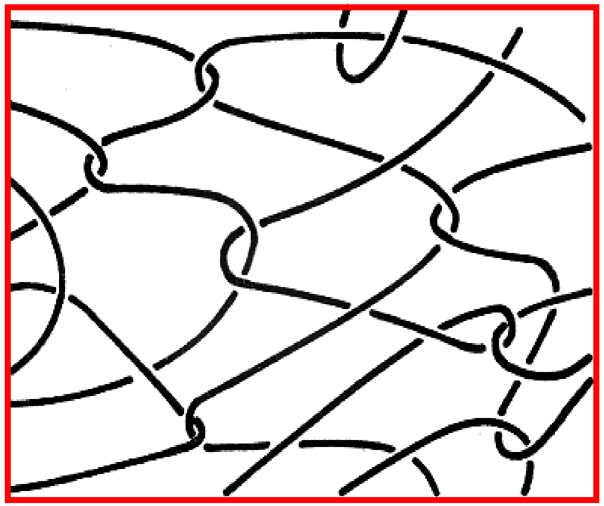
Network of entangled polymers



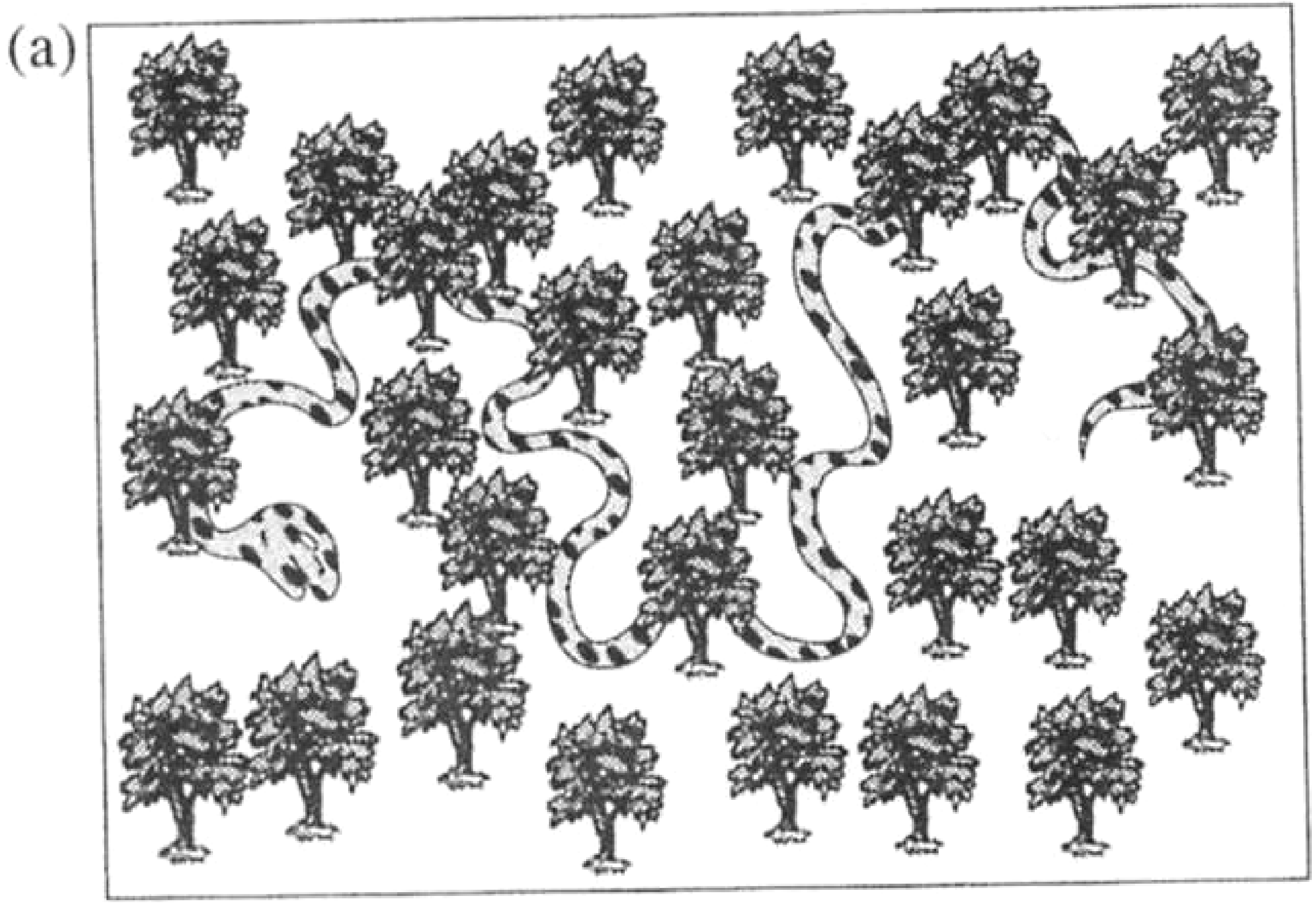
Long polymers in the state of melt or of concentrated solution are entangled, forming a network as depicted in the figure. The network is impermanent since chains are not chemically linked, and will eventually separate to form new entanglements with different partners. Yet, the entangled network deserves a special treatment.

First we redefine the elastic modulus G, which here is still given by νkT as in the rubber, provided ν is no longer interpreted as the number of chains per unit volume but rather as the number of subchains, where a subchain (or chain segment, or strand) connects two consecutive entanglements along the chain. Indeed, upon a sudden deformation, entanglements are expected to behave like crosslinks, and hence also in the entangled network the initial stress response to a sudden strain generating a Finger tensor **B** is equal to G**B**.

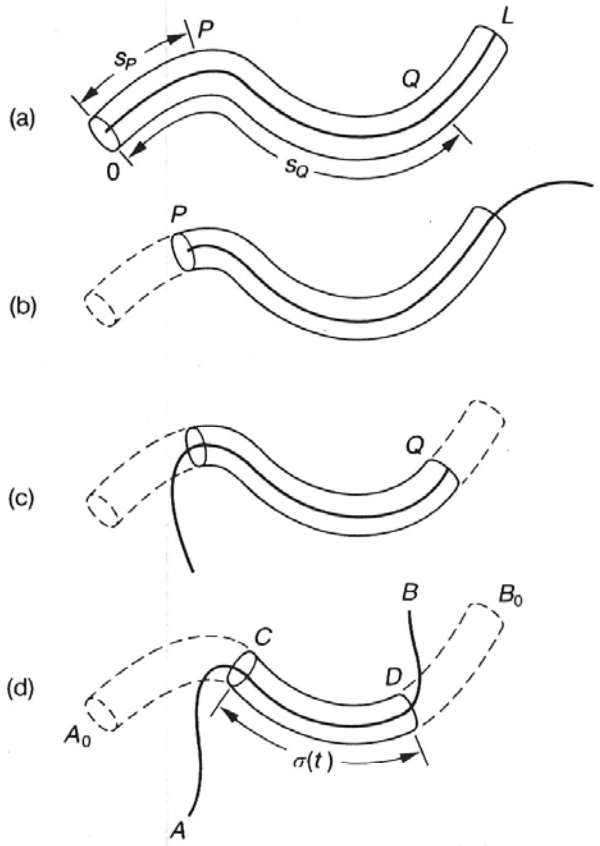
How the chain “feels” the topological constraints: the “tube” idea (Edwards 1967)

The characteristic dimension of the entangled chain: the tube diameter = *a*

How the chain renews the tube in the course of time: Reptation dynamics (de Gennes 1971)



Reptation



Random direction

Fig. 6.4. Four successive situations of a reptating chain. (*a*) The initial conformation of the primitive chain and the tube which we call the original tube. (*b*) and (*c*) As the chain moves right or left, some parts of the chain leave the original tube. The parts of the original tube which have become empty of the chain disappear (dotted line). (*d*) The conformation at a later time *t*. The tube segment vanishes when it is reached by either of the chain ends: e.g., the tube segment *P* and *Q* vanish at the instance (*b*) when $\xi(t) = s_P$ and at (*c*) when $\xi(t) = s_Q - L$, respectively.

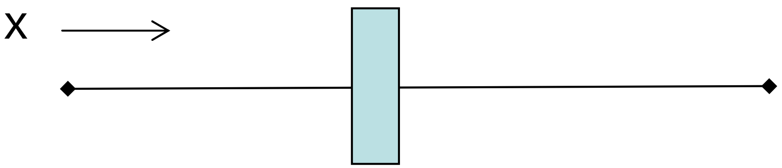
$L \propto M$

Memory of past is kept by tube, not by chain

Back-and-forth diffusion of chain progressively destroys old pieces of tube, which are replaced by new randomly oriented ones.

The “longitudinal” diffusion coefficient of the chain is: $D = kT/\zeta \propto M^{-1}$

Equivalently, *D* can be assigned to tube segments diffusing along the chain



$0 < x < L$

The “old” tube segments vanish when they reach one of the chain ends.

Given a chain population, call F(x, t) the fraction of old tube segments at x surviving at time *t*

At *t* =0, by definition all segments are present $\Rightarrow F(x,0) = 1 \qquad \forall x$

F then changes in time, obeying:

$$\frac{\partial F}{\partial t} = D\frac{\partial^2 F}{\partial x^2}$$

with “absorbing” boundary conditions: F=0 at x=0 and x=L

This diffusion problem is the same of thermal conduction in a slab of thickness L (see, e.g., the treatise of Carslaw e Jaeger)

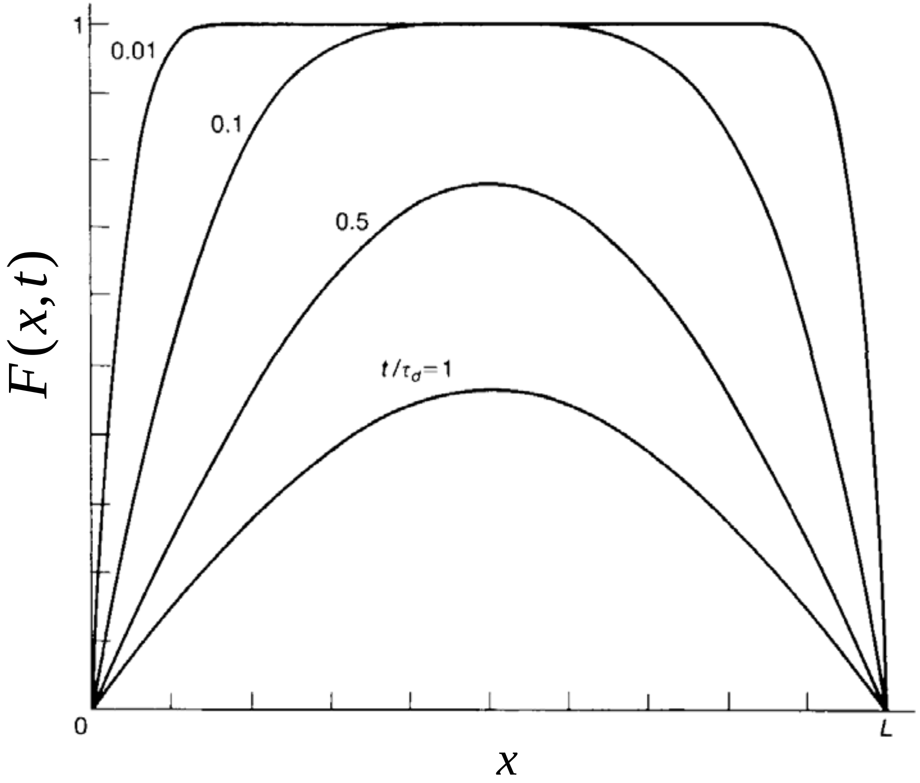
$$F(x,t)=\frac{4}{\pi}\sum_{p=0}^{\infty}\frac{1}{2p+1}\exp\left[-\left(2p+1\right)^2\pi^2\frac{Dt}{L^2}\right]\sin\frac{\left(2p+1\right)\pi x}{L}$$

