

# Microscopic dynamic models

Microscopic basis  $\Rightarrow$  macroscopic properties

통계 열역학 : “ fluctuation and dissipation theorem ”

$\Rightarrow$  relation between the microscopic dynamics in thermal equilibrium and macroscopic response function

## 6.1 the fluctuation-dissipation theorem

부피  $v$  를 가지는 subsystem  $\leftarrow$  macroscopic  $\leftarrow$  통계 열역학 적용 가능

$\Rightarrow$  time dependent fluctuation

ex) shape of the volume  $\Rightarrow$  local strain internal strain  $E$ , total dipole moment, local stress

polar sample 에서 fluctuation of the dipole moment 와 melt 상태에서 fluctuation of stress 의 관계

$$\mathbf{p}_v = \sum_i \mathbf{p}_i$$

subsystemd 의 total dipole moment

$P_i$  group dipole moment

$\Rightarrow$  second order time correlation function

$$\langle p_v(0)p_v(t) \rangle = \frac{\langle \mathbf{p}_v(0) \cdot \mathbf{p}_v(t) \rangle}{3}$$

fluctuation independently  $x, y, z$

$P_v$   $t' \sim t'+t$   $t'$ : 열평형 이 homogeneous

$P = \epsilon_0 \Delta \epsilon(t) E_0$  : zero time the polarization

$P = \epsilon_0 \Delta \epsilon(\infty) E_0$  : equilibrium

Electric field off --- polarization --- 0 : time dependent process

$P = \epsilon_0 \Delta (\epsilon(\infty) - \Delta \epsilon(t)) E_0$   $t$  : time elapsed (moment of switching off)

Fluctuation-dissipation theorem : decay function of the polarization

$$\langle p_v(0)p_v(t) \rangle = v k T \epsilon_0 (\Delta \epsilon(\infty) - \Delta \epsilon(t))$$

The correlation function of the fluctuation of the component of the total dipole moment along the field direction,  $p_v$

Left-hand side : correlation function associated with the spontaneous fluctuations in thermal equilibrium.

Right-hand side : response function; external field 가 가해질 때 reaction of the sample

정지상 melt 에서 stress fluctuation  $\Rightarrow$  the shear component  $\sigma_{zx}$

$$\langle \sigma_{zx}(0)\sigma_{zx}(t) \rangle = kT \frac{G(t)}{v}$$

t=0 에서의 variances of the fluctuating variables

$$\langle p_v \rangle = v\varepsilon_0 \Delta\varepsilon(\infty)kT$$

$$\langle \sigma_{zx} \rangle = kT \frac{G(0)}{v}$$

: characteristic difference

total dipole moments represent an extensive variable

$\Rightarrow$  variance  $\propto$  size of the subsystem

local stress : intensive variables

$\Rightarrow$  variance  $\propto$  1/size of the subsystem

$\Rightarrow$  systems of infinite size

time  $\Rightarrow$  frequencies

:  $X_v$  = extensive variable  $\Psi$  : field

$$X_v(t) = v\alpha(t)\psi_0$$

(  $t \geq 0$  ) with  $\alpha(t)$  as general time dependent susceptibility

general form

$$\langle X_v(0)X_v(t) \rangle = vkT(\alpha(\infty) - \alpha(t))$$

“Wiener – Chinchin theorem” : fourier transform

$$\langle X_v(0)X_v(t) \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle X_v(\omega)^2 \rangle \exp i\omega t d\omega$$

$$\langle X_v(\omega)^2 \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle X_v(0)X_v(t) \rangle \exp i\omega t d\omega$$

$$\alpha(t \rightarrow \infty) = \alpha'(\omega = 0)$$

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} \langle X_v(\omega)^2 \rangle d\omega = vkT\alpha'(\omega = 0)(t = 0)$$

Kramers-Kronig dispersion relation

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} \langle Xv(\omega)^2 \rangle d\omega = vkT \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\alpha''(\omega)}{\omega} d\omega$$

Second form of the fluctuation-dissipation theorem

$$\langle Xv(\omega)^2 \rangle = \frac{2vkT}{\omega} \alpha''(\omega)$$

⇒ spectral density of the fluctuation of  $X_v$  to the imaginary part

spectral density of the field fluctuation

$$\langle \Psi(\omega)^2 \rangle = \frac{2kT}{v\omega} a''(\omega)$$

$$a^* := \frac{1}{\alpha^*}$$

## 6.2 The Rouse – Model

The transition back to an isotropic coil increase the number of available rotational isomeric state and thus entropy

