Dynamics of Polymers

Lecture 10.05.2006

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- **Oszillator chain**

- **Rouse-model**

- **Reptation-model**

- **Experimental examples**

The Rouse-Model

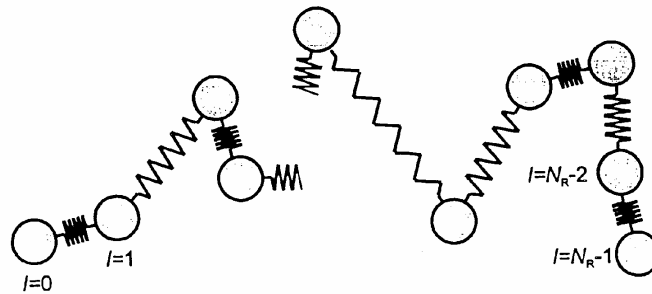The polymer chain is treated as a "bead and spring"-model (Fig. 1).

Fig. 1: Rouse-chain composed of N_R beads connected by springs

The force f between the beads is given by "entropic" forces (s. last lecture)

$$f = b_R \Delta r \qquad \text{with} \qquad b_R = \frac{3k_B T}{\langle \Delta r^2 \rangle} \qquad (1)$$

where $\langle \Delta r^2 \rangle$ is the mean squared end-to-end distance.

The chain is assumed to be surrounded by other chains. This interaction is summarized by a "friction coefficient" ζ with

$$f = \zeta u \qquad (2)$$

where u is the velocity of a bead.

The "segmental friction coefficient ζ" is assumed to be proportional to the viscosity of the melt

$$\zeta \sim \eta_S \qquad (3)$$

In the "Rouse-model" the chain is subdivided in N_R "Rouse-sequences", each being long enough so that Gaussian properties are ensured. Neglecting inertia effects the equation of motion reads as

$$\underbrace{\zeta_R \frac{d\vec{r}_l}{dt}}_{\substack{\text{viscous} \\ \text{damping}}} = \underbrace{b_R \left(\vec{r}_{l+1} - \vec{r}_l \right) + b_R \left(\vec{r}_{l-1} - \vec{r}_l \right)}_{\text{restoring forces}} \qquad (4)$$

b_R is defined for a "Rouse-sequence" with a mean squared end-to-end distance a_R^2

$$b_R = \frac{3k_B T}{a_R^2} \qquad (4a)$$

ζ_R denotes the friction coefficient per bead.

Assuming isotropy $\vec{r}$ can be replaced by – let's say – z

$$\zeta_R \frac{dz_I}{dt} = b_R \left(z_{I+1} - z_I \right) + b_R \left(z_{I-1} - z_I \right) \tag{5}$$

For a chain of infinite length one has translational symmetry in terms of I. Then there must be a wave-like solution.

$$z_I \sim \exp\left(-\frac{t}{\tau} \right) \exp\left(iI\delta \right) \tag{6}$$

δ describes the phase shift between adjacent beads and τ is a relaxational time.

Inserting (6) into (5) yields

$$\tau^{-1} = \frac{b_R}{\zeta_R} \left(2 - 2\cos\delta \right) = \frac{4b_R}{\zeta_R} \sin^2 \frac{\delta}{2} \tag{7}$$
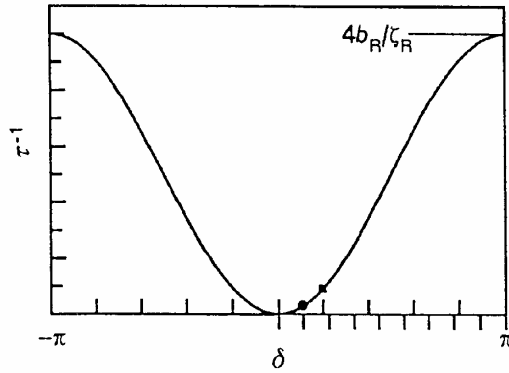