Or equivalently

$$F(x,t)=\frac{4}{\pi}\sum_{p\,\mathrm{odd}}\frac{1}{p}\exp\left[-p^2\pi^2\frac{Dt}{L^2}\right]\sin\frac{p\pi x}{L}$$

Disengagement time:

$$\tau_d=\frac{L^2}{\pi^2 D}\propto M^3$$



Relaxation modulus G(t)

Sum over x of F(x,t) gives:

$$\psi(t) = \frac{1}{L}\int_0^L F(x,t)\,dx = \frac{8}{\pi^2}\sum_{p\,\mathrm{odd}}\frac{1}{p^2}\exp\left(-p^2t/\tau_d\right)$$

where ψ(t) represents the overall fraction of surviving old tube.

Hence:

$$G(t) = G(0)\psi(t) = G\frac{8}{\pi^2}\sum_{p\,\mathrm{odd}}\frac{1}{p^2}\exp\left(-p^2t/\tau_d\right)$$

where:

$$G = \nu_{subchain}kT = \frac{\rho RT}{M_e}$$

M_e being the molar mass of the entangled subchains.

Note that, differently from Rouse relaxation, the first exponential of the sum (*p*=1) dominates over all others.

Rouse vs. reptation dynamics

$$G_{Rouse}(t) = \nu_{chain} kT \sum_p \exp\left(-p^2 t / \tau_{Rouse}\right) \qquad G_{reptation}(t) = G \frac{8}{\pi^2} \sum_{p\,\mathrm{odd}} \frac{1}{p^2} \exp\left(-p^2 t / \tau_d\right)$$

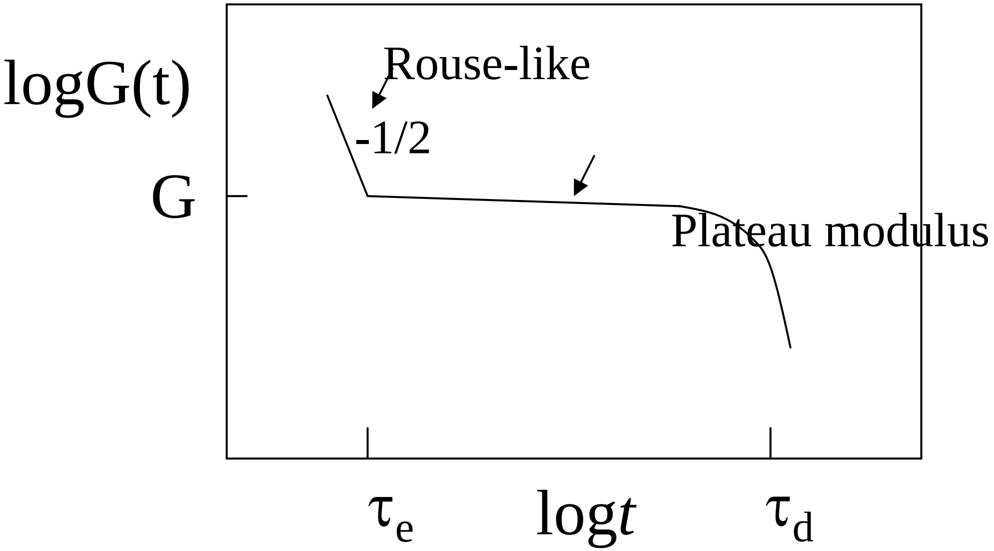
Notice that, for *t*→0

$$G_{Rouse}(t) = \nu_{chain} kT \sqrt{\frac{\tau_{Rouse}}{t}} \qquad G_{reptation}(0) = G = \nu_{subchain} kT = \frac{M}{M_e} \nu_{chain} kT$$

(plateau modulus)

$$G_{Rouse}(t) = G_{reptation}(t)$$

$$at\ t = \frac{\tau_{Rouse}}{\left(M/M_e\right)^2} = \tau_e$$



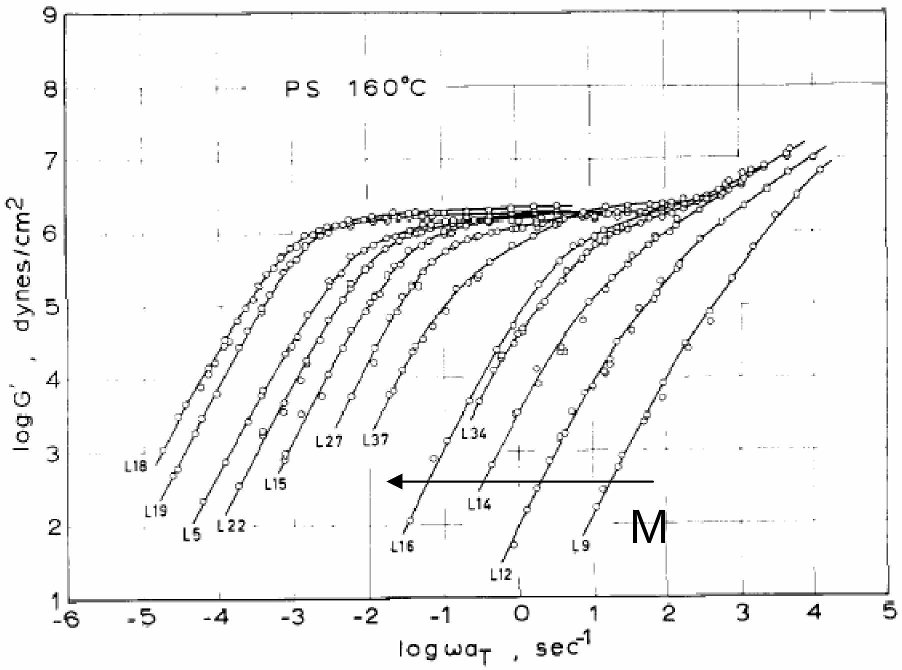
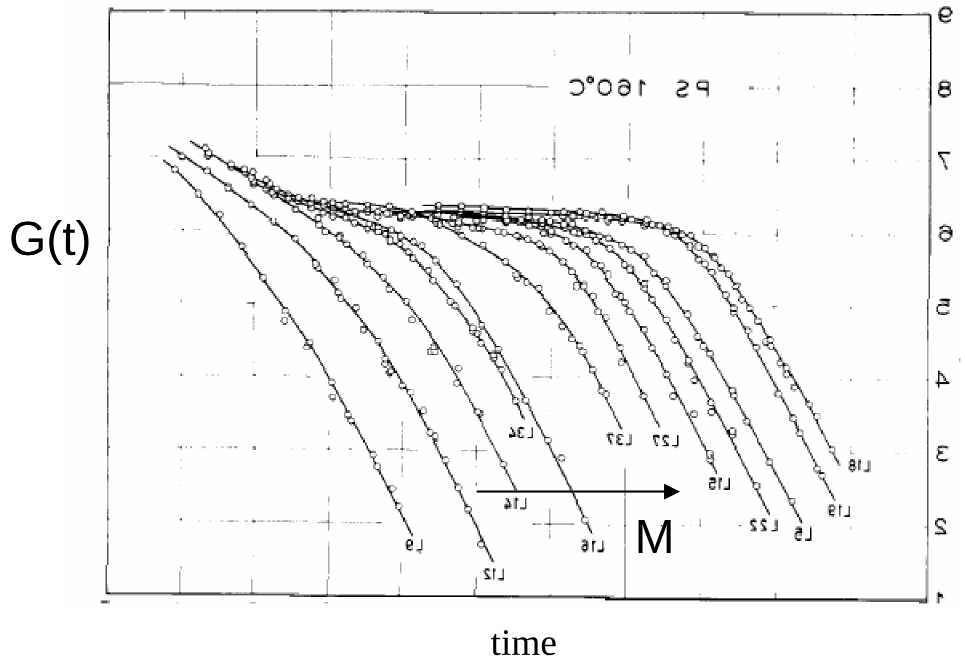


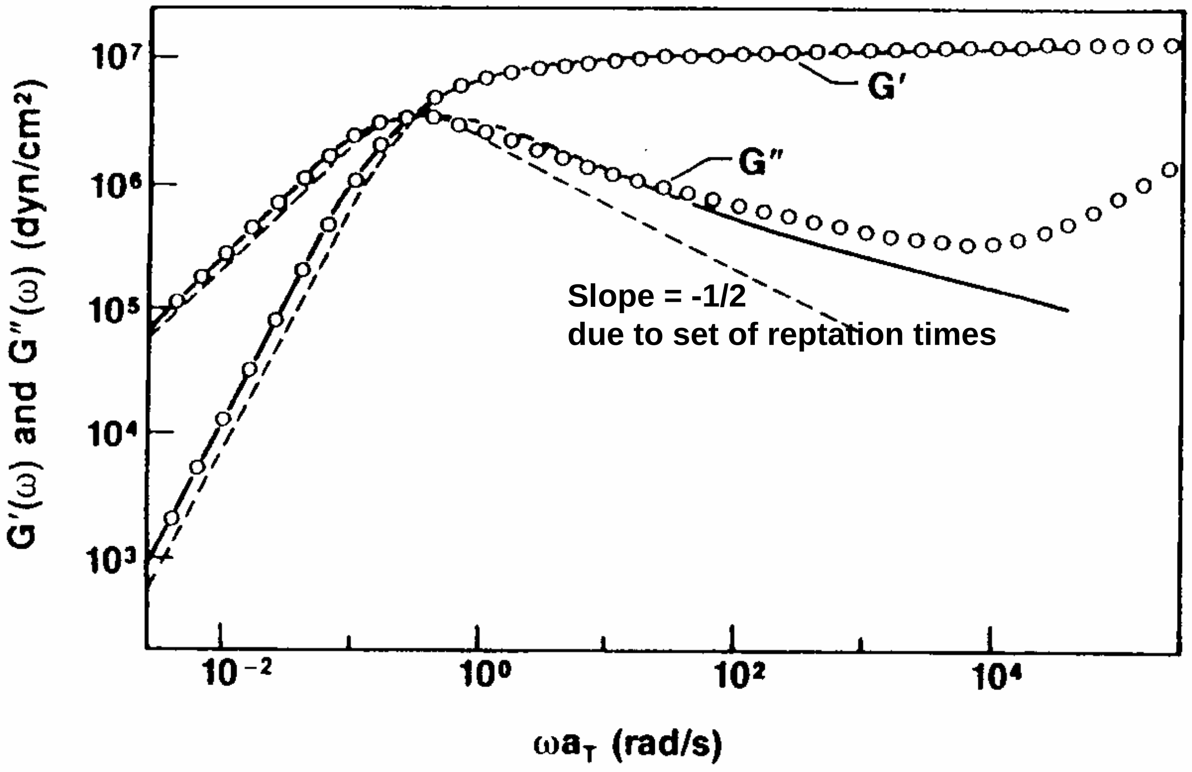
Figure 2. Master curves of G' for narrow-distribution polystyrenes having different molecular weights. The reference temperature is 160°.

