}{kT} = cste + \frac{3}{2Nb^2}|\underline{R_0}|^2 \text{ (free energy)}$$

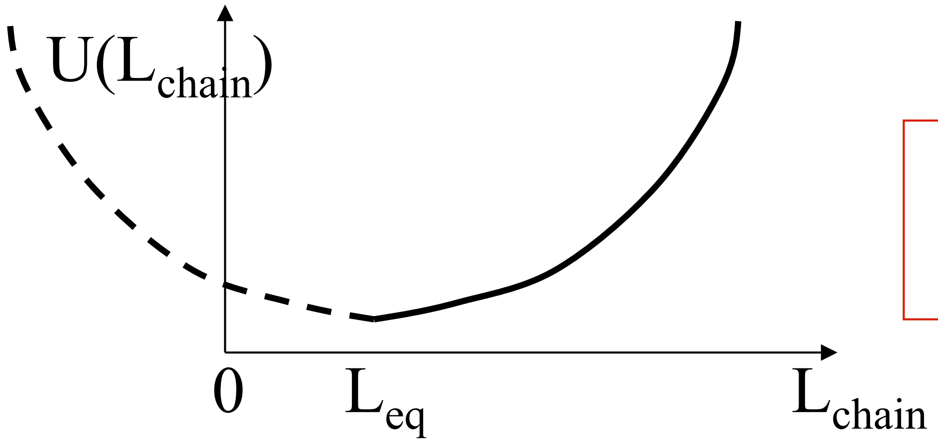


Constitutive equation of a polymer melt

For a polymer melt:

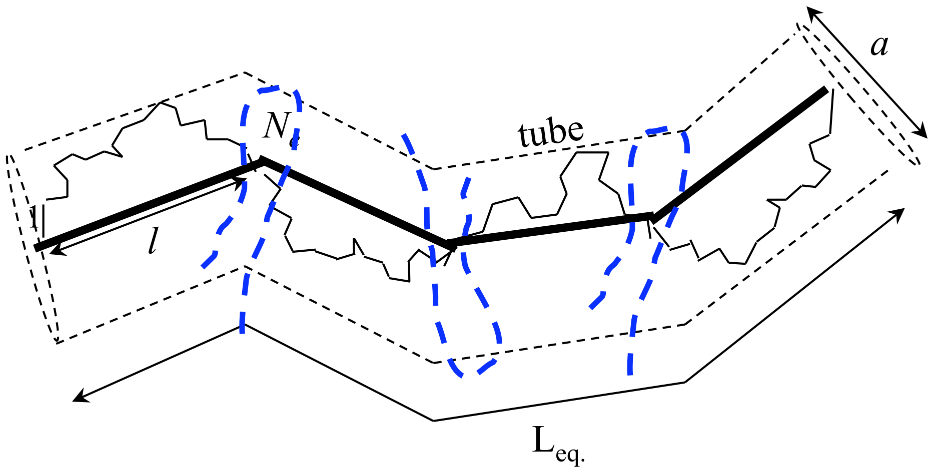
Additional boundary conditions: $\psi(R) = 0$ on the tube surface

$$\boxed{\frac{U(L_{chain})}{kT} = cste - \frac{3Nb^2}{a^2} + \frac{3}{2Nb^2} L_{chain}{}^2}$$



At equilibrium (U min.):
$Nb^2 \approx a.L_{eq}$

Equilibrium state in a polymer melt: parameters



$$\boxed{L_{eq} = Z \cdot l = \frac{N}{N_e} \cdot l}$$

L_{eq} = length of the primitive path

Z = number of segments between two ent.

l = length of a segment between two ent.

a = tube diameter

b = length of a Khun segment

N_e = number of Khun segments between two entanglements

N = total number of Khun segments in the chain

Gaussian chain in solution: $R_0^2 = Nb^2$

Gaussian chain in a melt or concentrated solution: $\boxed{l^2 \approx N_e b^2}$ $\boxed{Nb^2 \approx a.L_{eq}}$

$$\boxed{l \approx a}$$

Material parameters in the tube model

$\longrightarrow$ Defined at the "equilibrium state" of the polymer

- The molecular weight between two entanglements: M_e

- The plateau modulus:

$$\boxed{G_N^0 = \frac{\rho \; N_A \; kT}{M_e} = \frac{\rho \; R \; T}{M_e}} \qquad (\text{x } 4/5)$$

- The relaxation time of a segment between two entanglements:

$$\tau_e \approx \tau_0 N_e^{\;2} \qquad\qquad \tau_e = \frac{\zeta b^2}{3\pi^2 kT} N_e^{\;2}$$

Very simplified coarse-grained model

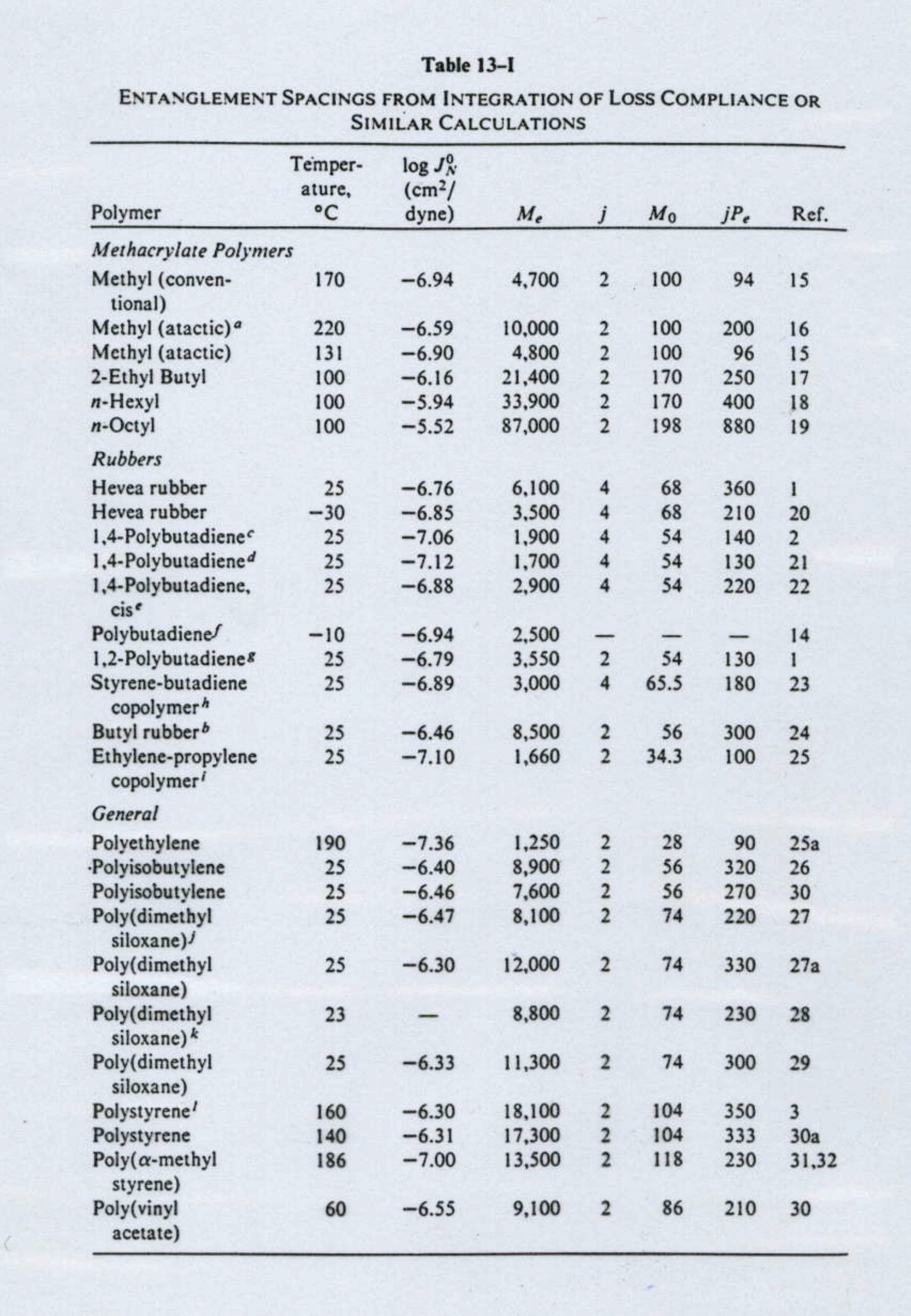
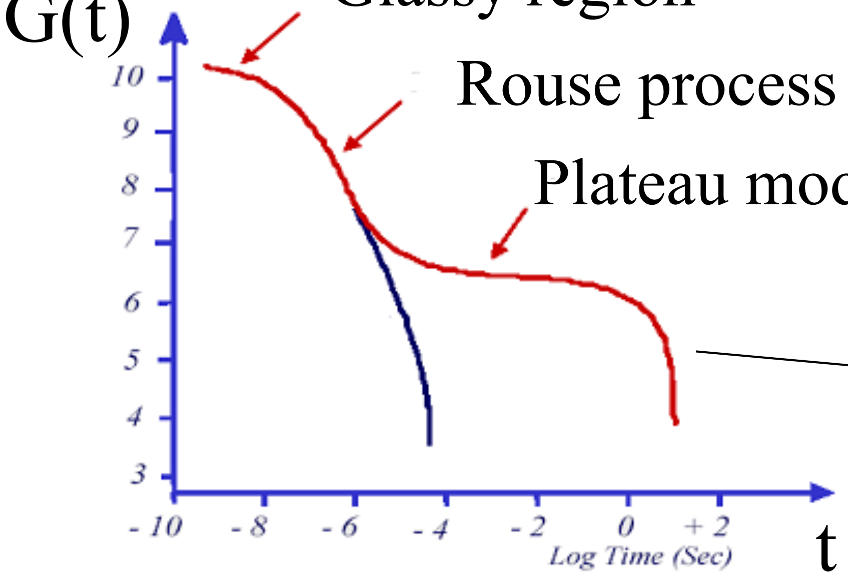