Fig. 2: Relaxation rates of Rouse-modes as a function of the phase-shift δ. Marks on the inside of the abscissa show the mode positions for a **cyclic chain** with $N_R = 10$ beads, the marks on the outside give the modes of a linear chain with the same length. The lowest order Rouse-modes of the two chains with relaxation rates τ_R^{-1} are especially indicated, by a *filled circle* and a *filled square*

A formal means of accounting for the finite size of a chain while maintaining the wave-like solution is provided by the introduction of cyclic boundary conditions

$$z_I = z_{I+N_R} \tag{8}$$

which is satisfied if

$$N_R \delta = m 2\pi \tag{9}$$

hence

$$\delta_m = \frac{2\pi}{N_R} m \quad ; \quad m = -\left(\frac{N_R - 1}{2}, \quad ...... \frac{N_R}{2} \right) \tag{10}$$

Fig. 2 shows the locations for a chain with $N_R = 10$.

For **linear** chains one has **free** ends where the tensile forces on the end segment vanish.

$$z_l - z_0 = z_{N_{R-1}} - z_{N_{R-2}} = \text{const.}$$

(11)

or in differential form

$$\frac{dz}{dl}(l=0) = \frac{dz}{dl}(l=N_R-1) = 0$$

(12)

For the real and imaginary part of (6) one finds

$$z_l \sim \cos l\delta \exp\left(-\frac{t}{\tau}\right)$$

$$z_l \sim \sin l\delta \exp\left(-\frac{t}{\tau}\right)$$

(13)

The boundary condition at l = 0 is only fulfilled by the cosine solution;

$$\frac{dz_l}{dl}(l=0) \Box \exp\left(-\frac{t}{\tau}\right)(-\delta)\sin(l\delta)$$

(13a)

It vanishes for l = 0; the condition for the upper end l = N_R-1 then selects

$$\frac{dz_l}{dl}(l=N_R-1) \Box \sin\big((N_R-1)\delta\big) = 0$$

(14)

or

$$(N_R-1)\delta = m\pi$$

(15)

Thus one obtains for a linear chain with free ends the following eigenvalues

$$\delta_m = \frac{\pi}{N_R-1}m \qquad m = 0, 1, 2, ...N_R - 1$$

(16)

For the linear chain one finds hence N_R independent solutions, the so-called "Rouse-modes". For the relaxation rate of these modes on obtains with (16) and (7) for the lowest order mode with m = 1 having a relaxation rate τ_R^{-1}

$$\tau_R^{-1} \Box \frac{b_R}{\zeta_R} \frac{\pi^2}{(N_R-1)^2}$$

(17)

if one assumes that $\dfrac{\pi}{(N_R-1)\cdot 2}$ is small.

With (4a) follows

$$\tau_R^{-1} = \frac{3k_B T\pi^2}{\zeta_R a_R^2 (N_R-1)^2}$$

(18)

and hence

$$\tau_R \Box (N_R-1)^2 \Box M^2$$

(19)

What are in summary the assumptions of the "Rouse-model"?

1. The chain is treated by a "bead and spring" model with entropic forces between nearest neighbours.

2. The interaction with the other surrounding chains is described by a frictional coefficient ζ with $f = \zeta \cdot u$

3. Inertia-effects are neglected, but as well hydrodynamic interactions.

4. The chain must be long.

How to prove experimentally the validity of the "Rouse-model"? There are so-called type-A polymers which have a dipole moment along the chain contour. This is for instance the case for cis-1,4-polyisoprene (PI).
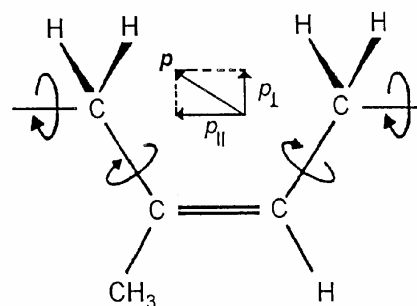

Fig. 3: Stereochemical constitution of a monomer unit of cis-PIP. The electric dipole moment, split into a longitudinal and a transverse component, is indicated.