$G'(\omega)$ for polystyrenes of different molar mass M

Data of $G'(\omega)$ can be looked upon as $G(t)$ by changing from frequency ω to time $t \cong 1/\omega$



G’ and G’’ for an entangled polymer (nearly a Maxwell model)



Slope = -1/2
due to set of reptation times

FIG. 7.—The dynamic shear moduli, $G'(\omega)$ and $G''(\omega)$, for polybutadiene of molecular weight 360 000 at 27°C. The dashed line is the original reptation theory derived from Equation (4.10). The solid line includes the effect of fluctuations. The short time response of process A has not been included. (See Reference 64.)

Viscosity of entangled networks

- Viscosity is approximately given by

$$\eta \sim G\ \tau_d$$

- Indeed, in a steady flow with a shear rate $\dot{\gamma}$ the deformation stored in the network is:

$$\gamma = \dot{\gamma}\tau_d$$

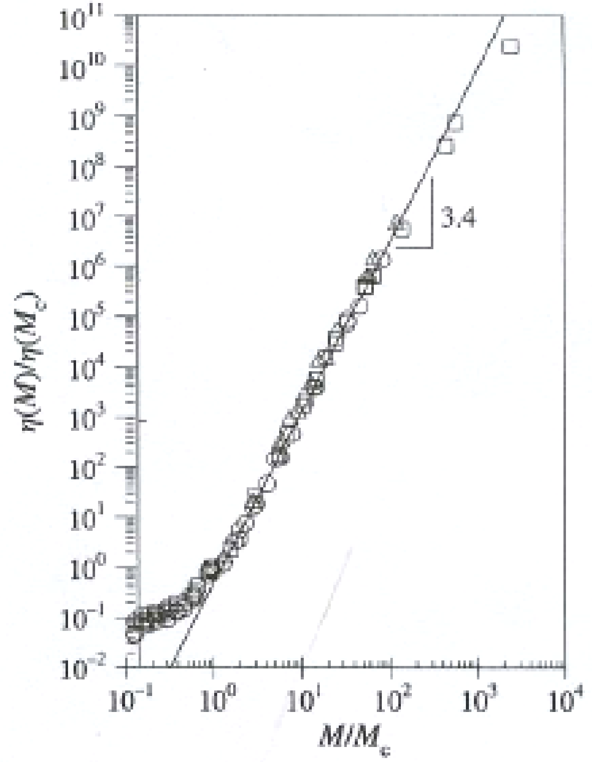
- As in the rubber, the shear stress is then

$$\sigma = G\gamma = G\tau_d\dot{\gamma} = \eta\,\dot{\gamma}$$

Zero-shear viscosity

$$\eta_0 = \int_0^\infty G(t)dt$$

$$\eta_{0,Rouse} = \frac{\pi^2}{6}\frac{\rho RT}{M}\tau_{Rouse} \propto M \qquad \eta_{0,reptation} = \frac{\pi^2}{12}\frac{\rho RT}{M_e}\tau_{reptation} \propto M^3$$



Why the power is 3.4
instead of 3 ?!?

Tube length fluctuations

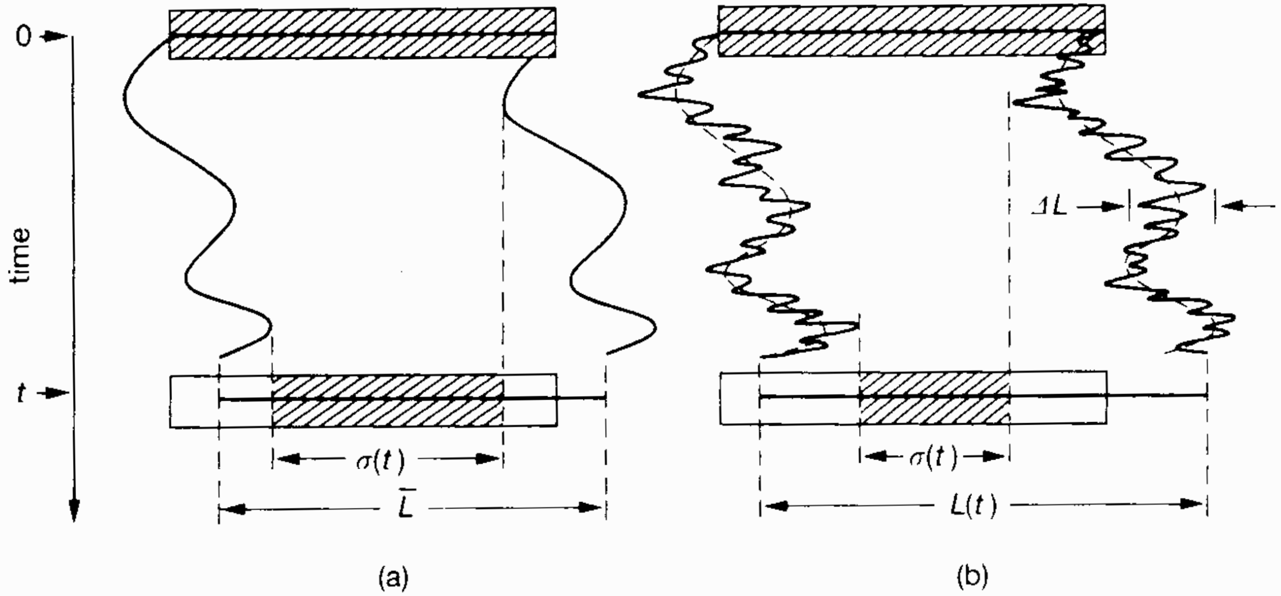
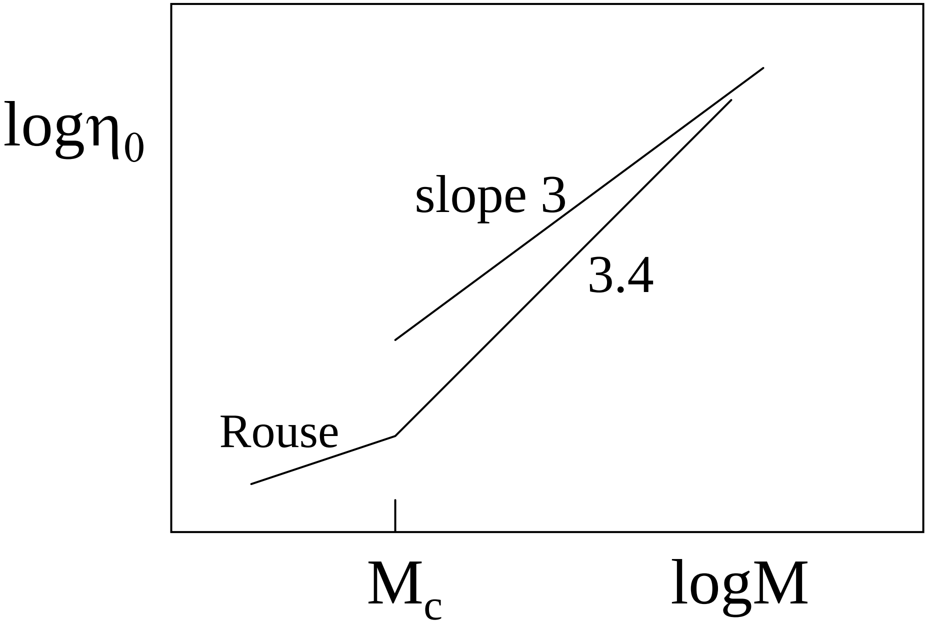


Fig. 6.9. The Brownian motion of a primitive chain with (*a*) fixed contour length, and (*b*) fluctuating contour length. The oblique lines denote the region that has not been reached by either end of the primitive chain. Obviously the length of this region $\sigma(t)$ decreases faster in (*b*) than in (*a*). Reproduced from ref. 15.

