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

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

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

How can we generate such “spin coherences”?
\[
B_{\text{eff}}(\omega) = \sqrt{(B_0 - \omega/\gamma)^2 + B_1^2}
\]

\[B_{\text{eff}}(\omega = \gamma B_0) = B_1\]

\[\vec{\omega}_1 = -\gamma \vec{B}_1\]
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
diffusometry, transverse relaxation, residual spin couplings

field cycling relaxometry

rot. frame relax.

corr. relaxometry

$\tau$ $10^{-1}$ $10^{-2}$ $10^{-3}$ $10^{-4}$ $10^{-5}$ $10^{-6}$ $10^{-7}$ $10^{-8}$ $10^{-9}$

$\omega$ $10^1$ $10^2$ $10^3$ $10^4$ $10^5$ $10^6$ $10^7$ $10^8$ $10^9$ rad Hz
translational diffusion

?  ?

rotational diffusion of nuclear magnetic dipole pairs or electric quadrupoles in anisotropic heterogeneous media

spin-lattice relaxation
Spin-lattice relaxometry
Field-cycling NMR relaxometry

- Frequency: \( \omega = \gamma B_0 \)
- Relaxation rate: \( \frac{1}{T_1} = C[I(\omega) + 4I(2\omega)] \)
- Spectral density: \( I(\omega) = F_r \{ G(t) \} \)
- 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 correlation function: \( G(t) = \left\langle Y_2^m(0)Y_2^{-m}(t) \right\rangle \)

- Field: \( B_0/T \) with polarization and relaxation
- Time: \( t \) with detection
- RF: ~s

Frequency ranges:
- Dipolar: \( 10^3 \) Hz < \( \frac{\omega}{2\pi} \) < 4 \times 10^8 Hz
- Quadrupolar: \( 10^2 \) Hz < \( \frac{\omega}{2\pi} \) < 6 \times 10^7 Hz
102 109
NMR relaxometry
ν/Hz

300
segment fluctuations (comp. A)

chain modes (comp. B)

center-of-mass motions (comp. C)

10^2
NMR relaxometry

10^4
10^5
M_w

T/ K
400
300
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

damping buffers against building vibrations

favorable if

a) $T_2$ short ($\approx 100 \ \mu s$)

b) $\sqrt{\langle R^2 \rangle}$ small ($\approx 100 \ \text{nm}$)

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

\begin{align*}
  \mathbf{K}(\mathbf{2r}_n - \mathbf{r}_{n+1} - \mathbf{r}_{n-1}) - \zeta \frac{\partial \mathbf{r}_n}{\partial t} + \mathbf{F}_n &\approx \mathbf{K} \frac{\partial^2 \mathbf{r}_n}{\partial \mathbf{r}^2} - \zeta \frac{\partial \mathbf{r}_n}{\partial t} + \mathbf{F}_n = 0
\end{align*}

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

**Solution:** Superposition of discrete Rouse relaxation modes with time constants

\[ \tau_p = \frac{\zeta b^2 N^2}{3\pi^2 k_B T p^2}, \text{ where } p = 1 \cdots N \]

NMR measurand laws predicted by the Rouse model:

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

<table>
<thead>
<tr>
<th>Relaxation</th>
<th>Diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \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} )</td>
<td>[ \langle R^2 \rangle \propto M^0 t^{1/2} ] for ( \tau_s \ll t \ll \tau_R )</td>
</tr>
<tr>
<td>[ \frac{1}{T_1} = \frac{1}{T_2} = C_1 + C_2 \tau_s \ln (M^2) ] for ( \omega \ll \frac{1}{\tau_R} )</td>
<td>[ \langle R^2 \rangle \propto M^{-1} t ] for ( t \gg \tau_R )</td>
</tr>
</tbody>
</table>

(\( \tau_s \) local segment fluctuation time; 
\( \tau_R \) longest Rouse relaxation time)

T. N. Khazanovich, Polymer Sci. USSR 4 (1963) 727
PIB, $M_w = 4700$, $T = 357$ K

$\tau_s = 1.4 \times 10^{-9}$ s

$\omega \tau_s = 1$

PDMS, $M_w = 5200$, $T = 293$ K

$\tau_s = 9.8 \times 10^{-11}$ s

$\omega \tau_s = 1$

PIB, $\nu = 90$ MHz

15% PDMS + 85% CCl$_4$, $M_w = 423000$, $T = 293$ K

$\tau_s = 9.7 \times 10^{-12}$ s

$\omega \tau_s = 1$

melts $M < M_c$

conc. solution
Renormalized Rouse formalism
“Entangled” polymers ($M >> M_c$)

many-chain problem

“tagged chain” in a “matrix”

Renormalized Rouse formalism
\[
\tilde{F}_n(t) = -\frac{3k_B T}{b^2} \frac{\partial^2 \tilde{r}_n(t)}{\partial n^2} + \zeta \frac{\partial \tilde{r}_n(t)}{\partial t} + \zeta t \sum_m \Gamma_{nm}(t-\tau) \frac{\partial \tilde{r}_m(t)}{\partial t} d\tau
\]