Table 13–I

ENTANGLEMENT SPACINGS FROM INTEGRATION OF LOSS COMPLIANCE OR SIMILAR CALCULATIONS

Polymer	Temperature, °C	log J_N^0 (cm^2/dyne)	M_e	j	M_0	jP_e	Ref.
Methacrylate Polymers							
Methyl (conventional)	170	−6.94	4,700	2	100	94	15
Methyl (atactic)[a]	220	−6.59	10,000	2	100	200	16
Methyl (atactic)	131	−6.90	4,800	2	100	96	15
2-Ethyl Butyl	100	−6.16	21,400	2	170	250	17
n-Hexyl	100	−5.94	33,900	2	170	400	18
n-Octyl	100	−5.52	87,000	2	198	880	19
Rubbers							
Hevea rubber	25	−6.76	6,100	4	68	360	1
Hevea rubber	−30	−6.85	3,500	4	68	210	20
1,4-Polybutadiene[c]	25	−7.06	1,900	4	54	140	2
1,4-Polybutadiene[d]	25	−7.12	1,700	4	54	130	21
1,4-Polybutadiene, cis[e]	25	−6.88	2,900	4	54	220	22
Polybutadiene[f]	−10	−6.94	2,500	—	—	—	14
1,2-Polybutadiene[g]	25	−6.79	3,550	2	54	130	1
Styrene-butadiene copolymer[h]	25	−6.89	3,000	4	65.5	180	23
Butyl rubber[b]	25	−6.46	8,500	2	56	300	24
Ethylene-propylene copolymer[i]	25	−7.10	1,660	2	34.3	100	25
General							
Polyethylene	190	−7.36	1,250	2	28	90	25a
Polyisobutylene	25	−6.40	8,900	2	56	320	26
Polyisobutylene	25	−6.46	7,600	2	56	270	30
Poly(dimethyl siloxane)[j]	25	−6.47	8,100	2	74	220	27
Poly(dimethyl siloxane)	25	−6.30	12,000	2	74	330	27a
Poly(dimethyl siloxane)[k]	23	—	8,800	2	74	230	28
Poly(dimethyl siloxane)	25	−6.33	11,300	2	74	300	29
Polystyrene[l]	160	−6.30	18,100	2	104	350	3
Polystyrene	140	−6.31	17,300	2	104	333	30a
Poly(α-methyl styrene)	186	−7.00	13,500	2	118	230	31,32
Poly(vinyl acetate)	60	−6.55	9,100	2	86	210	30

II.3. Relaxation processes in linear chains



Glassy region

Rouse process

Plateau modulus G_0^N : tube effect

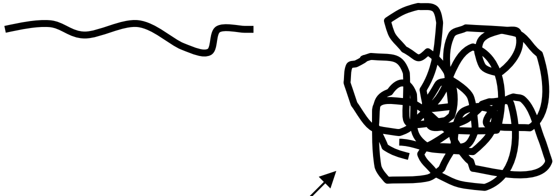
Relaxation of the polymer (as Reptation)