Two end group of a polymer chain a held at a certain distance, a tensile force arises due to the net moment transfer onto the ends

the tensile force

$$f = b_R \Delta r$$

$$b_R = \frac{3kT}{\langle \Delta r^2 \rangle} \quad : \text{force constant}$$

⇒ sequence behave like spring ; 힘 과 extension 이 linear relation

dynamic of a colloid in a solvent

⇒ molecule 의 모든 interaction 을 점성도로 설정 ← mesoscopic size

$$f = \zeta u \quad u = \text{velocity of the colloid}$$

$$\zeta \sim \eta_s : \text{마찰 계수}$$

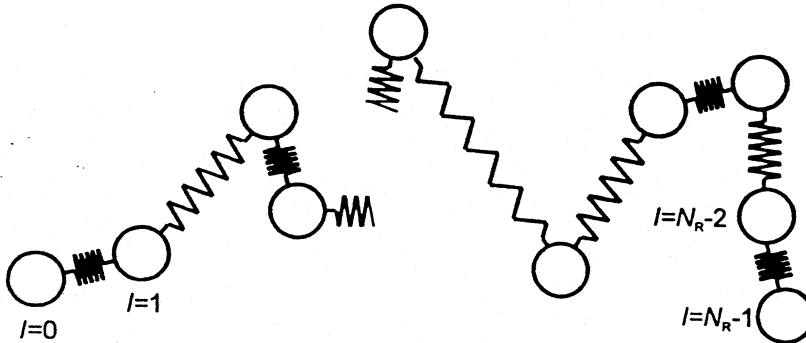


Fig. 6.1. Rouse-chain composed of  $N_R$  beads connected by springs

Rouse model

1. chain is subdivided in  $N_R$  : Rouse sequence  
; each sequence being sufficiently long so that gaussian properties are ensured
2. bead ( friction force) and spring (elastic tensile force)

motion of Rouse chain

$$\zeta_R \frac{dr_l}{dt} = b_R(r_{l+1} - r_l) + b_R(r_{l-1} - r_l)$$

left-hand side: viscous force      right-hand side: elastic force

$\zeta_R$  : friction coefficient per bead

force constant  $b_R$

$$b_R = \frac{3kT}{a_R^2} : a_R^2 : \text{spring 에 의존하는 mean square end to end distance}$$

differential equation : x,y,z (decoupled and equivalent)

z- direction

$$\zeta_R \frac{dz_l}{dt} = b_R(z_{l+1} - z_l) + b_R(z_{l-1} - z_l)$$

1. chain with infinite length : translational symmetry in terms of l

⇒wave-like solution of the form

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

⇒an exponential time dependence---relaxation process

$\delta$  : phase shift between adjacent beads

the dependence of relaxation rate  $\tau^{-1}$  on  $\delta$

$$\tau^{-1} = \frac{b_R}{\zeta_R} (2 - 2 \cos \delta) = \frac{4b_R}{\zeta_R} \sin^2 \frac{\delta}{2} \quad 6.28$$

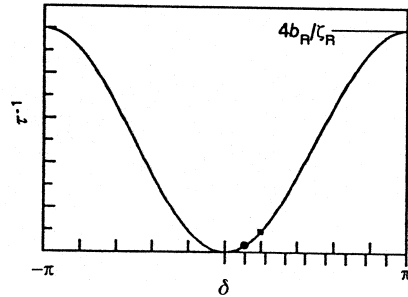


Fig. 6.2. Relaxation rates of Rouse-modes as a function of the phase shift  $\delta$ . Marks on the inside of the abscissa show the mode positions for a cyclic chain with  $N_R = 10$  beads, the marks on the outside give the modes of a linear chain with the same length. The lowest order Rouse-modes of the two chains with relaxation rates  $\tau_R^{-1}$  are especially indicated, by a filled circle and a filled square