Renormalized Rouse formalism

random force
entropic spring force

Rouse ↓

friction

memory function

matrix/entanglement effects

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
\((p < N/6\pi)\)
\(T_1 \propto M^0(\omega \tau_s)^{1/5 \cdots 1/3}\)
("region II")

diffusion

high-mode number limit
\((p > N/6\pi)\)
\(\langle R^2 \rangle \propto M^0 t^{1/4}\)

low-mode number limit
\((p < N/6\pi)\)
\(\langle R^2 \rangle \propto M^0 t^{1/3 \cdots 2/5}\)
spin-lattice relaxation dispersion of polyisobutylene melts $M_w > M_c$


"Renormalized Rouse"

$T_1, T_{1\rho} \frac{T_1}{S}$

PIB

$\nu \propto \nu^0.5 (I)$

$\nu \propto \nu^{0.25} (II)$

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

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

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

$M_w, T$

$\nu, \nu_1 \frac{\text{Hz}}{\text{s}}$
Spin-lattice relaxation dispersion of polyethylene oxide melts


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

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

\[
\left\langle r_s^2(t) \right\rangle \propto t^{1/3 \cdots 2/5}
\]

region III:

\[
T_{1,\text{inter}} \propto \nu^{0.4 \cdots 0.5}
\]
protons: intra- and intersegment interactions
deuterons: only intrasegment interactions

\[ T_1 \sim v^{0.25} \]

polyethyleneoxide

protons

\[ T_1 \sim v^{0.5} \]

deuterons

polybutadiene

protons

\[ T_1 \sim v^{0.3} \]

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

Polybutadiene

$M_w = 65500$
spin-lattice relaxation
dispersion of polymer melts
with $M_w \leq M_c$  
(“entangled” polymers)

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

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

region I: $T_1 \propto M_w^{0.05 \pm 0.05} \nu^{0.5 \pm 0.05}$
region II: $T_1 \propto M_w^{0.05 \pm 0.05} \nu^{0.25 \pm 0.1}$
region III: $T_1 \propto M_w^{0.05 \pm 0.05} \nu^{0.45 \pm 0.05}$

a) limits b) power laws c) universal

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

<table>
<thead>
<tr>
<th></th>
<th>limits</th>
<th>mean squared segment displacement</th>
<th>spin-lattice relaxation time</th>
</tr>
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<tbody>
<tr>
<td>(I)(_{DE})</td>
<td>(\tau_s \leq \left(t, \frac{1}{\omega}\right) \leq \tau_e)</td>
<td>(\langle R^2 \rangle \propto M^0 t^{1/2})</td>
<td>(T_1 \propto -M^0 / \ln(\omega \tau_s))</td>
</tr>
<tr>
<td>(II)(_{DE})</td>
<td>(\tau_e \leq \left(t, \frac{1}{\omega}\right) \leq \tau_R)</td>
<td>(\langle R^2 \rangle \propto M^0 t^{1/4})</td>
<td>(T_1 \propto M^0 \omega^{3/4})</td>
</tr>
<tr>
<td>(III)(_{DE})</td>
<td>(\tau_R \leq \left(t, \frac{1}{\omega}\right) \leq \tau_d)</td>
<td>(\langle R^2 \rangle \propto M^{-1/2} t^{1/2})</td>
<td>(T_1 \propto M^{-1/2} \omega^{1/2})</td>
</tr>
<tr>
<td>(IV)(_{DE})</td>
<td>(\tau_d \leq \left(t, \frac{1}{\omega}\right))</td>
<td>(\langle R^2 \rangle \propto M^{-2} t^1)</td>
<td>(T_1 \propto M^{-\alpha} \omega^0)</td>
</tr>
</tbody>
</table>
NMR diffusometry and the tube/reptation concept

\[ E(\vec{k}, t) = \left\langle e^{i\vec{k} \cdot \vec{r}(t)} \right\rangle_r = \left\langle e^{i\vec{k} \cdot \vec{r}_{s}(t)} \right\rangle_{r_s} + \exp(-k^2D_c t) \left\langle e^{i\vec{k} \cdot \vec{r}_{c}(t)} \right\rangle_{r_c} \]

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

- **anomalous segment diffusion**

\[ E_s(\vec{k}, t) = \int \left( \frac{4\pi}{3} P_{d_t} \right)^{-3/2} e^{\frac{t^2}{d_t|s|}} e^{i\vec{k} \cdot \vec{r}_{s}(t)} d^3\vec{r}_s = \exp \left\{ k^4 d_t^2 \frac{\langle s^2(t) \rangle}{72} \right\} \text{erfc} \left\{ k^2 d_t \sqrt{\langle s^2(t) \rangle} \frac{6\sqrt{2}}{6\sqrt{2}} \right\} \]

- **mean square curvilinear segment displacements**

\[ \langle s^2(t) \rangle = \frac{2D_0 t}{N} + \frac{2b\sqrt{D_0 t}}{\sqrt{3\pi} + 18 \sqrt{D_0 t}} \]