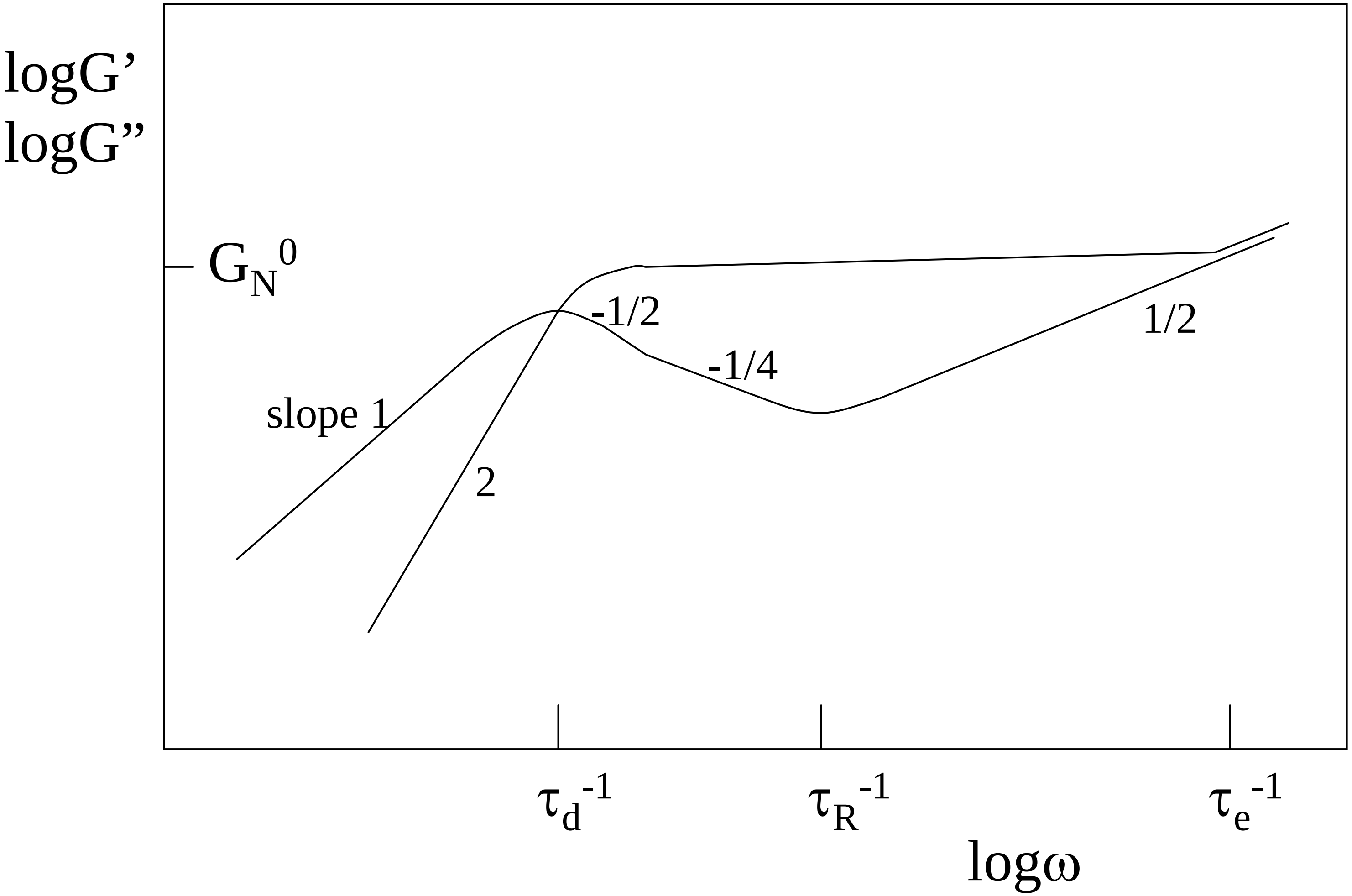
Effect of chain-end fluctuations Doi (1981)

Chain-end fluctuations are faster than reptation. Hence they decrease the viscosity with respect to reptation prediction.

Chain-end fluctuations are more effective in short chains. By increasing chain length, they progressively loose importance.



Frequency response



Also G” is influenced by fluctuations

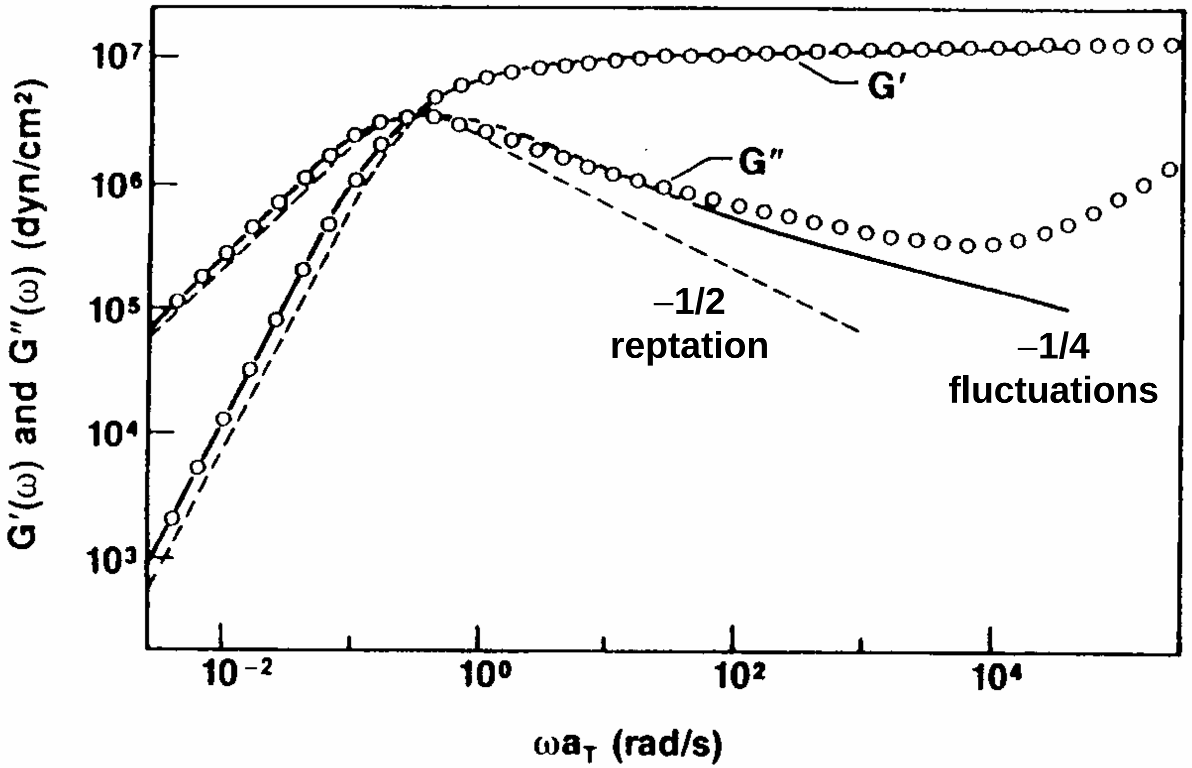


FIG. 7.—The dynamic shear moduli, $G'(\omega)$ and $G''(\omega)$, for polybutadiene of molecular weight 360 000 at 27°C. The dashed line is the original reptation theory derived from Equation (4.10). The solid line includes the effect of fluctuations. The short time response of process *A* has not been included. (See Reference 64.)

Nonlinear response

For small deformations or deformation rates the response is linear. The entangled network differs from the equilibrium situation only because of a slight anisotropy. In other words, subchains are only slightly oriented.

On the contrary, for large deformations and deformation rates, the response is nonlinear, i,.e., subchains become strongly oriented as well as stretched. Indeed chain stretch is a second-order effect, which is negligible at small deformations and very important at large ones.

Let's indicate with r_0 and r the end-to-end distance of a subchain at and out of equilibrium, respectively, and assume that r_0 goes into r affinely.

For example, for a shear deformation γ we find: $\langle r^2 \rangle = \langle r_0^2 \rangle (1+\gamma^2/3)$

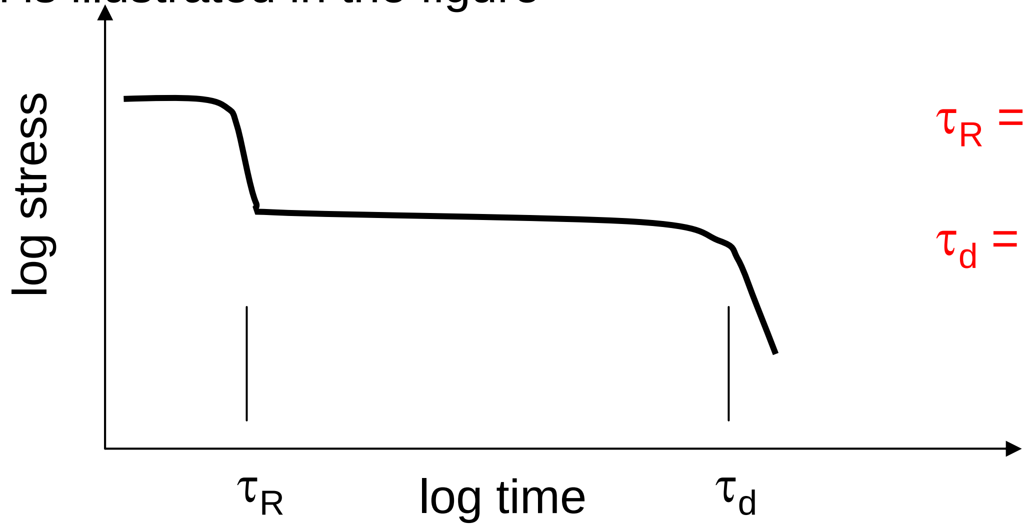
Similarly, for a uniaxial elongation $\lambda = 1+\varepsilon$, it is: $\langle r^2 \rangle = \langle r_0^2 \rangle (1+\varepsilon^2/2)$

Notice that, the effect being quadratic, chain length always increases.

A peculiarity of entangled networks is fast retraction of stretched chains

Although entanglements do not allow a fast reorientation of subchains, they do not constitute an obstacle to a fast relaxation of chain stretch. Chain stretch relax by friction only, hence essentially in a time of the order of the Rouse time.

If a step deformation is applied, large enough to generate both chain stretch and chain orientation, that part of the stress **T** linked to chain stretch will soon relax by chain retraction, while that due to the orientational anisotropy will relax much later, when chains disengage from the existing entanglements and create new ones, and hence generate new random orientations of the subchains. Such a two-step relaxation is illustrated in the figure