The fact that one has a dipole moment which add up along the chain contour gives rise to a dielectric relaxation process corresponding to a fluctuation of the end-to-end vector of the chain. For the component of the dipole moment perpendicular to the chain axis one has another process being assigned to segmental fluctuations, which is called as well the segmental mode. It has the character of an α-relaxation being identical to the dynamic glass transition. Both processes are well separated from each other in frequency and their temperature dependence (Fig. 4).
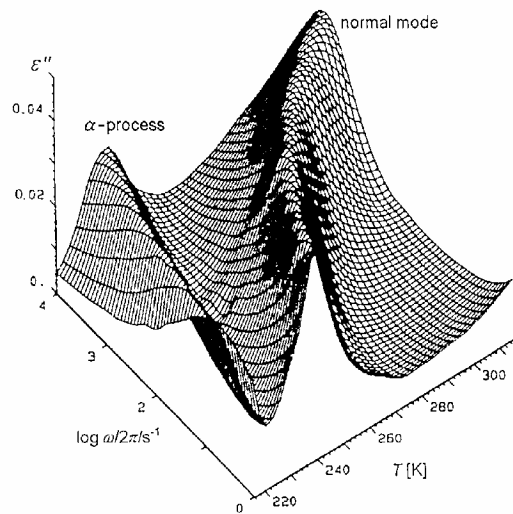
Fig. 4: Frequency- and temperature dependence of the dielectric loss in cis-PIP (M = 1.2 · 10^4), indicating the activity of two groups of relaxatory modes.

For the relaxation rate of both processes one finds – as expected – that the segmental fluctuation ("α-process") does **not** depend in the molecular weight of the chain, while the normal mode (fluctuation of the end-to-end vector) shows a pronounced effect (Fig. 5). Displaying the relaxation time of the normal mode (at a fixed temperature) in dependence on the molecular weight M one finds (Fig. 6) that for M being smaller than a critical molecular weight M_c

$$\tau \square M^2$$

in full accordance to the predictions of the Rouse theory. For $M > M_c$

$$\tau \square M^{3.3}$$
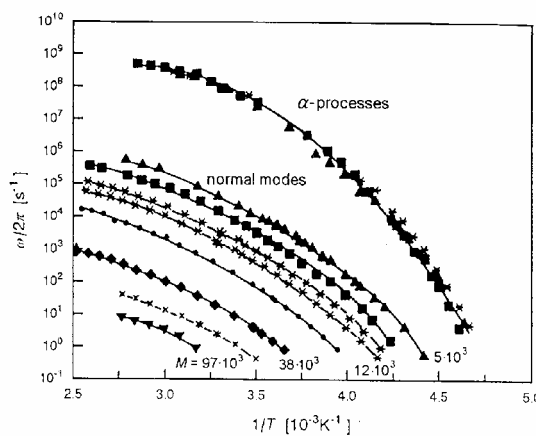
is found which is attributed to

Fig. 5: Temperature dependence of the relaxation rates of the dielectric α-process and the normal mode, observed for samples of cis-PIP with different molecular weights (four values are indicated).

reptational dynamics; for cis-PIP M_c = 10.000 g/mol. For more details see "Broadband Dielectric Spectroscopy" (Eds. F. Kremer & A. Schönhals, Chapter 7, Springer Verlag 2002).
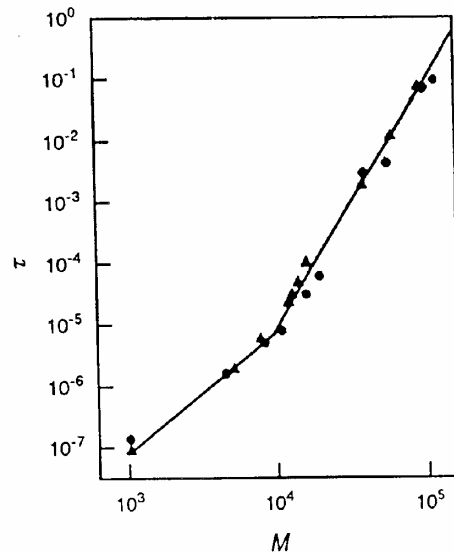

Fig. 6: Molecular weight dependence of the relaxation time of
the dielectric normal mode in cis-PIP.

