NMR relaxation and dynamics of polymer systems. NMR relaxation dispersion signatures of models for entangled polymer systems.

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N.F. Fatkullin
Kazan State University
Thanks to R. Kimmich for many years collaboration.

Nail.Fatkullin@ksu.ru
The basic concepts of polymer physics

- Linear homopolymers are molecules composed from chemically bounded repeated units, for example:
  - Polyethylene  
    \[ \left[ -CH_2 - CH_2 - \right]_n \]
  - Poly(oxyethelene)  
    \[ \left[ -CH_2 - CH_2 - O - \right]_n \]
- The number of repeat units, \( n \), called the degree of polymerization, which  
  - can be very large  
    \( n \sim 10^3 \div 10^6 \)
- A great number degrees of freedom. How to describe analytically?

Course grained description of polymer chains

- Kuhn segment is an elementary unit in physical description of long wavelength static properties of polymer chains.

Fig. 2. Distribution function of Kuhn segment length
Universality of the ideal chain’s static properties in the limit $N \gg 1$

- For long enough ideal chains only the second moment of segmental distribution function $w(r)$ is important.

- $b^2 \equiv \left\langle r^2 \right\rangle_s \equiv \int r^2 w(|\vec{r}|) d\vec{r}$

- $b$ is the Kuhn segment length by definition.

- The Flory Radius distribution function is Gaussian:

$$W(\bar{R}; N) = \frac{1}{\left( \frac{2\pi}{3} Nb^2 \right)^{3/2}} \exp \left\{ -\frac{3}{2} \cdot \frac{R^2}{Nb^2} \right\}$$
Experimental procedure for determination of the Kuhn segment length

- For ideal chains, $\langle R_F^2 \rangle = N b^2 = L b = C_\infty l_0^2 n$

$L = n l_0 \langle \sin(\theta/2) \rangle \quad \langle \sin(\theta/2) \rangle \approx 0.83 \quad b = \frac{C_\infty l_0}{\langle \sin(\theta/2) \rangle}$

Fig. 3 Extended polymer chain

- $C_\infty$ is the characteristic ratio

Figure 4. Typical dependence of Kuhn segment length from molecular mass.
Some examples

- For PE
  \[ l_0 = 1.54A^0, C_\infty \approx 7.0, b = C_\infty l_0 / \sin(\theta/2) \approx 13A^0 (10.7A^0) \]
  - \( m_b \approx 140 \) is approximately the molecular mass of one Kuhn segment,
  - If molecular mass \( M=1000000 \), \( R_F \approx 760A^0 \)

- For PEO
  \[ l_0 = 1.45A^0, C_\infty \approx 5.59, b = C_\infty l_0 / \sin(\theta/2) \approx 9.7A^0 (8.1A^0) \]
  - \( m_b \approx 120 \)
  - If molecular mass \( M=1000000 \), \( R_F \approx 900A^0 \)

- Radius of gyration of macromolecule.
  \[ R_g^2 = \frac{1}{6} b^2 N = \frac{1}{6} R_F^2 \]

- Hydrodynamic radius of macromolecule.
  \[ R_H = \sqrt{\frac{3\pi}{2^7}} b\sqrt{N} = \sqrt{\frac{3\pi}{2^7}} R_F \]
Some special models of ideal polymer chains.

1. The freely joined model. This model corresponds to segmental distribution function described by the following expression:

\[ w_{fj}(|\vec{r}|) = \frac{1}{4\pi^2b^2} \delta(|\vec{r}| - b) \]

Freely joined chain is composed by Kuhn segments with fixed length. Any Kuhn segment can rotates to any angle respectively it’s neighbours. Actually just this model was originally suggested by W. Kuhn.

2. The Gaussian chain.

\[ w_G(|\vec{r}|) = \frac{1}{\left(\frac{2\pi^2}{3}b^2\right)^{3/2}} \exp \left\{ -\frac{3}{2} \frac{r^2}{b^2} \right\} \]
How does the spin-lattice relaxation reflects the polymer segment dynamic?

- The spin-lattice relaxation rate can be calculated using the standard and very general relation:

\[
\frac{1}{T_1} = \frac{1}{\hbar^2} \int_0^\infty dt \mathbf{T} \mathbf{r}_{\text{spin}} \left\langle \left[ \hat{I}_z, \hat{V}_{sl}(t) \right] \left[ \hat{V}_{sl}(0), \hat{I}_z \right] \right\rangle_{\text{eq}}
\]

- \( \hat{I}_z \) is the z coordinate of the total spin operator of the system, \( \hat{I} = \sum_{k,i} \hat{I}_{k,i} \)

- \( \hat{V}_{sl}(t) \) is the Hamiltonian effective for spin-lattice relaxation in Dirac representation.

molecular motion

pair of nuclear dipoles

molecule

"intra"

"inter"
Calculations with the Hamiltonian of magnetic dipole-dipole interaction

- In general case the spin-lattice relaxation rate contains two main contributions:

\[
\frac{1}{T_1(\omega)} = \frac{1}{T_{1\text{ intra}}(\omega)} + \frac{1}{T_{1\text{ inter}}(\omega)}
\]

\[
\frac{1}{T_{1\text{ intra}}(\omega)}
\]

is the contribution from spins belonging to same macromolecule

\[
\frac{1}{T_{1\text{ inter}}(\omega)}
\]

is the contribution from spins belonging to different macromolecule
The intra-segment contribution into spin-lattice relaxation rate

• Consider the case of proton spin-lattice relaxation, the corresponding Hamiltonian:

\[
\hat{H}_{k;ij} = \frac{\gamma^2 \hbar^2}{r_{k;ij}^3} \left\{ \hat{I}_{k;i} \cdot \hat{I}_{k;j} - 3 \left( \hat{I}_{k;i} \cdot \vec{e}_{k;ij} \right) \left( \hat{I}_{k;j} \cdot \vec{e}_{k;ij} \right) \right\}
\]

• \(r_{k;ij}\) is the internuclear distance \(\vec{e}_{k;ij} = \frac{\vec{r}_{k;ij}}{r_{k;ij}}\)

• \(k\) is the number of polymer segment, \(i\) and \(j\) are numbers of spins from considering segment,

• For flexible macromolecules Kuhn segment length \(b \sim 5 - 15 A^0\)

• and \(r_{k;ij} \approx 1.8 A^0\) for nearest spins.