$$\boxed{G(t) = G_{Rouse}(t) + G_0^N \cdot \Phi(t)}$$

Plateau modulus

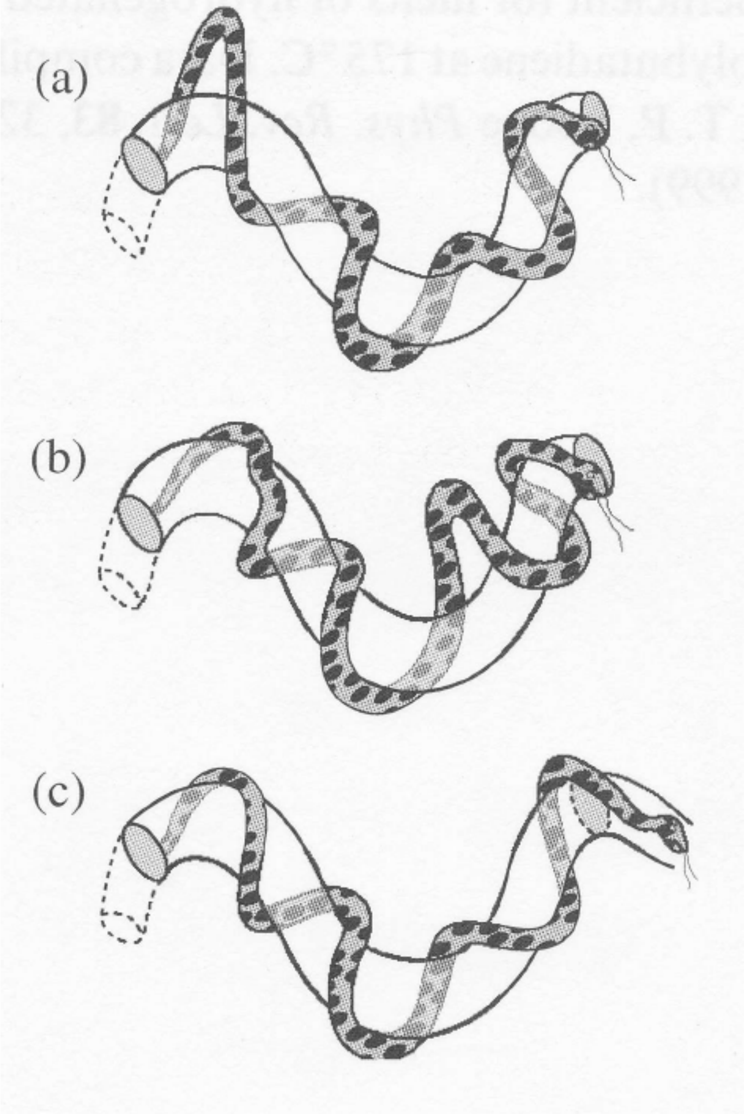
Unrelaxed fraction of the polymer melt

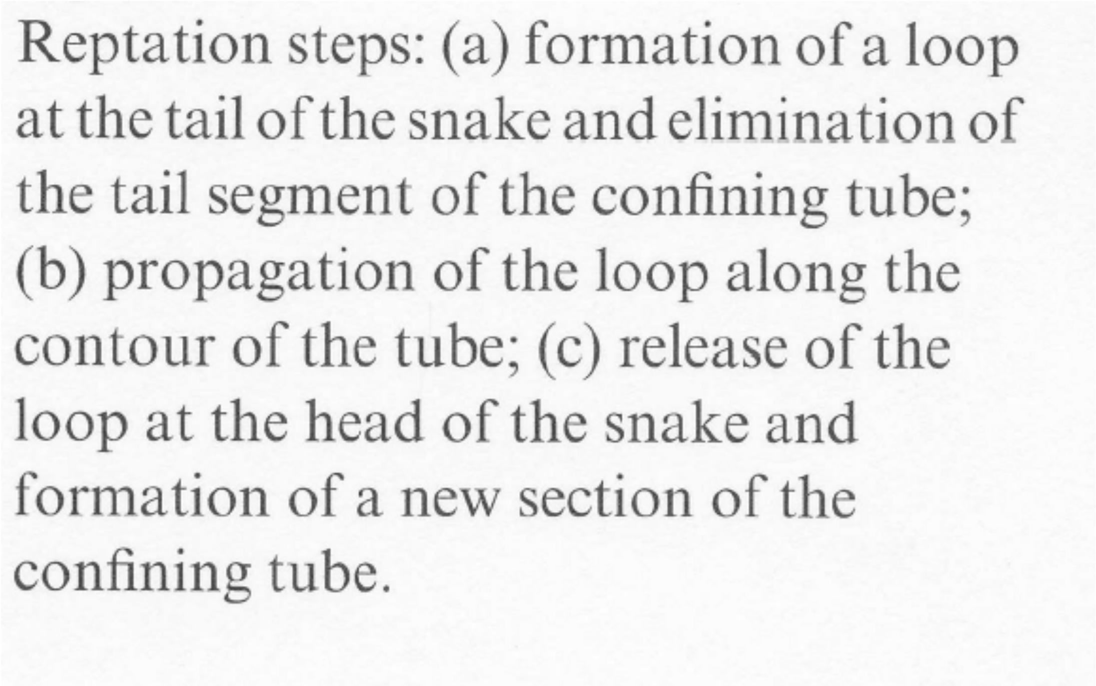
$\Phi = 1$ → $\Phi = 0$



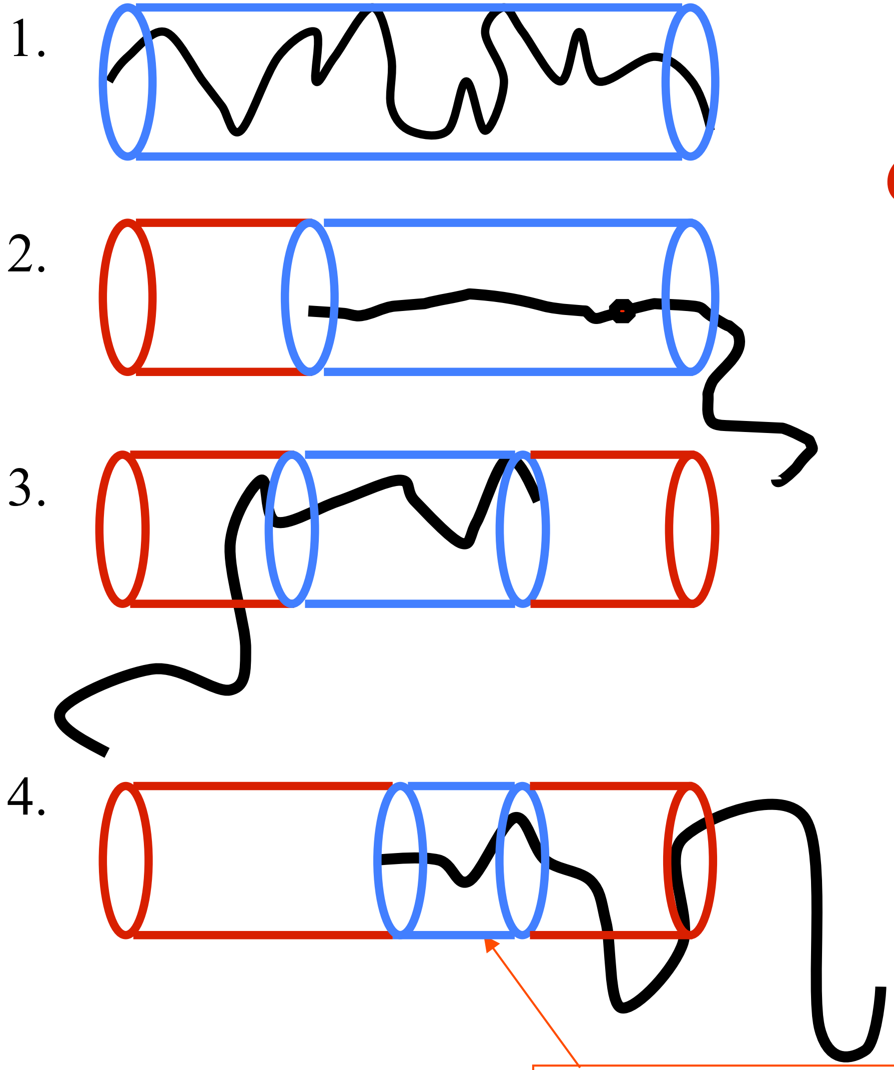
Not anymore memory of the initial deformation

II.3.1. Main relaxation process in linear chain: Reptation




Reptation steps: (a) formation of a loop at the tail of the snake and elimination of the tail segment of the confining tube; (b) propagation of the loop along the contour of the tube; (c) release of the loop at the head of the snake and formation of a new section of the confining tube.

Reptation



Part of the initial tube

1-D curvilinear diffusion

As the primitive chain diffuses out of the tube, a new tube is continuously being formed, starting from the ends.

This new tube portion is randomly oriented even if the starting tube is not.

+ Movie

Reptation

Curvilinear diffusion coefficient:

$$D_e = \frac{kT}{\zeta_{tot}} = \frac{kT}{N\zeta_0}$$

Total friction of the chain

Monomeric friction

$$\Rightarrow$$

Reptation time:

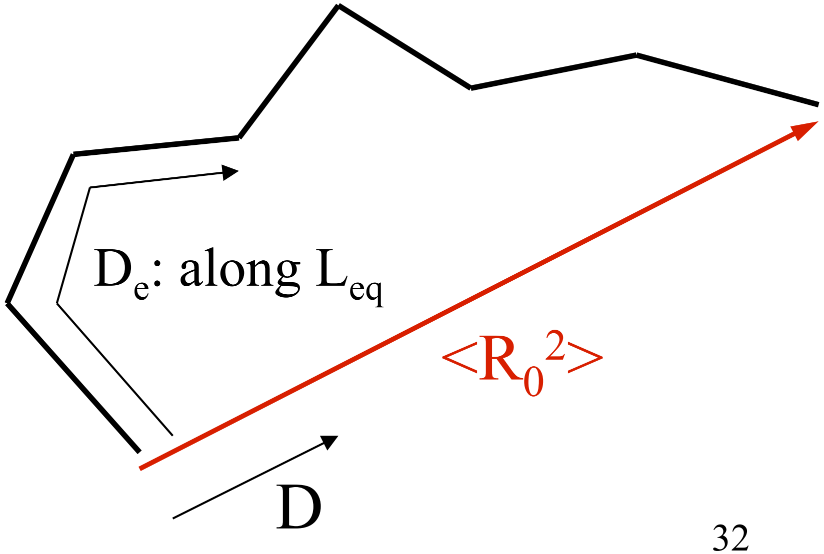
$$\boxed{\tau_{rept}} = \frac{L_{eq}^{\;2}}{D_e} \propto \frac{N^2}{N^{-1}} = \boxed{N^3}$$

$$\boxed{\tau_{\mathrm{Re}\,pt} \approx \tau_e \left(\frac{N}{N_e}\right)^3}$$

$$D \approx \frac{R^2}{\tau_{rept}}$$

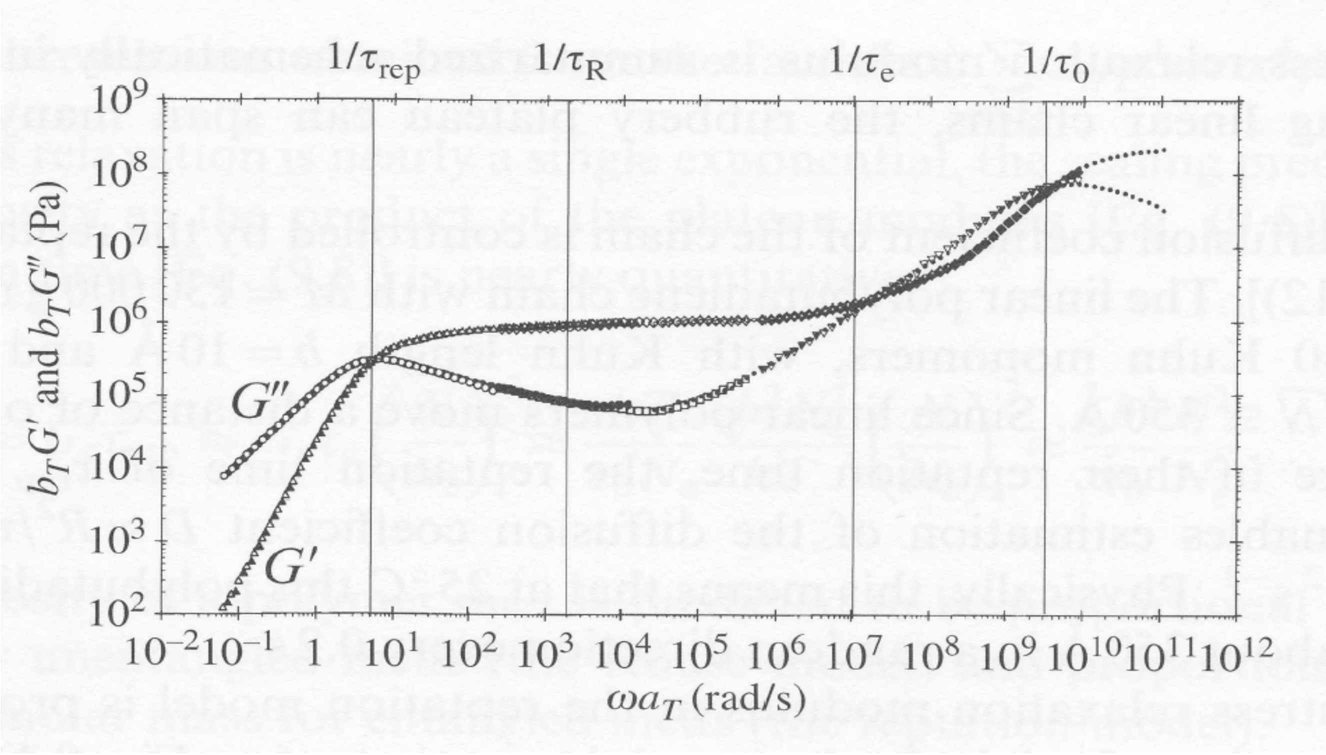
In solution:

$$\boxed{\tau_{Rouse}} = \frac{\langle R_0 \rangle^2}{D_e} \propto \frac{Nb^2}{N^{-1}} \propto \boxed{N^2}$$



Reptation

PBD, 130 kg/mol.

