

NMR signatures of polymer chain dynamics in bulk and under nanoscopic confinements

Rainer Kimmich

University of Ulm

Outline

- Short introduction to NMR methods
- Polymer dynamics theories
- Bulk polymer melts
- Confined polymer melts
- Simulations

"Magnetic Resonance" (magnetic dipole moment in a magnetic field)

$$E = -\vec{\mu} \cdot \vec{B}$$

(Zeeman-energy)

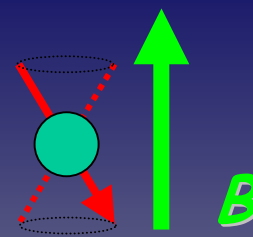
$$\vec{\mu} = \gamma \hbar \vec{I}$$

RF quantum

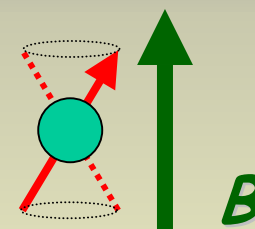
$$\hbar \omega_0$$

B_0

B
(magnetic flux density)



spin $\frac{1}{2}$ "down"



spin $\frac{1}{2}$ "up"

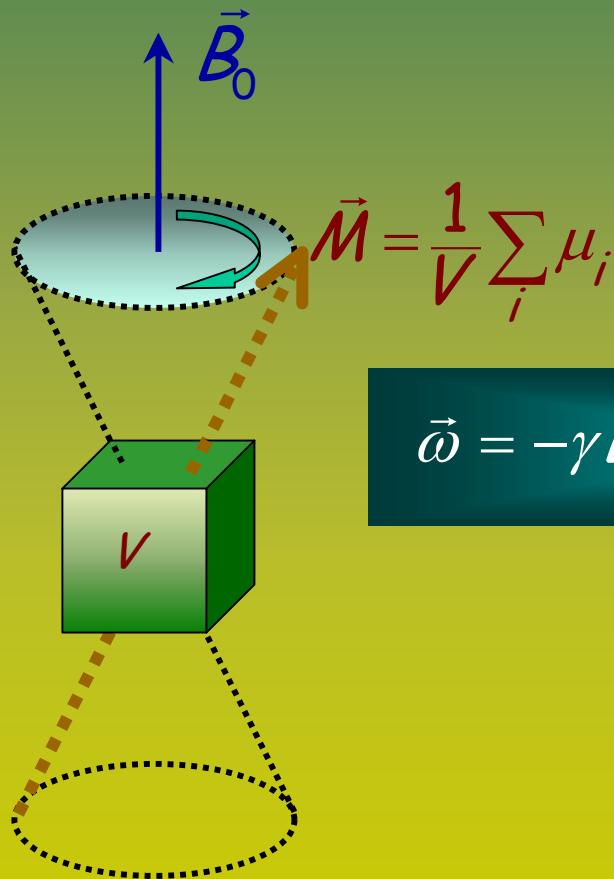
(positive gyromagnetic ratio γ assumed)

$$\text{resonance condition: } \omega_0 = \gamma B_0$$

assume: magnetization tilted against \vec{B}_0

→ precesses with a certain Larmor frequency

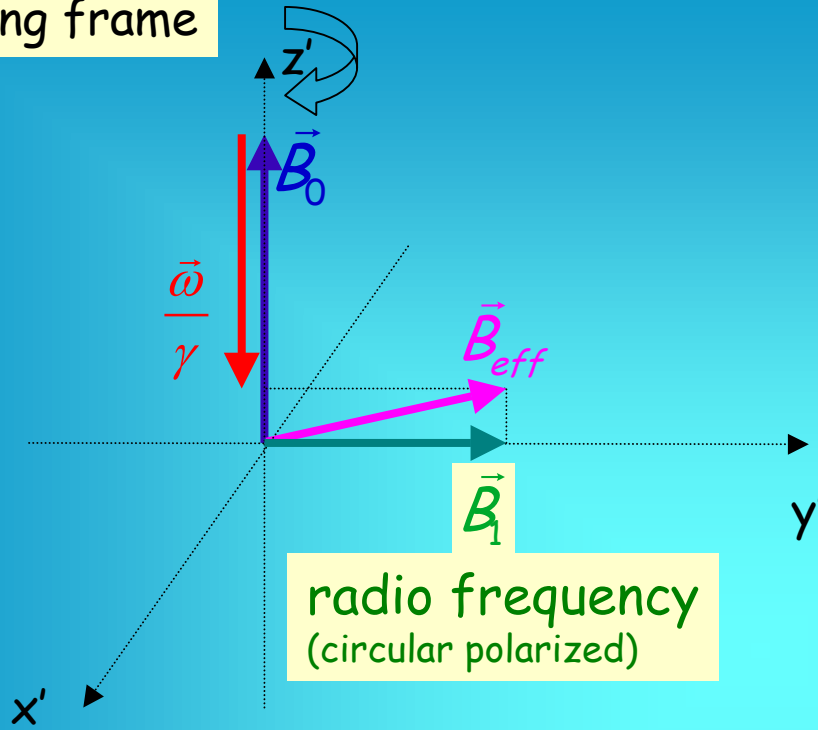
and a certain precession phase



$$\vec{\omega} = -\gamma \vec{B}_0 \text{ and } \varphi = \omega t + \varphi_0$$

How can we generate such "spin coherences"?

Rotating frame

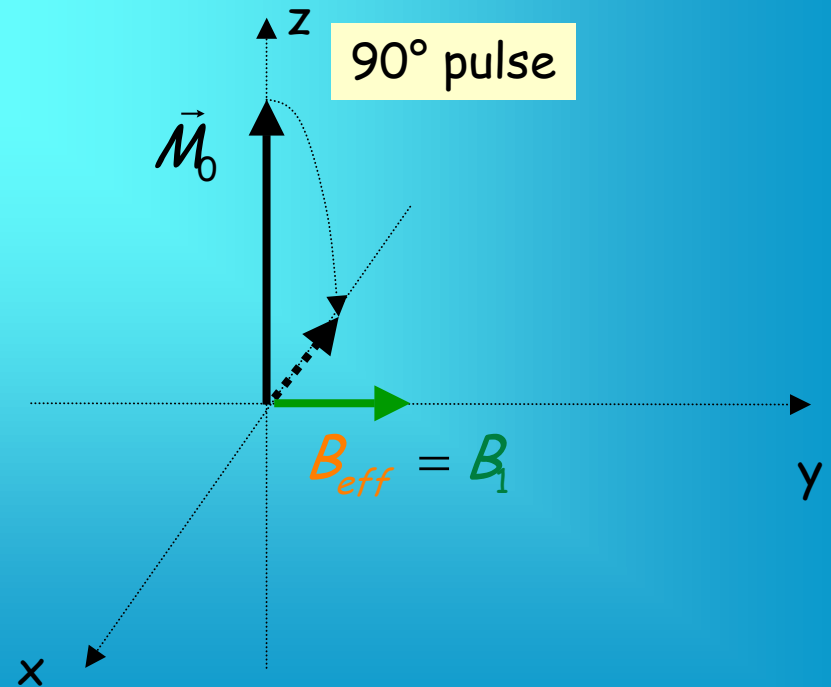
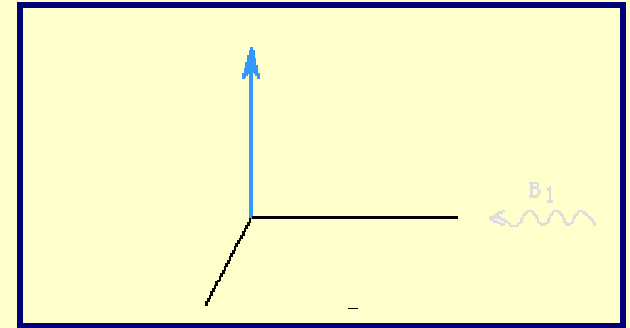


$$B_{eff}(\omega) = \sqrt{\left(B_0 - \frac{\omega}{\gamma}\right)^2 + B_1^2}$$

$$B_{eff}(\omega = \gamma B_0) = B_1$$

$$\vec{\omega}_1 = -\gamma \vec{B}_1$$

Laboratory frame

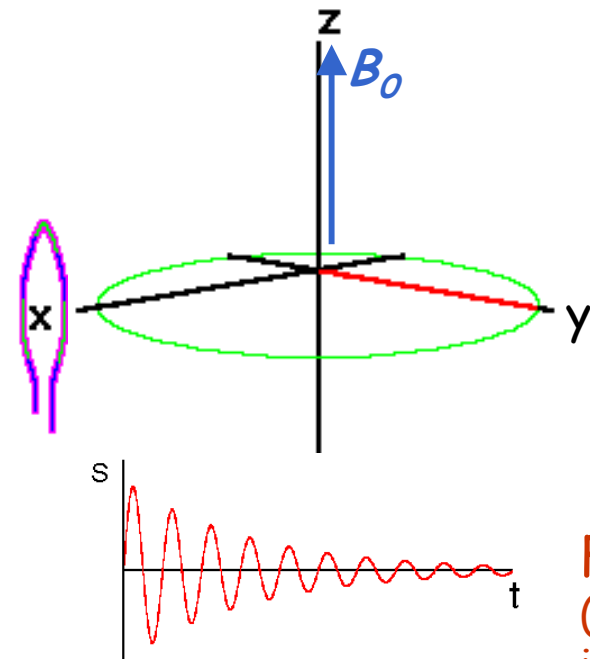


Free induction signal:

magnetization precesses

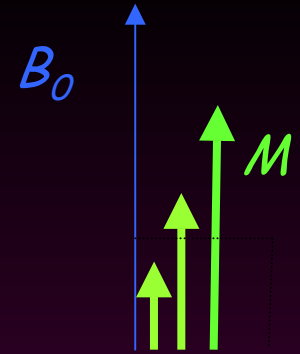
=> flux in an RF pick-up coil oscillates

=> signal voltage is induced



FID
(free
induction
decay)

NMR measurands of interest:



a) the spin-lattice relaxation time T_1

... is the time constant with which thermal equilibrium of the longitudinal magnetization is approached

... is due to energy transfer between spins and mechanical degrees of freedom

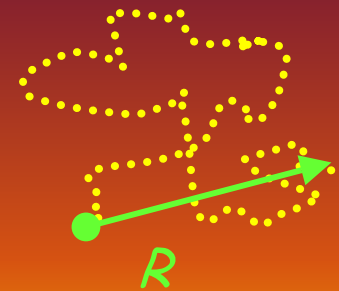
... is caused by induced spin transitions "up" \rightarrow "down" and "down" \rightarrow "up"

... reflects motions of chain segments at the resonance frequency

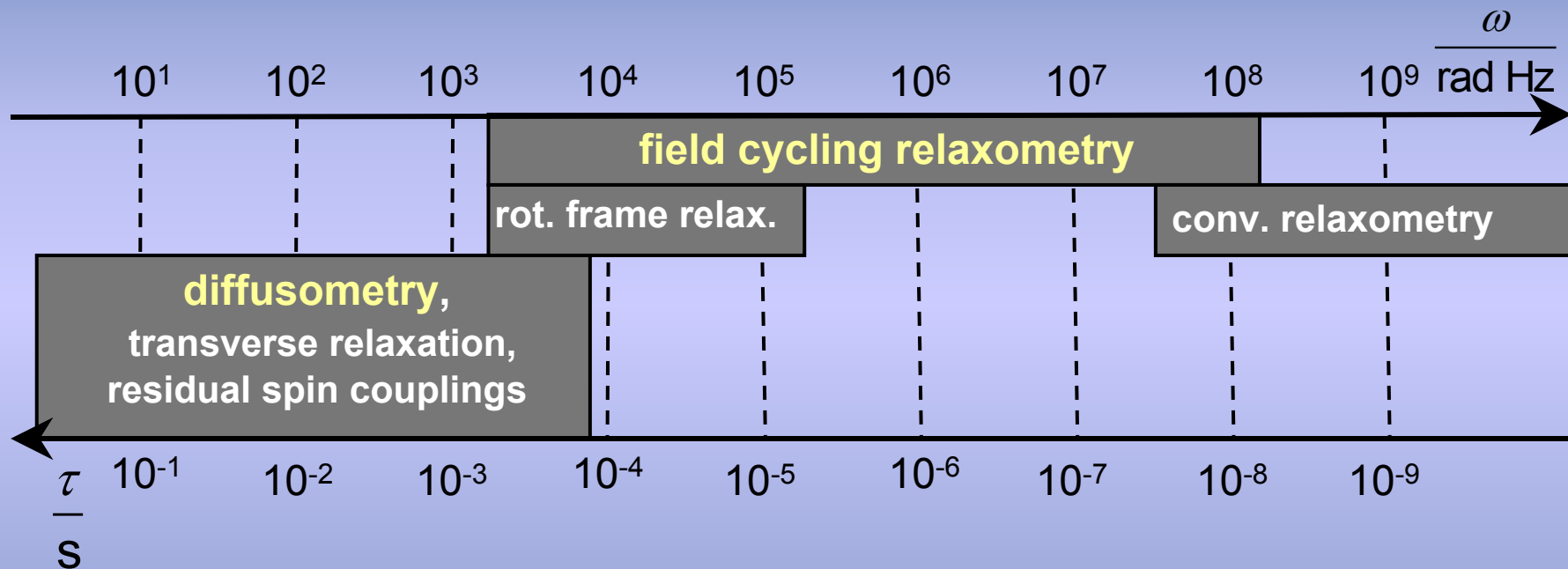
b) the mean square displacement $\langle R^2 \rangle$

... is the second moment of the probability density function

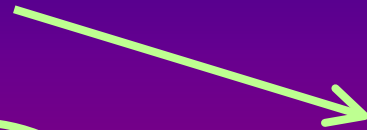
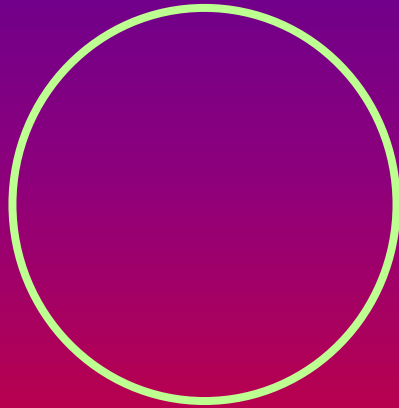
... is due to self-diffusion of chain segments



NMR



translational diffusion



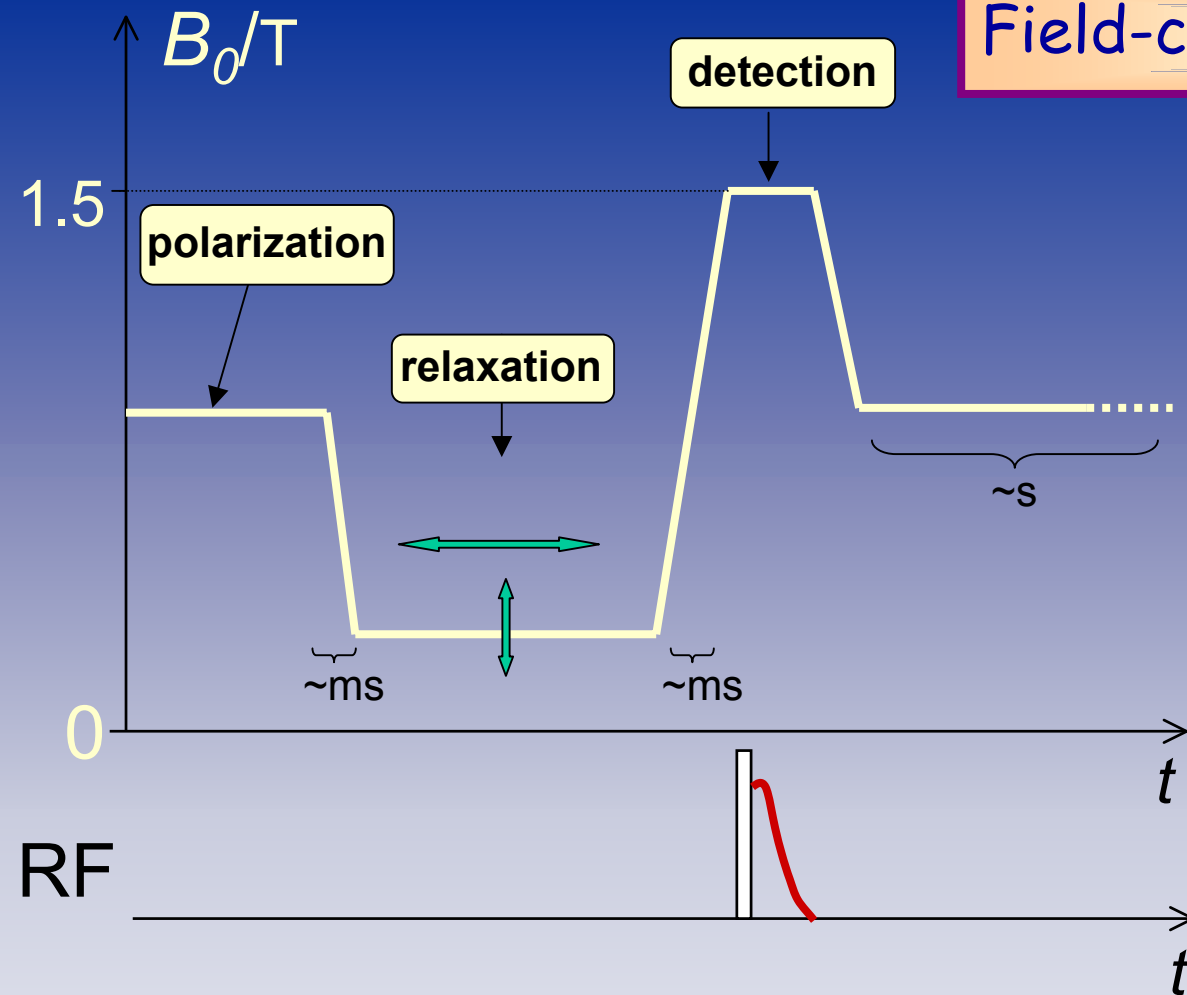
rotational diffusion
of nuclear magnetic
dipole pairs or electric
quadrupoles in
anisotropic hetero-
geneous media