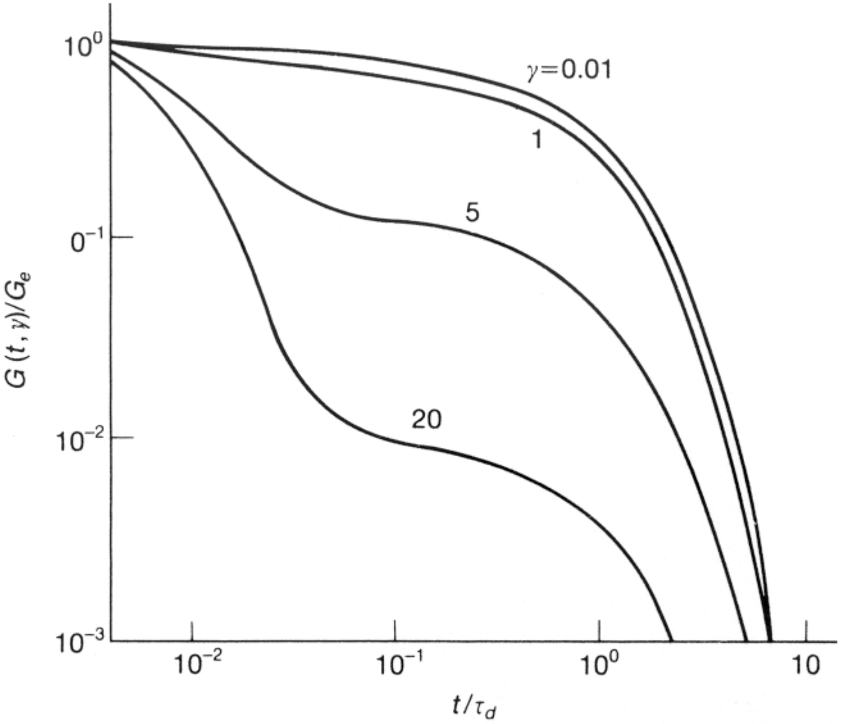


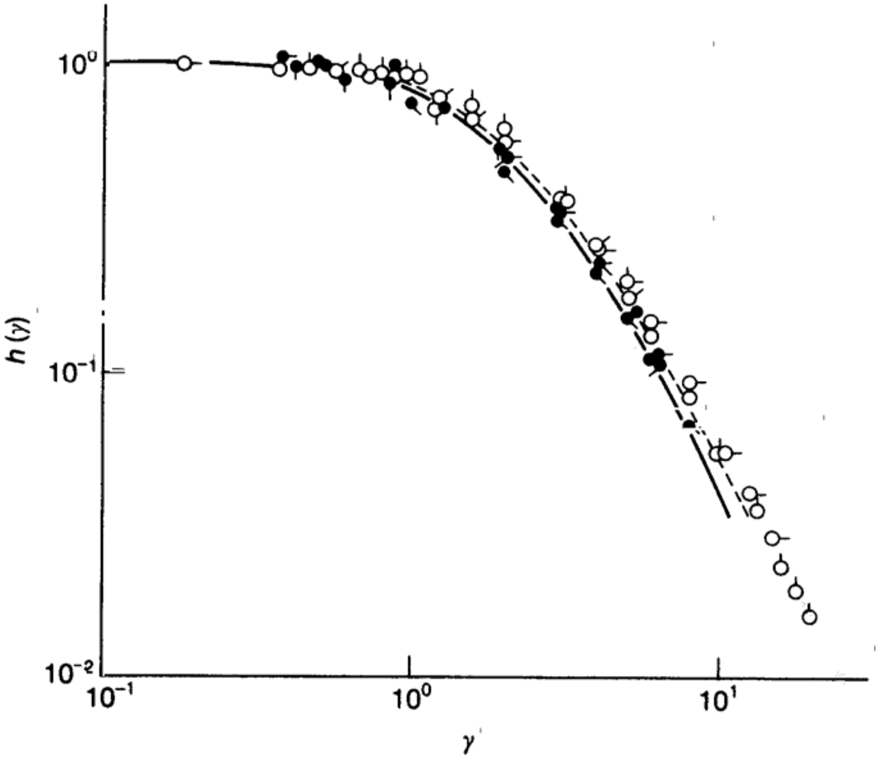
τ_R = retraction time

τ_d = disengagement time

Doi and Edwards introduced this crucial difference between stretch and orientation. In their basic constitutive theory, they simplified the problem by setting $\tau_R = 0$, i.e., by assuming that chains retract virtually instantly. **Stress is simply due to orientation.**

Large-strain relaxation occurs in two steps: stretch relaxation (Rouse time τ_R) orientation relaxation (disengagement time τ_d)





Time-deformation separability at long times defines the “damping function”

Splitting deformation into stretch and orientation

We have seen previously that, for a network of Gaussian chains, the stress tensor **T** has the expression:

$$\mathbf{T} = 3\nu kT\left\langle \frac{\mathbf{rr}}{nb^2} \right\rangle$$

The orientation of a subchain is described by the unit vector **u** = **r**/r. Hence we may rewrite **T** as:

$$\mathbf{T} = 3\nu kT\left\langle \frac{r^2}{nb^2}\mathbf{uu} \right\rangle = 3\nu kT\left\langle \Lambda^2\,\mathbf{uu} \right\rangle \qquad (1)$$

where Λ is the stretch of a subchain. If the stretch is relaxed (as in Doi-Edwards constitutive equation), Λ = 1, and previous **T** expression reduces to:

$$\mathbf{T} = 3\nu kT\left\langle \mathbf{uu} \right\rangle = 3\nu kT\,\mathbf{S} = G\,\mathbf{S}$$

where **S** = <**uu**> is the orientation tensor of the entangled network, and the modulus G has been redefined to include the factor of 3. Notice that **S** has a unit trace, and reduces to **I**/3 in the isotropic equilibrium state.

Doi-Edwards constitutive equation

Doi and Edwards derived a new tensor, called **Q**(**E**)**,** that describes the orientation in an entangled network soon after a step strain **E**, when chain stretch is relaxed. (Since **Q** is not easy to use, we will later look for simpler approximate forms.) Hence, for the step strain, it is **S** = **Q** at t = 0^+. Next, during orientational relaxation due to disengagement, **S**(t) is given by:

$$\mathbf{S}\left(t\right)-\mathbf{I}/3=\psi\left(t\right)\left(\mathbf{Q}-\mathbf{I}/3\right)\cong\exp\left(-t/\tau_d\right)\left(\mathbf{Q}-\mathbf{I}/3\right)$$

where ψ(t) gives the fraction of chain segments that at time t have not yet disengaged from the old entanglements. For simplicity, ψ(t) can be approximated by the single negative exponential that dominates reptation dynamics.

Similarly to what we have done for impermanent networks, for a general flow or deformation history, we find

$$\mathbf{S}\left(t\right)=\frac{1}{\tau_d}\int_{-\infty}^{t}\exp\left(-\frac{t-t'}{\tau_d}\right)\mathbf{Q}\left[\mathbf{E}\left(t,t'\right)\right]dt' \qquad (2)$$

which, except for the restriction to a single exponential, is the Doi-Edwards C.E.

More on chain stretch

We can define a mean stretch λ of network strands through the average ratio:

$$\lambda^2 = \left\langle \frac{r^2}{nb^2} \right\rangle \tag{3}$$

which is unity at equilibrium. It is easy to calculate **λ for a step strain** with the affinity assumption. In rubber elasticity theory we found that, as a consequence of a deformation **E**, the end-to-end vectors **r** of the network strands obey:

$$\left\langle \frac{\mathbf{rr}}{nb^2} \right\rangle = \frac{1}{3}\mathbf{B}$$

where **B** is the Finger tensor. We now take the trace of this equation, obtaining:

$$\lambda^2 = \frac{1}{3}\mathrm{tr}\mathbf{B} \tag{4}$$

For example, for the shear case, the B-matrix previously calculated gives:

$$\lambda^2 = \mathrm{tr}\mathbf{B}/3 = 1 + \gamma^2/3$$

Approximate splitting of stress into stretch and orientation. Approximations for tensor **Q**

We now take the stress expression in Eq.(1) and approximate it as follows:

$$\mathbf{T} = 3\nu kT\left\langle \Lambda^2 \mathbf{uu} \right\rangle \approx 3\nu kT\, \lambda^2 \left\langle \mathbf{uu} \right\rangle = G\,\lambda^2\, \mathbf{S} \qquad (5)$$

Furthermore, since in a step strain (before stretch relaxes) **T** is proportional to **B**, and λ^2 is given by Eq.(4), it is tempting to approximate the orientational tensor **Q** of Doi-Edwards theory as:

$$\tilde{\mathbf{Q}} = \frac{\mathbf{B}}{\mathrm{tr}\mathbf{B}}$$

and hence, in a general flow or deformation the orientation **S** would be given by:

$$\mathbf{S}(t) = \frac{1}{\tau_d}\int_{-\infty}^{t} \exp\left(-\frac{t-t'}{\tau_d}\right)\tilde{\mathbf{Q}}\left[\mathbf{E}(t,t')\right]dt' \qquad (6)$$

The approximate form of tensor **Q** is easy to calculate, and Eq.(6) correctly predicts a non-Newtonian viscosity, as well as deviations of N_1 from the quadratic form. However N_2 remains zero, differently from when the correct **Q** is used.

Convective constraint release (CCR)

Another nonlinear effect should be included in constitutive equations for entangled polymers, namely CCR.

CCR arises from chain retraction. Indeed, retraction of any given chain removes entanglements from other chains, which can then relax orientation more quickly than in the absence of CCR. If the velocity gradient of the flow is the tensor **k**, <u>in the absence of chain stretch</u> the mean retraction rate is given by the scalar product of **k** to the orientation tensor **S**, i.e., by **k:S**.

For example, in a shear flow it is: $\mathbf{k}:\mathbf{S} = \dot{\gamma}\, S_{xy}$

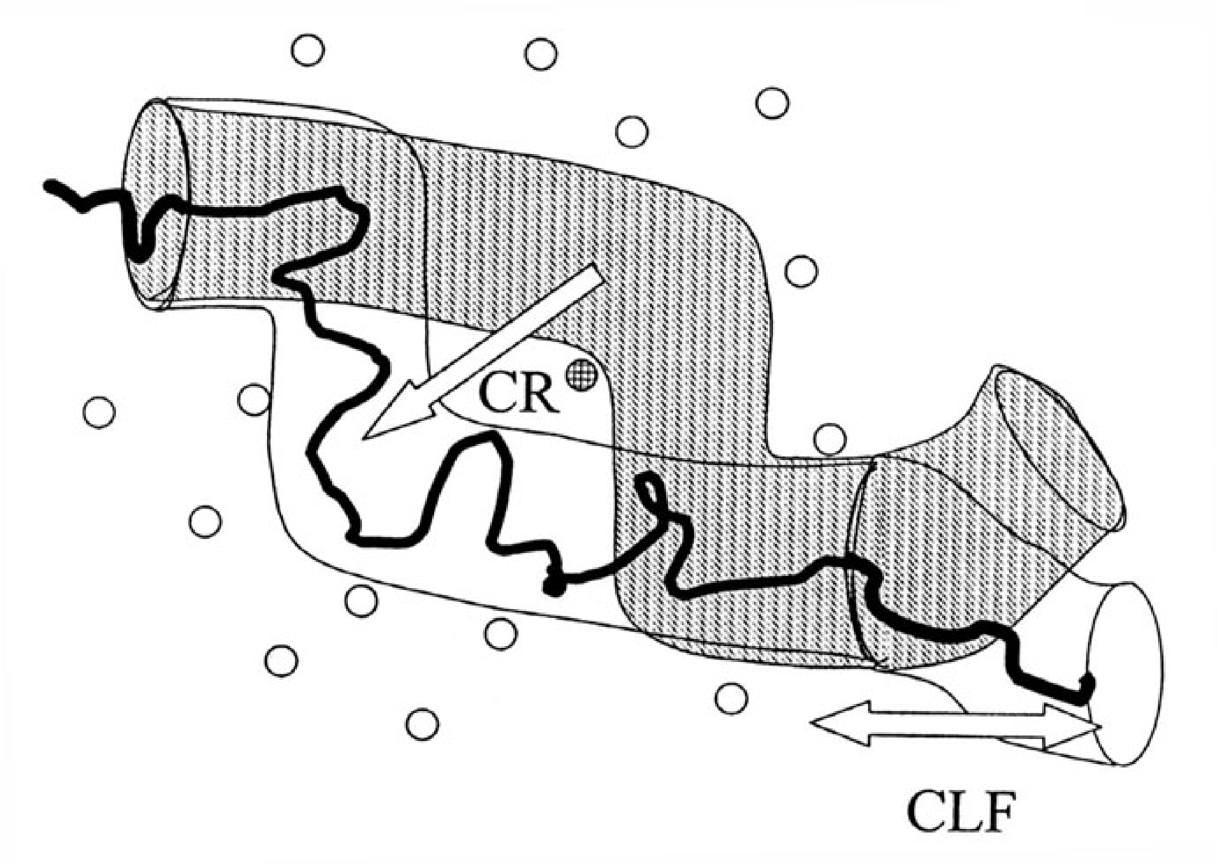
By assuming that thermal motions and convective motions are independent from one another, we calculate the rate $1/\tau$ of orientation renewal as a sum:

$$\frac{1}{\tau} = \frac{1}{\tau_d} + \beta\, \mathbf{k}:\mathbf{S} \qquad (7)$$

where β is an unknown numerical factor of order 1.