## 2. finite size of a chain

⇒ while maintaining the wave-like solution is provided by the introduction of cyclic boundary conditions

for chain with  $N_R$  beads

$$z_l = z_l + N_R \Leftrightarrow N_R \delta = m 2\pi$$

$N_R$  discrete value of the phase shift

$$\delta_m = \frac{2\pi}{N_R} m, m = -\left(\frac{N_R}{2} - 1\right), \dots, \frac{N_R}{2}$$

linear chain : free ends

⇒ tensile force vanish so the boundary condition

$$z_l - z_0 = z_{N_R-1} - z_{N_R-2} = 0$$

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

$$z_l \sim \cos l\delta \cdot \exp -\frac{t}{\tau}$$

$$z_l \sim \sin l\delta \cdot \exp -\frac{t}{\tau}$$

boundary condition ( $l=0$ ) ; cosine solution

the condition for the upper end :  $l=N_R-1$

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

linear chain with with free ends : eigenvalues  $\delta_m$

$$\delta_m = \frac{\pi}{N_R - 1} m \quad m=0,1,2,\dots,N_R-1 \quad \text{: linear chain } N_R \text{ independent solution}$$

$\Rightarrow$  Rouse Model

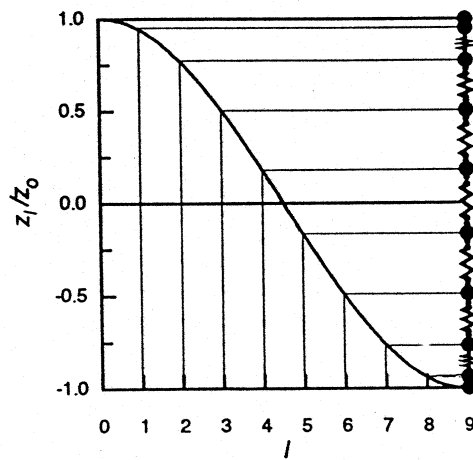


Fig. 6.3. Displacement pattern of the primary Rouse-mode

Displacement pattern associated with the lowest order Rouse mode with  $m = 1$

$\Rightarrow$  relaxation rate : 'Rouse-rate'  $\tau_R^{-1}$

$$\tau_1^{-1} := \tau_R^{-1} = \frac{3kT\pi^2}{\zeta_R a_R^2 (N_R - 1)^2}$$

freedom of choice 의 제거

$$R_0^2 = a_R^2 (N_R - 1)$$

Rouse time  $\tau_R$

$$\tau_R = \frac{1}{3\pi^2} \frac{(\zeta_R / a_R^2)}{kT} R_0^4$$

$\Rightarrow \zeta_R / a_R^2$  : independent of the choice of sequence

the friction coefficient of a sequence has to be proportional to the number of

monomer unit.

Dependence of the Rouse-time on the degree of polymerization

$$R_0^2 = a_0^2 N \Rightarrow \tau_R \sim N^2$$

$$\tau_{N_R-1} = \frac{\zeta_R a_R^2}{12kT} = \frac{(\zeta_R / a_R^2)}{12kT} a_R^4$$

: cut-off at the short-time end which depend on  $a_R$

In a dynamic equilibrium state : Rouse-modes become thermally excited and it is instructive to calculate their mean-squared amplitudes. The displacement pattern of mode m is given by

$$z_l = Z_m \cos l \delta_m$$

$Z_m$  : 'normal coordinate'

Bead-and-spring model, the change in free energy per polymer chain :  $\Delta f_p$

$$\begin{aligned} \Delta f_p &= \frac{b_R}{2} \sum_{l=0}^{N_R-2} (z_{l+1} - z_l)^2 \\ &= \frac{b_R}{2} Z_m^2 \sum_{l=0}^{N_R-2} (\cos(l+1)\delta_m - \cos l \delta_m)^2 \\ &= \frac{b_R}{2} Z_m^2 \delta_m^2 \sum_{l=0}^{N_R-2} \sin^2 \delta_{ml} = \frac{b_R}{2} \frac{N_R-1}{2} Z_m^2 \delta_m^2 \end{aligned}$$

: determines the probability distribution  $p(Z_m)$  for the amplitude  $Z_m$

$$\langle \Delta f_p \rangle = \frac{kT}{2}$$

ideal chain :  $\langle Z_m^2 \rangle$  independent of temperature

$$\langle Z_m^2 \rangle = \frac{2}{3\pi^2} \frac{R_0^2}{m^2}$$

amplitude of Rouse-modes rapidly decrease with increasing mode order m . If we consider the contributions of the different Rouse-modes to the known total mean

squared end-to-end distance,  $\langle R^2 \rangle = R_0^2$ , we find that a large part is already

provided by the three lowest order Rouse-modes. Contribution to the the end-to-end

distance in the z-direction,  $\langle R_z^2 \rangle = \frac{R_0^2}{3}$ , come from all z-polarized Rouse-modes

with odd m's

$$\langle (z_{N_R-1} - z_0)^2 \rangle = \langle (2Z_1)^2 \rangle + \langle (2Z_3)^2 \rangle + \dots$$

$$\langle (z_{N_R-1} - z_0)^2 \rangle = \frac{8}{\pi^2} \cdot \frac{R_0^2}{3} \left(1 + \frac{1}{9} + \dots\right) = \frac{R_0^2}{3}$$