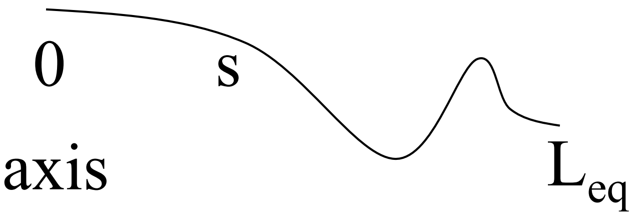


M (Kuhn segment): 105 g/mol → N=1240 Kuhn segments

τ_0 = 0.3 ns. τ_e = 0.1 μs. M_e=1900g/mol. N_e=18. M/M_e= 68 entanglements

Reptation: Doi and Edwards model

- First passage problem
- diffusion of a chain along the tube axis



$$\boxed{\frac{\partial\ p(s,t)}{\partial\ t} = D_e \cdot \frac{\partial^2 p(s,t)}{\partial\ s^2}}$$

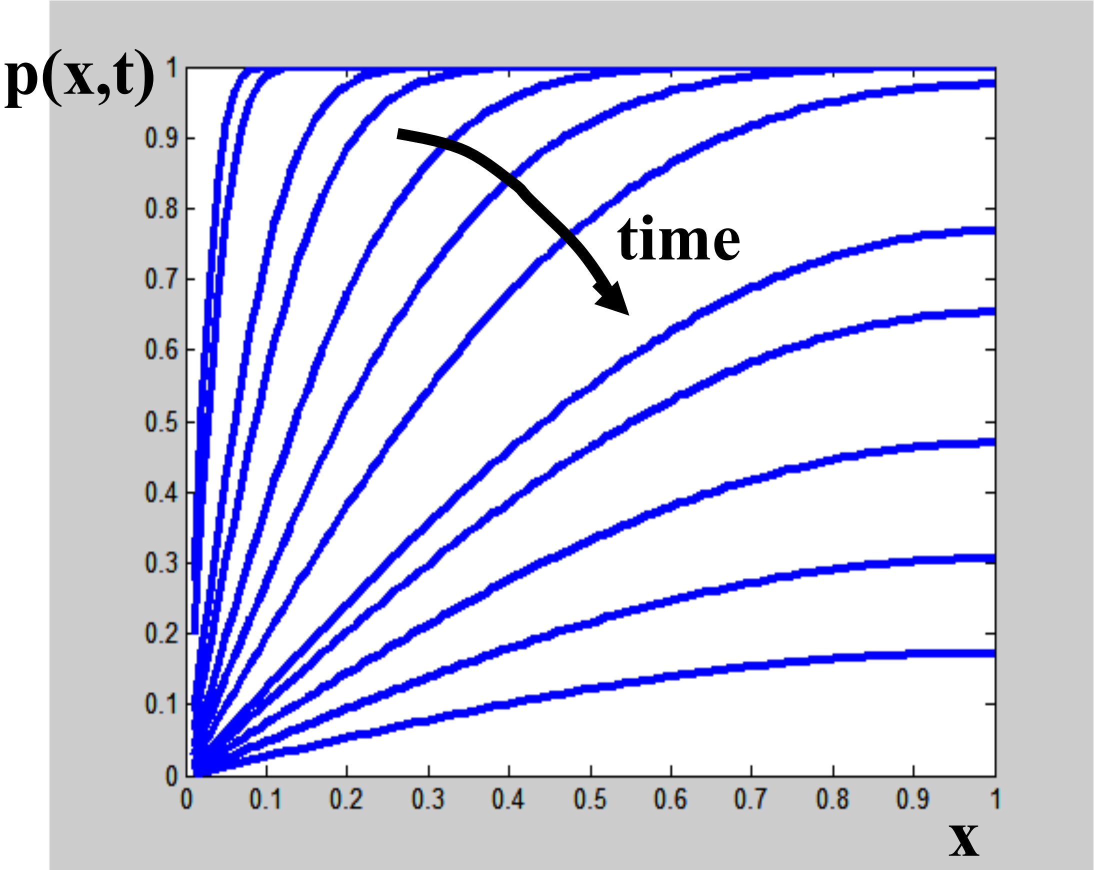
$$\boxed{\begin{array}{l} p(0,t) = p(L,t) = 0 \\ p(x,0) = 1,\ \ \forall x \in (0,L) \end{array}}$$

p(s,t): survival probability of a initial tube segment localized at a distance s.

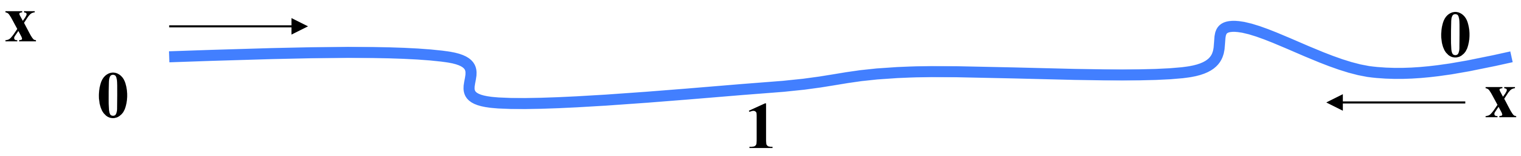
$$\xrightarrow[\textit{Variables separability}]{} \quad \boxed{p(s,t) = \sum_{i\ odd} \frac{4}{p\pi} \cdot \sin\left(\frac{i\pi s}{L_{eq}}\right) \cdot \exp\left(\frac{-i^2\pi^2 D\ \ t}{{L_{eq}}^2}\right)}$$

$$\longrightarrow \quad \boxed{p_{rept}(t) = \int_0^L\ p(s,t)ds = \frac{8}{\pi^2} \sum_{i\ odd} \frac{1}{i^2} \exp\left(\frac{-i^2 D\ \ t}{{L_{eq}}^2}\right)}$$

Doi and Edwards model



Using the usual coordinate system



Doi and Edwards model

$$\boxed{p_{rept}(t) = \int_0^L p(s,t)ds = \frac{8}{\pi^2}\sum_{p\ odd}\frac{1}{p^2}\exp\left(\frac{-p^2 D\ t}{L_{eq}^{\ 2}}\right)}$$

Relaxation modulus:

$$\boxed{G(t) = \frac{8}{\pi^2}G_N^0\sum_{p\ odd}\frac{1}{p^2}\exp\left(\frac{-p^2 t}{\tau_{rept}(M)}\right)}$$

$$\tau_{rept}(M) = 3\tau_e\left(\frac{N}{N_e}\right)^3 \qquad \tau_e = \frac{\zeta b^2}{3\pi^2 kT}N_e^{\ 2}$$

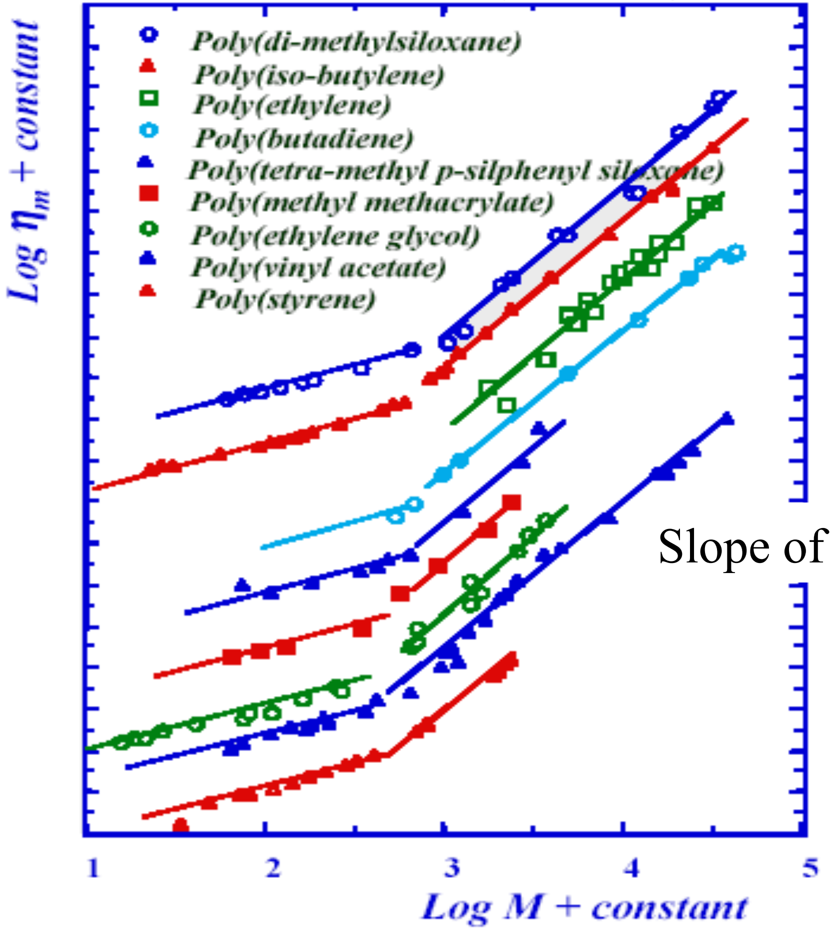
Related viscosity:

$$\boxed{\eta = \int_0^\infty G(t)dt = \frac{8}{\pi^2}G_N^0\sum_{p\ odd}\frac{1}{p^2}\int_0^\infty \exp\left(\frac{-p^2 t}{\tau_{rept}}\right)dt = \frac{\pi^2}{12}G_N^0\tau_{rept}}$$

$$(\sum_{p\ odd} 1/p^4 = \pi^4/96)$$

$$\begin{cases}\eta \sim M & \text{for M < M}_\text{c} \\ \eta \sim M^3 & \text{for M > M}_\text{c}\end{cases} \qquad \eta \sim M^{3.4}\ \text{ in the real case}$$