Because of CCR, in Eq.(6) we should replace τ_d with τ as given by Eq.(7). The problem is that **S**, hence τ, is a function of time, and therefore Eq.(6) is no longer explicit in the unknown orientation **S**(t) resulting from a given **k**(t). Time differential CE’s, instead of integral ones like Eq.(6), are therefore preferable.

Constraint release accelerates relaxation



Contributions from chain stretch

We have discussed so far of the CE for entangled networks under the assumption that chains are not stretched. However, if the flow is really fast, specifically if the magnitude of the velocity gradient **k** approaches the retraction rate $1/\tau_R$, then also chain stretch becomes important in determining the stress **T**.

We have seen in Eq.(5) that, approximately, $\mathbf{T} = G\,\lambda^2\,\mathbf{S}$. Hence we also need an equation to predict λ. The simplest such equation is written as:

$$\frac{d\lambda}{dt} = (\mathbf{k} : \mathbf{S})\lambda - \frac{\lambda - 1}{\tau_R} \qquad (8)$$

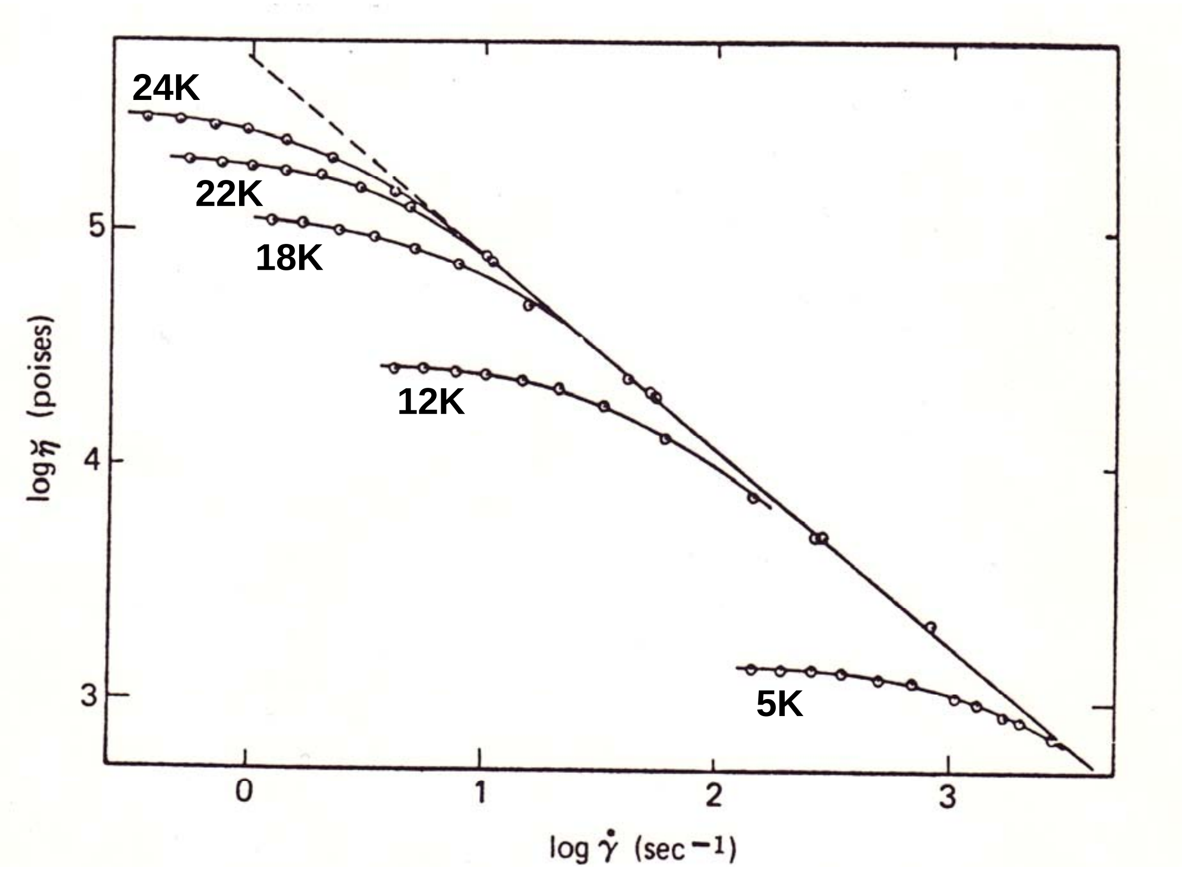
The first term on the r.h.s. of Eq.(8) is the positive forcing term, driving λ towards values larger than unity, i.e., towards chain stretch. The last (negative) term describes relaxation of the stretch λ back to unity. Equations more complex than Eq.(8) have also been suggested.

The other change to be considered is due to the effect of chain stretch on CCR. When chain stretch is not negligible, Eq.(7) becomes

$$\frac{1}{\tau} = \frac{1}{\tau_d} + \beta\left(\mathbf{k} : \mathbf{S} - \frac{1}{\lambda}\frac{d\lambda}{dt}\right) \qquad (9)$$

Because of Eqs.(8) and (9), λ and **S** are coupled, and hence the equations describing the change in time of **S** and λ must be solved simultaneously.

Example of nonlinear behavior

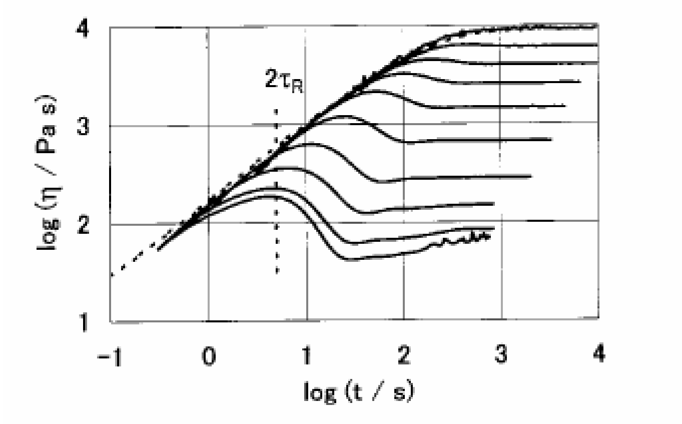


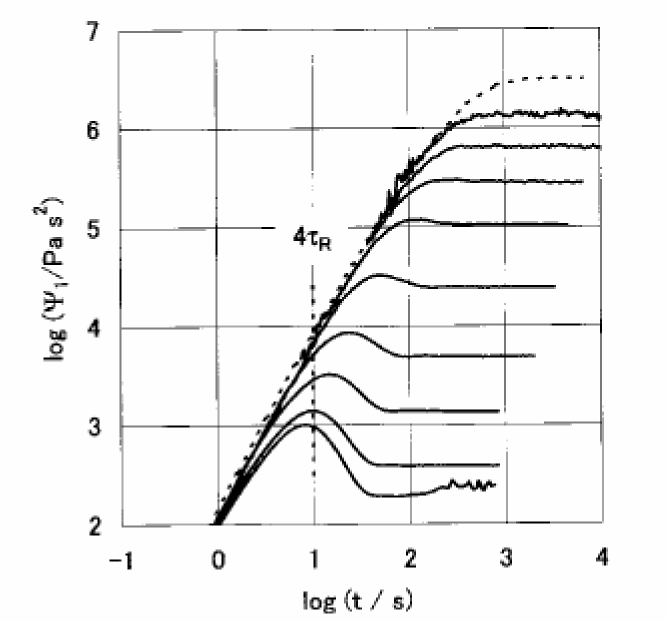
Bending over of the curves from the zero-shear viscosity is described by the basic Doi-Edwards theory.

