



Free induction decays in entangled polymer melts

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ABSTRACT

The relaxation of the transverse magnetization components caused by both dipolar interactions between the spins of different polymer chains and the dipolar coupling between CH-protons on an isolated Kuhn segment along a single polymer chain have been calculated. Explicit expressions for the transverse relaxation function are given in terms of the absolute mean squared displacement of the Kuhn segment during melt $g_r(t)$, the tangent vector dynamical correlation function $\langle \mathbf{b}_n(t)\mathbf{b}(0) \rangle$, the segmental relaxation time τ_s , the Kuhn segment length b , the bond length a_0 , the internuclear distance d , and the spin number density ρ_s . It is shown that the functional dependence of the intramolecular relaxation function on $\langle \mathbf{b}_n(t)\mathbf{b}(0) \rangle$ is fairly weak. The time-dependence of the intramolecular contribution to the transverse relaxation function is dominated by the probability density distribution function of the end-to-end vector of the Kuhn segment. The long-time decay of the intramolecular contribution to the transverse relaxation function is found to scale as $t^{-3/2}$ for $\tau_s \ll t \ll \tau_{\max}$, where τ_{\max} is the maximum relaxation time of polymer chains in melts. For times much less than the spin-spin relaxation time, $T_2 \approx 10^{-3} - 10^{-2}$ s, we show that the intermolecular contribution to the relaxation function is given by the following expression: $\exp(-\lambda_1(b, \tau_s, \rho_s)t^2/g_r^{3/2}(t))$. Both the numerical coefficient and the functional dependence of λ_1 on b , τ_s and ρ_s reproduce the expression obtained from the frequently used second cumulant approximation. For longer times ($T_2 \leq t \ll \tau_{\max}$), the intermolecular contribution is determined by the following relation: $\exp(-\lambda_2(b, \tau_s, \rho_s, t)g_r(t))$. We show that λ_2 increases logarithmically with t . The molecular mass independence of λ_1 and λ_2 shows that, in polymer melts with molecular masses M_w far above the critical value M_c , the relevant experimental window for the decay of the intermolecular relaxation function is connected with the anomalous diffusion regime. Comparison with the experimental data suggests that the intermolecular contribution plays a significant role in the NMR relaxation process in polymer systems close to the melting point.

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1. Introduction

One of the fundamental problems of magnetic resonance in polymer systems is the calculation of the transverse relaxation function. Currently, detailed theories of free induction decay (FID) are only developed for systems with very short or very long local field modulation correlation times $\delta\tau_c \ll 1$ or $\delta\tau_c \gg 1$, where δ is the width of an absorption line. The first case is typical of simple liquids; the second one occurs in crystal lattices. For the intermediate correlation times $\delta\tau_c \sim 1$ that occur in melts with molecular masses M_w far above the critical value M_c , the general expression for the transverse relaxation function has not yet been obtained.

Magnetic relaxation in melts of low molecular mass polymers ($M_w \ll M_c$) is well described with the Bloch–Redfield–Wangsness approach [1–7]. According to this method, the diffusion processes are assumed to be very fast relative to the experimentally relevant time scale; thus, the magnetization decay is very slow. For fast modulations $\delta\tau_c \ll 1$, Gaussian stochastic processes lead to the motional

narrowing limit, in which the Bloch–Redfield–Wangsness theory is applicable.

Entangled polymer melts ($M_w \gg M_c$) have been successfully treated by the method of cumulants [8–16]. For Gaussian stochastic processes, the cumulant expansion holds whether fast or slow motion is assumed. For relatively long correlation times, the magnetic resonance line shape has been found to be very similar to that of a Gaussian function.

Another facet of the problem is the consideration of intra- and intermolecular contributions to magnetic relaxation in polymer systems. Generally, spin-spin interactions within a single Kuhn segment (intramolecular interactions) are expected to dominate in relaxation processes because the intermolecular dipole-dipole interactions decrease with r , exhibiting an r^{-3} dependence. Nevertheless, recent experimental research [17,18] has shown that for low resonance frequencies, $\nu \sim 10^2 - 10^8$ Hz, intermolecular contributions can be greater than intramolecular contributions. This result is also supported by the theoretical estimate of the spin-lattice relaxation rate for low frequencies [19,20]: $(1/T_1)_{\text{int ra}} \sim \nu^{-1/3}$ and $(1/T_1)_{\text{int er}} \sim \nu^{-1/2}$, where $\tau_{\max}^{-1} < \nu < \tau_s^{-1}$. Here, $\tau_s = 10^{-10} - 10^{-9}$ s is a typical value of the Kuhn segment relaxation time at room temperature,

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$\tau_{\max} \approx \tau_s N^{3+3.4}$ is the maximum relaxation time of polymer chains in melts, and N is the number of Kuhn segments per polymer chain.