90% of the total mean squared end-to-end distance of a chain originates from the lowest order Rouse-modes

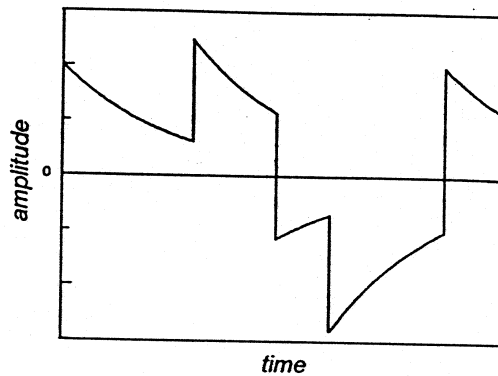


Fig. 6.4. Time dependence of the amplitude  $Z_m$  of a Rouse mode (schematic)

the time correlation function for the normal coordinate  $Z_m$

$$\langle Z_m(0)Z_m(t) \rangle = \langle Z_m^2 \rangle \cdot \exp\left(-\frac{t}{\tau_m}\right) = \frac{2R_0^2}{3\pi^2 m^2} \exp\left(-\frac{t}{\tau_m}\right)$$

### 6.2.1 Stress Relaxation

shear stress relaxation modulus,  $G(t)$ .

$$\langle \sigma_{zx}(0)\sigma_{zx}(t) \rangle = kT \frac{G(t)}{\nu}$$

in thermal equilibrium

fluctuations of an intensive variable  $\Rightarrow$  stress depend upon the size of the chosen subsystem : ( ex ) orthogonal edge,  $l_x, l_y, l_z$



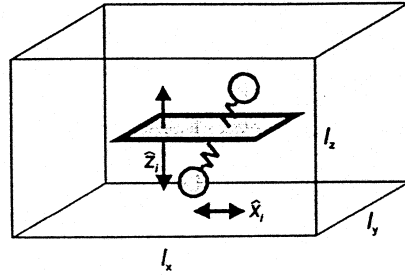


Fig. 6.5. Notions used in the calculation of the tensile stress  $\sigma_{zx}$  associated with a system of Rouse-chains: Reference volume  $v = l_x l_y l_z$ ; unit area, crossed by the spring  $i$  with extensions  $\hat{x}_i$  and  $\hat{z}_i$  along  $x$  and  $z$

shear stress  $\sigma_{zx}$

contributions arise from all springs which have a non-vanishing component of extension in  $x$ -direction.

Mean value of  $\sigma_{zx}$

$$\sigma_{zx} = \sum_i \frac{1}{l_x l_y} \frac{\hat{z}_i}{l_z} \cdot f_{x,i}$$

stress on this plane is produced by all springs which cross it

$$\frac{1}{l_x l_y} \frac{\hat{z}_i}{l_z}$$

the probability that spring  $i$ , with an extension  $\hat{z}_i$  along  $z$ , crosses the unit area. When crossing this area, the spring contribution a force  $f_{x,i}$  to  $\sigma_{zx}$

$$\sigma_{zx} = \frac{1}{v} \sum_i \hat{z}_i f_{x,i} = \frac{b_R}{v} \sum_i \hat{z}_i \hat{x}_i$$

$\sigma_{zx}$  : spatial average in a volume  $v$ , represents a fluctuating quantity which shows different values in different subsystems

the ensemble  $E$  vanishes

$$\langle \hat{z}_i \hat{x}_i \rangle = \langle \hat{z}_i \rangle \langle \hat{x}_i \rangle = 0$$

time correlation function of the fluctuation of the shear stress

$$\langle \sigma_{zx}(0) \sigma_{zx}(t) \rangle = \frac{1}{v^2} b_R^2 \sum_{k,l,k',l'} \langle \hat{x}_{k,l}(0) \hat{z}_{k,l}(0) \rangle \langle \hat{x}_{k',l'}(t) \hat{z}_{k',l'}(t) \rangle$$

\*fluctuation-dissipation theorem : shear relaxation modulus.

$$G(t) = c_p kT \sum_m \frac{\langle X_m(0) X_m(t) \rangle}{\langle X_m^2 \rangle} \cdot \frac{\langle Z_m(0) Z_m(t) \rangle}{\langle X_m^2 \rangle}$$

$G(t)$  to the magnitudes and the time dependencies of the fluctuations of the Rouse-modes in thermal equilibrium.

