On the NMR relaxation-behaviour of solid and molten polymers

Theoretical methods and model calculations

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With 9 figures and 3 tables

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1. Introduction

Molecular motion of polymers is anisotropic according to the structural properties. The purpose of this paper is to discuss the relaxation features arising from the anisotropic motion of the main chain of solid and molten polymers. Some simplified models of chain motion will be taken as basic components for the calculation of the frequency (and temperature) dependence of the longitudinal relaxation time $T_1$.

According to Pechhold's “concept of kinks” (1), localized chain defects can be considered as the mobile elements of polymer microstructure. A well known defect is the $g g$ sequence (kink), the stability of which recently has been shown by energy minimization (2, 3). Other defect structures potentially those due to more extended chain torsions are also compatible with the following consideration.

2. Definitions

The longitudinal relaxation rate in dependence of the Larmor frequency $\omega_L$ of an ensemble of interacting spins is given by a perturbation theoretical description assuming an ensemble of uncorrelated two-spin-systems as (4, 5)

$$\frac{1}{T_1} = \frac{9}{8} \gamma^4 \eta^2 \sum \{ J_{\text{L}}^{(1)}(\omega_L) + J_{\text{L}}^{(2)}(\omega_L) \} \tag{1}$$

where the sum comprises all nuclei interacting with the reference nucleus.

Dipolar interaction leads to intensity functions

$$j^{(i)}_k(\omega_L) = \int_{-\infty}^{+\infty} \phi_k^{(i)}(\tau_k(0)) \phi_k^{(-i)}(\tau_k(\tau)) e^{i\omega(1)\tau} d\tau$$

$$i = 1, 2$$

$$\omega^{(1)} = \omega_L$$

$$\omega^{(2)} = 2 \omega_L$$

$$j = \pm 1$$

depending on the dipolar interaction functions

$$\phi_k^{(\pm 1)} = \frac{1}{r_k^3} \cos \theta_k \sin \theta_k e^{\pm j q_k}$$

$$\phi_k^{(\pm 2)} = \frac{1}{r_k^2} \sin^2 \theta_k e^{\pm 2 j q_k} \tag{3}$$

$\gamma$ magnetogyric ratio, $r_k$, $\theta_k$, $\phi_k$ spherical coordinates of the spin-spin-vector.

The autocorrelation function, given as the ensemble averaged product of the dipolar interaction functions at time 0 and $\tau^1$, can be written as (ref. 5 p. 271)

$$G_k(\tau) = \frac{\phi_k^{(0)}(\tau(0)) \phi_k^{(-i)}(\tau(\tau))}{\int \{ W(r', 0 | r^*, \tau) \phi_k^{(0)}(r^*) \}}$$

where $r'$, $r^*$ denote the spin-spin-vectors.

The probability that at time 0 the two spins taken into consideration are connected by $r'$ and at time $\tau$ by $r^*$ can be split into

$$W(r', 0 | r^*, \tau) = p(r') W_b(r', r^*, \tau) \tag{5}$$

1) Read $\tau$ as the absolute value of the considered period $t_2 - t_1$. 

(\(p(\mathcal{r})\)): a priori probability of finding \(\mathcal{r}'\),
\(W_b(\mathcal{r}', \mathcal{r}'', \tau)\): conditional probability of finding \(\mathcal{r}''\) at time \(\tau\) if there was \(\mathcal{r}'\) at time \(\delta\).

Well known correlation functions (5) are those for rotational diffusion (continuous isotropic desorientation of \(\mathcal{r}\) at constant length) and for translational diffusion (continuous change of |\(\mathcal{r}\)| in addition). Molecular motion can be described by such continuous diffusion processes or, at the other extreme, as a jump process between \(N\) discrete positions (or conformations) having different interaction functions, while transition times are neglected. In this case the integrals in eq. [4] can be replaced by a sum

\[
G_k^{(i)}(\tau) = \sum_{l=1}^{N} \sum_{m=1}^{N} p(\mathcal{r}_l) W_b(\mathcal{r}_l, \mathcal{r}_m, \tau) \phi_k^{(i)}(\mathcal{r}_l) \phi_k^{(i)}(\mathcal{r}_m)
\]

Eq. [6] can be written in matrix form (the spin-spin-vectors of the various states are replaced by numbers)

\[
G_k^{(i)}(\tau) = (\sum_{l=1}^{N} p(\mathcal{r}_l)) \phi_k^{(i)}(1) \begin{pmatrix}
W_b(1,1,\tau) & \cdots & W_b(1,N,\tau) \\
\vdots & \ddots & \vdots \\
W_b(N,1,\tau) & \cdots & W_b(N,N,\tau)
\end{pmatrix} \begin{pmatrix}
\phi_k^{(i)}(1) \\
\vdots \\
\phi_k^{(i)}(N)
\end{pmatrix}
\]

According to equ. [2] the intensity functions are given by

\[
J_k^{(i)}(\omega_L) = (\sum_{l=1}^{N} p(\mathcal{r}_l)) \phi_k^{(i)}(1) \begin{pmatrix}
\mathcal{F}^{(i)}\{W_b(1,1,\tau)\} & \cdots & \mathcal{F}^{(i)}\{W_b(1,N,\tau)\} \\
\vdots & \ddots & \vdots \\
\mathcal{F}^{(i)}\{W_b(N,1,\tau)\} & \cdots & \mathcal{F}^{(i)}\{W_b(N,N,\tau)\}
\end{pmatrix} \begin{pmatrix}
\phi_k^{(i)}(1) \\
\vdots \\
\phi_k^{(i)}(N)
\end{pmatrix}
\]

\([\mathcal{F}^{(i)}\{\ldots\}]\) denotes Fourier transformation with respect to frequency \(\omega^{(i)}\) (see equ. [2]). Alternatively the a priori probabilities can be enclosed in the middle matrix).

In the following sections we shall assume jump models keeping in mind, that the modulation of this "rectangular" time dependence of the dipolar interaction functions with oscillations (6) to produce smoother transitions would be closer to reality. Furthermore, we shall avoid at this stage any distribution of correlation functions (2) i.e. we consider homogeneous subsystems of nuclei.

3. Matrix method for calculation of the conditional probabilities \(W_b\)

3.1. Two conformation jump model

The problem of determination of the relaxation rates has been reduced to the calculation of conditional probabilities. At first let us treat a simple two conformation jump model.

Assume a molecule being able to jump with frequencies \(\alpha\) and \(\beta\) between two conformations 1 and 2 which are characterized by two sets of dipolar interaction functions (fig. 1). In order to retain general validity we admit different energies of conformation. In fig. 2 one exemplary time evolution of conformations between the times \(t = 0\) and \(t = \tau\) is shown. Subdividing the time axis in infinitesimal intervals \(\Delta t \leq \frac{1}{\alpha, \beta}\) we may treat this