Zero-shear viscosity vs. log (M)



Slope of 3.4

Discrepancy between theory and experiments: inclusion of the contour length fluctuations process

Initial D&E model (with CR)

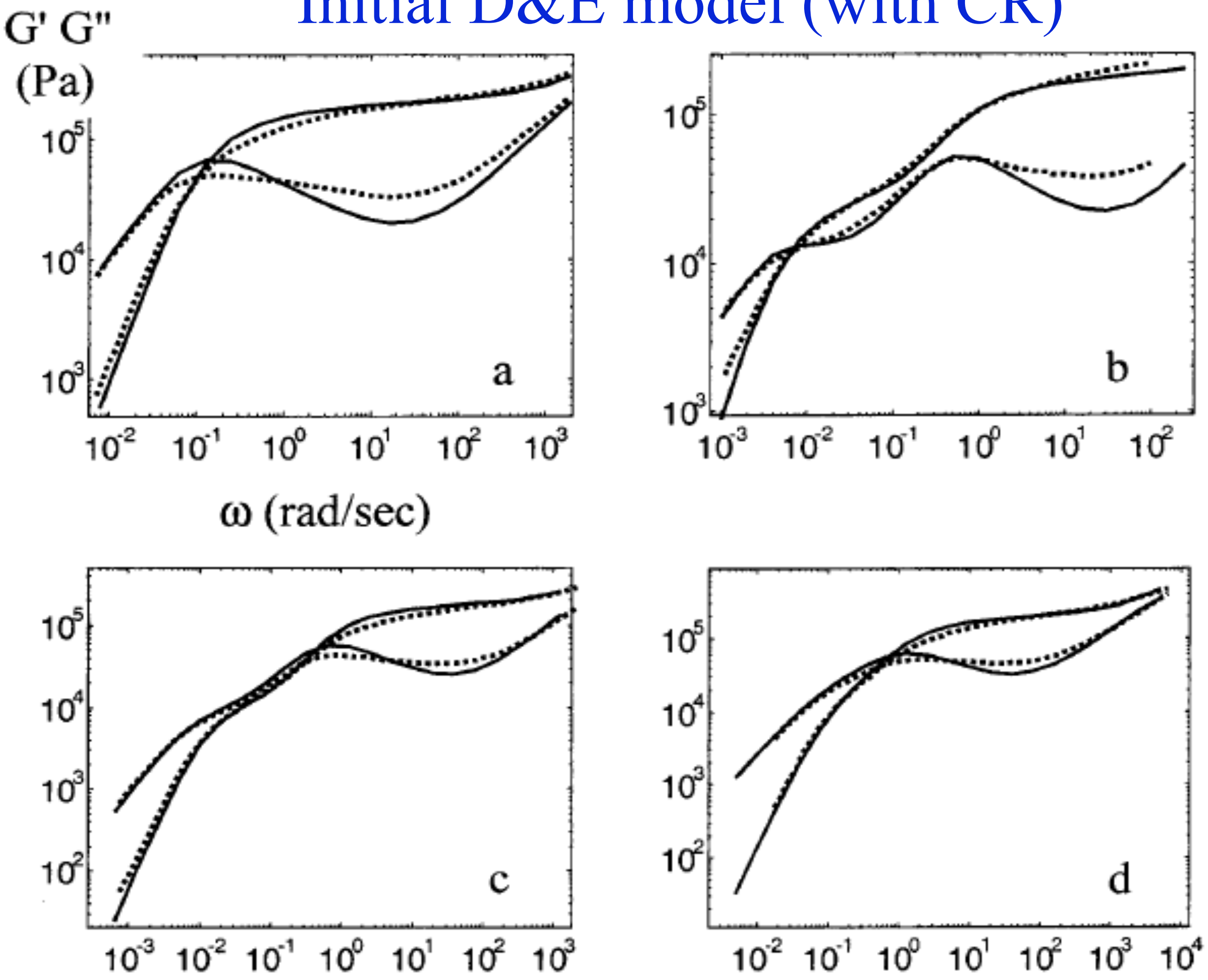


Figure 2. Experimental (···) and predicted (—) dynamic moduli using the Doi and Edwards kernel (eq 2) and double reptation (eqs 1 and 5) for (a) PS1, (b) PS9, (c) PS12, and (d) PS13.

	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

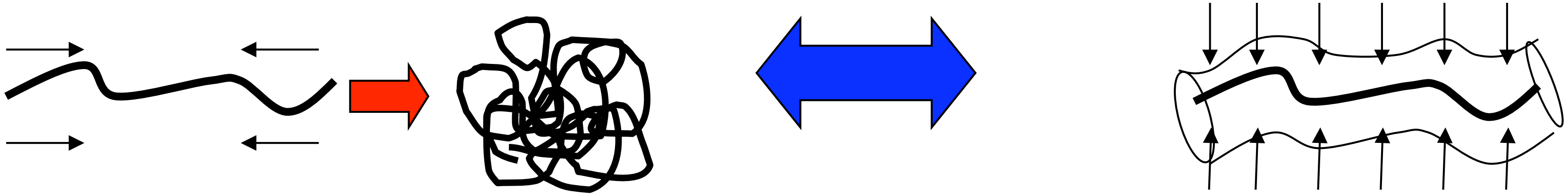
	composition
PS9	50% PS2, 50% PS3
PS10	20% PS4, 80% PS5
PS11	80% PS4, 20% PS5
PS12	65% PS2, 35% PS8
PS13	30% PS7, 30% PS2, 40% PS1

II.3.2. Contour length fluctuations

Equilibrium length of an arm:

Entropical force:

Topological force:

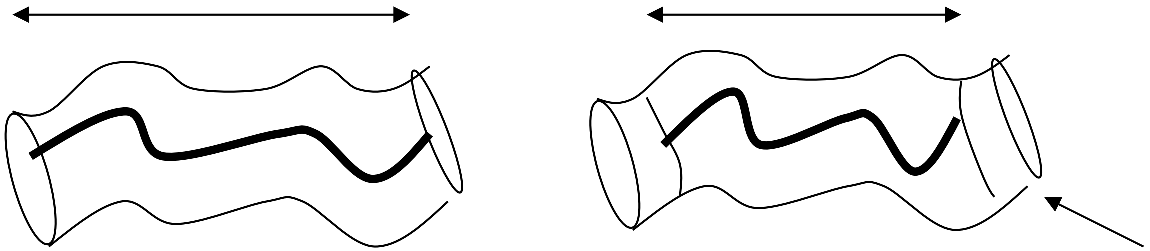


$$L_{eq} = Z \cdot l = \frac{N}{N_e} \cdot l$$

L_{eq} = the most probable length

Equilibrium length L_{eq}

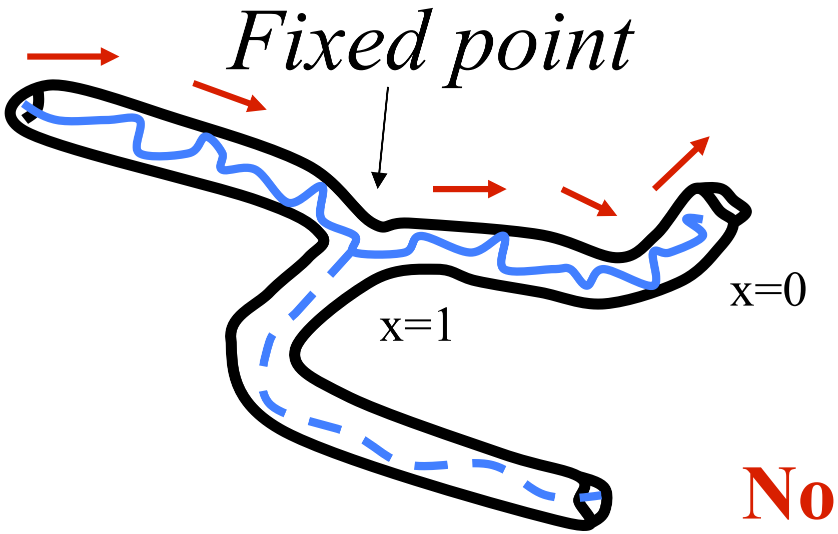
real length



This part of the
initial tube is lost

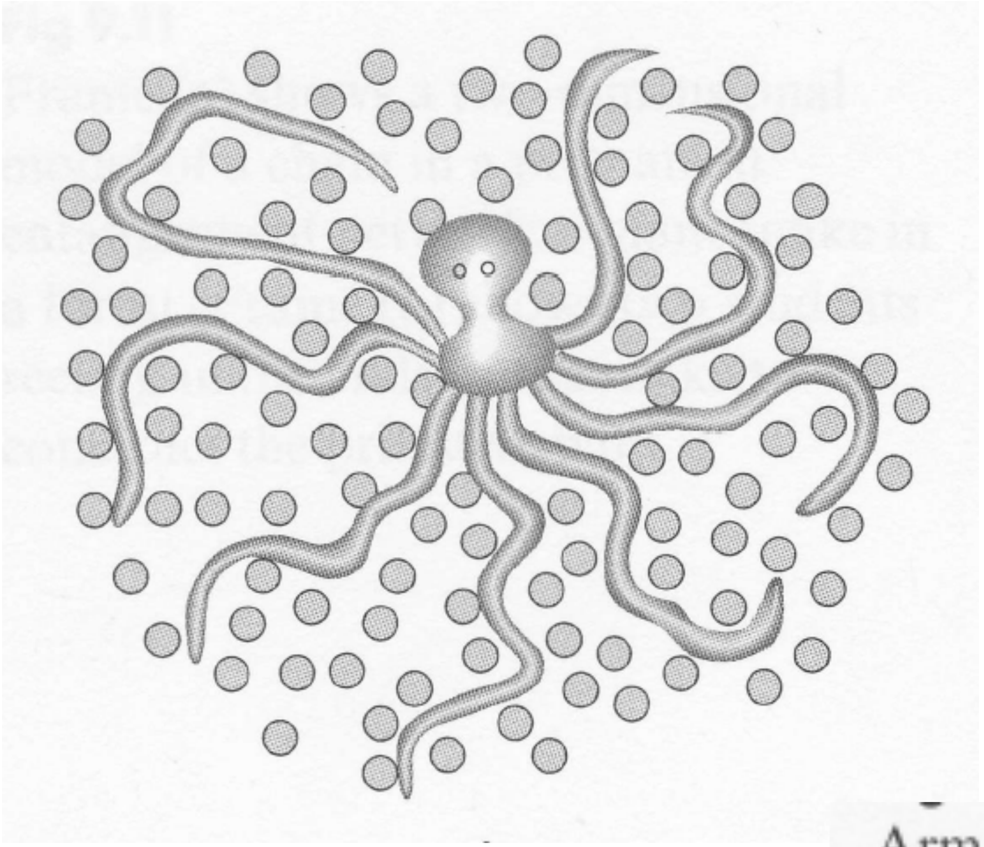
II.3.2. Contour length fluctuations

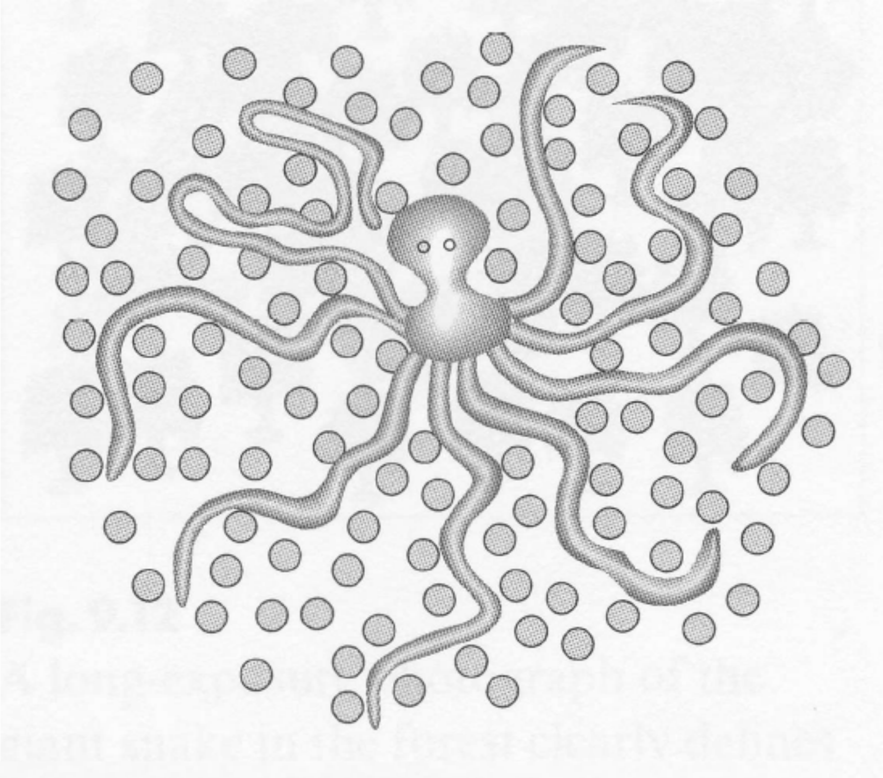
Symmetric star:



No Reptation
Only fluctuations
(see the next lesson)

II.3.2. Contour length fluctuations

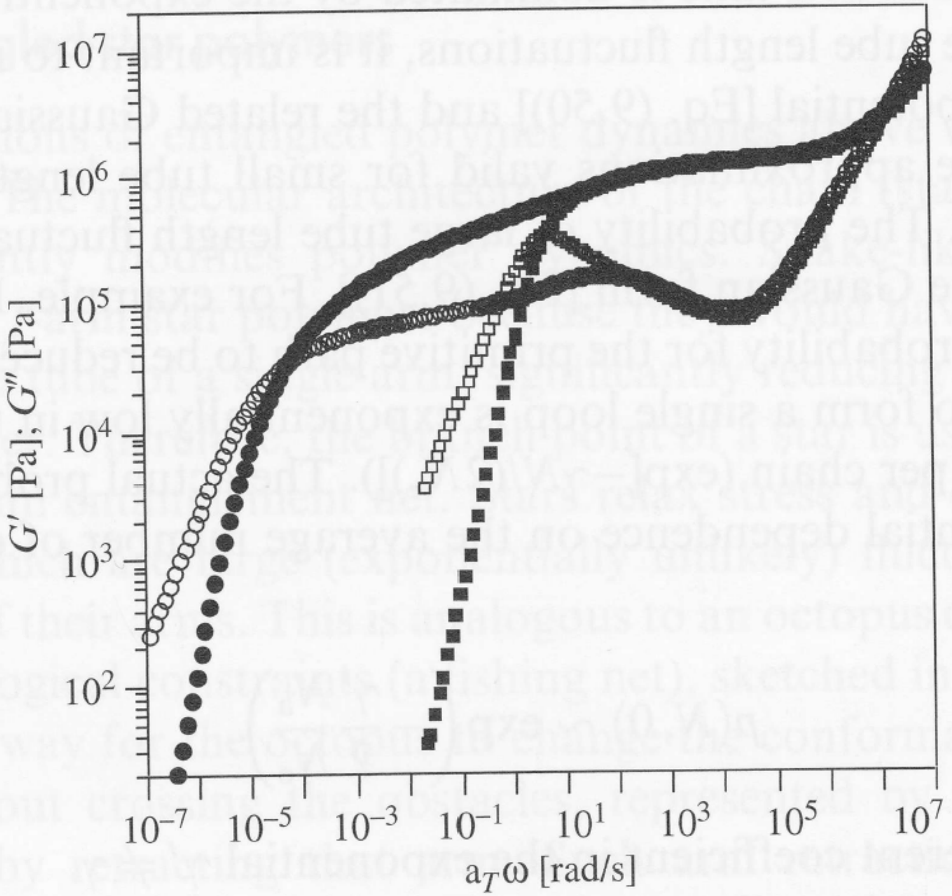




Arm retraction of entangled star polymers demonstrated by an octopus in a fishing net. The circles are permanent topological constraints.

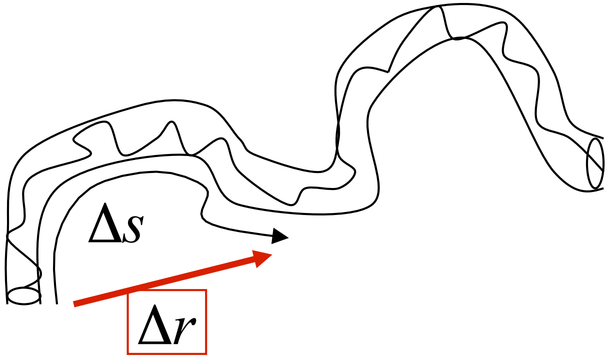
+ movie

Storage modulus (filled symbols) and loss modulus (open symbols) for linear 1,4-polybutadiene with $M_w = 160\,000\ \mathrm{g\,mol^{-1}}$ (squares) and a 6-arm star 1,4-polybutadiene with $M_a = 77\,000\ \mathrm{g\,mol^{-1}}$ (circles), both at a reference temperature of 28 °C. The linear polymer was chosen because it's molar mass is approximately the span molar mass of the star polymer. Data courtesy of L. Archer.



Linear chains: Doi and Edwards model including the contour length fluctuations (CLF):

- the environment of the molecule is considered as fixed.