spin-lattice relaxation

Spin-lattice relaxometry

Field-cycling NMR relaxometry



1H
 $10^3 \text{ Hz} < \frac{\omega}{2\pi} < 4 \times 10^8 \text{ Hz}$

2H
 $10^2 \text{ Hz} < \frac{\omega}{2\pi} < 6 \times 10^7 \text{ Hz}$

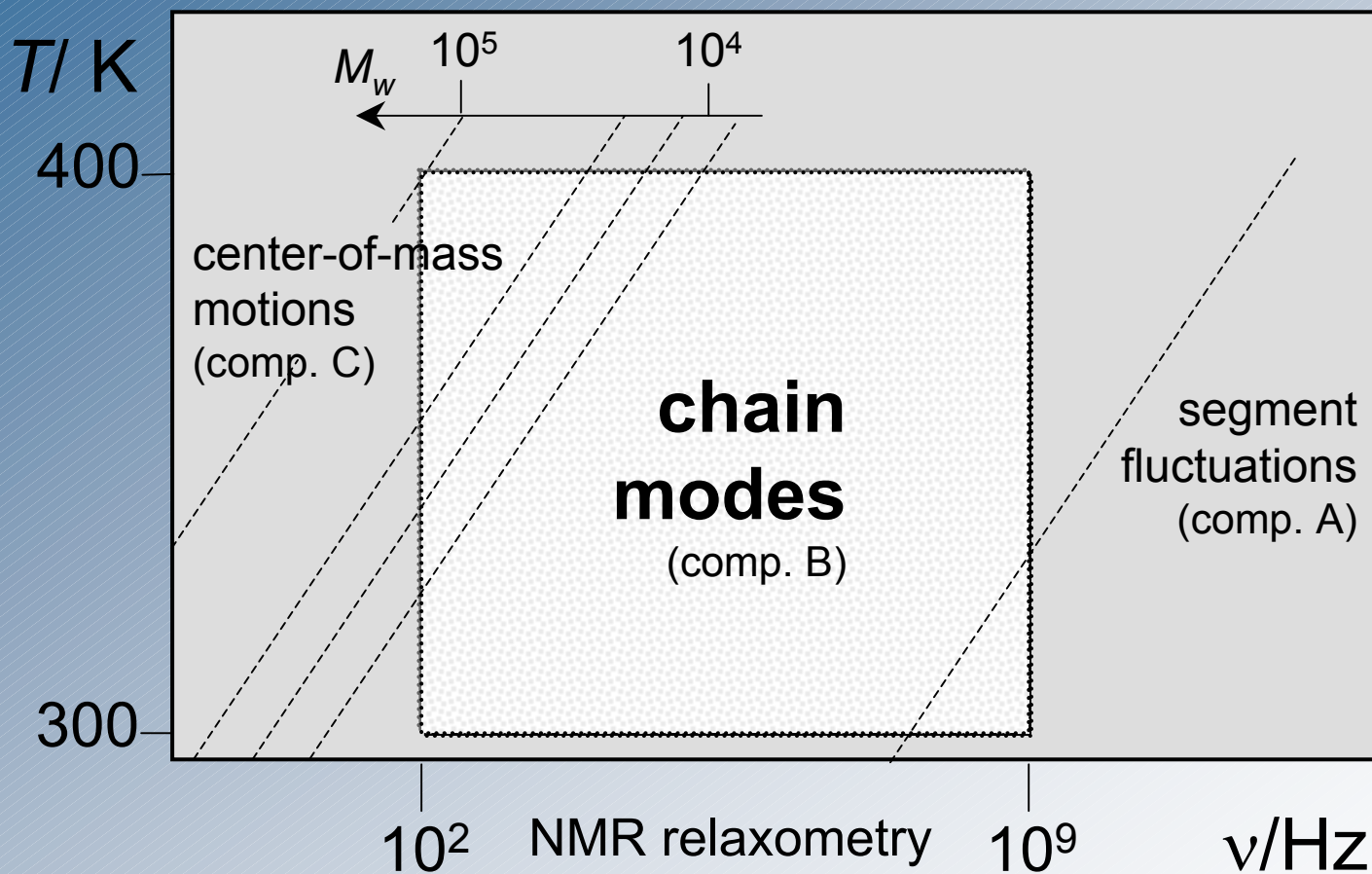
frequency: $\omega = \gamma B_0$

relax. rate: $\frac{1}{T_1} = C [I(\omega) + 4I(2\omega)]$

spectr. dens.: $I(\omega) = F_t \{G(t)\}$

dipolar correlation function:
 $G(t) = \left\langle \frac{y_2^m(0)y_2^{-m}(t)}{r^3(0)r^3(t)} \right\rangle$

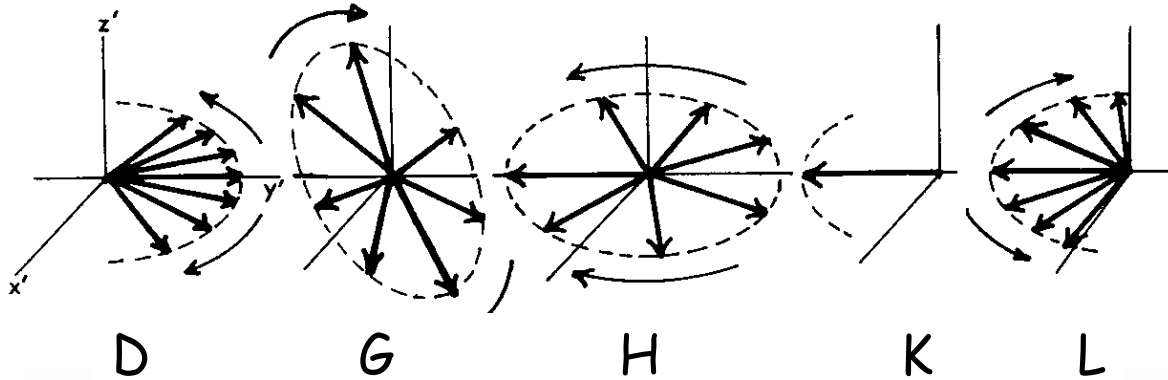
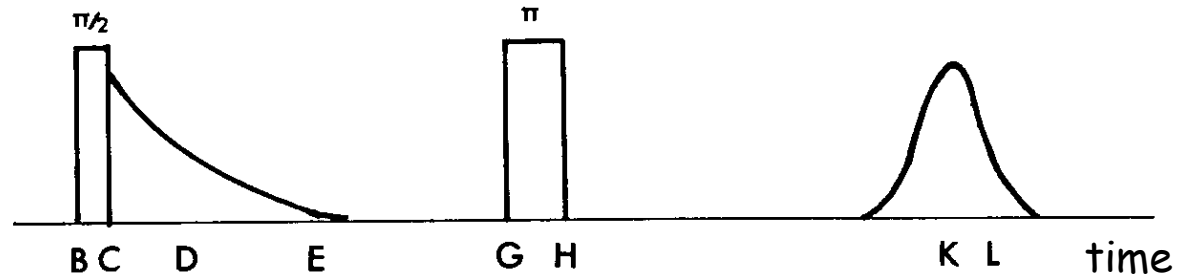
quadrupolar corr. function:
 $G(t) = \langle y_2^m(0)y_2^{-m}(t) \rangle$



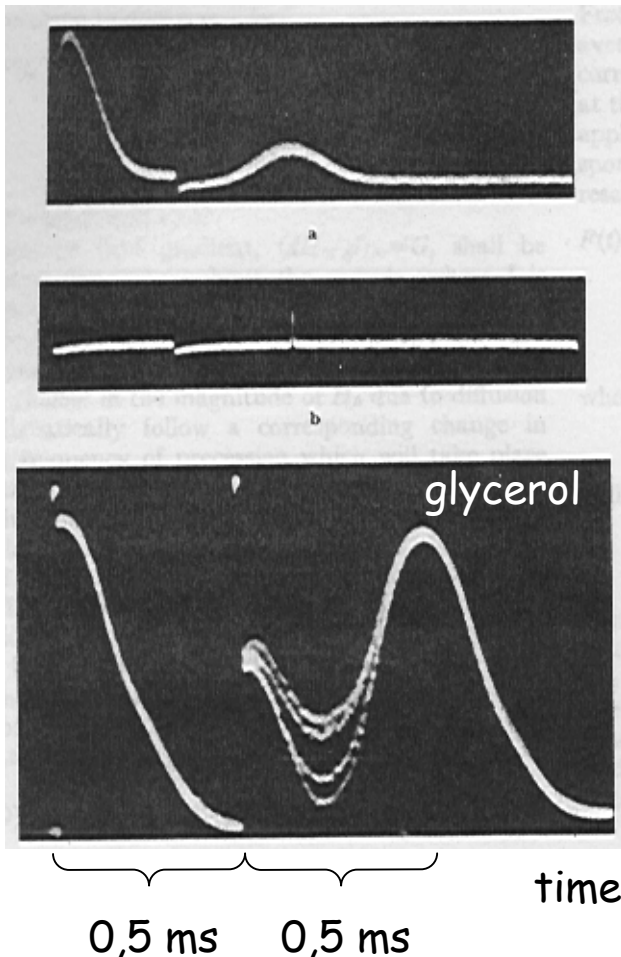
Field-gradient NMR diffusometry

Spin-Echoes

E. L. Hahn, 1950



- reversible refocusing of the transverse magnetization in an inhomogeneous magnetic field
- refocusing incomplete in the presence of translational diffusion
- echo attenuation indicative for translational diffusion



Diffusion measurements in the fringe field of an ordinary superconducting magnet

89 mm

9.4 T,
400 MHz,
 10^{-5} T/m

4.7 T,
200 MHz,
60 T/m



favorable if

- a) T_2 short ($\cong 100 \mu s$)
- b) $\sqrt{\langle R^2 \rangle}$ small ($\cong 100$ nm)

(the physical limit,
i.e. $\approx 10^{-15} \text{ m}^2/\text{s}$,
is reached!)

damping buffers
against building
vibrations

three model theories for polymer chain modes:

- Rouse model

(chain in a viscous medium; no hydrodynamic backflow;
no "entanglements" i.e. $M < M_c$)

- Renormalized Rouse formalism

(chains subject to "entanglements" i.e. $M > M_c$)

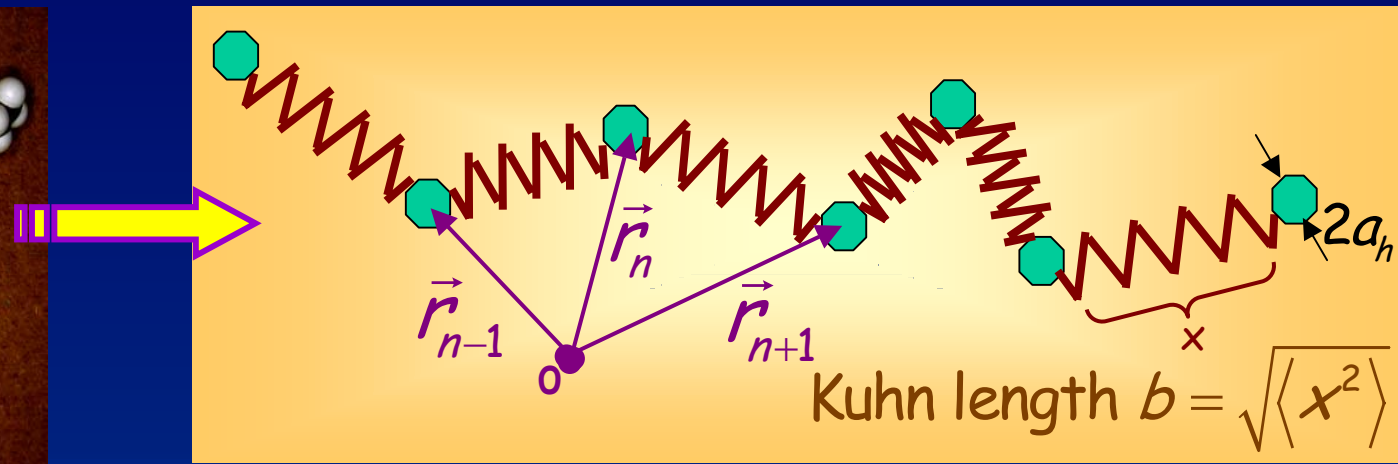
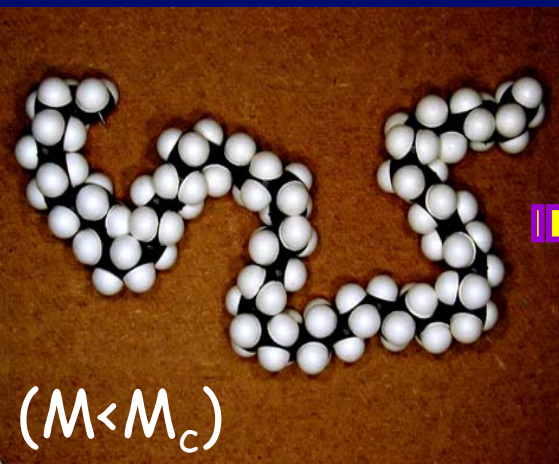
- Tube/reptation concept

(chains confined in nanoscopic tubes)

Rouse model

Rouse model:

Bead-and-spring chain in a viscous medium without backflow



equation of motion for the n -th bead:

$$K(2\vec{r}_n - \vec{r}_{n+1} - \vec{r}_{n-1}) - \zeta \frac{\partial \vec{r}_n}{\partial t} + \vec{F}_n \approx K \frac{\partial^2 \vec{r}_n}{\partial n^2} - \zeta \frac{\partial \vec{r}_n}{\partial t} + \vec{F}_n = 0$$

(entropic spring const. $K = \frac{3k_B T}{b^2}$; friction coeff. $\zeta = 6\pi\eta a_h$; random force \vec{F}_n)

Solution: Superposition of discrete Rouse relaxation modes with time constants

$$\tau_p = \frac{\zeta b^2 N^2}{3\pi^2 k_B T p^2}, \quad \text{where } p = 1 \dots N$$

NMR measurand laws predicted by the Rouse model:

(polymer chains in a viscous medium
without "entanglements" and hydrodynamic backflow)

relaxation: $\frac{1}{T_1} = C_1 + C_2 \tau_s \ln\left(\frac{1}{\omega \tau_s}\right)$ for $\frac{1}{\tau_R} \ll \omega \ll \frac{1}{\tau_s}$