• It is necessary to connect course grained variables \(\vec{b}_k(t)\)

• with microscopic \(\vec{r}_{k;ij}(t)\).

• How does the spin-lattice relaxation reflects the polymer segment dynamic?
Answer can be done with the aid of the Zwanzig-Mori projection operator formalism.

- If we have two physical quantities $A$ and $B$ we can extract from $B$ maximal part which statistically correlate with $A$ by following way:

$$
\hat{P}_A B \equiv A \frac{\langle A^* B \rangle_{eq}}{\langle A^* A \rangle_{eq}}
$$

- $\hat{P}_A \equiv |A\rangle \frac{1}{\langle A^* A \rangle_{eq}} \langle A|$ is the projection operator on $A$.

- By definition, the projection operator acts on functions of atomistic space variables according to

$$
\hat{P}_A B \equiv A \frac{\langle A^* B \rangle_{eq}}{\langle A^* A \rangle_{eq}} = |A\rangle \frac{1}{\langle A^* A \rangle_{eq}} \langle A|B\rangle
$$

In the case of proton spin-lattice relaxation

- The relevant projection operator on polymer segment with number k is

\[ \hat{P}_k \equiv \sum_{m=-2,...,+2} \left| \begin{array}{c} B_k^m \\ 1/b^4_k \end{array} \right\rangle \left\langle B_k^m \right| \]

- The components of the irreducible second order tensor, i.e.

\[ \left| B_k^m \right\rangle \]

and

\[ B_k^m = b_k^2 Y_{2;m} \left( \frac{\vec{b}_k}{b_k} \right) \]

\[ \left\langle B_k^m \right| B_k^l \left\rangle = \delta_{ml} \left\langle b^4_k \right| \right. \]
The total Hamiltonian for the spin pair under consideration is composed of the sum

\[ \hat{H}_{k;ij} = \hat{H}_{k;ij}^b + \hat{H}_{k;ij}^{loc} \]

- The first one, reflecting polymer segment’s dynamics is

\[ \hat{H}_{k;ij}^b = \hat{P}_k \hat{H}_{k;ij} = \]

\[ \frac{\gamma^2 \hbar^2}{\langle b^4_\lambda \rangle_s} \left( \frac{b^2_\lambda}{r^3_\lambda:ij} \right)_s \cdot \left( \langle \left( \hat{I}_{k;i} \cdot \hat{I}_{k;j} \right) b^2_k - 3 \left( \hat{I}_{k;i} \cdot \vec{b}_k \right) \left( \hat{I}_{k;j} \cdot \vec{b}_k \right) \rangle_s \right) \]

- where

\[ S_{ij} = \frac{1}{2} \left( \frac{3 \left( \vec{e}_{\lambda;ij} \cdot \vec{n}_\lambda \right)^2 - 1}{b_\lambda^2} \right) \left( \frac{b^2_\lambda}{r^3_\lambda:ij} \right)_s \]

- is the spin-segment coupling parameter,

\[ \vec{n}_\lambda = \frac{\vec{b}_\lambda}{b_\lambda} \]
If to neglect by fluctuations of $b_\lambda$ and $r_{k:ij}$

- The spin-segment coupling parameter is
  \[ S_{ij} = \frac{1}{2} \left\langle 3 \left( \vec{e}_{\lambda;ij} \cdot \vec{n}_s \right)^2 - 1 \right\rangle_s \]

- and
  \[ \hat{H}^b_{k;ij} = \frac{\gamma^2 h^2}{r_{ij}^3} S_{ij} \left\{ \left( \hat{I}_{k;i} \cdot \hat{I}_{k;j} \right) - 3 \left( \hat{I}_{k;i} \cdot \vec{n}_k \right) \left( \hat{I}_{k;j} \cdot \vec{n}_k \right) \right\} \]

- For $S_{CH_2} \approx -\frac{1}{2}$ and $S_{CH_3} \approx \frac{1}{4}$

\[ \vec{n}_k = \frac{\vec{b}_k}{b} \]
Contribution into spin-lattice relaxation rate from the effective Hamiltonian for spin-segment coupling

- The effective Hamiltonian for spin-segment coupling is

\[
\hat{H}^b = \frac{\gamma^2 h^2}{\langle b^4_\lambda \rangle_s} \left( \frac{b^2_\lambda}{r^3_{\lambda;ij}} \right)_s \sum_{k;i<j} S_{ij} \left( \langle \hat{I}_{k;i} \cdot \hat{I}_{k;j} \rangle b^2_k - 3 \langle \hat{I}_{k;i} \cdot \hat{b}_k \rangle \langle \hat{I}_{k;j} \cdot \hat{b}_k \rangle \right)
\]

- The corresponding contribution into spin-lattice relaxation rate

\[
w^b = \frac{\tilde{M}^b_2}{\langle b^4_\lambda \rangle_s} \sum_{k} \frac{1}{N} \int_0^\infty dt \left\{ \cos(\omega t) \langle b^z_k(t) b^z_k(0) b^+_k(t) b^-_k(0) \rangle + \cos(2\omega t) \left\langle \left( b^+_k(t) \right)^2 \left( b^-_k(0) \right)^2 \right\rangle \right\}
\]

- \[\tilde{M}^b_2 = \frac{3\gamma^4 h^2 I(I+1)}{\tilde{N}_s} \sum_{i<j} \frac{S^2_{ij}}{\langle b^4_\lambda \rangle_s} \left( \frac{b^2_\lambda}{r^3_{\lambda;ij}} \right)_s \]

  characterizes the strength of the intrasegmental dipole-dipole interaction. \(\tilde{N}_s\) is the number of spins in a Kuhn segment and differs from the residual part of the intrasegmental second moment only by a numerical coefficient of order one, \(\sim 5\).
Contribution from intrasegmental local fluctuations

- The corresponding part of total Hamiltonian contains only fast local variables

\[ \hat{H}^{loc} \equiv \hat{H}^{intra}_{dd} - \hat{H}^b = (1 - \hat{P}) \hat{H}^{intra}_{dd} \]