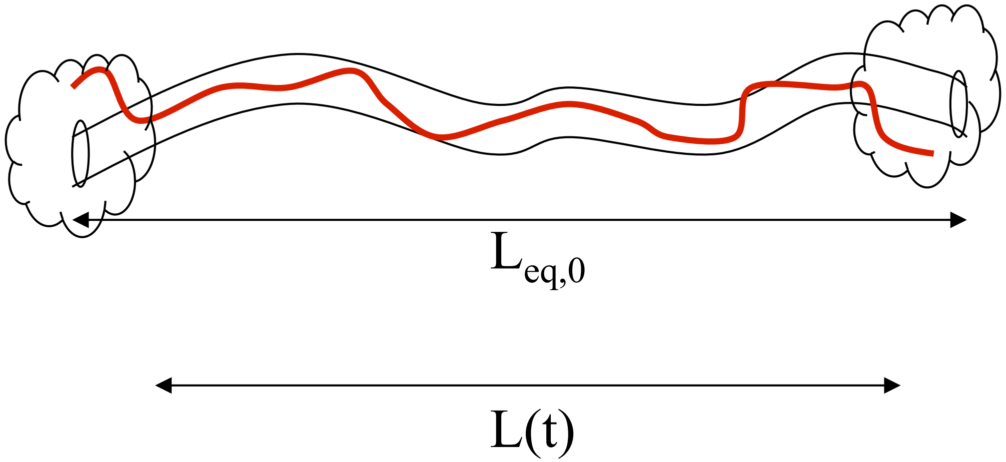
Rouse-like motion of the chain ends:

Displacement along the curvilinear tube:

$$\left\langle \Delta s^2 \right\rangle \approx b^2 \left(\frac{t}{\tau_0} \right)^{\frac{1}{2}} \approx a^2 \left(\frac{t}{\tau_e} \right)^{\frac{1}{2}}$$ For $t < \tau_R$

➡ *Displacement of a monomer in the 3D space:* $\left\langle \Delta r^2 \right\rangle \approx a^2 \left(\frac{t}{\tau_e} \right)^{\frac{1}{4}}$

Rem/ Before $t = \tau_{Rouse}$, the end-chain does not know that it belongs to the whole molecule



$$\left\langle \Delta L^2 \right\rangle \approx b^2 \left(\frac{t}{\tau_0}\right)^{\frac{1}{2}} \approx a^2 \left(\frac{t}{\tau_e}\right)^{\frac{1}{2}}$$

Partial relaxation of the stress:

$$G(t) \approx G_N^0 \frac{L(t)}{\langle L \rangle} \approx G_N^0 \frac{\langle L \rangle - \sqrt{\left\langle \Delta L(t)^2 \right\rangle}}{\langle L \rangle} \approx G_N^0 \left(1 - \frac{a}{\langle L \rangle}\left(\frac{t}{\tau_e}\right)^{1/4}\right) \approx G_N^0 \left(1 - \frac{N_e}{N}\left(\frac{t}{\tau_e}\right)^{1/4}\right)$$

For $\tau_e < t < \tau_R$

At time $t = \tau_R$:

$$G(\tau_R) \approx G_N^0 \left(1 - \frac{N_e}{N}\left(\frac{\tau_R}{\tau_e}\right)^{1/4}\right) \approx G_N^0 \left(1 - \mu\sqrt{\left(\frac{N_e}{N}\right)}\right)$$

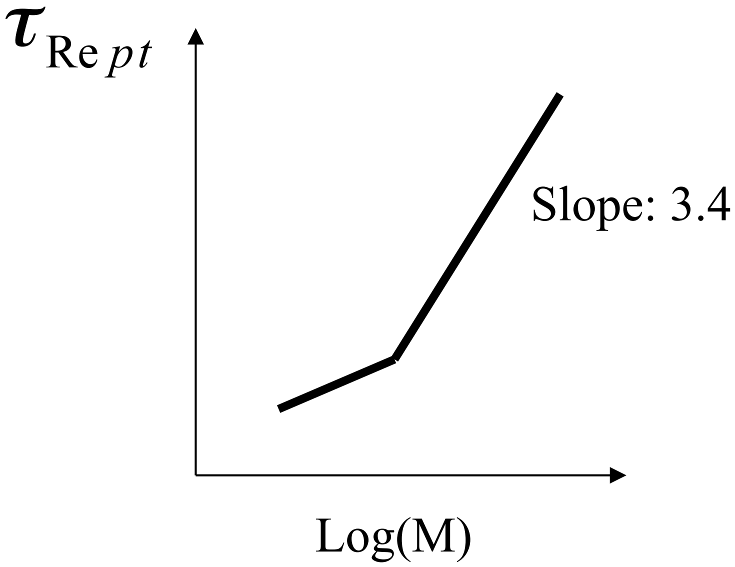
With μ close to 1

In the same way:

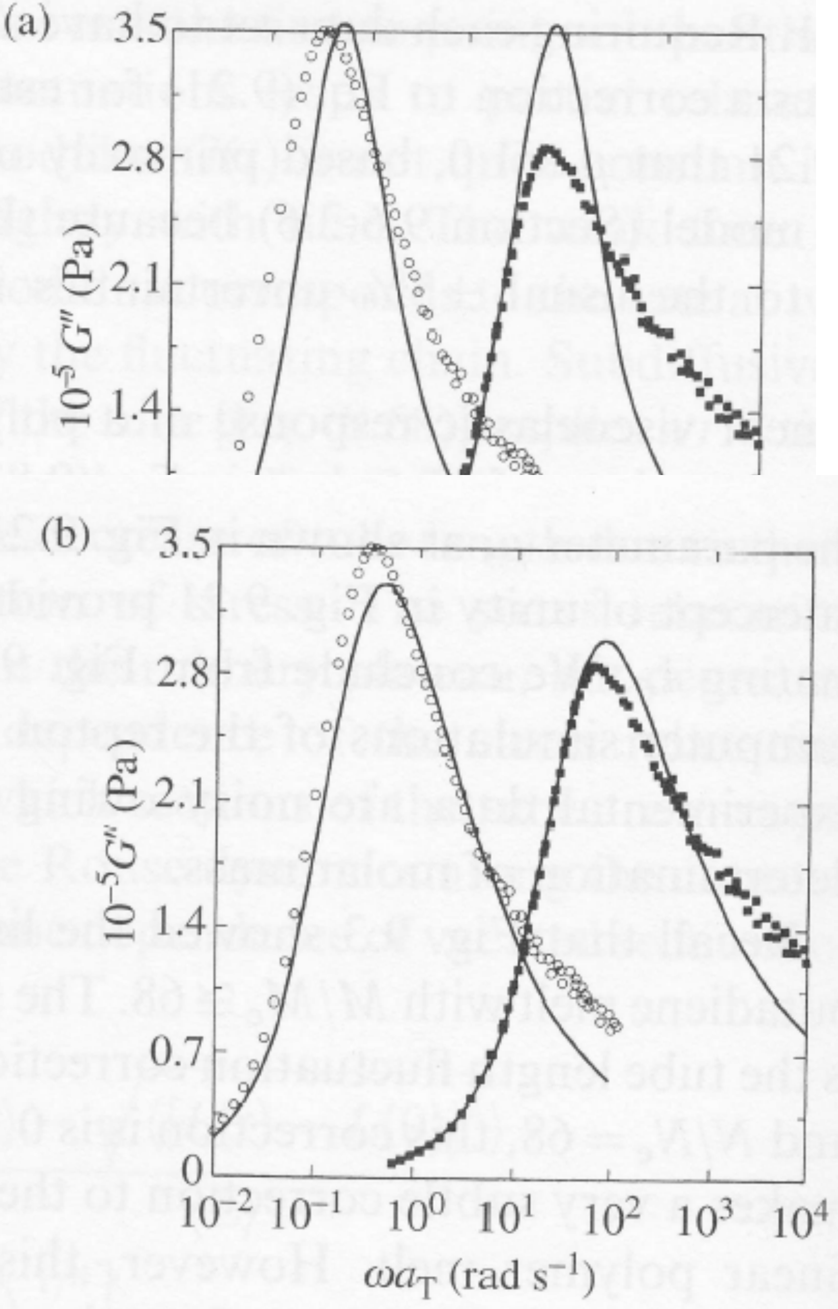
$$\boxed{G(\tau_{\mathrm{Re}\,pt}) \approx G_N^0\left(1-\mu\sqrt{\left(\frac{N_e}{N}\right)}\right)}$$

$$\boxed{\tau_{\mathrm{Re}\,pt} \approx \frac{\langle L\rangle^2\left[1-\mu\sqrt{N_e/N}\right]^2}{D_c} \approx \tau_0\,\frac{N^3}{N_e}\left(1-\mu\sqrt{\left(\frac{N_e}{N}\right)}\right)^2}$$

Rescale of the reptation time in order to account for the fluctuations process



Simultaneous fit of loss modulus data for the two monodisperse polybutadiene samples at 30 °C by (a) the Doi–Edwards equation and (b) the Doi tube length fluctuation model. Lines are the fitting results. Open circles are data for $M = 355\,000\ \mathrm{g\,mol^{-1}}$. Filled squares are data for $M = 70\,900\ \mathrm{g\,mol^{-1}}$. Data from M. Rubinstein and R. H. Colby, *J. Chem. Phys.* **89**, 5291 (1988).