$\Rightarrow$  the time correlation function

$$\langle Z_m(0)Z_m(t) \rangle = \langle Z_m^2 \rangle \exp\left(-\frac{t}{\tau_m}\right)$$

and equivalent

$$\langle Z_m(0)Z_m(t) \rangle = \langle Z_m^2 \rangle \exp\left(-\frac{t}{\tau_m}\right)$$

$$\Rightarrow G(t) = c_p kT \sum_m \exp\left(-2\frac{t}{\tau_m}\right)$$

: shear stress relaxation modulus associated with a system of Rouse-chains. The result has a remarkably simple structure, as all Rouse-modes contribute to  $G(t)$  with the same weight.

$\Rightarrow$  disregard the short-time range : reduced to the contribution of the low order Rouse-modes

$$\tau_m^{-1} \approx \tau_R^{-1} \cdot m^2$$

$$\Rightarrow G(t) \approx \int_{m=1}^{N_R^{-1}} dm \exp\left(-2\tau_R^{-1} m^2 t\right) \approx \int_{m=0}^{\infty} dm \exp\left(-2\tau_R^{-1} m^2 t\right)$$

with the substitution

$$u := m\left(\frac{t}{\tau_R}\right)^{1/2} \Rightarrow G \sim \left(\frac{\tau_R}{t}\right)^{1/2} \int_{u=0}^{\infty} \exp\left(-2u^2\right) du$$

$\cong$

$$G(t) \sim t^{-1/2} \Rightarrow \text{power law : relaxation of Rouse-chains : in polymer melts}$$

:The center of the glass-rubber transition, as observed in stress relaxation experiments

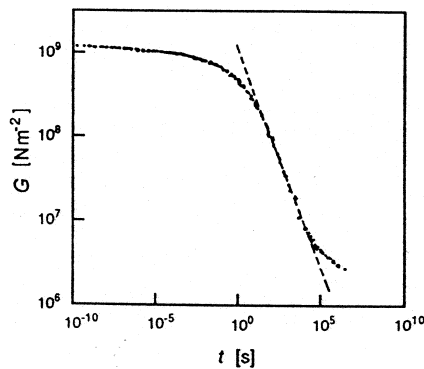


Fig. 6.6. Time dependent shear modulus of PVC. Master curve set up for  $T_g = 65^\circ\text{C}$  as the reference temperature. The *dashed line* indicates the slope predicted by the Rouse-model. Data from Eisele [66]

viscosity at zero shear rate

$$\begin{aligned}\eta_0 &= \int_0^\infty G(t) dt \\ &= kTc_p \sum_{m=1}^{N_R-1} \frac{\tau_m}{2} \\ &\approx kTc_p \frac{\tau_R}{2} \sum_{m=1}^\infty \frac{1}{m^2} = kTc_p \tau_R \frac{\pi^2}{12}\end{aligned}$$

$\Rightarrow$  a linear dependence of  $\eta_0$  on the degree of polymerization

$$\eta_0 \sim \frac{c_m}{N} N^2 \sim N$$

$\Rightarrow$  non entangled melts

intrinsic limitation at short times

: the unrelaxed modulus is determined by the number of Rouse-sequences,  $c_R$

$$G(0) = c_p kT(N_R - 1) = c_R kT$$

the correct value follows only from both parts together

$$G(t) = \Delta G_{mic}(t) + G_{Rouse}(t)$$

; short time properties

### 6.3 Entanglement Effect

chains are linearly connected objects which cannot cross each other, their individual motions become constrained and for the chain as a whole it is therefore impossible to

move freely in all directions

the motion perpendicular to the chain contour

⇒ the chain dynamics as a motion in a tube. This tube is set up by those of the adjacent polymers which represent obstacles for the lateral motion and thus models the confinement range.

- The occurrence of the rubber-elastic plateau in the time-and frequency dependent mechanical response function
- The change in the molecular weight dependence of the viscosity
- The change in the molecular weight dependence of the relaxation time of the dielectric normal mode

Effect of entanglement : elastic & viscous

$M_c$  : critical molecular weight at the entanglement weight

⇒  $M < M_c$ : no entanglement effect

Quasi-elastic neutron scattering experiment

⇒ the change in the dynamics from a free Rouse- to a constrained tube motion, occurring at a certain sequence length.

Spatial resolution 1~10nm; frequency resolution GHz

: deuterium and hydrogen have different scattering cross-section

in dilute solution of protonated chains in a deuterated matrix

yield the intermediate scattering law  $S(\mathbf{q}, t)$

related by a Fourier transformation to the time dependent pair correlation function of the monomers in protonated chains,  $g(\mathbf{r}, t)$

$$S(\mathbf{q}, t) = \int \exp i \mathbf{q} \cdot \mathbf{r} \cdot (g(\mathbf{r}, t) - \langle c_m \rangle) d^3 \mathbf{r}$$

$g(\mathbf{r}, t)$  : pair correlation function of the monomers of one chain : motion of individual chain

the motion of the chain in the melts is not restricted

⇒ the limit of the pair correlation function for long periods of time

$$g(\mathbf{r}, t \rightarrow \infty) = \langle c_m \rangle$$

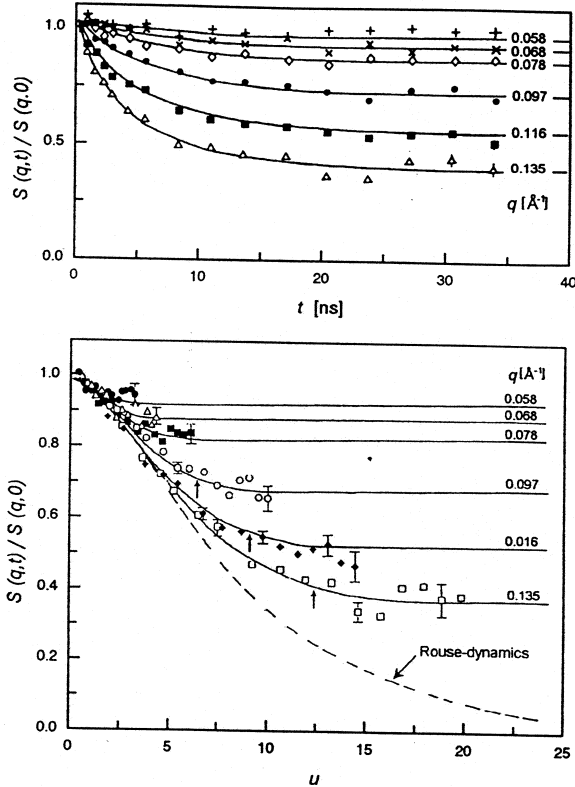
$$S(\mathbf{q}, t \rightarrow \infty) = 0$$

the motion of the chains remains confined

$$g(\mathbf{r}, t \rightarrow \infty) \neq \langle c_m \rangle$$

:  $\mathbf{r}$  which located within the confinement range

$\mathbf{r}$  out side this zone  $\Rightarrow$  eq 6.104



**Fig. 6.8.** Results of a quasielastic neutron scattering experiment on a melt of poly(ethylene-co-propylene) at 199 °C (10% protonated chains dissolved in a deuterated matrix;  $M = 8.6 \cdot 10^4$ ): Intermediate scattering laws measured at the indicated scattering vectors (*top*); data representation using the dimensionless variable  $u = q^2(12kTa_R^2t/\zeta_R)^{1/2}$  (*bottom*). From Richter et al.[67]

$\Rightarrow$  curve belong to different scattering vector  $q$

: decay times decrease with increasing  $q$  : all kind of diffusive motions

the intermediate scattering law : system of Rouse-chains

$\Rightarrow$  function of one dimensionless variable

$$u = q^2 a_R^2 (\tau^{-1} (\delta = \pi) t)^{1/2} = q^2 (12kTa_R^2 t / \zeta_R)^{1/2}$$

$\Rightarrow \tau^{-1}(\pi)$  is the maximum relaxation rate of the Rouse-chain

$\Rightarrow$  when using the variable  $u$ , measurement at different  $q$ 's must coincide and contribute to one common curve

- ⇒ the short term dynamics is indeed Rouse- like
- ⇒ with longer times : curves deviate from the Rouse scattering law

limiting value for long periods the size of the confinement range

$$S(q, t \rightarrow \infty) = \int \exp iqr \cdot (g(r, \infty) - \langle c_m \rangle) d^3 r$$

non-vanishing values only for distance  $r$  within the confinement range.