- It’s contribution into spin-lattice relaxation rate can be estimated as

\[ w^{loc} = \frac{2}{3} M_2^{near} (1 - S_{ij}^2) \tau_{loc} \left\{ \frac{1}{1 + (\omega \tau_{loc})^2} + \frac{4}{1 + (2 \omega \tau_{loc})^2} \right\} \]

- \( M_2^{near} \) is the contribution into second moment from nearest spins

- \( \tau_{loc} \) is the characteristic relaxation time for local fluctuations

- \( S_{ij} \) is the spin-segment coupling parameter of nearest spins
Some numerical estimations

- If $\omega \tau_{loc} \ll 1$

  \[ W_{loc} = \frac{10}{3} M_2^{near} \left(1 - S_{ij}^2\right) \tau_{loc} \]

- For $CH_2$, $M_{2CH_2} \approx 8 \cdot 10^9 s^{-2}$, for $CH_3$, $M_{2CH_3} \approx 1.5 \cdot 10^{10} s^{-2}$

- Then $w_{loc}^{CH_2} \approx 2 \cdot 10^{10} s^{-2} \tau_{loc}$ and $w_{loc}^{CH_3} \approx 5 \cdot 10^{10} s^{-2} \tau_{loc}$

- If temperature is high enough and contributions are relatively small $\tau_{loc} \leq 10^{-11} s$ this
Intermolecular contribution

- Calculations show (M. Kehr, N. Fatkullin, R. Kimmich, J. Chem. Phys. 126, 09403 (2007), ) for times $t \gg \tau_s$

$$
\frac{1}{T_{1\text{inter}}(\omega)} = \frac{32\pi^2}{45} \gamma_H^4 \hbar^2 I(I+1) \rho_s \int_0^\infty dt \tilde{W}(0; t) \left[ \cos(\omega t) + 4 \cos(2\omega t) \right]
$$

- The propagator of relative motions two spins from different macromolecules is here main quantity

$$
\tilde{W}(\vec{r}, \vec{r}'; t) = \tilde{W}(\vec{r}' - \vec{r}; t) g(r')
$$

- Approximation for the radial distribution function:

$$
g(r) = \begin{cases} 
1 & \text{for } r > \sigma \\
0 & \text{for } r \leq \sigma 
\end{cases}
$$

$\sigma$ is an effective diameter of chain
If the propagator is Gaussian

• Then

\[
\tilde{W}(\vec{r}; t) = \frac{1}{\left(\frac{2\pi}{3} \langle \vec{r}^2(t) \rangle\right)^{3/2}} \exp \left\{ -\frac{3}{2} \frac{r^2}{\langle \vec{r}^2(t) \rangle} \right\}
\]

\[
\frac{1}{T_{1 \text{inter}}(\omega)} = \frac{16}{15} \sqrt{2 \gamma_H^4 \hbar^2 I (I + 1)} \rho_s \int_0^\infty dt \frac{\cos(\omega t) + 4 \cos(2\omega t)}{\left(\sigma^* + \langle \vec{r}^2(t) \rangle^{1/2}\right)^3}
\]

• For low molecular mass liquids at times \( t \gg \tau_s = 10^{-11} \div 10^{-9} \text{s} \)

• diffusion has normal character \( \langle \vec{r}^2(t) \rangle = 12 D t \) and main contribution comes from short times.

• \( \sigma^* \propto \sigma \) takes in a qualitative manner a short wave length effects
Situation is essentially different in polymer melts


- For times \( \tau_s \ll t \ll \tau_1 \), where \( \tau_1 \propto \tau_s N^{2-3.5} \):

- we have strongly subdiffusive behavior:

\[
\left\langle \tilde{r}^2(t) \right\rangle = \tilde{b}^2 \left( \frac{t}{\tau_s} \right)^\alpha, \quad (1/4 \leq \alpha \leq 1/2)
\]

- where \( \tilde{b} \) is a characteristic length of an order of the Kuhn segment length. The main contribution comes from times of order \( t \sim \omega^{-1} \)
The Rouse model.


- The Rouse model is the simplest generalization of Langeven equations for Brownian motion of system with internal degrees of freedom. At temperatures $T \sim 300K$ the de Broglie thermal length of a polymer segment $\lambda = \frac{h}{\sqrt{2\pi mk_BT}} \ll 1A^0$ and system can be described by classical equations of motions:

$$m\ddot{r}_n = \vec{F}_{n}^{\text{intra}} + \vec{F}_{n}^{\text{inter}}$$

- $\vec{F}_{n}^{\text{intra}}$ is the effective intramolecular force acting on bead with number $n$ (mean force),

- $\vec{F}_{n}^{\text{inter}}$ is the intermolecular force acting on
How to calculate $F_{n}^{\text{intra}}$ and $F_{n}^{\text{inter}}$?

- The intramolecular part is closely connected with equilibrium distribution function describing the course gained conformation $\tilde{W}(\{\vec{r}_n\})$:

  $$F_{n}^{\text{intra}} = k_B T \frac{\partial}{\partial \vec{r}_n} \ln\left(\tilde{W}(\{\vec{r}_n\})\right) \lambda^{3N}$$

- For ideal chains we have

  $$\tilde{W}(\{\vec{r}_i\}) = \prod_{i=0}^{N} w(|\vec{r}_{i+1} - \vec{r}_i|) = \prod_{i=0}^{N} w(|\vec{r}_{i+1}; i|)$$

- In Rouse model is assumed the Gaussian distribution function for the Rouse segment

  $$w_G \left(|\vec{r}|\right) = \frac{1}{\left(\frac{2\pi^2}{3} b^2\right)^{3/2}} \exp \left\{-\frac{3}{2} \frac{r^2}{b^2}\right\}$$
The intermolecular force is most difficult for treatment

- In Rouse model postulated that the intermolecular force consist from friction and stochastic Langeven forces.

\[ m \dddot{\vec{r}}_n(t) = \frac{3k_B T}{b^2} \left\{ \vec{r}_{n+1}(t) + \vec{r}_{n-1}(t) - 2\vec{r}_n(t) \right\} - \zeta \dot{\vec{r}}_n(t) + \vec{F}^{L}_n(t) \]