\( d_t \) 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)

$E_{\text{diff}}(k,t)$

$E_{\text{diff}}(k,t)$ vs. $k^2$ [1/m$^2$] for PEO 11,200 in PHEMA at 353 K

$t$/ms: 10, 15, 30, 60

$k = \gamma G \delta$

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

echo attenuation formalism:
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

$T_1$ (s) vs. $\nu$ (MHz)

- **PEO 2,000 bulk, $M < M_c$**
- **confined**
- **PEO 2,000 to 10,000 in nanopores from 8 to 60 nm**

$T_1 \propto M^0 \nu^{3/4}$ (reptation)

The graph shows the relaxation time ($T_1$) as a function of frequency ($\nu$) for PEO in different environments. The data points are differentiated between bulk and confined states, with a clear distinction in behavior at different frequency ranges.
polymers confined in pores \[ \rightarrow \text{melts in bulk ("entangled" polymers)} \]

PEO-d4 in porous PHEMA, deuteron relaxation at 80°C

\[
T_1 / s \propto \nu^{0.75}
\]

PEO-d4 (entangled) deuteron relaxation at 80°C

\[
\propto \nu^{0.34}
\]

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

$\delta_{\text{pore}} \approx 8 \ldots 60 \text{ nm}
\text{(NMR diffusometry, 10 \ldots 300 ms)}$

$\delta_{\text{tube}} \approx 0.6 \text{ nm}
\text{(NMR relaxometry, 10^{-9} \ldots 10^{-4} s)}$

the “corset effect”
The system dimensions

mobile linear polyethylene oxide:

PEO 2,000: \( R_F = 4 \text{ nm} \)
PEO 10,000: \( R_F = 9 \text{ nm} \)

nearest neighbor distance \( 0.5 \text{ nm} \)

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

"tube" effective for diffusion
"tube" effective for relaxation
random coil for \( M_w=1665 \) \( (R_F=N^{1/2}b) \)
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

\[ <n^2> - <n>^2 = k_B T \rho_m \kappa_T <n> \]

\[ \rho \approx 10^{1/3} \]

Effective tube diameter

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

Bulk dynamics for

\[ d_{\text{pore}} \left( \frac{b^3}{k_B T \kappa_T} \right)^{1/3} R_F \approx 10 R_F \]
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 $10^{-2} \ldots 3 \times 10^{-1}$ s
      (8 \ldots 60 \text{ nm})
   = “tight tube” for $10^{-9} \ldots 10^{-4}$ s
      (~0.6 nm)

predicted confined-to-bulk crossover for pore diameters $\gg 10 \, R_F$

rigid wall is sensed over at least 60 polymer chain diameters
"corset effect":
impenetrable pore walls
   + excluded volume of polymer chains
   + low compressibility
Collaborators:

Esteban Anoardo
Ioan Ardelean
Uwe Beginn
Bogdan Buhai
Alexei Denissov
German Farrher
Nail Fatkullin
Elmar Fischer
Ravinath Kausik
Elke Kossel
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Carlos Mattea
Hernan Tiraboschi

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Recent review articles from our group:

a) **Diffusion Methods**


b) **Field-cycling NMR Relaxometry**


c) **Polymer Dynamics**


d) **General Dynamics**

NMR probing into length scales of structure and dynamics

- NMR in the field
- Diagnostic magnetic resonance imaging
- Magnetic resonance microscopy ($q$ space)
- Field-gradient diffusometry
- Field-cycling relaxometry
- NOESY, MQC

- Confinement + surf. effects
PEO melt ($M_\text{w}=10,170$) in 21 nm strands embedded in a solid methacrylate matrix at 85°C

- measured as prepared
- evacuated overnight

$T_1 \propto \nu^{3/4}$
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:**

\[
\left( \frac{1}{T_1} \right)_{\text{meas.}} = \left( \frac{1}{T_1} \right)_{\text{motion A}} + \left( \frac{1}{T_1} \right)_{\text{motion B}}
\]

*This is wrong!*

**different time scale limit:**

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

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

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

\[
\approx a_{\text{fast, restr.}}(t)B_{\text{slow}}(0) + a_{\text{fast, restr.}}(\infty)B_{\text{slow}}(t)
\]

\[
\Rightarrow \left( \frac{1}{T_1} \right)_{\text{meas.}} \approx \frac{b_0}{T_1} + \frac{a_{\infty}}{T_1}
\]
Tube/Reptation concept
Plots of the familiar BPP relaxation formulas for a single process with an exponential correlation function:

\[ \frac{1}{T} = k_B \Delta E \ln \left( \frac{\tau}{\tau_c^0} \right) \]

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

PEO-d4 in porous PHEMA
deuteron relaxation at 80°C

\[ T_1 / s \propto \nu^{0.75} \]

\( M_w = 7,400 \)
\( M_w = 17,300 \)
\( M_w = 43,200 \)

\[ T_1 \propto M_{PEO}^0 \omega^{3/4} \]

experiment:

\[ T_1 \propto M_{PEO}^{0+0.05} \omega^{0.75+0.02} \]