Approaching a common asymptote at high shear rates is explained by CCR

Other examples of nonlinear behavior

Overshoots in viscosity and normal stresses in start up of shear flows



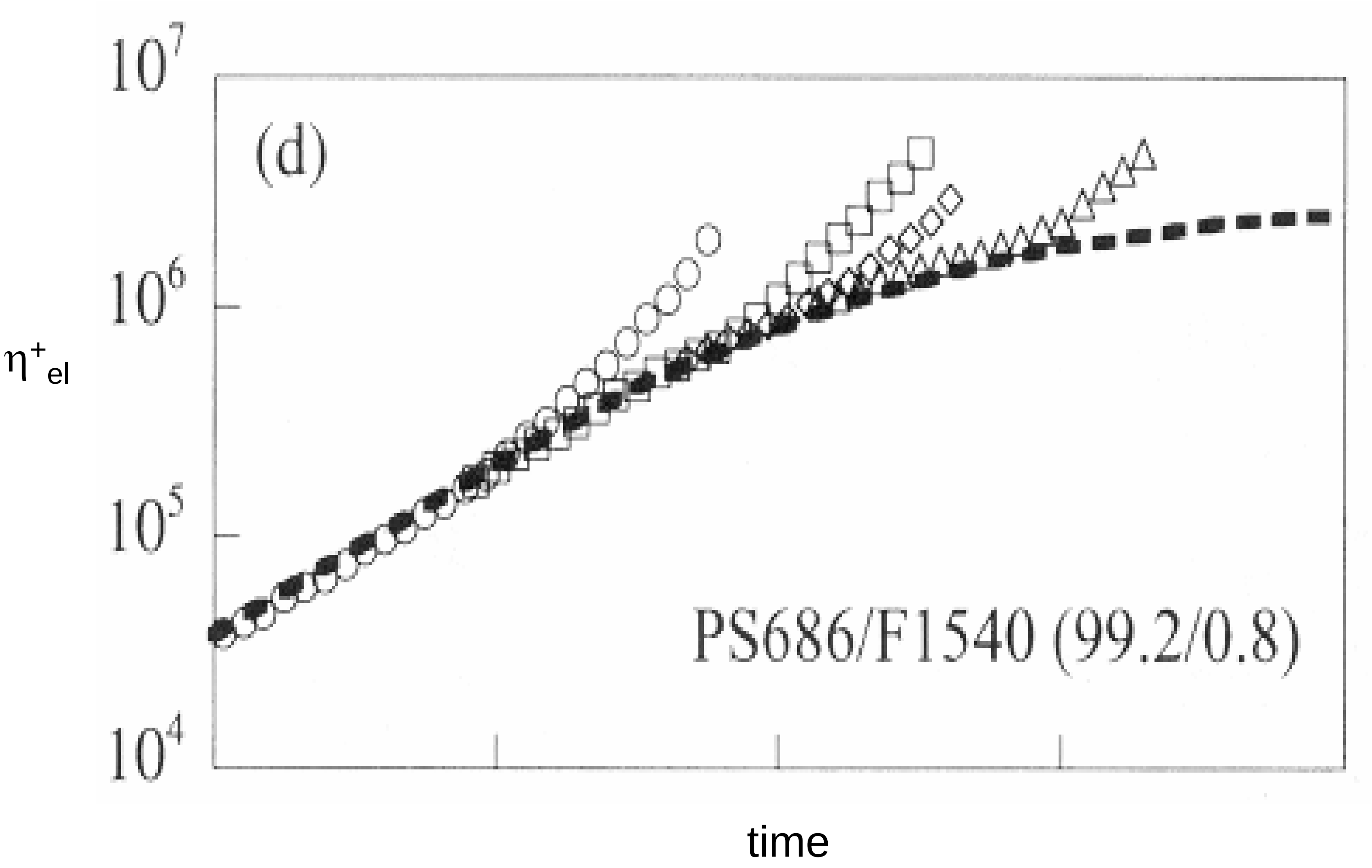


PS of M ≈ 5,5·10^6 in TCP at c ≈ 50 kg/m^3. Data from Osaki *et al.*, *J. Polym. Sci.: Polym. Phys.* 2000. Shear rates range from 0.00065 s^{-1} (top curve) to 4.9 s^{-1} (lowest curve)

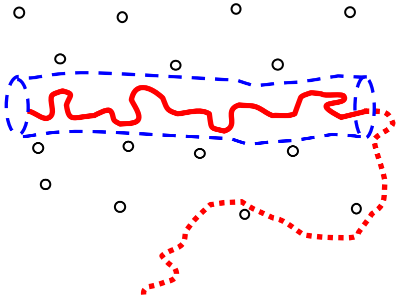
Maxima shown by the curves are understood in terms of tube orientation and chain stretching

Start up of elongational flows

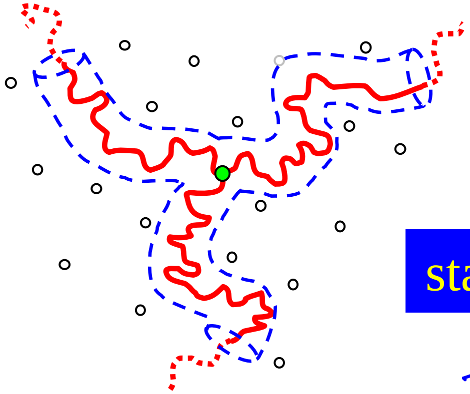
Deviations upwards from the linear curve (strain hardening)
are understood in terms of chain stretch



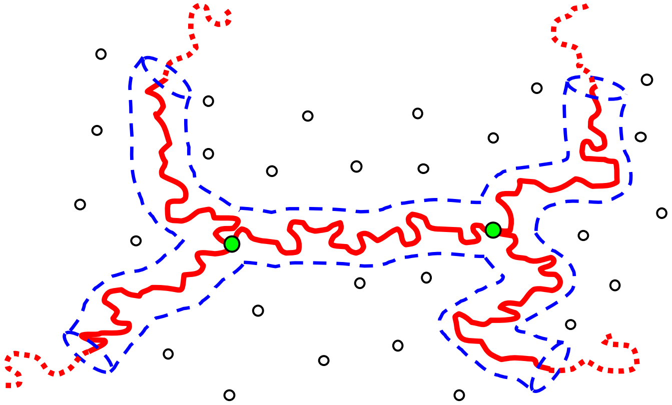
Polimeri ramificati



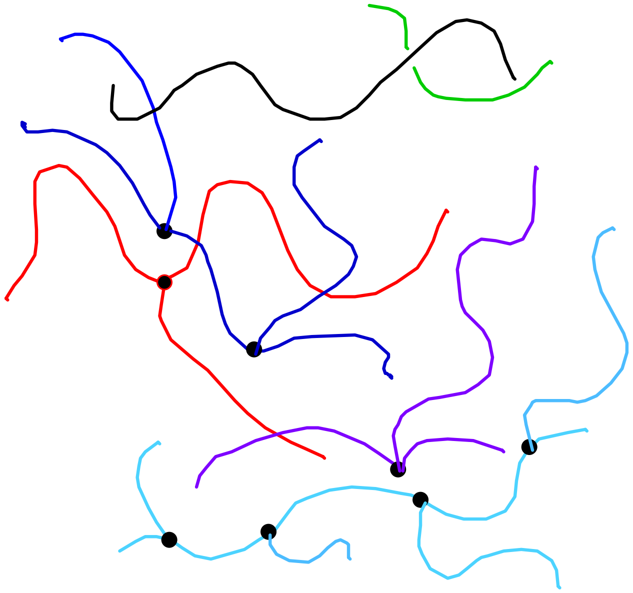
linear



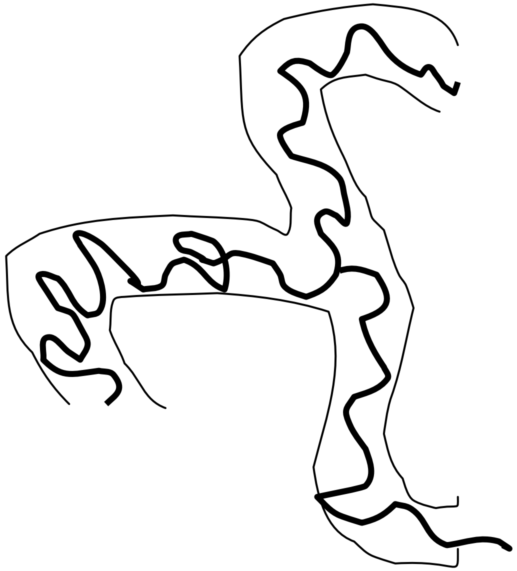
star



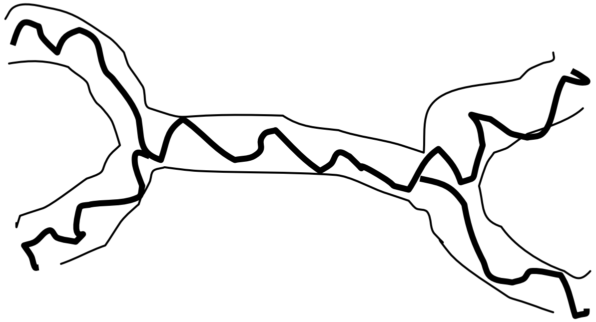
“H”



Entangled branched polymers

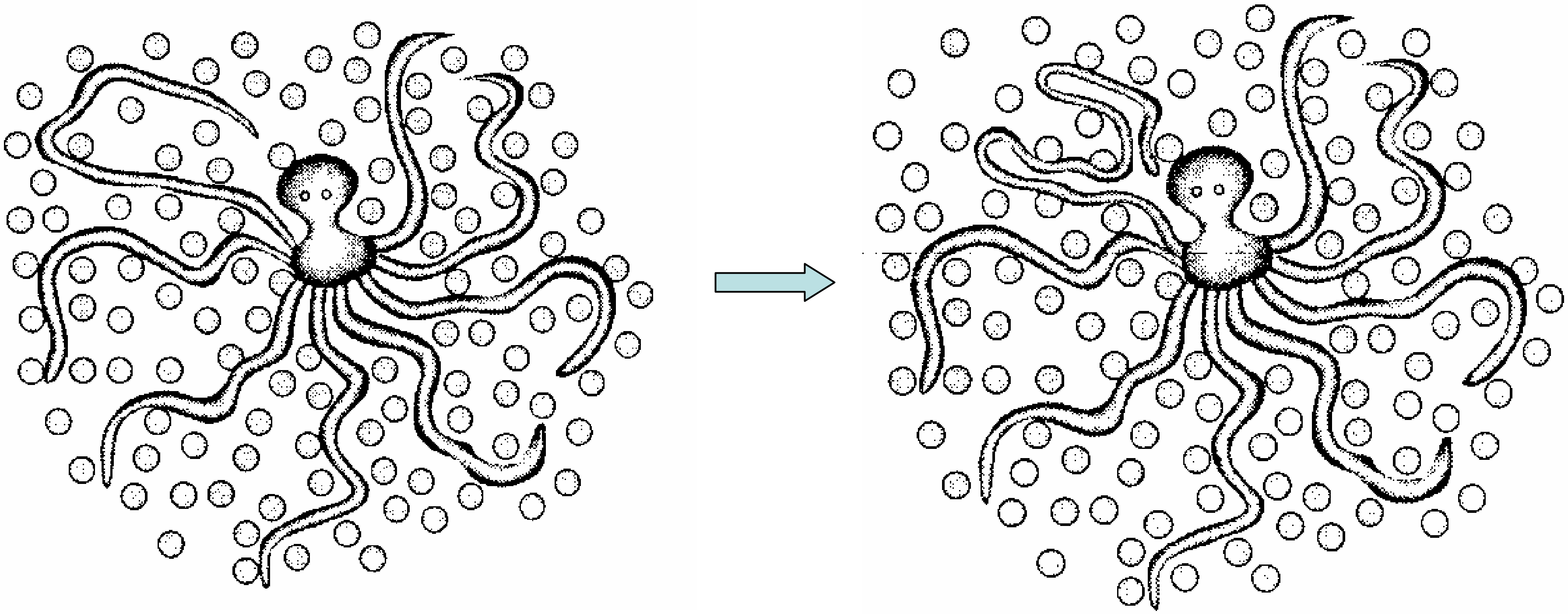


In star-like polymers the relaxation time grows <u>exponentially</u> with M (instead of the power-law $M^{3.4}$). Reptation is suppressed. Relaxation occurs through deep arm fluctuations.