- \( \zeta \) is sub-chain frictional coefficient,
- \( \vec{F}^{L}_n(t) \) is the stochastic Langevin force acting on the bead, connected with the friction coefficient by the fluctuation-dissipative theorem.
- For \( N \gg 1 \) and \( \frac{m}{\zeta} \gg 10^{-12} - 10^{-13} s \) the continuum approximation without inertia term is asymptotically exact

- \( \zeta \dot{\vec{r}}_n(t) = \frac{3k_B T}{b^2} \frac{\partial^2 r_n(t)}{\partial n^2} + \vec{F}^{L}_n(t) \), \( \left. \frac{\partial}{\partial n} \vec{r}(t) \right|_{n=0,N} = 0 \)
The Rouse normal modes

- The Rouse normal modes are special type of generalized coordinates:

\[
\tilde{X}_p(t) = \frac{1}{N+1} \sum_{n=1}^{N+1} \cos \left( \frac{\pi}{N+1} p \left( n - \frac{1}{2} \right) \right) \tilde{r}_n(t), \quad p = 0, 1, \ldots, N
\]

- The Rouse normal modes binary correlation function decay exponentially:

\[
C_{pq}(t) = \langle \tilde{X}_p(t) \cdot \tilde{X}_q(0) \rangle = \langle \tilde{X}_p^2 \rangle \exp \{-w^R_p t \} \delta_{pq}
\]

- with relaxation times

\[
\tau^R_p \equiv \frac{1}{w_p} = \frac{\zeta \langle r^2 \rangle_s}{12k_BT \sin^2 \left( \frac{\pi p}{2(N+1)} \right) N \langle r^2 \rangle_s} \rightarrow \tau_s \left( \frac{N}{p} \right)^2
\]

\[
\langle \tilde{X}_p^2 \rangle = \frac{\langle r^2 \rangle_s}{8(N+1) \sin^2 \left( \frac{\pi p}{2(N+1)} \right)} \rightarrow \frac{N \langle r^2 \rangle_s}{2 \pi^2 p^2}
\]

\[
\tau_s = \frac{\zeta \langle r^2 \rangle_s}{3 \pi^2 k_BT}
\]
Most important dynamical characteristics of the Rouse model

- The mean squared displacement

\[
\left\langle (\vec{r}_n(t) - \vec{r}_n(0))^2 \right\rangle = \left\langle (\vec{X}_0(t) - \vec{X}_0(0))^2 \right\rangle + 8 \sum_{p=1}^{N-1} \left[ C_p(t) - C_p(0) \right] \cos^2 \left( \frac{\pi pn}{N} \right)
\]

- \( \left\langle (\vec{r}_n(t) - \vec{r}_n(0))^2 \right\rangle = \frac{2}{\pi^{3/2}} b^2 \sqrt{\frac{t}{\tau_s}} \), if \( \tau_s \ll t \ll \tau_R = \tau_s N^2 \)

- \( \left\langle (\vec{r}_n(t) - \vec{r}_n(0))^2 \right\rangle = 6D_R t = 6 \frac{k_B T}{\zeta N} t = 6 \frac{b^2}{3\pi^3 N} \frac{t}{\tau_s} \), if \( \tau_R \ll t \)
The Kuhn segment tangent vector autocorrelation function

- By the definition

\[ \bar{b}_n(t) = \bar{r}_{n+1}(t) - \bar{r}_n(0) = -4 \sum_{p=1}^{N} \bar{X}_p \sin \frac{np\pi}{N+1} \sin \frac{p\pi}{2(N+1)} \]

\[ \frac{\partial \bar{r}_n(t)}{\partial n} = -\frac{2\pi}{N} \sum_{p=1}^{N-1} p\bar{X}_p(t) \sin \left( \frac{\pi pn}{N} \right) \]

\[ \langle \bar{b}_n(t) \cdot \bar{b}_n(0) \rangle = \frac{\sqrt{\pi} b^2}{2} \left( \frac{\tau_s}{t} \right)^{1/2} \quad \tau_s \ll t \ll \tau_R = \tau_s N^2 \]

\[ \langle \bar{b}_n(t) \cdot \bar{b}_n(0) \rangle = \frac{b^2}{N^2} \exp \left\{ -\frac{t}{\tau_R} \right\} \quad \tau_R \ll t \]
The Rouse and Kuhn segments are essentially same
N.Fatkullin, T.Shakirov, N.Balakirev, Polymer Science A (in press)

- It is possible to prove rigorously, that initial decay of the binary correlation functions for any ideal nonentangled chain is Rousian:

\[
\langle \bar{X}_p(t) \cdot \bar{X}_p(0) \rangle = \left(1 - w_p^R t + \ldots\right) \langle \bar{X}_p^2(0) \rangle
\]

- For any times

\[
w_p^R \frac{\langle r^2 \rangle_s}{3} \frac{\langle r^{-2} \rangle_s}{s} \leq w_p(t) \leq w_p^R = \frac{1}{\tau_R}
\]
For Fraenkel chains, having distribution

\[ w_{fr}(r) \approx \frac{1}{4\pi b^2} \sqrt{\frac{\kappa}{2\pi}} \exp\left\{ -\frac{\kappa(r-b)^2}{2}\right\} \]

- 1-simulations N=20,
- 2-Rouse model predictions,
- 3 – Rouse model predictions shifted on the factor \( \langle r^2 \rangle_s \langle r^{-2} \rangle_s \)}
Initial nonexponentiality of decay normal modes with high numbers

1. results of simulations for $p=20$, 3 - Rouse model predictions.
Intramolecular contribution into spin-lattice relaxation rate in Rouse model

- The general expression ( \( b_k^+ = b_k^z + ib_k^x; b_k^- = b_k^z - ib_k^x \) ):

\[
\frac{1}{T_{1;\text{intra}}} = \frac{\tilde{M}_2^b}{\langle b^A \rangle_s} \frac{1}{2N} \sum_k \int_0^\infty dt \left\{ \cos(\omega t) \langle b_k^- (t) b_k^z (0) b_k^+ (t) b_k^- (0) \rangle + 4 \cos(2\omega t) \langle (b_k^+ (t))^2 (b_k^- (0))^2 \rangle \right\}
\]