Based on the reptation model [21] and the twice renormalized Rouse model [22], Fenchenko [16] derived the relations for the second ($\tilde{M}_2(t)$) and fourth ($\tilde{M}_4(t)$) cumulants, considering both the intramolecular and intermolecular contributions. The results proved to be in a good agreement with experimental data in the time interval $0 < t < T_2$ for molecular masses $M_w \gg M_c$. A reasonable estimate for the spin-spin relaxation time in polymer melts with molecular masses $M_w \gg M_c$ is $T_2 \approx 10^{-3} - 10^{-2}$ s. However, the theoretical values of the transverse relaxation function within the relevant experimental window $T_2 < t < \tau_{\max}$ differ from the experimental data by a factor greater than ten.

Using the stochastic trajectory method, Brereton [23–25] calculated the transverse relaxation function for an isolated spin pair that is rigidly connected to a monomer of a polymer chain. Although this method allows both short ($t < T_2$) and long ($t > T_2$) times to be considered, it only takes into account intramolecular interactions and neglects intermolecular ones.

All perturbation theories address the first few orders of expansion. For polymer melts, the stochastic effects are not assumed to be strong compared to the constant Zeeman interaction. However, this assumption is only valid in the case of either intramolecular (“internal”) relaxation or short-time ($t < T_2$) intermolecular effects. A theoretical description of slow stochastic processes may require additional terms in the expansion series; thus, the regime of relatively slow motion ($\delta\tau_c \sim 1$) is still beyond the scope of perturbation theory.

In this paper, we present a new perturbation technique for the investigation of the transverse relaxation characterized by intermediate times $\tau_s \ll t \ll \tau_{\max}$. In the given approach, both the intramolecular and intermolecular contributions are considered. We argue that the probability distribution of the end-to-end vector of the Kuhn segment is manifested in the contribution of intramolecular interactions to the relaxation processes. Using the method described by Alexandrov–Karamjan [26] for the case of intermolecular (“external”) relaxation in a system with a diffusion-modulated interaction, it is shown that the intermolecular contribution to the transverse relaxation function in polymer melts is described by a stretched exponential law. The theoretical results are in a good agreement with the experimental results.

2. Mathematical formulation of the problem

2.1. The intermolecular contribution

Initially, we consider the case of a frozen intra-group and segmental motion. In this case, the free induction decay can be treated by the method of moments [27,28] or the modified method of moment [29], e.g., by the methods commonly used for describing FID in solids.

The secular part of the magnetic dipole–dipole interaction Hamiltonian can be written in the following form:

$$\begin{aligned} \hat{H} &= \hbar(\hat{\alpha} + \hat{\beta}) \\ \hat{\alpha} &= \frac{1}{2N_0\hbar} \sum_{j \neq k} A_{jk} \mathbf{I}_j \mathbf{I}_k \\ \hat{\beta} &= \frac{1}{2N_0\hbar} \sum_{j \neq k} B_{jk} I_{zj} I_{zk} \\ B_{jk} &= -\frac{3\gamma^2 \hbar^2}{2r_{jk}^3} (3 \cos^2 \theta_{jk} - 1), A_{jk} = -\frac{1}{3} B_{jk} \end{aligned} \quad (1)$$

Here, I_x is the x component of the total moment operator, θ_{jk} is the angle between an external magnetic field \mathbf{B}_0 and the vector \mathbf{r}_{jk} connecting the j -th and k -th spins, γ is the magnetogyric ratio, and N_0 is the total number of spins in the volume sample V . Note that $[\hat{\alpha}, I_x] = 0$ and $[\hat{\beta}, I_x] \neq 0$.

The expansion of the transverse relaxation function in a power series of the commutator $[\hat{\alpha}, \hat{\beta}]$ leads to the following expression for FID in solids when $l = 1/2$ [29]:

$$\begin{aligned} F_{\text{solids}}(t) &= U_{\text{solids}}(t) S_{\text{solids}}(t) \\ U_{\text{solids}}(t) &= \prod_j \cos(B_{jk} t / (2\hbar)) \\ S_{\text{solids}}(t) &= 1 - \frac{1}{6} \left(\frac{t}{2\hbar}\right)^2 \frac{1}{N_0} \sum_{j \neq k \neq m} \left\{ \left[B_{jk} t g\left(\frac{B_{jk} t}{2\hbar}\right) \right] \left[B_{jm} t g\left(\frac{B_{jm} t}{2\hbar}\right) \right] - \right. \\ &\quad \left. - \left[B_{jk} t g\left(\frac{B_{jk} t}{2\hbar}\right) \right] \left[B_{km} t g\left(\frac{B_{km} t}{2\hbar}\right) \right] \right\} + \frac{1}{9} \left(\frac{t}{2\hbar}\right)^3 \frac{1}{N_0} \sum_{j \neq k \neq m} \left\{ 2B_{jk}^2 B_{km} - \right. \\ &\quad \left. - B_{jk}^2 B_{jm} - B_{jk} B_{jm} B_{km} \right\} t g\left(\frac{B_{km} t}{2\hbar}\right) - \frac{1}{12} \left(\frac{t}{2\hbar}\right)^4 \frac{1}{N_0} \sum_{j \neq k \neq m} \left\{ B_{jk}^2 B_{km}^2 - B_{jk}^2 B_{km} B_{jm} \right\} \\ &\quad + O(\{B^4\}) \end{aligned} \quad (2)$$