The reptation model

Fig. 7: Modelling the lateral constraints on the chain motion
imposed by the entanglements by a "tube". The average
over the rapid wriggling motion within the tube defines
the "primitive path" (*continuous dark line*)

The chain moves in the tube formed by the other chains and is thus highly restricted in its motion along the "primitive path" (Fig. 7). The chain can "disentangle" by reptative motion.
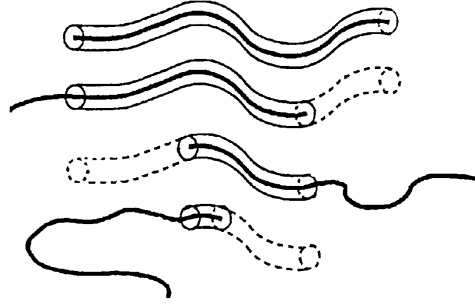
Fig. 8: Reptation model: Decomposition of the tube resulting
from a reptative motion of the primitive chain. The parts
which are left empty disappear.

Both the actual chain but as well the primitive path represent random coils, thus

$$R_0^2 = N_R a_R^2 = l_{pr} a_{pr} \qquad (20)$$

where l_{pr} is the contour length of the primitive path "l_{pr}" and an associated sequence
length a_{pr}, characterizing the stiffness of the "primitve path".

The process of disantanglement is envisaged in the reptation model as shown in Fig.
8. The associated curvilinear diffusion coefficient is given by the Einstein relation

$$D = \frac{k_B T}{\zeta_p} \qquad (21)$$

where ζ_p is the friction coefficient of the chain as a whole. As there are no
entanglements within the tube ζ_p equals the sum of the friction coefficients of all
beads

$$\zeta_p = N_R \zeta_R \qquad (22)$$

hence

$$D = \frac{k_B T}{N_R \zeta_R} \qquad (23)$$

The diffusion motion leads to a disentanglement of the chain. For DNA-chains it could
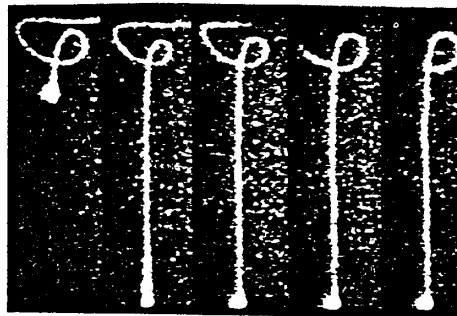be directly observed (s. Fig. 9).

Fig. 9: Series of images of a fluorescently stained DNA chain
embedded in a concentrated solution of unstained chains:

Initial conformation (*left*); partial stretching by a rapid move of the bead at one end (*second from the left*); chain recoil by a reptative motion in the tube (*subsequent pictures to the right*).

In order to disentangle fully a certain time is need

$$\tau_D \sim \frac{l_{pr}^2}{D} \tag{24}$$

With (26) and (23) follows

$$\tau_d \sim \varsigma_R N_R^3 \tag{25}$$

Experimentally a transition from a "Rouse-like"-dynamics

$$\tau_d \sim N_R^2 \tag{26}$$

to reptational dynamics

$$\tau_d \sim N_R^3 \tag{27}$$

is observed.

Summary of the lecture

"Dynamics of Polymers"

- The Rouse-model treats a polymer chain as a "bead-and-spring" model with entropic forces. As long as the molecular weight M_w is smaller than a critical specific molecular weight M_c

$$M_w < M_c$$

  the Rouse-model describes adequately the dynamics of a chain.

- For $M_w > M_c$ effects due to entanglements between the polymer chains come into play. The dynamics of the chain is then described by the reptation-model.