- The Rouse model allow decoupling:

\[
\langle b_n^z(t) b_n^z(0) b_n^x(t) b_n^x(0) \rangle = \langle b_n^z(t) b_n^z(0) \rangle \langle b_n^x(t) b_n^x(0) \rangle = \frac{1}{9} \langle \vec{b}_n(t) \cdot \vec{b}(0) \rangle^2
\]

\[
\frac{1}{T_{1;\text{intra}}} = \frac{\tilde{M}_2^b}{\langle b^A \rangle_s} \frac{2}{9N} \sum_k \int_0^\infty dt \langle \vec{b}_k(t) \cdot \vec{b}_k(0) \rangle^2 \left\{ \cos(\omega t) + 4 \cos(2\omega t) \right\}
\]

\[
\frac{1}{T_{1;\text{intra}}} \approx 0.63 \tilde{M} \tau_s \ln \left( \frac{0.95}{\omega \tau_s} \right) \quad \tau_R \ll \omega \ll \tau_s^{-1}
\]
First experimental observation

- First theoretical predictions:
  - 1. T.N.Khazanovich, Polymer Sci USSR (1963) 4, 727
Entangled and nonentangled regimes of motions in polymer melts

- Viscosity $\eta(M)$ of a polymer melt as function of molecular mass

- $M_c$ is the critical molecular mass, if $M < M_c$ system is called nonentangled,

- if $M > M_c$ system is called entangled. Number of Kuhn segments in the $M_c$

$$\ln \eta \propto M^{-3.4}$$

$PDMS \Rightarrow N_c \approx 83,$

$PE \Rightarrow N_c \approx 38,$

$PS \Rightarrow N_c \approx 50,$

$PEO \Rightarrow N_c \approx 53$

$PIB \Rightarrow N_c \approx 83,$

$Polypropilene \Rightarrow N_c \approx 40$

$$N_e = \frac{N_c}{2} \approx 5.5 \cdot 10^2 \left( \rho_s b^3 \right)^{-2}$$

- It is possible to extract from L.J.Fetters, D.J.Lohse, D.Richter, Macromolecules 27(1994),4640.
Tube/reptation concept by Doi and Edwards

(definition of 4 characteristic time constants)

Dynamical limits of tube reptation model

- **I. Short time nonentangled Rousian motion**
  \[ \tau_s \ll t \ll \tau_e \approx \tau_s N_e^2 \]
  \[ \left\langle \left( \vec{r}_n(t) - \vec{r}_n(0) \right)^2 \right\rangle = \frac{2}{\pi^{3/2}} b^2 \sqrt{\frac{t}{\tau_s}} \]

- **II. Noncoherent reptation inside tube**
  \[ \tau_e \ll t \ll \tau_R = \tau_s N^2 \]
  \[ \left\langle \left( \vec{r}_n(t) - \vec{r}_n(0) \right)^2 \right\rangle \propto b^2 N_e \left( \frac{t}{\tau_s} \right)^{1/4} \]

- **III. Coherent reptation inside tube**
  \[ \tau_R \ll t \ll \tau_1 \propto \tau_s N^3 / N_e \]
  \[ \left\langle \left( \vec{r}_n(t) - \vec{r}_n(0) \right)^2 \right\rangle \propto b^2 \left( \frac{N_e}{N} \frac{t}{\tau_s} \right)^{1/2} \]

- **IV. Normal diffusion**
  \[ \tau_1 \ll t \]
  \[ \left\langle \left( \vec{r}_n(t) - \vec{r}_n(0) \right)^2 \right\rangle = 6D_{rep} t = \frac{2k_B T}{\zeta} \frac{N_e}{N^2} t \]
Reptation model and spin-lattice relaxation dispersion

- The general expression is the same as for Rouse model

\[
\frac{1}{T_{1}^{\text{rep.int.ra}}} = \frac{\tilde{M}_2^b}{\langle b_2^4 \rangle_s} \frac{1}{N} \sum_k \int_0^\infty dt \left\{ \cos(\omega t) \langle b_k^z(t) b_k^z(0) b_k^z(t) b_k^z(0) \rangle + \cos(2\omega t) \langle (b_k^z(t))^2 (b_k^z(0))^2 \rangle \right\}
\]

- The decoupling is essentially different for \( \tau_e \ll t \ll \tau_s \propto \tau_s N^3 / N_e \)

\[
\langle b_n^\alpha(t) b_n^\alpha(0) b_n^\beta(t) b_n^\beta(0) \rangle \approx \frac{1}{9} \left\langle \bar{b}_n(\tau_e) \cdot \bar{b}(0) \right\rangle^2 P(t)
\]

- \( P(t) \propto \frac{bN_e^{1/2}}{\langle s^2(t) \rangle^{1/2}} \) is the probability to stay at initial part of tube

- \( \langle s^2(t) \rangle \) is the mean squared displacement inside tube

\[
P(t) \propto \frac{bN_e^{1/2}}{\langle s^2(t) \rangle^{1/2}} \propto \frac{b^2 N_e}{\langle r^2(t) \rangle}
\]
Intra and inter contributions into spin-lattice relaxation rate in reptation model

- Intramolecular contribution for \( \tau_e \ll t \ll \tau_1 \propto \tau_s N^3 / N_e \)

\[
\frac{1}{T_{1}^{\text{rep};\text{int} ra} (\omega)} \propto \tilde{M}^b_2 \left\langle b_n (\tau_e) \cdot \vec{b} (0) \right\rangle^2 b^2 N_e \int_0^\infty \frac{\cos (\omega t) + 4 \cos (2 \omega t)}{\left\langle r^2 (t) \right\rangle} dt
\]

- Intermolecular contribution:

\[
\frac{1}{T_{1}^{\text{rep};\text{inter} ra} (\omega)} \propto \gamma_H^4 h^2 I (I + 1) \rho_s \int_0^\infty dt \frac{\cos (\omega t) + 4 \cos (2 \omega t)}{\left\langle \tilde{r}^2 (t) \right\rangle^{3/2}}
\]

- One should expect:

\[
\frac{1}{T_{1}^{\text{rep};\text{int} ra} (\omega)} > \frac{1}{T_{1}^{\text{rep};\text{inter} ra} (\omega)}
\]
Frequency dependence of spin-lattice relaxation rate in reptation model