$\{B^4\}$ indicates that the series was cut off at the fourth order terms. The $U_{\text{solids}}(t)$ function that is connected with the $\hat{\beta}$ - component of the magnetic dipole-dipole interaction Hamiltonian presents direct quantum-mechanical transitions, which are defined in terms of the second order term of the perturbation expansion for FID. The $S_{\text{solids}}(t)$ function describes the three spin processes induced by the commutator of $\hat{\alpha}$ (the scalar exchange interactions) and $\hat{\beta}$ components. Crystals demonstrate the best agreement between Eq. 2 and the experimental data [28,29].

Now, let the segmental motions in the polymer melts be switched on, i.e., the spin system fluctuates in a spatial position with a rate of $\tau_c^{-1} \sim \delta$. For the sake of convenience, we introduce a procedure for the numeration of the spins in polymer melts. The vectors $\mathbf{r}_{\alpha n \Psi, \beta k \Omega}(t)$ connecting the spins Ψ and Ω (which belong to the n th and k th Kuhn segments of macromolecules α and β , respectively) at moment t are assumed to be random functions. We consider the system of spins coupled by dipole–dipole intermolecular interactions in which each Kuhn segment bears two $spin - 1/2$ nuclei. Averaging Eq. 2 over all possible values of the random functions $\mathbf{r}_{\alpha j \Psi, \beta k \Omega}(t)$ and expanding $t g(B_{\alpha n \Psi, \beta k \Omega} t / (2\hbar))$ in a power series to the first order, we obtain

$$\begin{aligned} F(t) &\approx \langle U_{\text{inter}}(t) U_{\text{intra}}(t) S(t) \rangle_t \approx \langle U_{\text{inter}}(t) \rangle_t \langle U_{\text{intra}}(t) \rangle_t \langle S(t) \rangle_t \\ F_{\text{inter}}(t) &\equiv \langle U_{\text{inter}}(t) \rangle_t = \left\langle \prod_{\beta=2n,k}^{n_M, N} \cos\left(\int_0^t d\tau B_{1n1, \beta k1}(\tau) / (2\hbar)\right) \right\rangle_t \\ F_{\text{intra}}(t) &\equiv \langle U_{\text{intra}}(t) \rangle_t = \left\langle \cos\left(\int_0^t d\tau B_{\alpha n1, \alpha n2}(\tau) / (2\hbar)\right) \right\rangle_t \\ \langle S(t) \rangle_t &= 1 - \frac{1}{36} (\tilde{S}_1(t) - \tilde{S}_2(t)) + O(\{B^4\}) \\ \tilde{S}_1(t) &\equiv \frac{1}{(2\hbar)^4} T \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \frac{1}{N_0} \left\langle \sum_{A \neq C \neq D} B_{AC}(t_1) B_{AC}(t_2) B_{AD}(t_3) B_{AD}(t_4) \right\rangle_t \\ \tilde{S}_2(t) &\equiv \frac{1}{(2\hbar)^4} T \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \frac{1}{N_0} \left\langle \sum_{A \neq C \neq D} B_{AC}(t_1) B_{AC}(t_2) B_{CD}(t_3) B_{AD}(t_4) \right\rangle_t \end{aligned} \quad (3)$$

where $\langle \dots \rangle_t$ is the average over $\mathbf{r}_{\alpha n \Psi, \beta k \Omega}(t)$; n_M is the number of macromolecules in the melt; $A, C,$ and D are complex indexes that describe all combinations of a number triple (α, n, Ψ) ; and \hat{T} is the time ordering operator. $B_{\alpha n1, \alpha n2}(t) = -(3\gamma^2 \hbar^2 / 2d^3) (3 \cos^2 \theta_{\alpha n1, \alpha n2}(t) - 1)$ is the coordinate part of the intrasegmental dipolar couplings at moment t , and d is the internuclear distance (for example, the distance between the protons in a CH_2 group is $d \approx 1.8 \text{ \AA}$). $B_{1n1, \beta k1}(t) = -(3\gamma^2 \hbar^2 / 2r_{1n1, \beta k1}^3(t)) (3 \cos^2 \theta_{1n1, \beta k1}(t) - 1)$ is the coordinate part of the intermolecular dipolar couplings modulated by the relative motions of macromolecules. Note that the second-order terms in expansions (2) and (3) are zero because of the commutation rules of moment operators; in addition, the stochastic independence of the relative motions of the protons on different chains and the Brownian rotation motions of the Kuhn segment are assumed. Here, the $F_{\text{inter}}(t)$

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