↔ relation at fourior transforms

⇒ measurement of the halfwidth  $\Delta q$  of  $S(q, \infty)$

⇒ diameter  $d$  of the confinement range

$$d \cong \frac{1}{\Delta q}$$

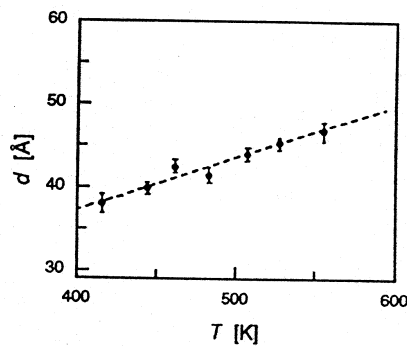


Fig. 6.9. Size  $d$  of the confinement range, as derived from the long term limits of the curves shown in Fig. 6.8 [67]

the time dependent shear modulus of an entangled polymer melt as being composed three parts

$$G(t) = \Delta G_{mic}(t) + c_p kT \sum_{m=m^*}^{N_{R,c}-1} \exp\left(-2 \frac{t}{\tau_m}\right) + c_p kT m^* \Phi\left(\frac{t}{\tau_d}\right)$$

1. the short-term contributions determined by the chemical microstructure of the chain

2. Rouse-model : dynamic for chain sequence

; shorter than the chain parts between entanglement

long enough to ensure that Gaussian properties hold.

Rouse-mode with the longest relaxation time : order  $m^*$

$$\delta_{m^*}(N_{R,c} - 1) \cong \pi \quad N_{R,c}: \text{contour length in Rouse unit corresponding to}$$

the  $M_c$

$$m^* \cong \frac{N_R - 1}{N_{R,c} - 1}$$

associated relaxation time

$$\tau_{m^*} \approx \tau_R \left( \frac{N_{R,c} - 1}{N_R - 1} \right)^2$$

3. this part remains unrelaxed after the decay of all modes with  $m > m^*$

⇒ correlation function for the long term part :  $\Phi(t/\tau)$

: similar to the Rouse-mode : controlled by a single characteristic time

; the disentangling time  $\tau_d$

$\Phi(t/\tau)$  is a general normalized function

$$\Phi(0) = 1$$

$$\int_{t=0}^{\infty} \Phi dt = \tau_d$$

$\tau_d$  exhibit a power law dependence on M

$$\tau_d \sim M^\nu \quad \text{with} \quad \nu \approx 3.4$$

formation of a gap in the spectrum of relaxation times, arising between the first two contributions and the long-term part.

⇒ plateau region

the extension in time is determined by the ratio  $\tau_d / \tau_{m^*}$

$$\frac{\tau_d}{\tau_{m^*}} \cong \frac{M^{3.4}}{M_c^{3.4}}$$

effect of the entanglement on the viscosity

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

shear viscosity is given by the relaxation strength and the mean relaxation times

$$\eta_0 = c_p kT [(N_R - m^*)\tau_\alpha + m^* \tau_d]$$

$$\eta_0 = G(0) \left( \frac{G(0) - G_{pl}}{G(0)} \tau_\alpha + \frac{G_{pl}}{G(0)} \tau_d \right)$$

$G_{pl}$  : plateau modulus

$\tau_\alpha$  : mean relaxation time of the Rouse-mode part

⇒ mean relaxation time of a Rouse-system of chains with  $N_R = NRc$   
 ⇒ first term on the right hand side is constant  
 ⇒ molecular weight dependence of the viscosity of entangled melts

$$\eta_0 = \beta_1 + \beta_2 \tau_d(M) = \beta_1 + \beta_3 M^\nu$$

In the molecular limit of high molecular weight,  $M \gg Mc$

$$\eta_0 \sim \tau_d \sim M^\nu$$

### 6.3.1 The Reptation Model

tube concept and the motion of the confined chains.

⇒ reptation model.



**Fig. 6.10.** 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*)

Chain motion component

1. rapid wriggling motion oriented along the cross section.

:dark-line in the tube center ; primitive path

⇒ shortest path connecting the end groups of the chain which is compatible with the topology of the entanglement as modeled by the tube

2. time dependent evolution of this primitive path

⇒ disentangling of the chain.

⇒ primitive path represent random coil : end-to-end distance equal.

$$R_0^2 = N_R a_R^2 = l_{pr} a_{pr}$$

$l_{pr}$  : contour length of the primitive path.