- Noncoherent reptation inside tube \( N^{-2} \ll \omega \tau_s \ll N_e^{-2} \)

\[
\frac{1}{T_{1}^{\text{rep.intra}}(\omega)} \propto \frac{\tilde{M}_2^b}{\langle b^4 \rangle_s} \frac{1}{N_e} \int_0^\infty dt \frac{\cos(\omega t) + 4 \cos(2\omega t)}{\langle r^2(t) \rangle} \propto \frac{\tilde{M}_2 \tau_s}{N_e^{3/2}} \frac{1}{(\omega \tau_s)^{3/4}}
\]

- Coherent reptation inside tube \( N^{-3}N_e \ll \omega \tau_s \ll N^{-2} \)

\[
\frac{1}{T_{1}^{\text{rep.intra}}(\omega)} \propto \frac{\tilde{M}_2^b}{\langle b^4 \rangle_s} \frac{1}{N_e} \int_0^\infty dt \frac{\cos(\omega t) + 4 \cos(2\omega t)}{\langle r^2(t) \rangle} \propto \frac{\tilde{M}_2 \tau_s}{N_e^{3/2}} \frac{N^{1/2}}{(\omega \tau_s)^{1/2}}
\]

- Normal diffusion \( \omega \tau_s \ll N^{-3}N_e \), \( \omega T_1 \gg 1 \), \( \omega r T_1 \gg \tau_1 \propto \tau_s \frac{N^3}{N_e} \)

\[
\frac{1}{T_{1}^{\text{rep.intra}}(\omega)} \propto \frac{\tilde{M}_2^b}{\langle b^4 \rangle_s} \frac{1}{N_e} \int_0^\infty dt \frac{\cos(\omega t) + 4 \cos(2\omega t)}{\langle r^2(t) \rangle} \propto \frac{\tilde{M}_2 \tau_s}{N_e^{3/2}} N^2
\]
Noncoherent reptation inside tube observed experimentally by NMR in porous systems


Experimental observation of coherent reptation inside tube by NMR in porous systems


- Perfluoropolyether melts confined in Vycor, a porous silica
- Glass of nominal pore dimension of 4 nm

![Graph](image)

**FIG. 2.** Fluorine spin-lattice relaxation dispersion curves in bulk PFPE and when confined in silanized Vycor porous glass. The solid line fitting the bulk data represents the Rouse model according to Eq. (33) with the segment fluctuation time $\tau_s=2 \times 10^{-9}$ s, $\tilde{M}_2=2.7 \times 10^{-9}$ s$^{-2}$, and $\tilde{M}_1=2.0 \times 10^{-9}$ s$^{-2}$. The data for the confined polymer can be described by a power law $T_1 \propto \nu^{0.45}$ above $10^5$ Hz which approaches limit III of the reptation model [see Eq. (36)].
Some literature connected with application of memory matrix to polymer dynamics

- Rostiashvili VG (1990) Sov Phys JETP 70: 563
- Pokrovskii VN (1992) Sov Phys Usp 35: 384
The Generalized Langevin Equation

An exact microscopic relation can be derived

\[ m \dddot{r}_n^i(t) = - \frac{\partial}{\partial \dddot{r}_n^i} W^* \left( \{ \dddot{r}_i(t) \} \right) - \sum_k \int_0^t d\tau \Gamma^{\alpha\beta}_{nk}(\tau; t - \tau) v_k^\beta(t - \tau) \hat{e}_\alpha + \vec{F}_n^Q(t) \]

- \( \frac{\partial}{\partial \dddot{r}_n^i} W^* \left( \{ \dddot{r}_i \} \right) \) is the effectively intra chain entropic force, acting on the \( n \)-th bead,
- \( \Gamma^{\alpha\beta}_{nk}(\tau; t - \tau) \) is the memory matrix,
- \( \hat{e}_\alpha \) is the unit vector aligned along the axis labeled \( \alpha = x, y, z \),
- \( v_k^\beta(t - \tau) \) is the component \( \beta \) of the \( k \)-th segment velocity at a time \( t - \tau \),
- \( \vec{F}_n^Q(t) \) is the Generalized stochastic Langevin term in analogy with the stochastic Langevin force in Rouse equations.
Exact structure of the memory matrix

• The exact expression for the memory matrix has the following structure:

\[
\Gamma^{\alpha\beta}_{nk}(\tau, t-\tau) = \frac{1}{k_B T} \left\langle F_k^{Q\beta}(0) \cdot F_n^{Q\alpha}(\tau) \right\rangle^* = \frac{1}{k_B T} \left\langle F_k^{Q\beta}(t-\tau) \cdot F_n^{Q\alpha}(t) \right\rangle^*_{\gamma_N(t-\tau)}
\]

• \( \langle \cdots \rangle^*_{\gamma_N(t-\tau)} \) is the conditional averaging over matrix variables under the condition, that phase variables of the tagged chain have constant values equal to their real values at time moment \( t - \tau \):

\[
\gamma_N(t-\tau) = \{ \tilde{\rho}_1(t-\tau), \ldots, \tilde{\rho}_N(t-\tau), \tilde{\eta}(t-\tau), \ldots, \tilde{\eta}_N(t-\tau) \}
\]
n-Renormalized Rouse Models

- After preaveraging approximation model becomes isotropic

\[
\langle F_k^{\alpha\beta}(0) \cdot F_n^{\alpha\varepsilon}(\tau) \rangle^*_{\gamma_{M(t-t)}} \approx \langle F_k^{\alpha\beta}(0) \cdot F_n^{\alpha\varepsilon}(\tau) \rangle_{\text{eq}} = \frac{1}{3} \langle \tilde{F}_k^{\alpha\beta}(0) \cdot \tilde{F}_n^{\alpha\varepsilon}(\tau) \rangle_{\text{eq}} \delta_{\alpha\beta}
\]

- The Rouse model can be considered as 0-renormalized, i.e. if to take

\[
\Gamma_{\alpha\beta}^{nk}(\tau; t - \tau) = 2 \zeta \delta(\tau) \delta_{\alpha\beta} \delta_{nk}
\]