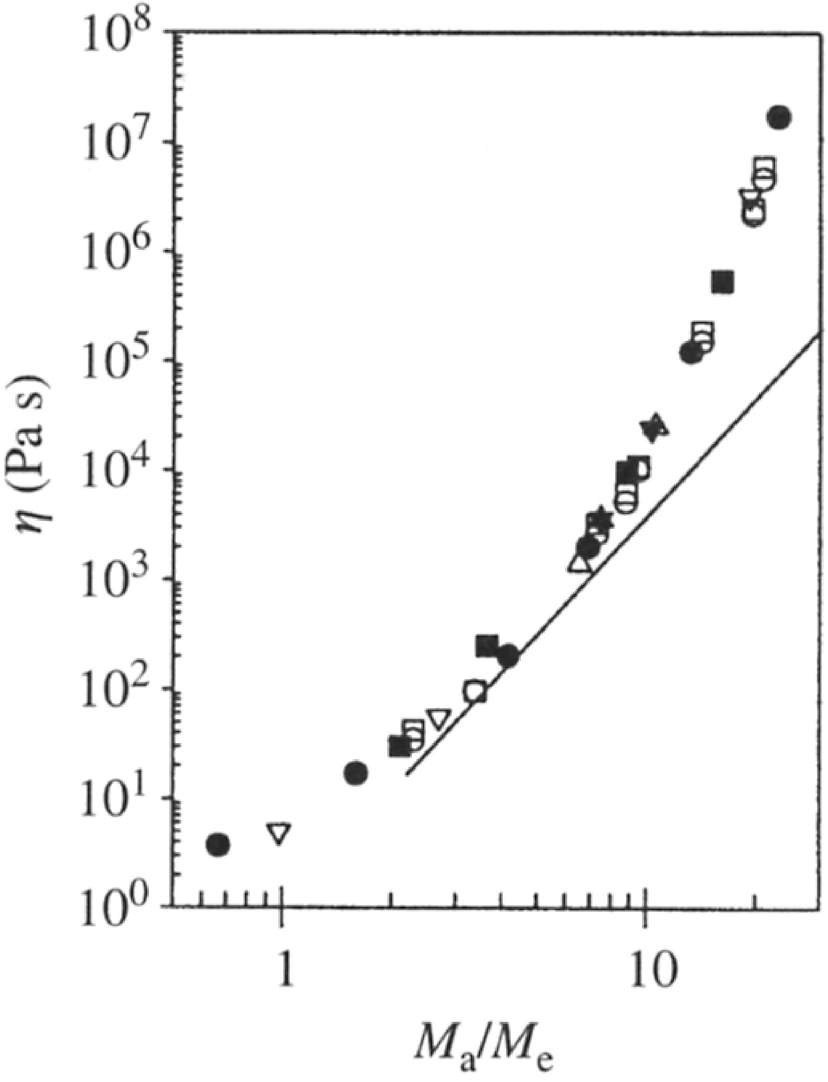
In other architectures of branched polymers, internal segments relax even more slowly

Rilassamento in una star

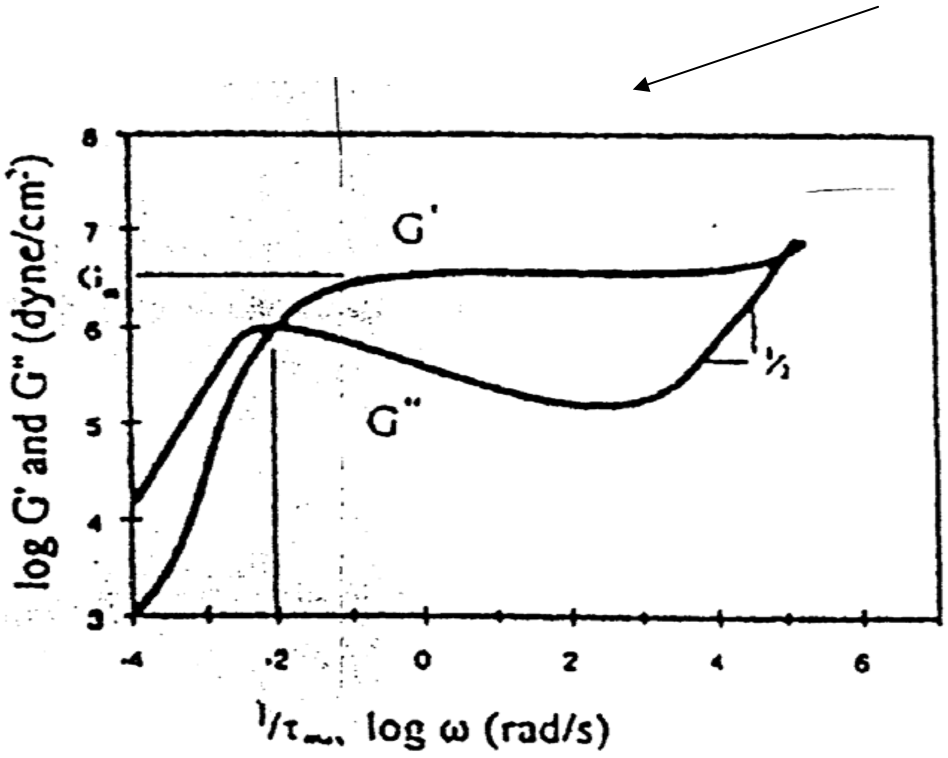


Arm retraction of entangled star polymers demonstrated by an octopus in a fishing net. The circles are permanent topological constraints.

Viscosity of starlike polymers vs. arm molecular weight



Comparison of linear vs. star polymers



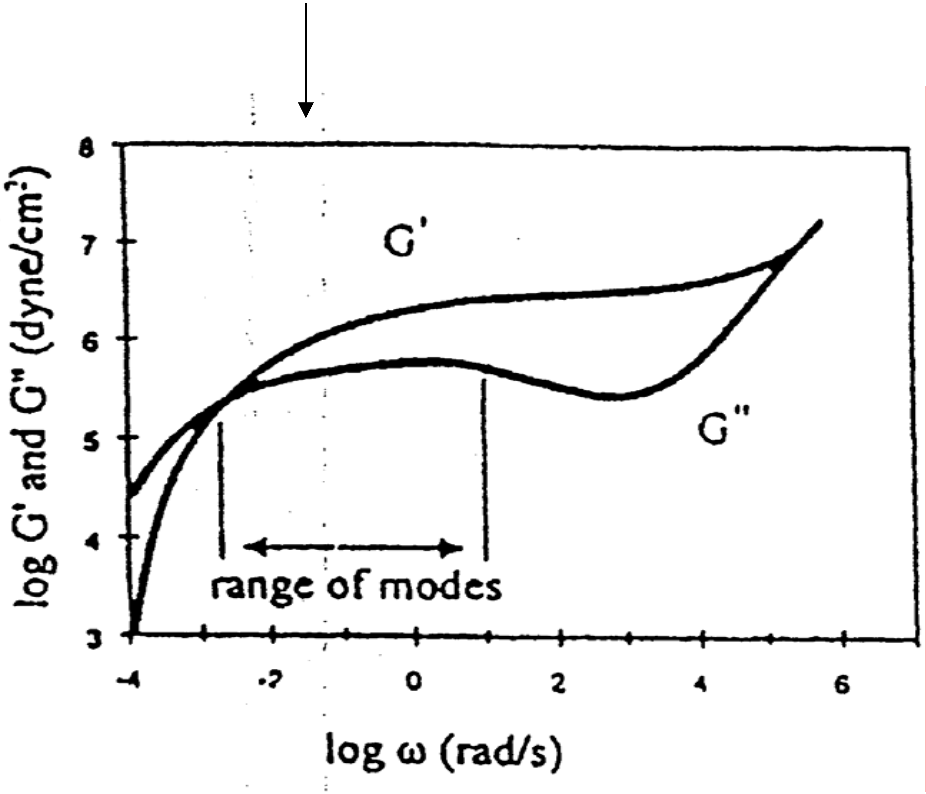
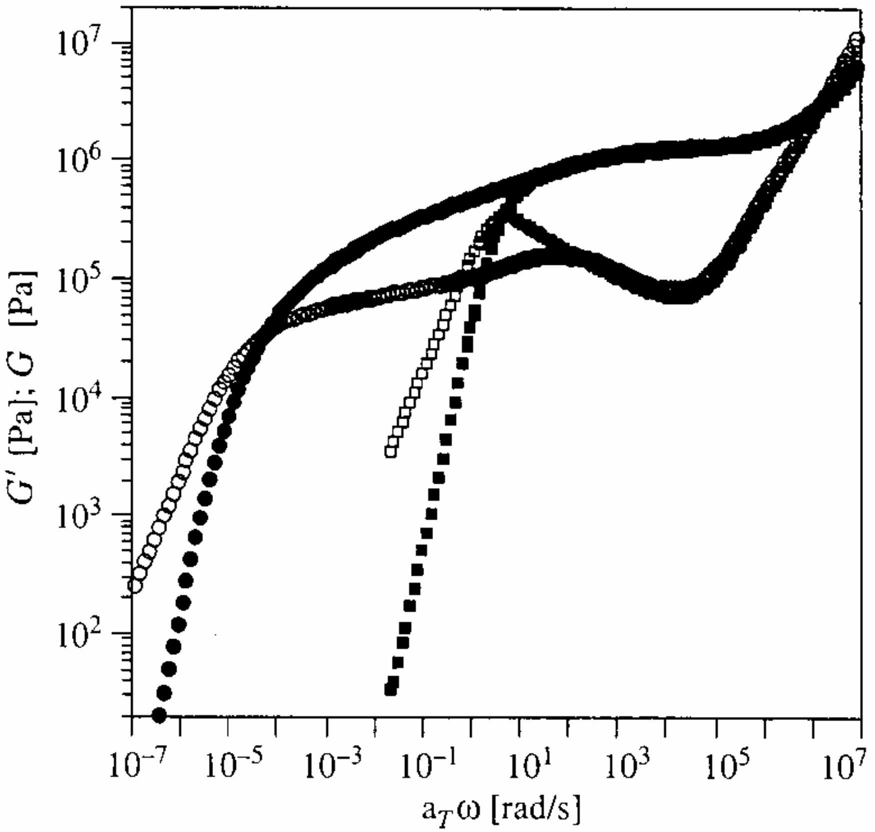


Fig. 5. The elastic modulus $G'(\omega)$ and dissipative modulus $G''(\omega)$ for linear (*top*) and three-arm-star branched (*bottom*) polyisoprene from [5]. Note the broad range of relaxation times indicated by the width of the peak in the star-polymer

Quantitative comparison of linear vs. star polymers

Fig. 9.15
Storage modulus (filled symbols) and loss modulus (open symbols) for linea 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 reference temperature of 28 °C. The linear polymer was chosen because it’ molar mass is approximately the span molar mass of the star polymer. Data courtesy of L. Archer.



PI data of G’-G” for an H polymer

(data and theory by McLeish *et al*)