D&E model with contour length fluctuations (with CR)

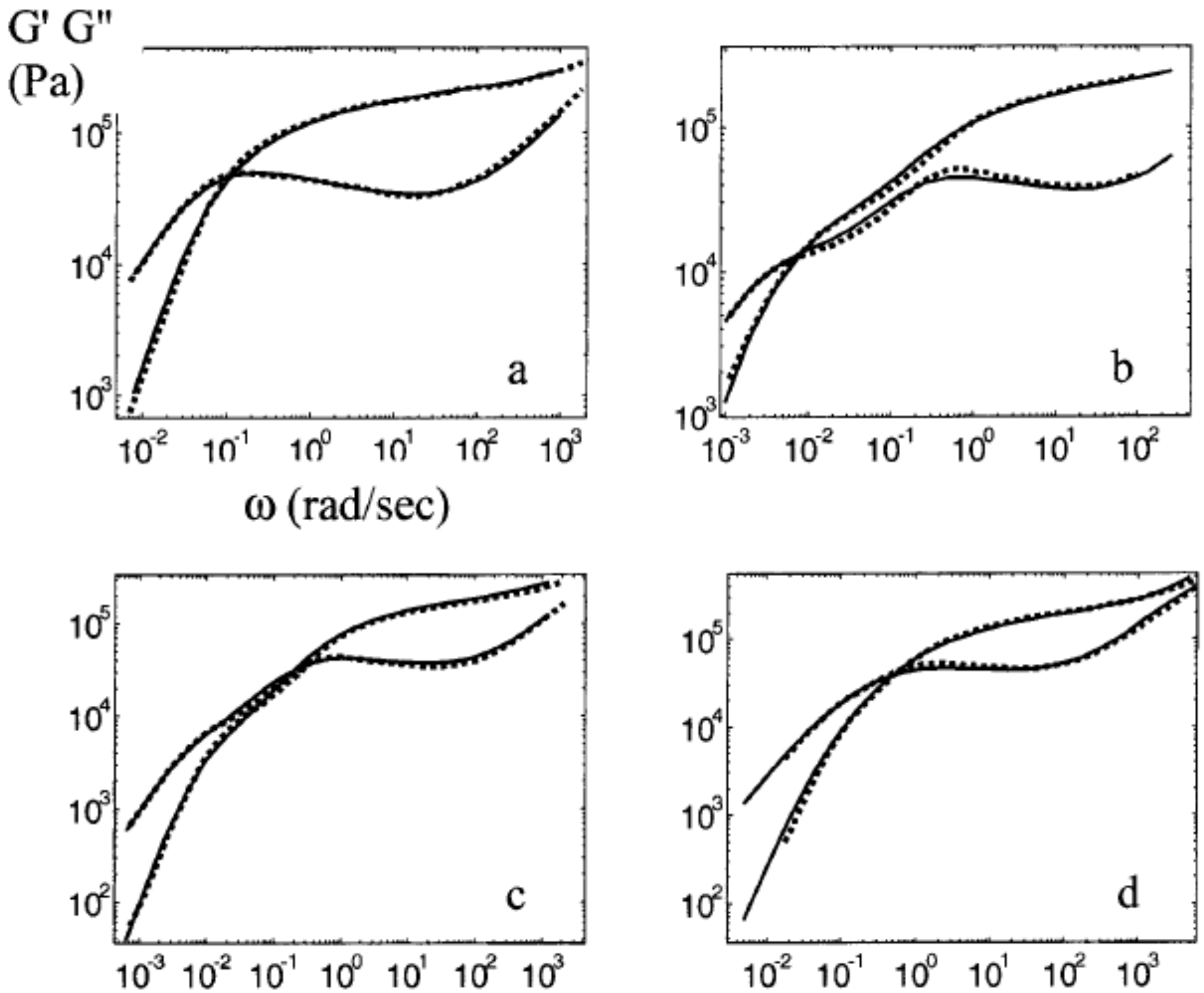
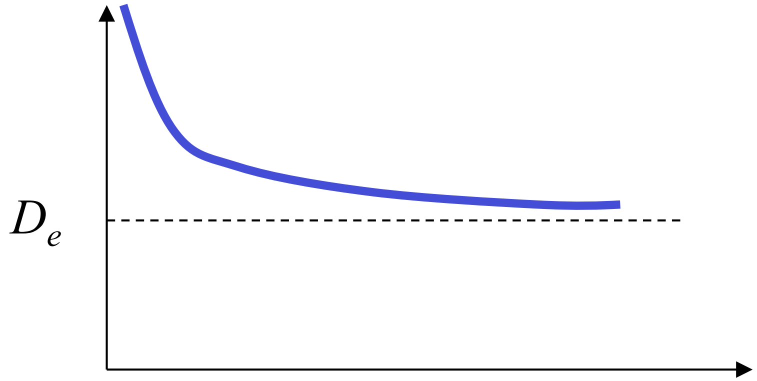


Figure 3. Experimental (···) and predicted (—) dynamic moduli using the Doi and Edwards kernel with fluctuations (eq 3) and double reptation (eqs 1 and 5) for (a) PS1, (b) PS9, (c) PS12, and (d) PS13.

Linear chains: model of des Cloizeaux:

Based on a time-dependent coefficient diffusion:

$$D(t) = D_e\left(1 + \sum_{n=1}^{\infty}\exp\left(\frac{-n^2 t}{\tau_i}\right)\right)$$



$$G(t) = G_N^0\,\frac{8}{\pi^2}\cdot\sum_{p\ odd}\frac{1}{p^2}\cdot\exp\left(-p^2\cdot U(t)\right)$$

$$U(t) = \frac{t}{\tau_{rept}} + \frac{1}{H}\cdot g\left(\frac{H\cdot t}{\tau_{rept}}\right)$$

$$g(y) = \sum_{n=1}^{\infty}\frac{1-\exp\left(-n^2\cdot y\right)}{n^2} \approx -y + y^{0.5}\cdot\left[y + \left(\pi\cdot y\right)^{0.5} + \pi\right]^{0.5}$$

Des Cloizeaux model (with CR)

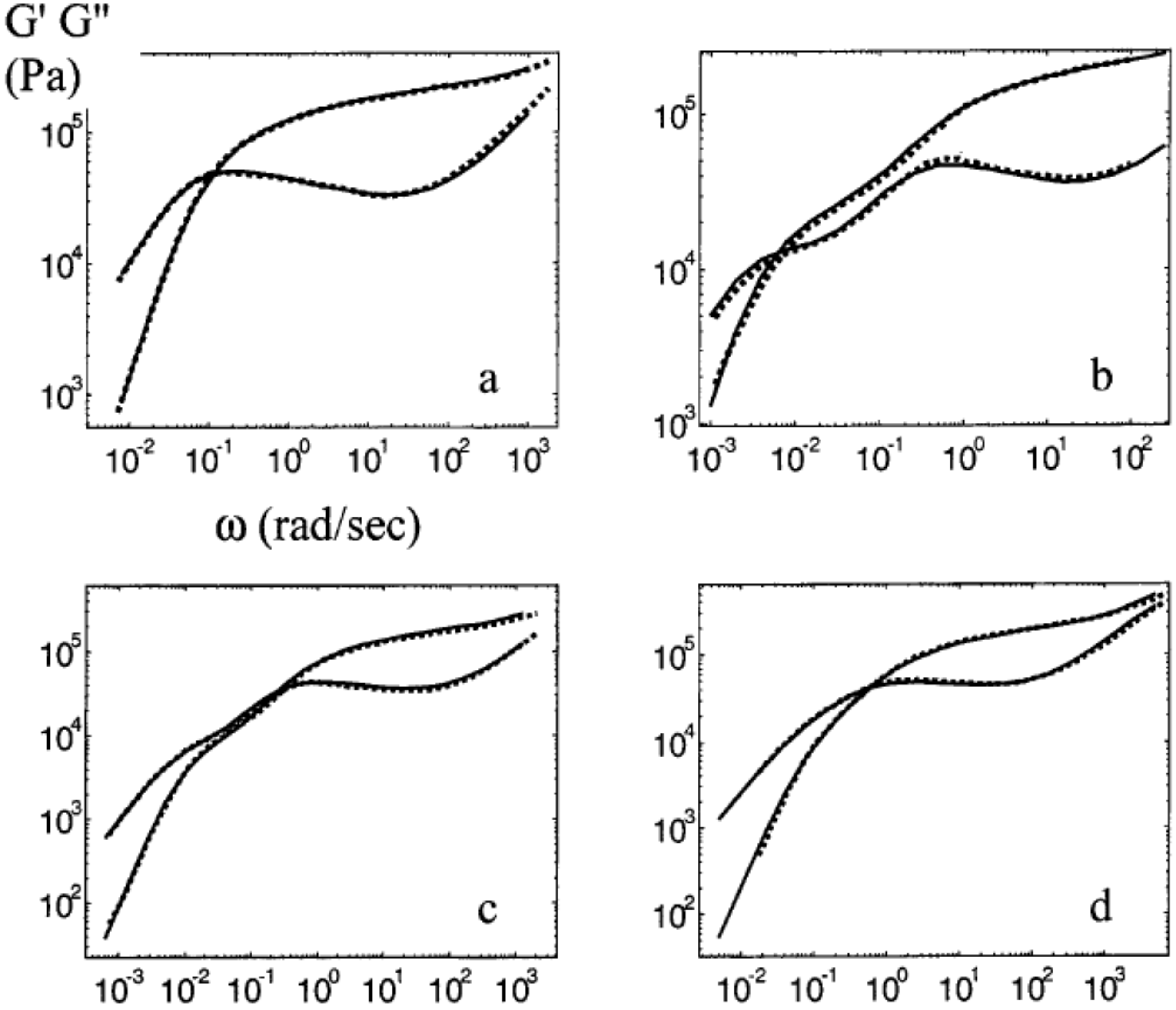


Figure 4. Experimental (···) and predicted (—) dynamic moduli using the des Cloizeaux kernel (eq 4) and double reptation (eqs 1 and 5) for (a) PS1, (b) PS9, (c) PS12, and (d) PS13.