- We will have exactly the Rouse equations

\[
m \dddot{\vec{r}}_n (t) = - \frac{\partial}{\partial \vec{r}_n} W^* \left( \{ \vec{r}_i (t) \} \right) - \zeta \ddot{\vec{v}}_n (t) + \tilde{F}_n^{\alpha\beta} (t)
\]

- For \(N \gg 1\)

\[
- \frac{\partial}{\partial \vec{r}_n} W^* \left( \{ \vec{r}_i (t) \} \right) = \frac{3 k_B T}{b^2} \frac{\partial^2 \vec{r}_n}{\partial^2 n}
\]
After extracting the fast decaying part of memory matrix

- We have for $N \gg 1$:

\[
m\ddot{r}_n(t) = \frac{3k_B T}{b^2} \frac{\partial^2 \tilde{r}_n(t)}{\partial^2 n} - \zeta \tilde{v}_n - \frac{1}{3k_B T} \sum_k \int_{t_0}^t d\tau \left< \tilde{F}_n^O(\tau) \cdot \tilde{F}_k^O(0) \right> \tilde{v}(t - \tau) + \tilde{F}_n^O(t)
\]

\[
\left< \tilde{F}_n^O(\tau) \cdot \tilde{F}_k^O(0) \right> = \int d\bar{r} \int d\bar{r}' \tilde{f}(\bar{r}) \cdot \tilde{f}(\bar{r}') \left< \delta \rho_n^O(\tau, \bar{r}) \delta \rho_k^O(0, \bar{r}') \right>
\]

$k, \bar{r}', t = 0, \delta \rho_k^O(\bar{r}')$.
Approximate structure of the memory matrix

- Using superposition approximation

\[
\Gamma_{nk}(t) = \Gamma_{n-k}(t) = \frac{8}{27} \rho_m k_B T d^6 g^2(d) \int_0^{b^{-1}} dkk^4 \hat{\omega}^Q_{nk}(k;t) \hat{S}^Q(k,t)
\]

- \(\rho_m\) is the density (concentration) of polymer segments
- \(d\) is the diameter of polymer segment
- \(g(d)\) is the radial intermolecular distribution function
- \(\hat{\omega}^Q_{nk}(k;t)\) is the single chain dynamic structure factor
- \(\hat{S}^Q(k,t)\) is the collective dynamical structure factor
Equation for the autocorrelation function of the Rouse normal modes

- Without contribution of inertia term:

\[
\frac{\partial}{\partial t} C_p(t) + \int_0^t \Gamma_p(\tau) \frac{\partial}{\partial t} C_p(t-\tau) d\tau = -\frac{1}{\tau_R} C_p(t)
\]

- Memory function corresponding to normal modes

\[
\Gamma_p(t) = \frac{1}{\zeta} \int_0^N \Gamma_m(t) \cos\left(\frac{\pi}{N} pm\right) dm =
\]

\[
\frac{16}{3/2} \frac{\psi b^3}{\tau_s \langle \ddot{R}^2(t) \rangle_{Q}} \frac{1}{\langle \dddot{R}^2(t) \rangle_Q} \int_0^{b^2} q^6 \exp\left\{-q^2\right\} q^4 + \left(\frac{2\pi \langle \dddot{R}^2(t) \rangle_Q}{Nb^2}\right)^2
\]

\[
\dot{\psi} \equiv \rho_m d^3 \left(\frac{d}{b}\right)^3 g^2(d) \hat{S}(0) \propto N_c^{-1/2} \quad \text{microscopic parameter describing the entanglement effects}
\]
Markovian approximation and n-renormalization

• The relaxation time of normal modes can be defined as

\[
\tau_{nR}^p \equiv \frac{\int_0^\infty C_p(t) \, dt}{C_p(0)}
\]

• Then

\[
\tau_{nR}^p \equiv \tau_p^R \left( 1 + \int_0^\infty \Gamma_p(t) \, dt \right)
\]

• But for \( t \to \infty \)

\[
\Gamma_p(t) \propto \frac{1}{\left< \bar{R}^2(t) \right>_Q^{5/2}} \propto \frac{1}{t^{n+3}}
\]

• And for \( n > 3 \) the integral is divergent.
Main predictions of n-Renormalized Rouse Models: Markovian approximation

• (Numerical study without Markovian approximation for n=2,1 see in M.A.Kroutieva, N.F.Fatkullun, R.Kimmcih, Polymer Science, Ser. A, 2005, v.47, № 6, p 1716-1727.)

• The relaxation time of the p-th normal mode:

\[
\tau_p^{nR} = \tau_p^R \left[1 + \left(\frac{N}{N_c p}\right)^{n/2}\right] \rightarrow \tau_s \left(\frac{N}{p}\right)^{\frac{4+n}{2}} N_c^{-n/2}
\]

• The self-diffusion coefficient

\[
D \propto \frac{R_F^2}{\tau_1} \propto \frac{b^2 N_c^{n/2}}{\tau_s^{2+n} N^{-n/2}}
\]

• For \(\tau_s N_c^2 \ll t \ll \tau_1\)

\[
\langle \overline{r^2}(t) \rangle \propto b^2 N_c^{\frac{n}{4+n}} \left(\frac{t}{\tau_s}\right)^{\frac{2}{4+n}} \quad \langle \overline{\vec{b}(t) \cdot \vec{b}(0)} \rangle \propto b^2 N_c^{-\frac{n}{4+n}} \left(\frac{\tau_s}{t}\right)^{\frac{2}{4+n}}
\]
Predictions of n-RRM for spin-lattice relaxation rate

• General expressions are like for Rouse Model:

\[
\frac{1}{T_{1}^{nR;\text{int}ra}} = \frac{M_{2}^{b}}{\langle b_{4}^{4} \rangle_{s}} \frac{2}{9 N} \sum_{k}^{\infty} \int_{0}^{\infty} dt \langle \vec{b}_{k}(t) \cdot \vec{b}_{k}(0) \rangle^{2} \left\{ \cos(\omega t) + 4 \cos(2\omega t) \right\} \\

\frac{1}{T_{1}^{nR;\text{inter}}(\omega)} = \frac{16}{15} \sqrt{\frac{3\pi}{2}} \gamma_{H}^{4} h^{2} I(I+1) \rho_{s} \int_{0}^{\infty} dt \left[ \frac{\cos(\omega t) + 4 \cos(2\omega t)}{\sigma + \langle \vec{r}^{2}(t) \rangle^{1/2}} \right]^{3}
\]