$a_{pr}$  : sequence length

⇒ stiffness of the primitive path

⇒ topology of the entanglement network



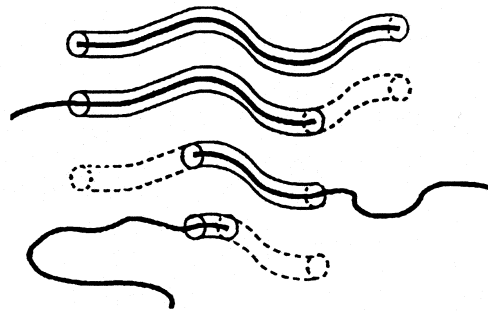


Fig. 6.11. Reptation model: Decomposition of the tube resulting from a reptative motion of the primitive chain. The parts which are left empty disappear

the motion of the primitive chain : diffusion along its contour length.  
: reptation.

Einstein relation

$\Rightarrow$  curvilinear diffusion coefficient.

$\Rightarrow$  independent dimension or topology

$$\hat{D} = \frac{kT}{\zeta_p}$$

$\zeta_p$  equals the sum of the friction coefficient of all beads : no entanglements within the

tube

$$\hat{D} = \frac{kT}{N_R \zeta_R} \quad \Leftarrow \quad \zeta_p = N_R \zeta_R$$

complete disentangling time

$\Rightarrow$  chains have to diffuse over a distance

$$\tau_d \cong \frac{l_{pr}^2}{\hat{D}}$$

molecular weight dependence of the disentangling time.

$$\tau_d \sim \zeta_R N_R^3$$

$$\Rightarrow \tau_d \sim M^v \quad v \approx 3.2-3.6$$

disentangling process of the primitive chain

in the case of Rouse motion

$\Rightarrow$  superposition of independent modes

⇒ one time constant :  $\tau_d$  (disentangling time) ⇒ set time scale for complete process

: longest relaxation time

time dependent shear modulus in the terminal flow region

$$G = G_{pl} \Phi\left(\frac{t}{\tau_d}\right)$$

$$\Phi = \frac{8}{\pi^2} \sum_{\text{oddm}} \frac{1}{m^2} \exp\left(-\frac{m^2}{\tau_d} t\right)$$

diffusion coefficient in the tube  $\Leftarrow$  curvilinear diffusion coefficient

⇒ no entanglement

$$D = \frac{kT}{N_R \zeta_R} \sim \frac{1}{M}$$

⇒ reptation model

⇒ disentangling process is associated with a shift of the center of mass of a polymer molecule over a distance in the order of  $l_{pr}$  along the primitive path

⇒ mean-squared displacement.

$$\langle \Delta r_c^2 \rangle \cong R_0^2 = l_{pr} a_{pr}$$

diffusion coefficient in 3-dimensions

$$D = \frac{\langle \Delta r_c^2 \rangle}{6\Delta t}$$

$$D \sim \frac{l_{pr}}{\tau_d} \sim \frac{N_R}{N_R^3} \sim \frac{1}{M^2}$$

the transition from a non-entangled to an entangled polymer melt should be accompanied by a change in the exponent of the power law for the diffusion coefficient

$$\Rightarrow D \sim M^{\nu} \quad \nu = -1 \sim -2$$

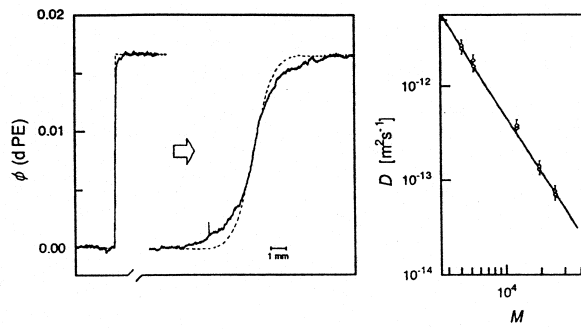


Fig. 6.12. Determination of diffusion coefficients of deuterated PE's in a PE matrix by infrared absorption measurements in a microscope. Concentration profiles  $\phi(x)$  obtained in the separated state at the begin of a diffusion run and at a later stage of diffusive mixing (the *dashed lines* were calculated for monodisperse components; the deviations are due to polydispersity) (*left*). Diffusion coefficients at  $T = 176^\circ\text{C}$ , derived from measurements on a series of d-PE's of different molecular weight (*right*). The *continuous line* corresponds to a power law  $D \sim M^2$ . Work of Klein [68]

# Microscopic Dynamic Model

6.1 the fluctuation-dissipation theorem

6.2 The Rouse – Model

6.3 Entanglement Effect