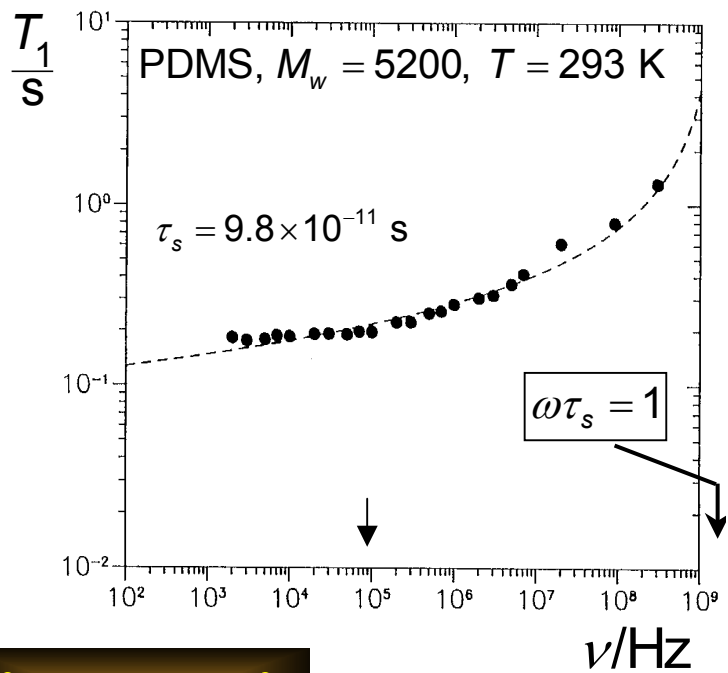
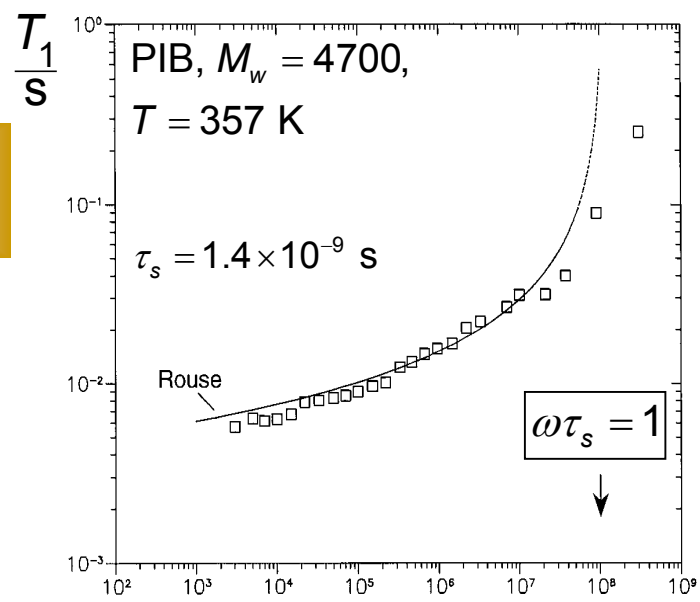
$\frac{1}{T_1} = \frac{1}{T_2} = C_1 + C_2 \tau_s \ln(M^2)$ for $\omega \ll \frac{1}{\tau_R}$

diffusion: $\langle R^2 \rangle \propto M^0 t^{1/2}$ for $\tau_s \ll t \ll \tau_R$

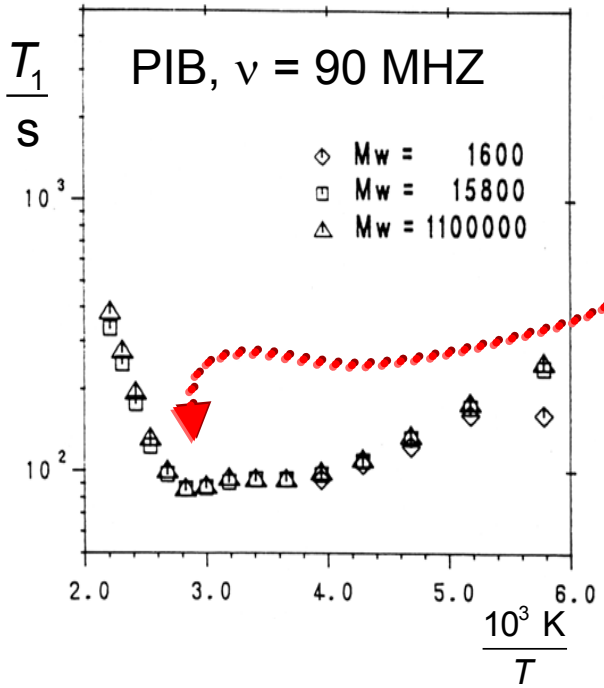
$\langle R^2 \rangle \propto M^{-1} t$ for $t > \tau_R$

(τ_s local segment fluctuation time;
 τ_R longest Rouse relaxation time)

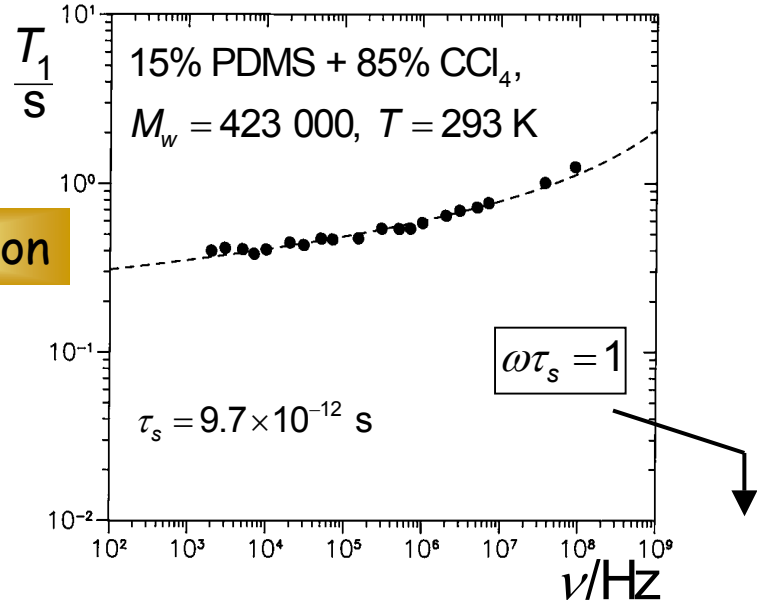
melts
 $M < M_c$



"Rouse"

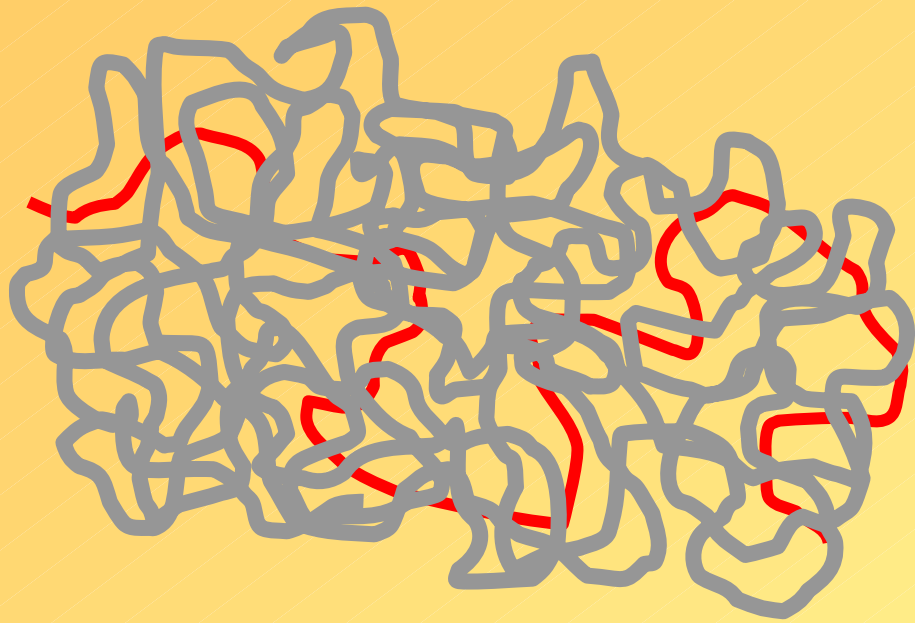


conc. solution



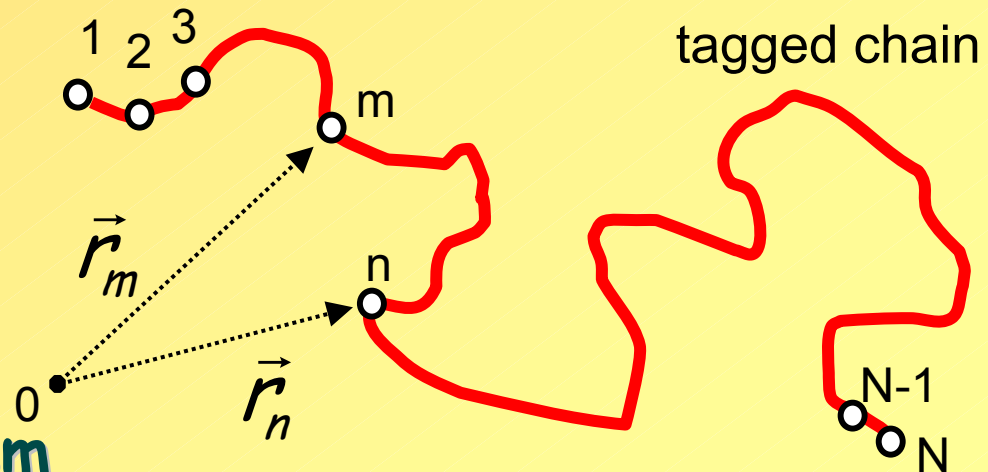
Renormalized Rouse formalism

"Entangled" polymers ($M \gg M_c$)



many-chain problem

"tagged chain" in a "matrix"



Renormalized Rouse formalism

(K. S. Schweizer, J. Chem. Phys. 91(1989)5802;
N. Fatkullin, R. Ki., J. Chem. Phys. 101(1994)822)

Renormalized Rouse formalism

$$\vec{F}_n(t) =$$

$$-\frac{3k_B T}{b^2} \frac{\partial^2 \vec{r}_n(t)}{\partial n^2}$$

random force

entropic spring force

Rouse \Downarrow

$$+ \zeta \frac{\partial \vec{r}_n(t)}{\partial t}$$

$$+ \zeta \int_0^t \sum_m \underbrace{\Gamma_{nm}(t-\tau)}_{\text{memory function}} \frac{\partial \vec{r}_m(t)}{\partial t} d\tau$$

\Downarrow
 matrix/entanglement effects

} friction

Generalized Langevin equation

spin-lattice relaxation

high-mode number limit

$$(p > N/6\pi)$$

$$T_1 \propto M^0 (\omega \tau_s)^{1/2}$$

("region I")

low-mode number limit

$$(p < N/6\pi)$$

$$T_1 \propto M^0 (\omega \tau_s)^{1/5 \dots 1/3}$$

("region II")

diffusion

high-mode number limit

$$(p > N/6\pi)$$

$$\langle R^2 \rangle \propto M^{0+1/4}$$

low-mode number limit

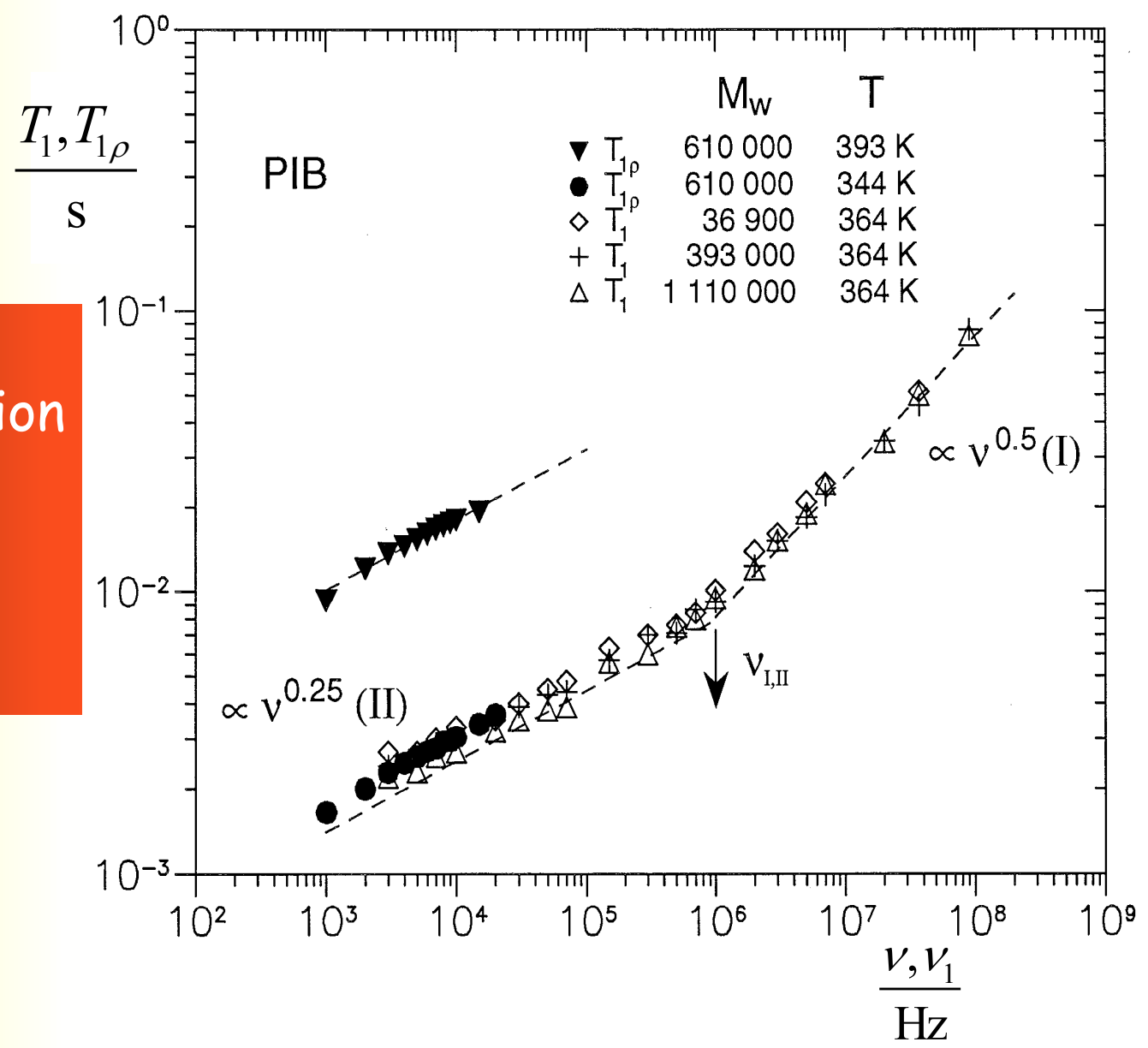
$$(p < N/6\pi)$$

$$\langle R^2 \rangle \propto M^{0+1/3 \dots 2/5}$$

"Renormalized Rouse"

spin-lattice relaxation dispersion of polyisobutylene melts $M_w > M_c$

(H.W. Weber, R. K.,
Macromolecules (26 (1993) 2597)

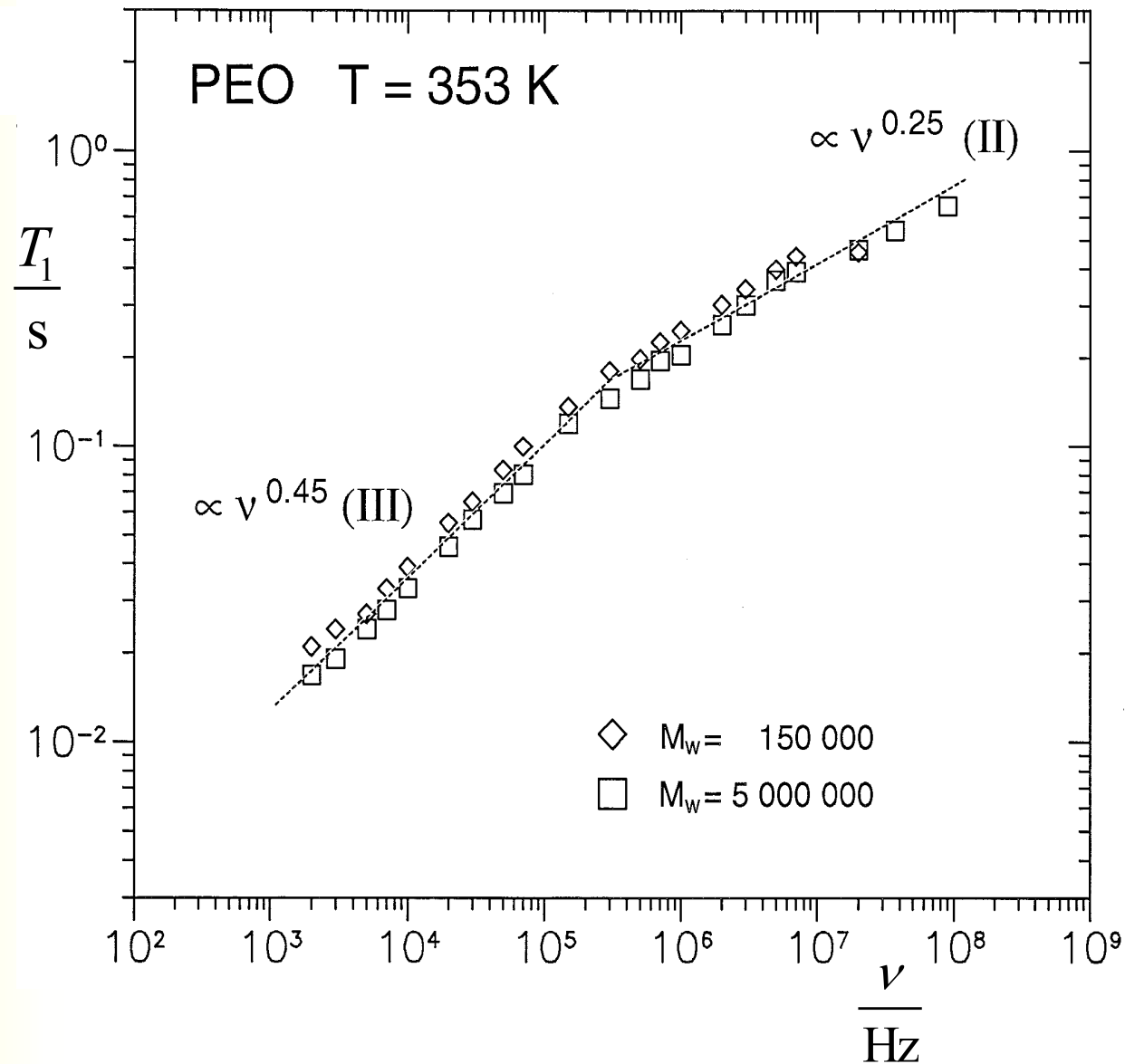


"high mode numbers" \Leftrightarrow "low mode numbers"

region I: $T_1 \propto M_w^{0.0} \nu^{0.5}$ \Leftrightarrow region II: $T_1 \propto M_w^{0.0} \nu^{0.25}$

spin-lattice relaxation dispersion of polyethylene oxide melts

(R. K., N. Fatkullin, R.-O. Seitter, K. Gille, J. Chem. Phys. 98 (1998) 2173)



high mode numbers

region II: $T_1 \propto M_w^0 \nu^{0.25}$



intersegment dipolar couplings

region III: $T_1 \propto M_w^0 \nu^{0.45}$

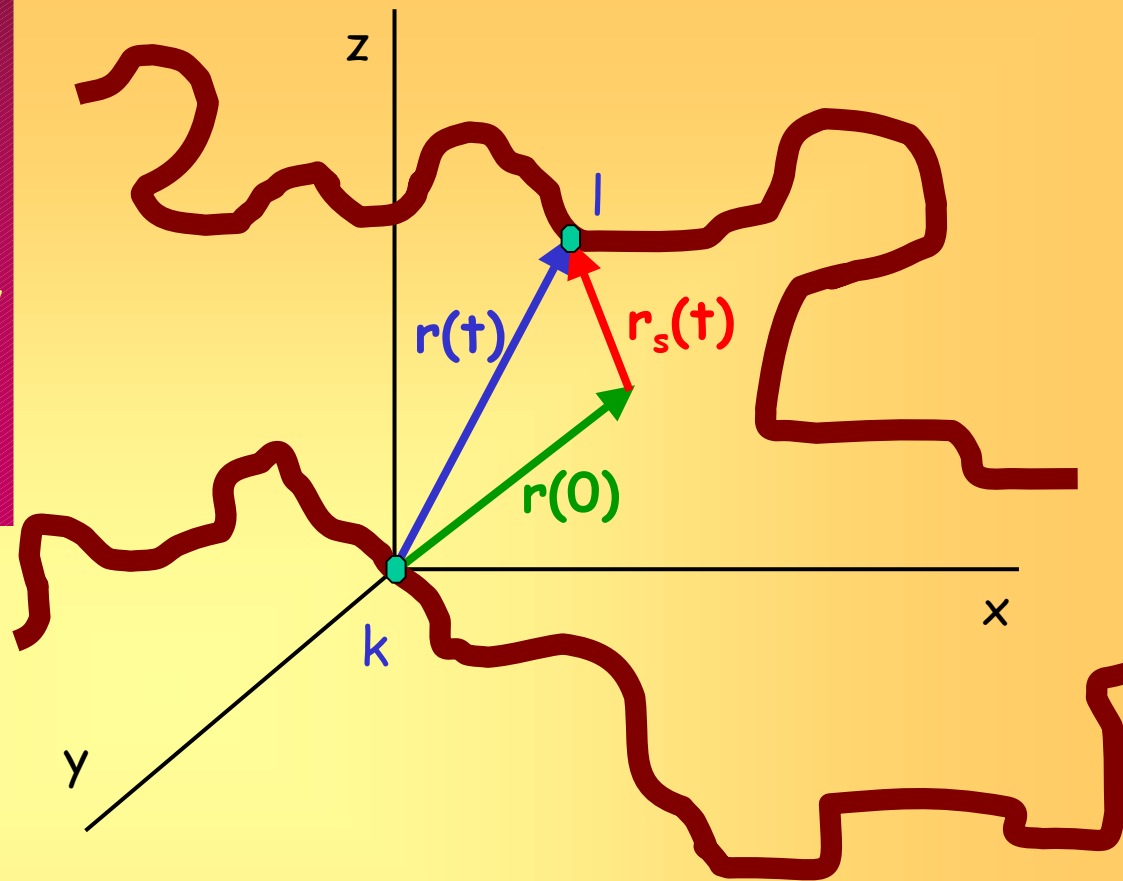
Intersegment

dipolar interactions:

correlation function

of the dipole pair k, l

$$G_{kl}^{(m)}(t) = \left\langle \frac{Y_{2,m}^*(t) Y_{2,m}(0)}{r^3(t) r^3(0)} \right\rangle$$



probability that
dipole l is still
in $V \propto r^3(0)$
around its
initial position



mean square displacement
relative to dipole k in the
low-mode number limit:

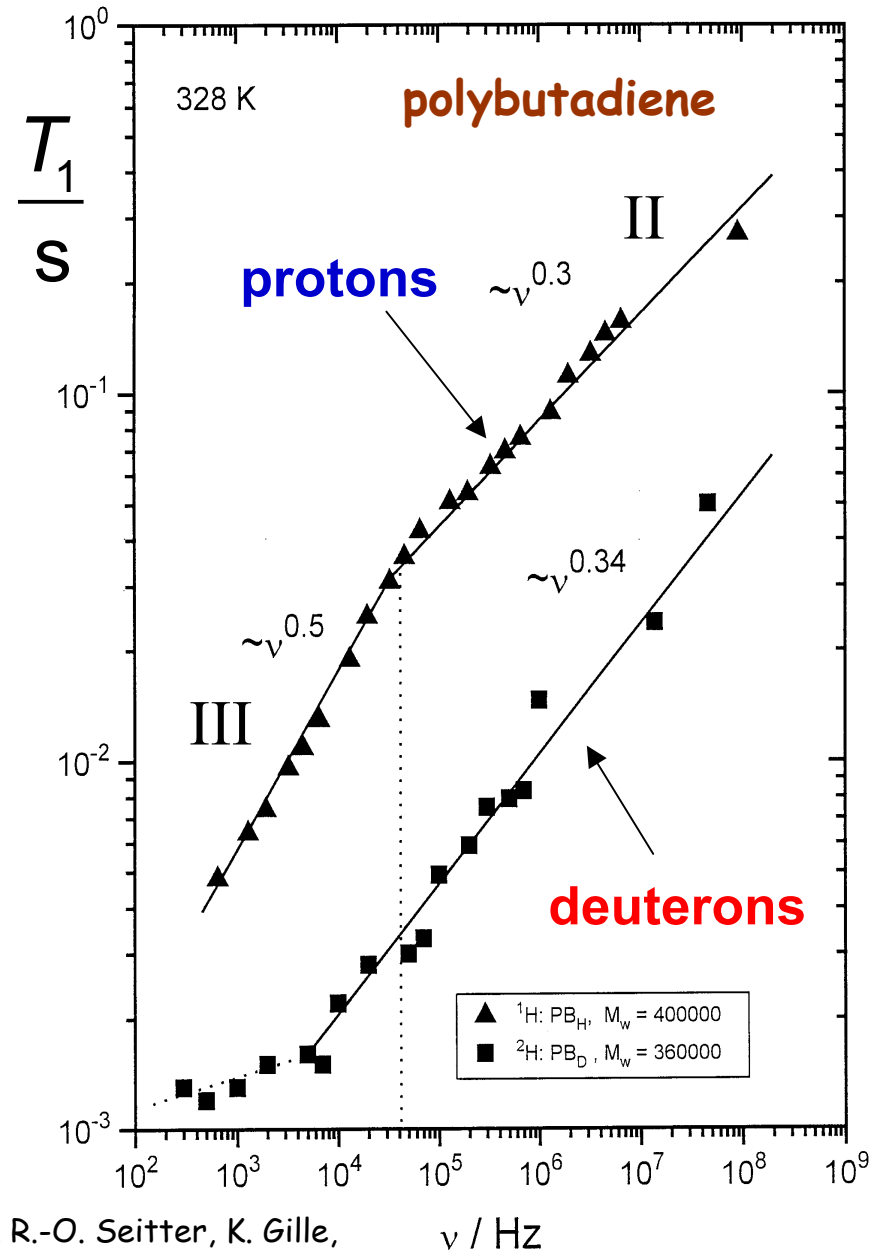
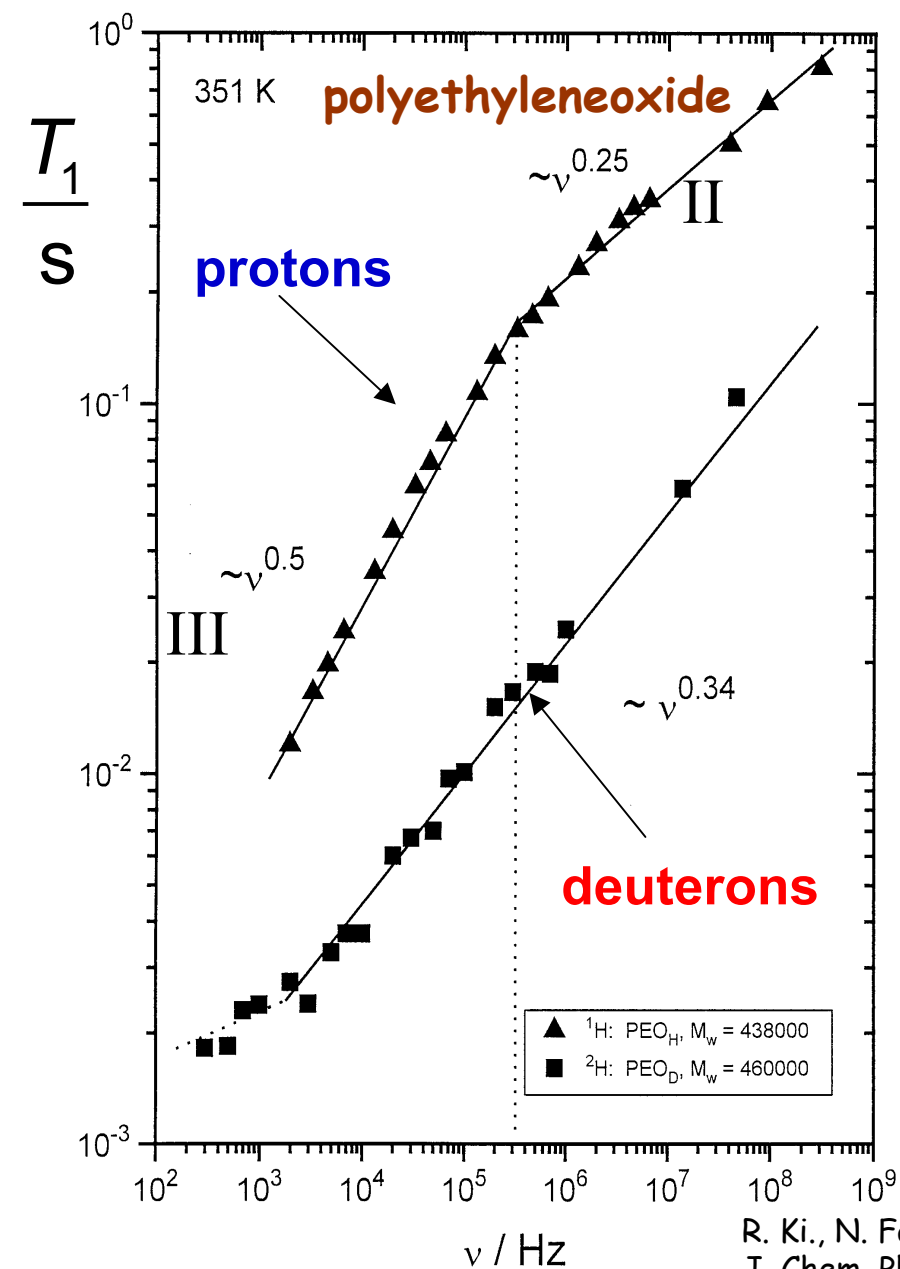
$$\langle r_s^2(t) \rangle \propto t^{1/3 \dots 2/5}$$

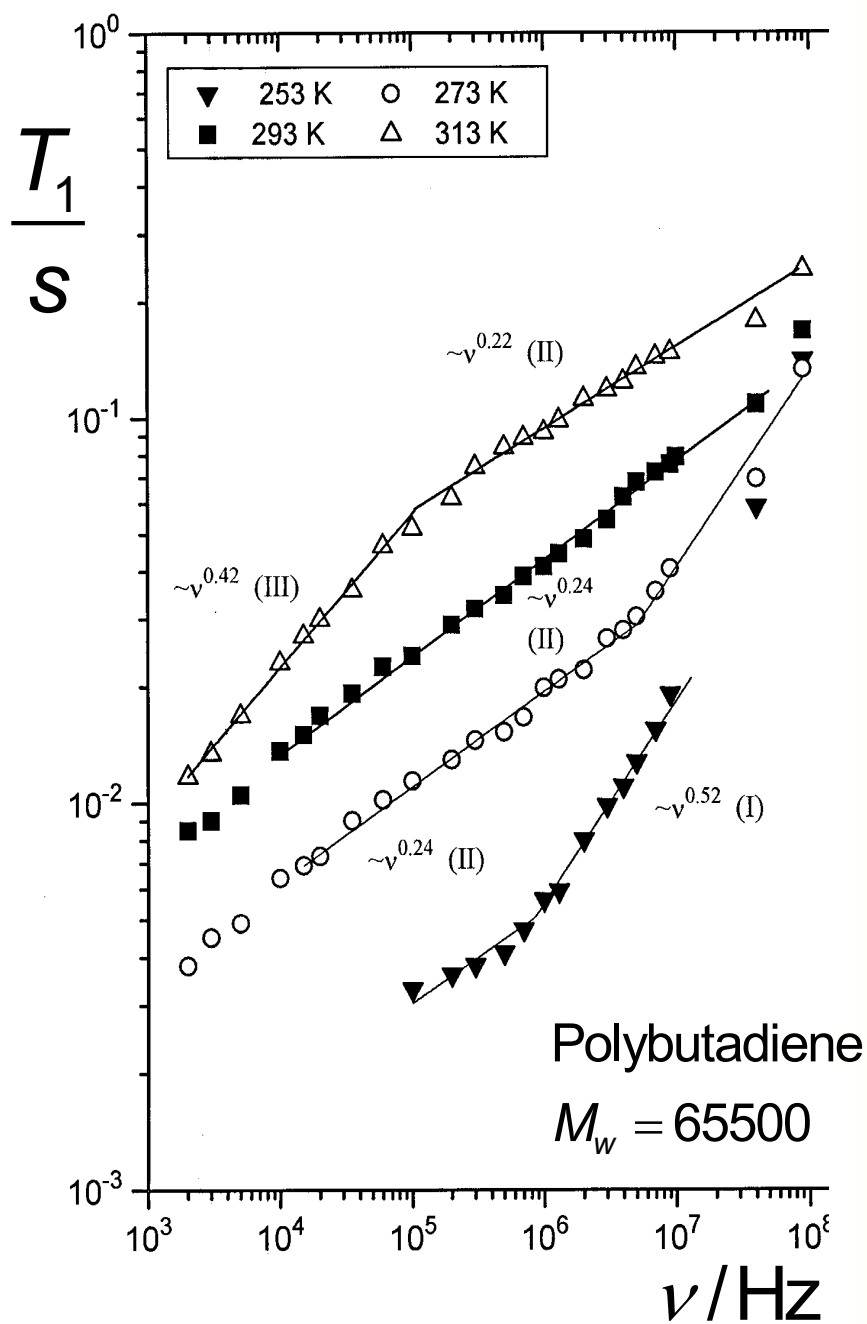


region III:

$$T_1^{\text{inter}} \propto \nu^{0.4 \dots 0.5}$$

protons: intra- and intersegment interactions
 deuterons: only intrasegment interactions





All three T_1 dispersion regions
 are shifted into the experimental
 window one by one upon
 temperature variation

spin-lattice relaxation
dispersion of polymer melts
with $M_w \gg M_c$
("entangled" polymers)

regions I, II, III
from high to low
frequencies or low to high
temperatures

region I: $T_1 \propto M_w^{0 \pm 0.05} \nu^{0.5 \pm 0.05}$

region II: $T_1 \propto M_w^{0 \pm 0.05} \nu^{0.25 \pm 0.1}$

region III: $T_1 \propto M_w^{0 \pm 0.05} \nu^{0.45 \pm 0.05}$

a) limits b) power laws c) universal

based on data for
PE, PEO, PDMS, PDES,
PIB, PTHF, PS, PB

regions I, II, III
do not coincide
with the Doi/Edwards limits
of the reptation concept!

Rouse

→ short chains in bulk melts

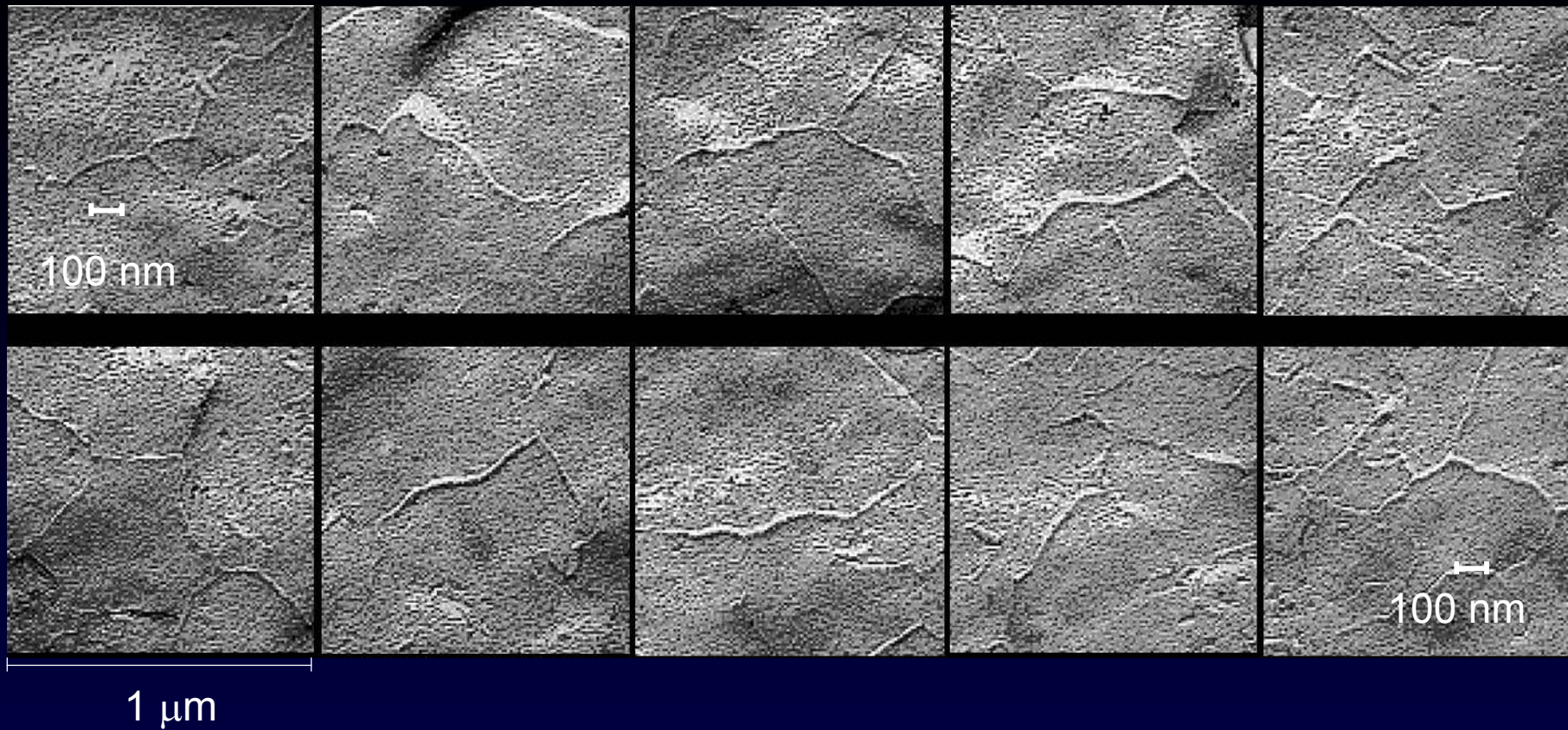
Ren. Rouse

→ long chains in bulk melts

Tube/reptation

→ ?

Polymer chain modes
under nanoscopic constraints

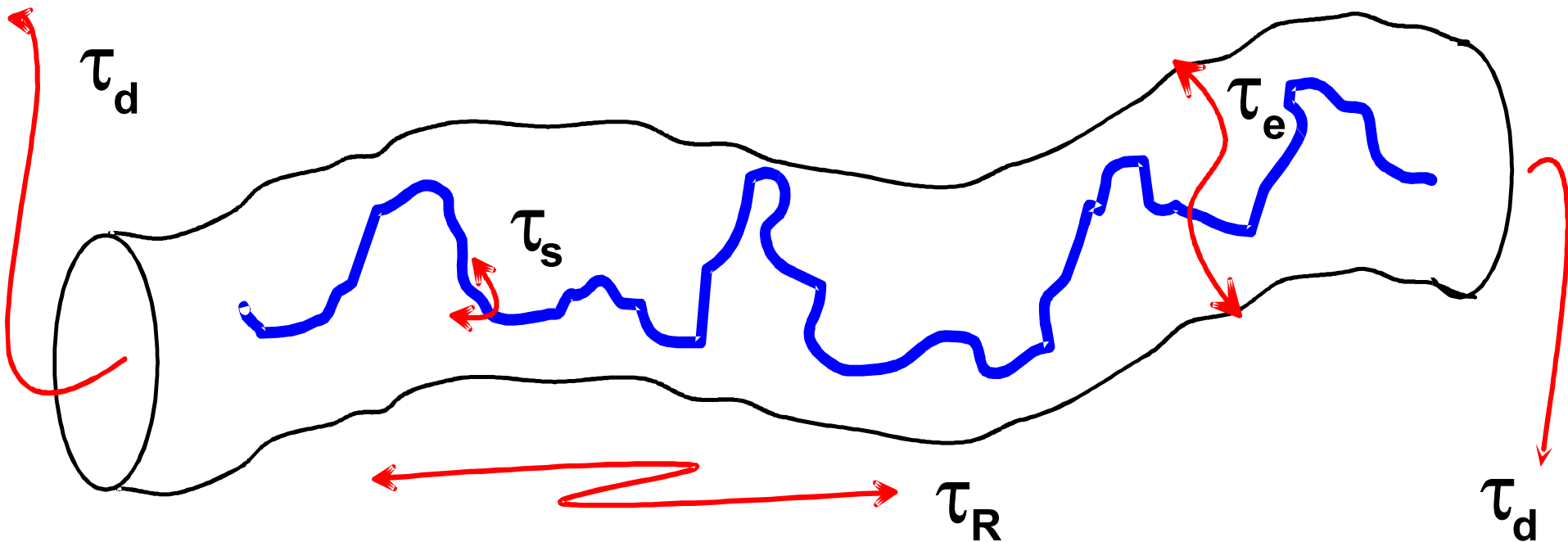


TEM, replica

pore width 10 nm

Linear polyethyleneoxide (PEO; $M_w=6000$)

in solid cross-linked polyhydroxyethylmethacrylate (PHEMA)



Doi/Edwards tube/reptation concept

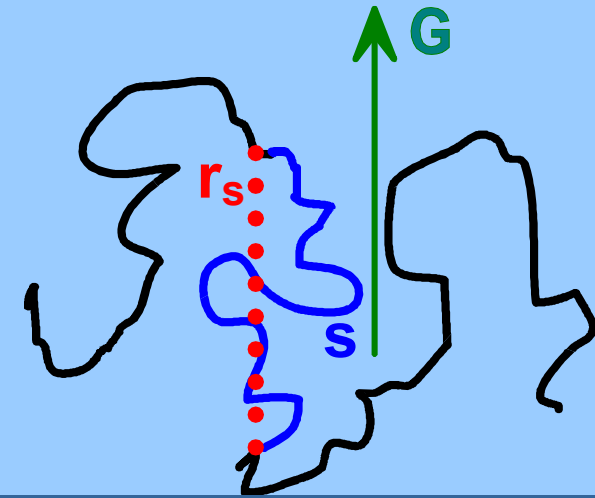
- Curvilinear displacements along tube: $s = s(t)$ for $\tau_e < t < \tau_d$
- Characteristic laws for $\langle R^2(t) \rangle$ and $T_1(\omega)$
- Originally: **Fictitious** tube is to represent "chain entanglements"
- Here: **Real "tube"** formed by nanopores in a solid polymer matrix
- Equivalent theory, same parameters

Predictions of the tube/reptation concept

| | limits | mean squared segment displacement | spin-lattice relaxation time |
|---------------------|---------------------------------------|--|---|
| (I) _{DE} | $\tau_s \ll (t, 1/\omega) \ll \tau_e$ | $\langle R^2 \rangle \propto M^0 t^{1/2}$ | $T_1 \propto -M^0 / \ln(\omega \tau_s)$ |
| (II) _{DE} | $\tau_e \ll (t, 1/\omega) \ll \tau_R$ | $\langle R^2 \rangle \propto M^0 t^{1/4}$ | $T_1 \propto M^0 \omega^{3/4}$ |
| (III) _{DE} | $\tau_R \ll (t, 1/\omega) \ll \tau_d$ | $\langle R^2 \rangle \propto M^{-1/2} t^{1/2}$ | $T_1 \propto M^{-1/2} \omega^{1/2}$ |
| (IV) _{DE} | $\tau_d \ll (t, 1/\omega)$ | $\langle R^2 \rangle \propto M^{-2} t^1$ | $T_1 \propto M^{-\alpha} \omega^0$ |

NMR diffusometry and the tube/reptation concept

$$E(\vec{k}, t) = \left\langle e^{i\vec{k} \cdot \vec{r}(t)} \right\rangle_r = \underbrace{\left\langle e^{i\vec{k} \cdot \vec{r}_s(t)} \right\rangle_{r_s}}_{E_s(\vec{k}, t) \text{ segments}} \underbrace{\left\langle e^{i\vec{k} \cdot \vec{r}_c(t)} \right\rangle_{r_c}}_{\exp(-k^2 D_c t) \text{ center-of-mass}}$$



(wave vector $\vec{k} = \gamma \vec{G} \tau$)

• anomalous segment diffusion

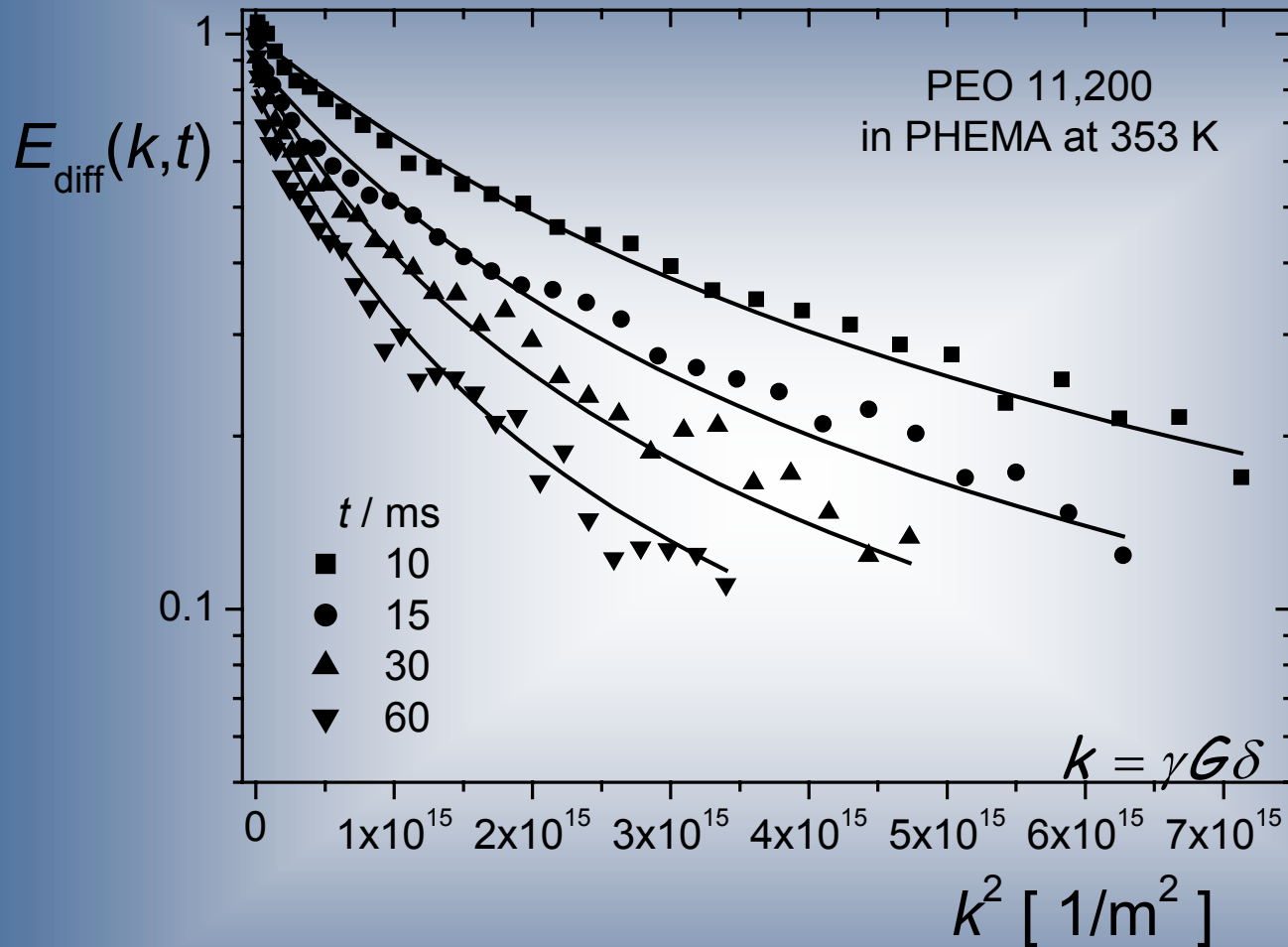
$$E_s(\vec{k}, t) = \left\langle \underbrace{\int \left(\frac{4\pi}{3} d_t |s| \right)^{-3/2} e^{r_s^2/d_t |s|} e^{i\vec{k} \cdot \vec{r}_s(t)} d^3 \vec{r}_s}_{\text{average over all } r_s \text{ for a given } s} \right\rangle_{\text{average over all } s} = \exp \left\{ \frac{k^4 d_t^2 \langle s^2(t) \rangle}{72} \right\} \text{erfc} \left\{ \frac{k^2 d_t \sqrt{\langle s^2(t) \rangle}}{6\sqrt{2}} \right\}$$

• mean square curvilinear segment displacements

$$\langle s^2(t) \rangle = \frac{2D_0 t}{N + \frac{12d_t^2 D_0 t}{N^2 b^4}} + \frac{2b\sqrt{D_0 t}}{\sqrt{3\pi} + 18 \frac{\sqrt{D_0 t}}{Nb}}$$

d_t tube diameter
(b, N, D_0 known)

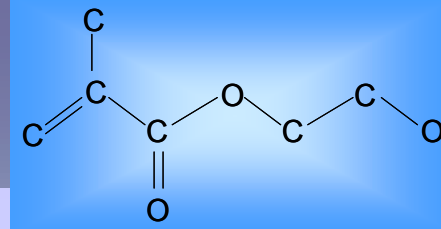
typical echo attenuation curves measured in linear PEO ($M_w=11,200$) confined in PHEMA pores at 80°C (fringe field technique; 60 T/m; 200 MHz)



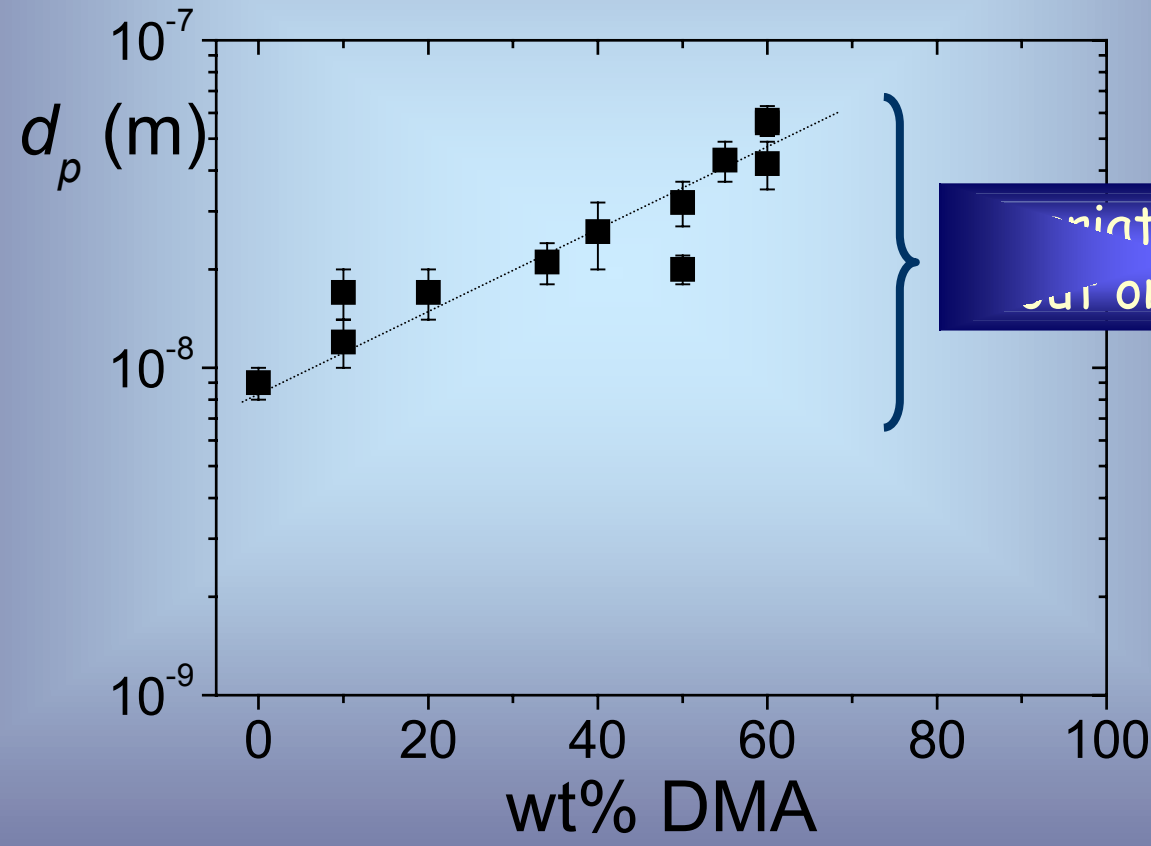
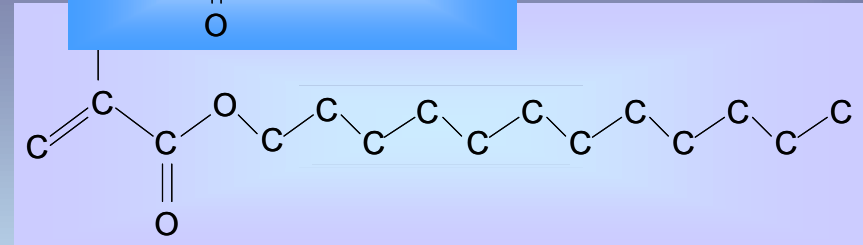
echo attenuation formalism:
(N. Fatkullin, R. Ki., Phys. Rev. E 52 (1995) 3273)

1 fitting parameter:
pore diameter $d_{\text{pore}} = (8 \pm 1) \text{ nm}$

solid matrix consists of cross-linked hydroxyethyl-methacrylate (= HEMA)



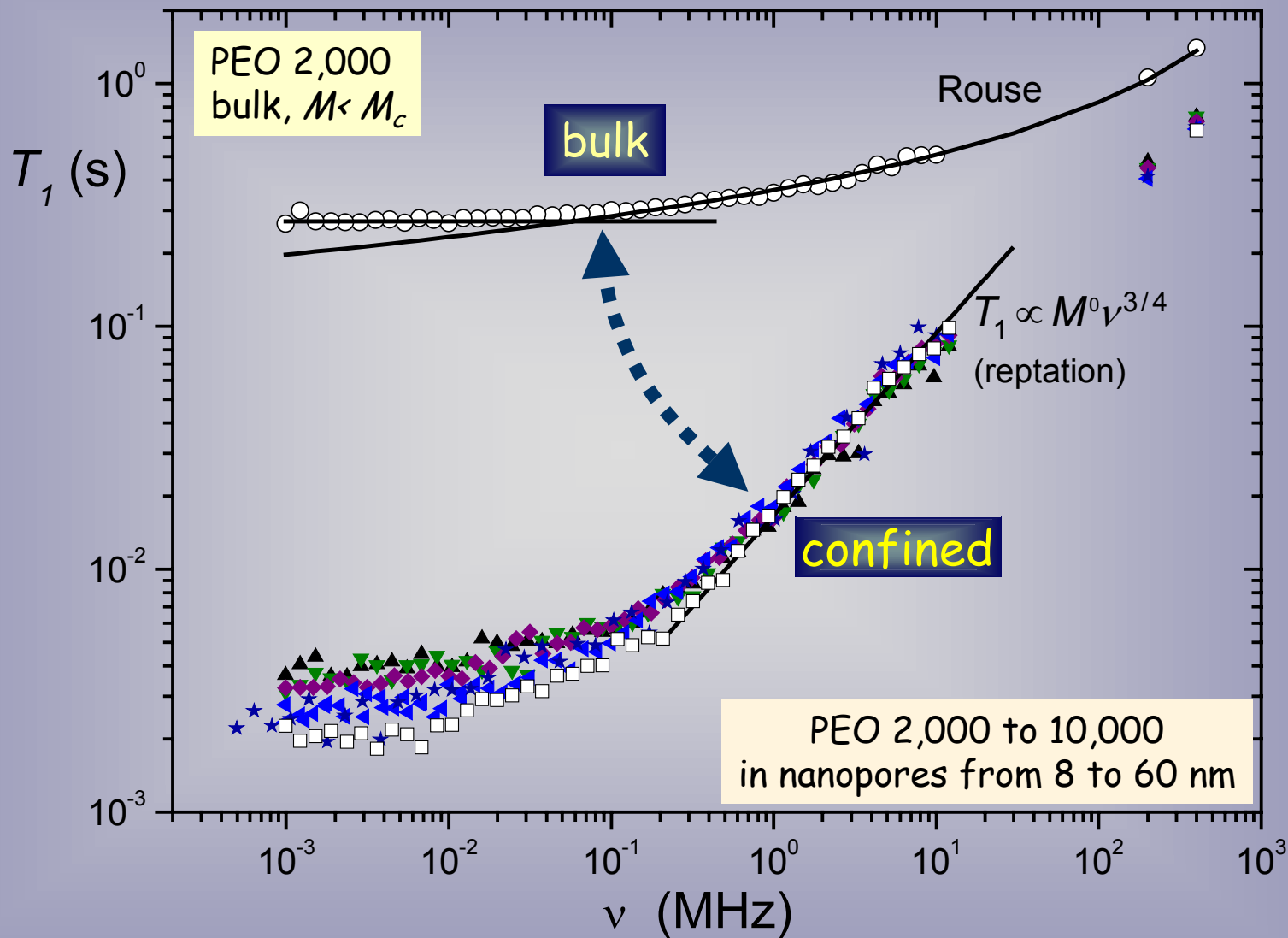
and dodecyl-methacrylate (= DMA)



(attenuation formalism modified for finite pore width $d_p > 10$ nm !)

"tube" = pore diameter d_p (on 10 ... 300 ms time scale)

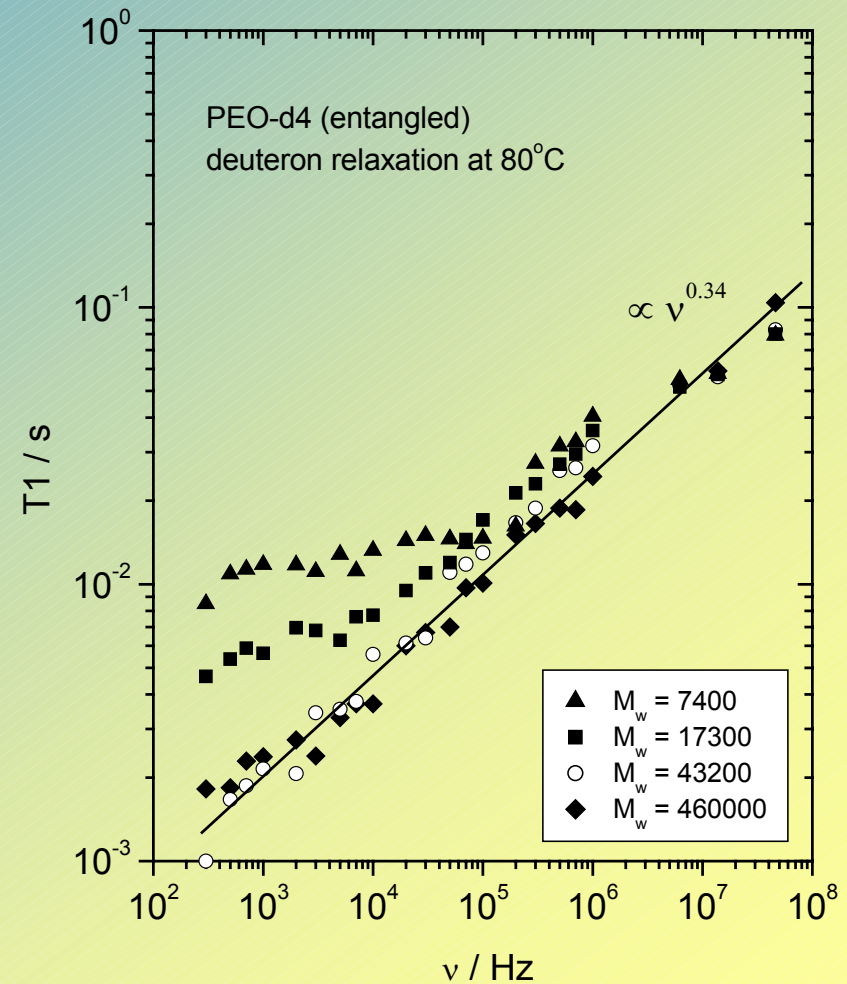
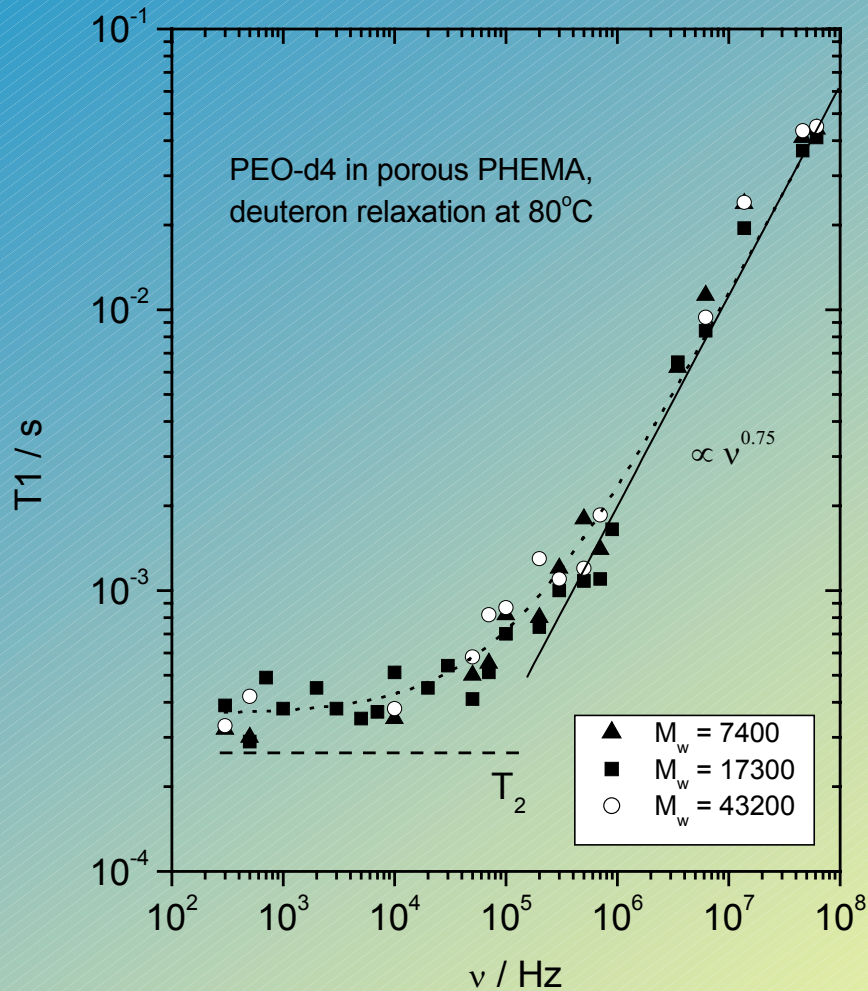
Field-cycling NMR relaxometry at 85°C

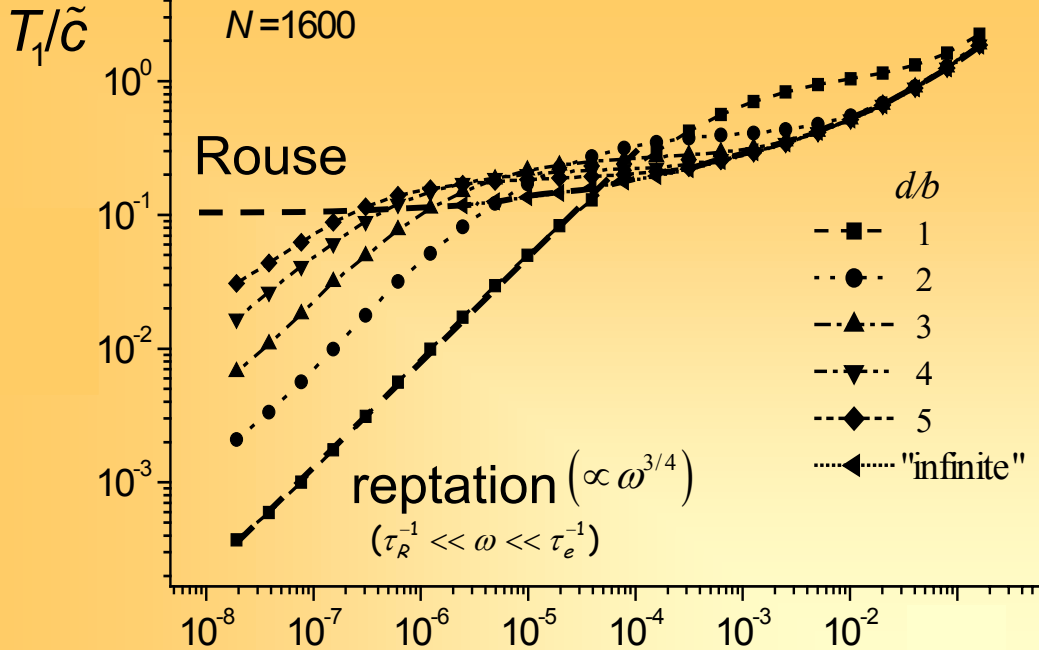


polymers confined
in pores



melts in bulk
("entangled" polymers)

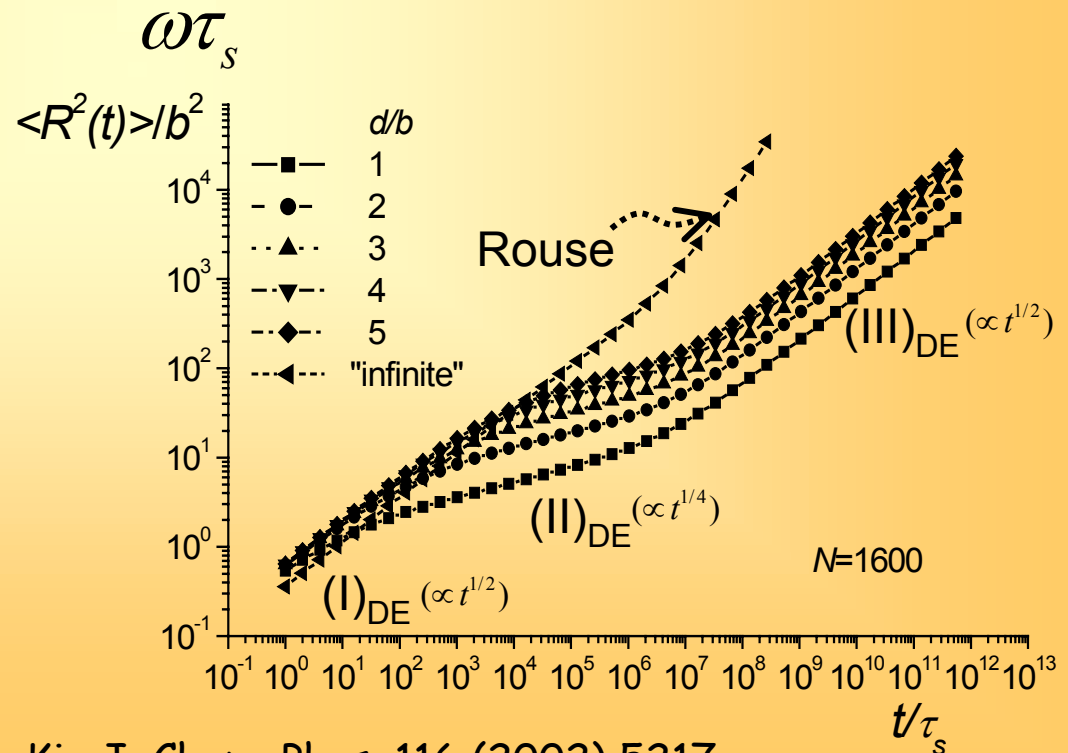




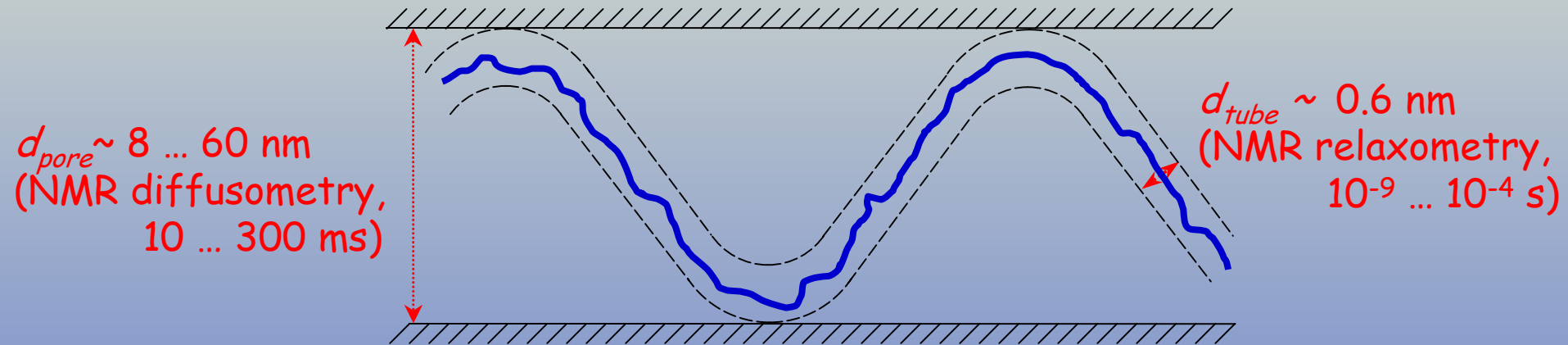
crossover from
reptation
to
Rouse
chain dynamics
with increasing
tube diameter

a) harmonic radial
potential theory

b) and Monte Carlo
simulations of a
modified Stockmayer
chain model in a
tube with hard walls)



experimental findings



the "corset effect"

The system dimensions

mobile linear polyethylene oxide:

PEO 2,000: $R_F = 4$ nm

PEO 10,000: $R_F = 9$ nm



nearest neighbor distance
0.5 nm

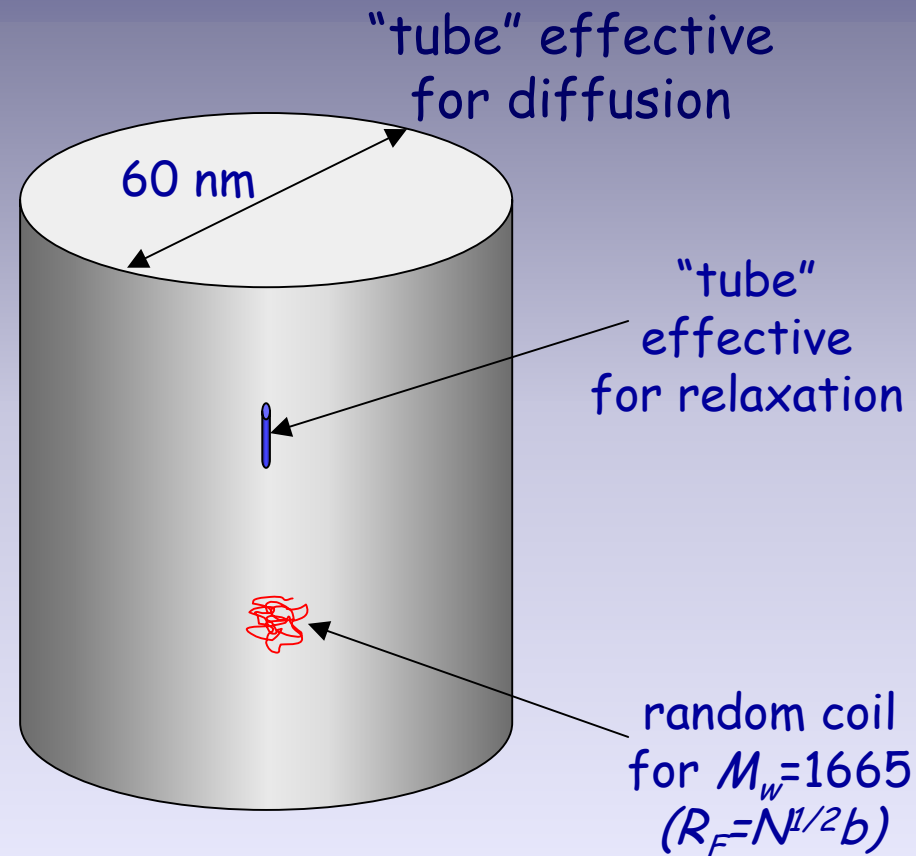
rigid crosslinked HEMA+DMA
methacrylate matrix:

pore diameters from 8 to 60 nm

that is:

... up to 122 PEO diameters

... up to 15 PEO radii of gyration



the corset effect - a finite size phenomenon

conformational changes require fluctuations of the free volume
~ fluctuations of the number of segments in the available volume

$$\langle n^2 \rangle - \langle n \rangle^2 = k_B T \rho_m \kappa_T \langle n \rangle$$

↑
compressibility

$\langle n \rangle$ small \rightarrow segments can only be displaced along the contour line of the chain

effective tube diameter

$$d_{\text{tube}} \approx \sqrt{b^2 \rho_m k_B T \kappa_T}$$

bulk dynamics for

$$d_{\text{pore}} \square \left(\frac{b^3}{k_B T \kappa_T} \right)^{1/3} R_F \approx 10 R_F$$

Summary

"bulk dynamics" versus (nanoscopically) "confined dynamics"

polymer melts, $M_w < M_c$, bulk,
Rouse dynamics

polymer melts, $M_w > M_c$, bulk,
Renormalized Rouse dynamics

polymer melts, M_w arbitrary,
nanoscopically confined,
reptation dynamics

"tube":
= "pore" for $10^{-2} \dots 3 \cdot 10^{-1} \text{ s}$
(8 ... 60 nm)
= "tight tube" for $10^{-9} \dots 10^{-4} \text{ s}$
(~0.6 nm)

rigid wall is sensed over at least
60 polymer chain diameters

"corset effect":

impenetrable pore walls

+ excluded volume of polymer chains

+ low compressibility

predicted confined-to-bulk
crossover

for pore diameters $\gg 10 R_F$

Collaborators:

Esteban Anoardo

Ioan Ardelean

Uwe Beginn

Bogdan Buhai

Alexei Denissov

German Farrher

Nail Fatkullin

Elmar Fischer

Ravinath Kausik

Elke Kossel

Margarita Kroutieva

Carlos Mattea

Hernan Tiraboschi



Funding:

Deutsche Forschungsgemeinschaft

Alexander-von-Humboldt Foundation

Volkswagen Foundation

Recent review articles from our group:

a) Diffusion Methods

I. Ardelean, R. Kimmich, Ann. Rep. NMR Spectr. 49 (2003) 43

I. Ardelean, R. Kimmich, Isr. J. Chem. 43 (2003) 9

b) Field-cycling NMR Relaxometry

R. Kimmich, E. Ansaldo, Progr. NMR Spectroscopy, 2004, in press

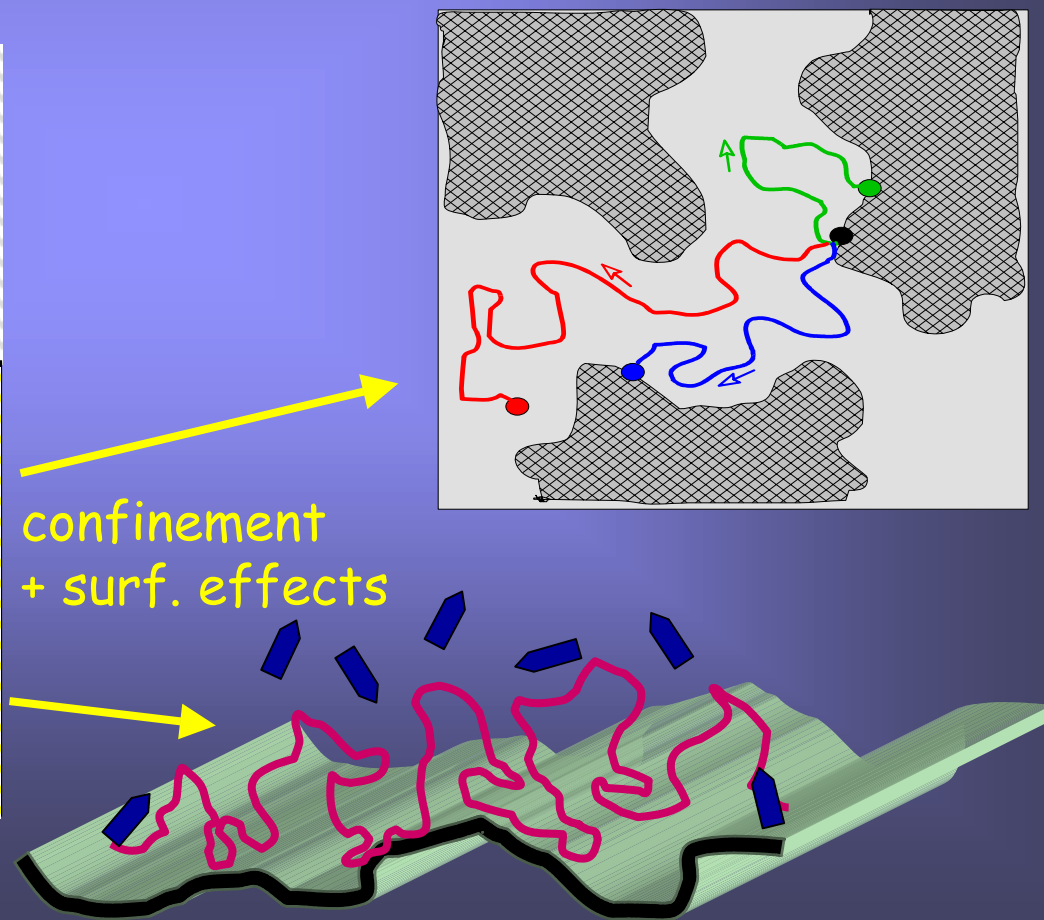
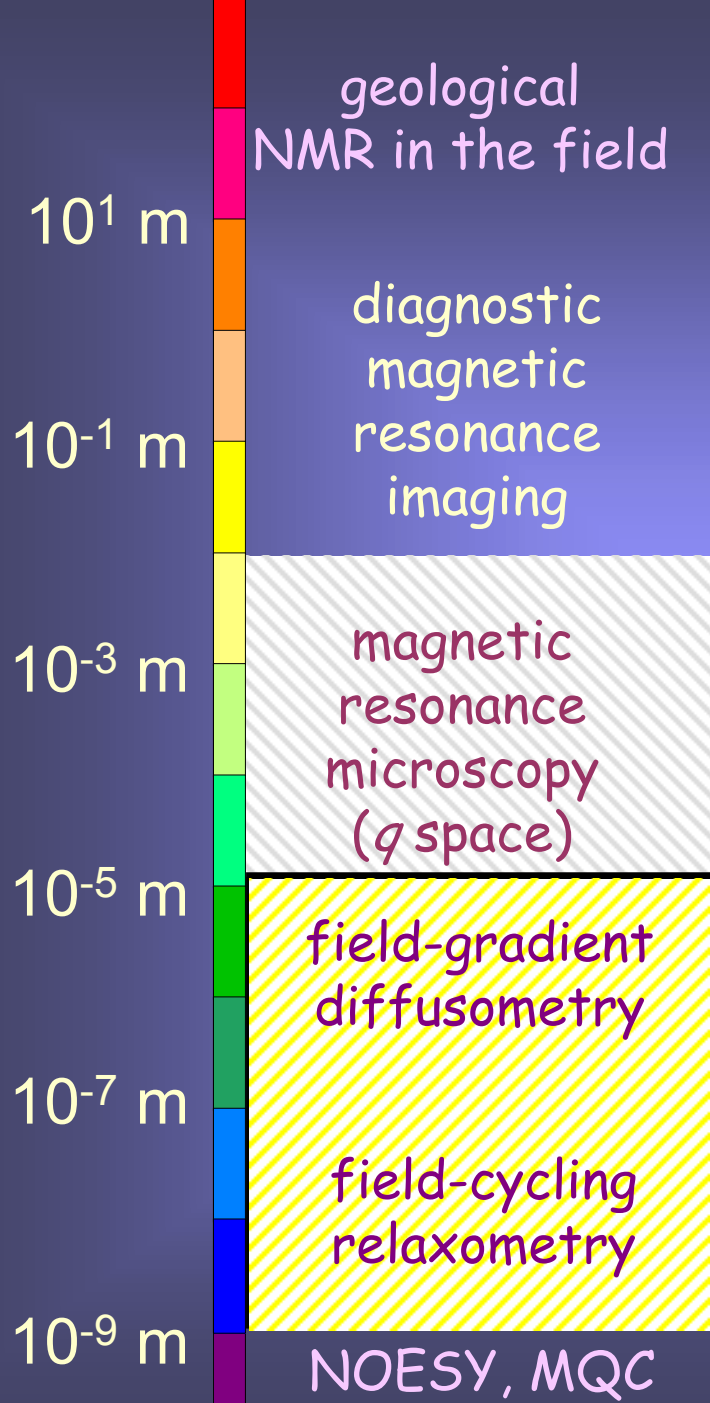
c) Polymer Dynamics

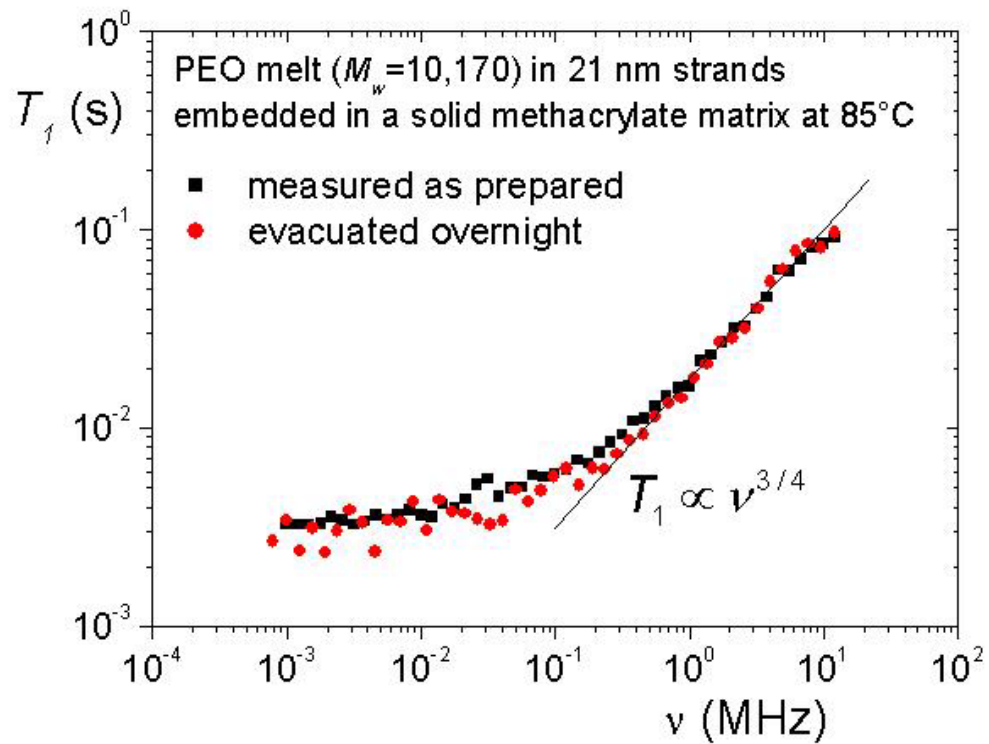
R. Kimmich, N. Fatkullin, Advan. Polym. Sci. 170 (2004)

d) General Dynamics

R. Kimmich, Chem. Phys. 284 (2002) 253

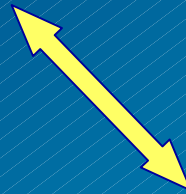
NMR probing into length scales of structure and dynamics



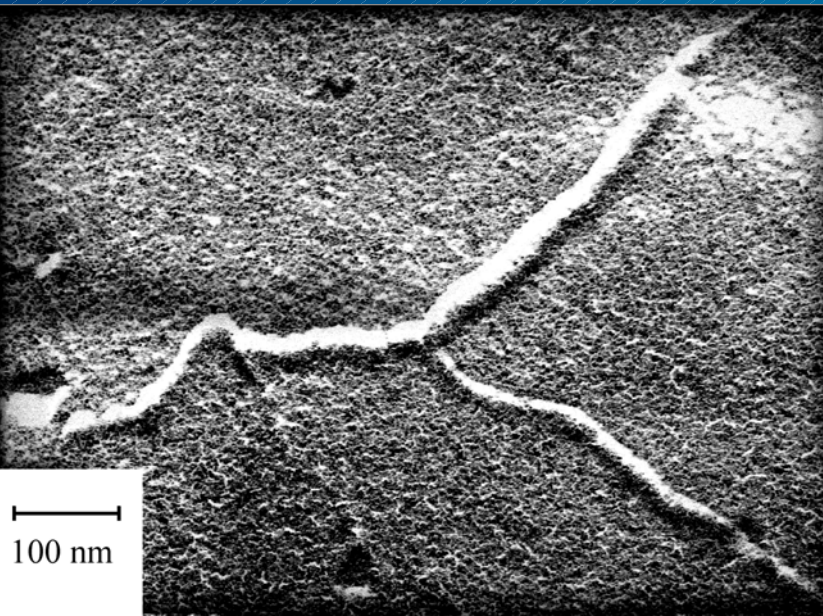


polymer chain dynamics:

polymer melts in bulk



polymer melts confined
in **nanoscopic pores**
in a solid,
impenetrable matrix



Complex systems → complex motions → relaxation?

examples:

- liquid crystals
→ restr. rot. diff. of individual molecules + collective modes
- porous media
→ restr. rot. diff. of molecules + surface diffusion (RMTD)
- polymers
→ local segment fluctuations + chain modes

literature:

often $\left(\frac{1}{T_1}\right)_{\text{measured}} = \left(\frac{1}{T_1}\right)_{\text{motion A}} + \left(\frac{1}{T_1}\right)_{\text{motion B}}$

this is wrong!

different time scale limit:

if motional components occur on **very different time scales** (implies **stochastic independence!**), then

$$G(t) = \langle Y_{2,m}(0) Y_{2,-m}(t) \rangle = A_{\text{fast, restr.}}(t) B_{\text{slow}}(t)$$

$$= \left[a_{\text{fast, restr.}}(t) + a_{\text{fast, restr.}}(\infty) \right] B_{\text{slow}}(t)$$

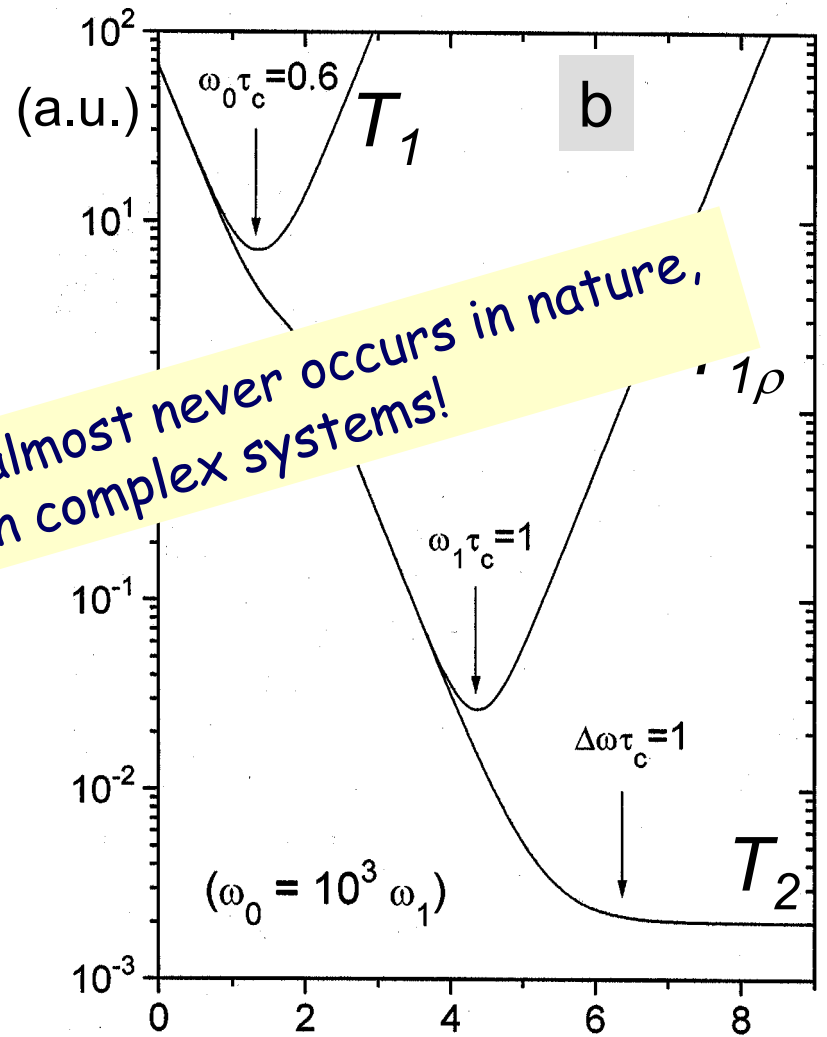
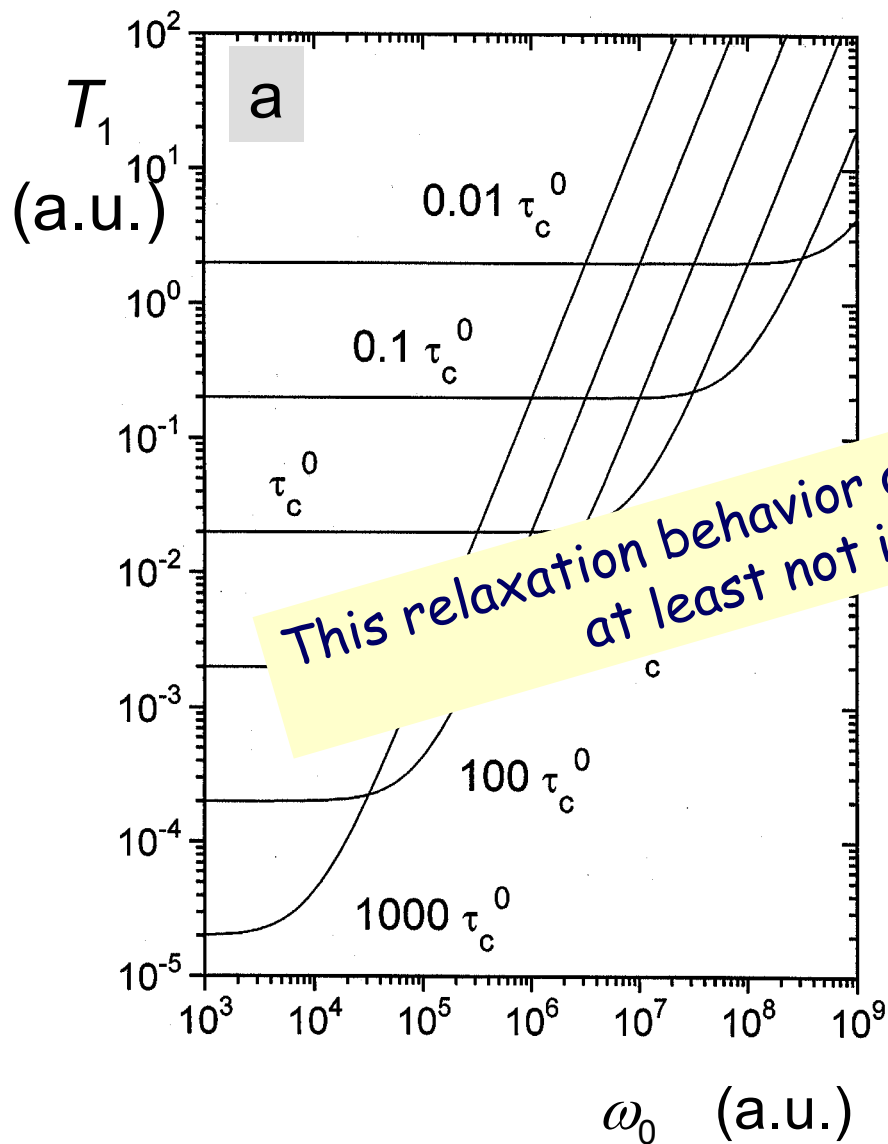
$$\approx a_{\text{fast, restr.}}(t) \underbrace{B_{\text{slow}}(0)}_{b_0} + a_{\text{fast, restr.}}(\infty) \underbrace{B_{\text{slow}}(t)}_{a_\infty}$$

$$\Rightarrow \left(\frac{1}{T_1}\right)_{\text{meas.}} \approx \left(\frac{b_0}{T_1}\right)_{\text{fast}} + \left(\frac{a_\infty}{T_1}\right)_{\text{slow}}$$

diff. time scales

Tube/Reptation concept

Plots of the familiar BPP relaxation formulas for a **single process** with an **exponential correlation function**:



This relaxation behavior almost never occurs in nature, at least not in complex systems!

$$\frac{1}{T} = k_B \Delta E \ln \left\{ \frac{\tau_c}{\tau_c^0} \right\} \quad (\text{a.u.})$$

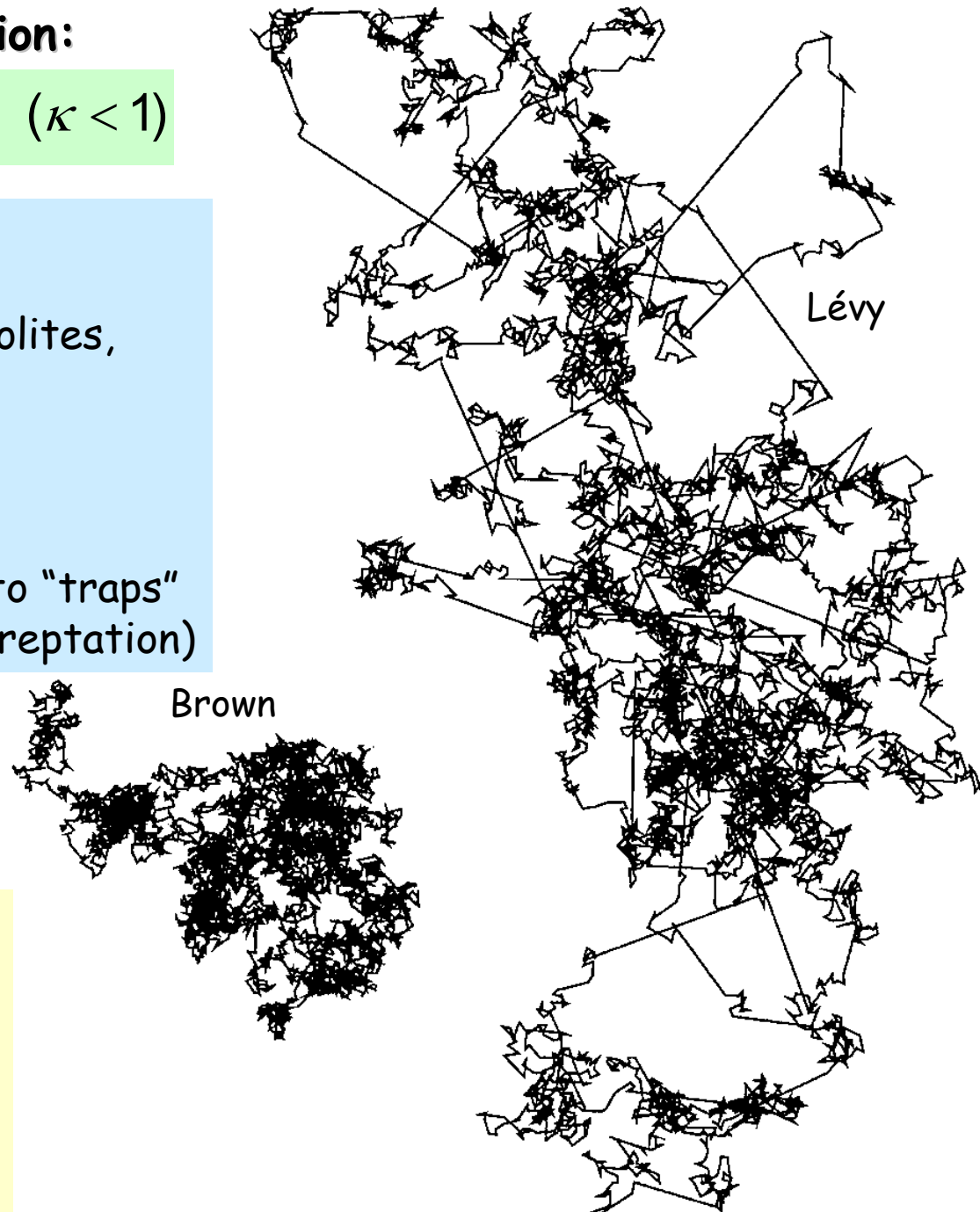
subdiffusive anomalous diffusion:

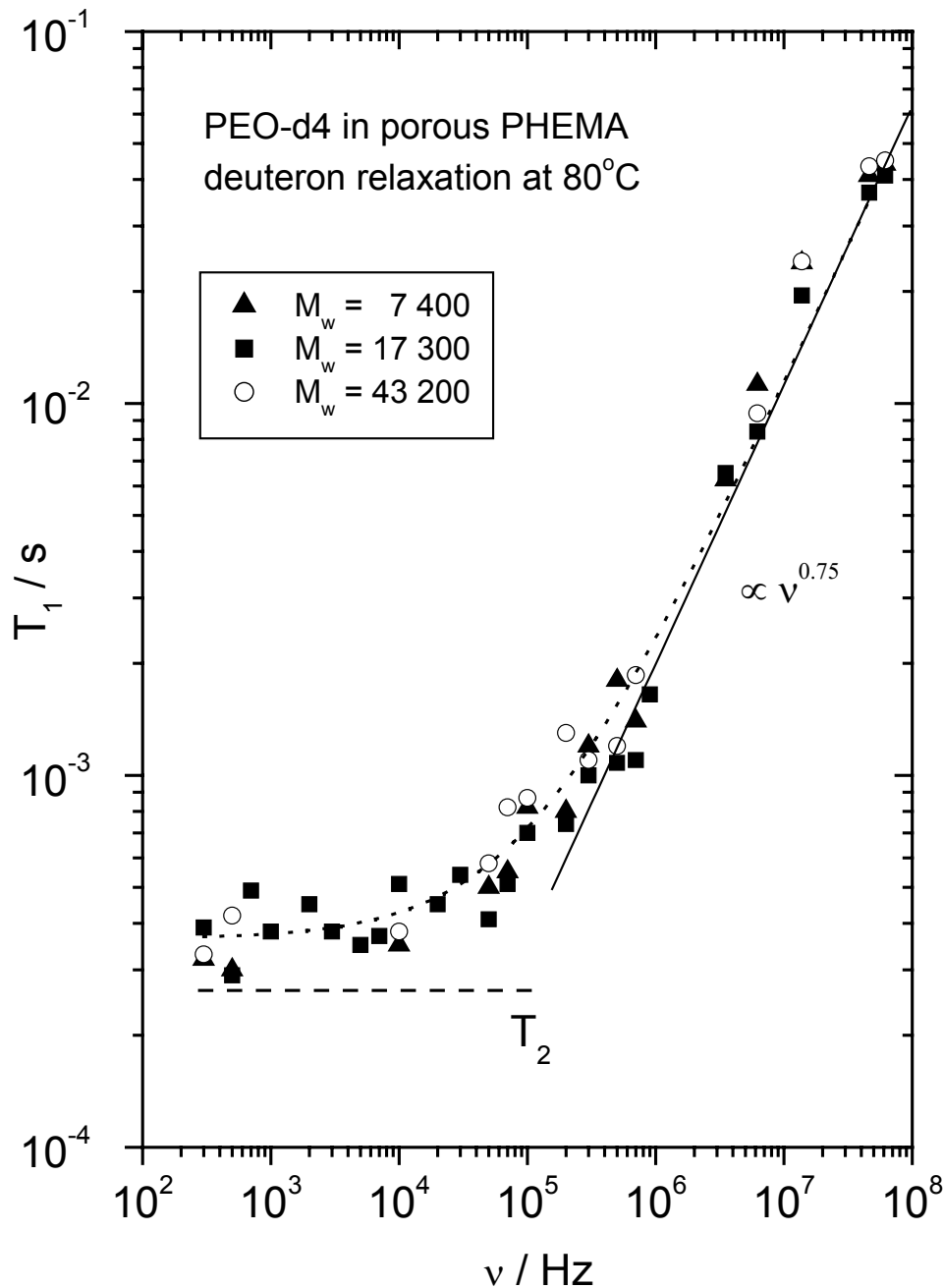
$$\langle r^2 \rangle \propto t^\kappa \quad (\kappa < 1)$$

- a) "(mutual) obstruction effect";
Gaussian propagator, $D=D(t)$
(e.g. single-file diffusion in zeolites,
Rouse mode based diffusion)
- a) "trapping effect";
non-Gaussian propagator;
waiting time distribution due to "traps"
(e.g. random walk on fractals, reptation)

reptation:

- "trapping effect"
- non-Gaussian propagators
- special evaluation theory for
spin echo attenuation required!
- Elmar Fischer





deuteron field-cycling relaxometry

de Gennes' prediction
of 1971 for the
tube/reptation concept:

limit (II)_{DE} : $\underbrace{\tau_e}_{\text{entanglement}} < 1/\omega < \underbrace{\tau_R}_{\text{Rouse}}$
 $\propto M_{PEO}^0$ $\propto M_{PEO}^2$

$$T_1 \propto M^0 \omega^{3/4}$$

experiment:

$$T_1 \propto M_{PEO}^{0 \pm 0.05} \omega^{0.75 \pm 0.02}$$