• For times \( \tau_{s} \ll t \ll \tau_{1} \) \n\[
\langle \vec{b}_{k}(t) \cdot \vec{b}_{k}(0) \rangle^{2} \propto \frac{b_{4}^{4}}{\langle r^{2}(t) \rangle^{2}}
\]

• Therefore if frequency is low enough \( \frac{1}{T_{1}^{nR;\text{inter}}(\omega)} > \frac{1}{T_{1}^{nR;\text{int}ra}(\omega)} \)

The frequency dependence of different contributions for n-RRM

• For $\tau_1^{-1} \ll \omega \ll N_e^{-2} \tau_s^{-1}$

$$
\frac{1}{T_{nR;\text{intra}}^{1}} \propto \tilde{M}_2 N_c^{-\frac{4n}{4+n}} (\omega \tau_s)^{-\frac{n}{4+n}} \quad \frac{1}{T_{nR;\text{inter}}^{1}} \propto \frac{\gamma^4 h^2 \rho_s}{b^3} N_c^{-\frac{3n}{4+n}} (\omega \tau_s)^{1+n}
$$

• For $\omega \ll \tau_1^{-1}$, $\omega T_1 \gg 1$, or $T_1 \gg \tau_1$

$$
\frac{1}{T_{nR;\text{intra}}^{1}} \propto \tilde{M}_2 \frac{\tau_1}{R_F^4} \propto \tilde{M}_2 \tau_s N_c^{-\frac{n}{2}} N^\frac{n}{2}
$$

$$
\frac{1}{T_{nR;\text{inter}}^{1}} \propto \gamma^4 h^2 \rho_s \frac{\tau_1}{R_F^3} \propto \frac{\gamma^4 h^2 \rho_s}{b^3} \tau_s N_c^{-\frac{n}{2}} N^{\frac{1+n}{2}}
$$
Experimental data for proton spin-lattice relaxation in PEO melts

- 95% PEO$_D$ + 5% PEO$_H$ (M$_w$ 460k, T=355K)

Graph showing $T_1^H$ vs. $\nu$ for 100% PEO$_H$ and 95% PEO$_D$ + 5% PEO$_H$ with exponents $\nu^{0.24}$, $\nu^{0.41}$, $\nu^{0.21}$, and $\nu^{0.46}$. 

$T_1^H$ [s]

$\nu$ [Hz]

$\sim \nu^{0.24}$

$\sim \nu^{0.41}$

$\sim \nu^{0.46}$

$\sim \nu^{0.21}$
Experimental data for proton spin-lattice relaxation in PB melts
(Polybutadiene: -CH₂-CH=CH-CH₂- )

\[ T_1^H \text{ [s]} \]

- 100% PB \(_h\)
- 95% PB \(_d\) + 5% PB \(_h\) (M\(_w\) 191k, T=355K)

~ ν\(^{0.23}\)
~ ν\(^{0.40}\)
~ ν\(^{0.45}\)
~ ν\(^{0.27}\)
$\frac{w_{\text{intra}}(\nu)}{w_{\text{inter}}(\nu)} \equiv \frac{T_{1\text{inter}}(\nu)}{T_{1\text{intra}}(\nu)}$

- Extracted from
  M.Kehr, N.Fatkullin, R.Kimmich,
  J.Chem.Phys. 126, 09403 (2007);
  127, 084911 (2007)

Poly(ethyleneoxide)
$M_w=460\,000;\, T=355K$
\[
\frac{W^{\text{intra}}(\nu)}{W^{\text{inter}}(\nu)} \equiv \frac{T^{\text{inter}}_1(\nu)}{T^{\text{intra}}_1(\nu)}
\]

- Extracted from
- M. Kehr, N. Fatkullin, R. Kimmich, J. Chem. Phys. 126, 09403 (2007);
- 127, 084911 (2007)
Results of model calculations

• The Trice Renormalized Rouse Model

\[
\frac{1}{T_1} = \int_0^\infty \left( \vec{b}(t) \cdot \vec{b}(0) \right)^2 (1 - \alpha)(\cos(\omega t) + 4\cos(2\omega t)) dt + \\
\int_0^\infty \frac{\alpha}{\left(b + \left<r^2(t)\right>^{1/2}\right)^3} (\cos(\omega t) + 4\cos(2\omega t)) dt + \\
\tau^{3R}_p = \tau^R_p \left( 1 + \left( \frac{N}{N_c p} \right)^{3/2} \right) \to \tau_s \left( \frac{N}{p} \right)^{3.5} N_c^{-1.5} \quad \text{D} \propto \frac{R_F^2}{\tau_1} \propto \frac{b^2 N_c^{3/2}}{\tau_s N^{2.5}} \quad \text{b} = 1
\]

\[
\tau_s \equiv \frac{\zeta b^2}{3\pi^2 k_B T} = 1
\]
N=4-1000, n=3  \( N_c = 80 \)  \( \alpha = 0 \)  \( N_c = 40 \)

- Trice Renormalized Rouse Model.
$N=4-1000, \ n=3 \quad N_c = 80 \quad \alpha = 0.05 \quad N_c = 40$

- Trice Renormalized Rouse Model.
N=4-1000, n=3

\( N_c = 80 \quad \alpha = 0.1 \quad N_c = 40 \)

\[ c_{N} = 1 \times 10^{-7} \quad 1 \times 10^{-6} \quad 1 \times 10^{-5} \quad 1 \times 10^{-4} \quad 1 \times 10^{-3} \quad 0.01 \quad 0.1 \quad 1 \quad 10 \]
\begin{itemize}
	\item Trice Renormalized Rouse Model
\end{itemize}

\begin{align*}
N=4-1000, \quad n=3 & \quad N_c = 80 \quad \alpha = 0.15 \quad N_c = 40
\end{align*}
Future directions.

- 1. Extensive investigations of the intermolecular magnetic dipole-dipole interactions contribution into proton spin-lattice relaxation rate in polymer melts.
- 2. The corset effect in confined polymer melts.

- Kazan, Kremlin: