Theory of stimulated spin echo in polymer systems

N. F. Fatkullin

Kazan State University

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A theory of stimulated spin echo with pulsed magnetic-field gradients is developed on the basis of the density-matrix formalism. Two effects vital for polymer systems of sufficiently large mass are predicted: an influence of spin-flop processes on the diffusion damping mechanism and an influence of pulsed magnetic-field gradients on the rates of the relaxation processes. The spin-diffusion coefficients are calculated for polymer melts; in contrast to low molecular liquid-phase systems they differ significantly from the macromolecule self-diffusion coefficients.

1. INTRODUCTION

Stimulated spin echo (SSE) with pulsed magnetic-field gradients is a traditional method of investigating the translational mobility of molecules with magnetic nuclei (see, e.g., Refs. 1–3). Its essence reduces to the following. The spin system of a substance is acted upon by a series of five magnetic-field pulses, of which three are 90-degree RF pulses and two are magnetic-field gradient pulses. Let τ_1 be the time between the first and second RF pulses, τ_2 the time between the second and third RF pulses, δ the duration of the gradient pulses, and g the amplitude of the gradient pulse. As is well known,[1-3] the response of the spin system of the investigated substance—the spin-echo amplitude—is measured at the instant $t = 2\tau_1 + \tau_2$ after the start of the experiment.

The SSE amplitude is measured as a rule phenomenologically, using either specially modified Bloch equations or methods of the "phase accumulation" type (see Refs. 1 and 2). Such calculations lead to the following expression for the normalized SSE amplitude of magnetically homogeneous systems:

$$A(g)=\exp\left(-\frac{2\tau_1}{T_2}\right)\exp\left(-\frac{\tau_2}{T_1}\right)\frac{1}{N_s}\sum_k\langle\exp[i(\varphi_{2k}-\varphi_{1k})]\rangle, \tag{1}$$

where T_1 and T_2 are the spin–lattice and spin–spin relaxation times, respectively, φ_{1k} and φ_{2k} are the phase shifts of the kth spin of the system during the actions of the first and second gradient pulses, and N_s is the total number of spins in the system.

The phase shifts φ_{1k} and φ_{2k} contain information on the spatial displacements of the spins:[1-3]

$$\varphi_{1k}=\gamma\int_0^\delta \mathbf{g}\mathbf{r}_k(\tau)\,d\tau,$$
$$\varphi_{2k}=\gamma\int_0^\delta \mathbf{g}\mathbf{r}_k(\tau_1+\tau_2+\tau)\,d\tau, \tag{2}$$

where γ is the gyromagnetic ratio, $\mathbf{g}$ is the magnetic-field gradient vector, $\mathbf{r}_k(\tau)$ is the radius vector of the kth spin at the instant τ, and $\langle\ldots\rangle$ stands for statistical averaging over all random realizations of the trajectories of the system's kth spin.

The first two factors in (1) are connected with relaxation damping and the third with diffusive damping of the SSE. The following procedure is customarily employed to separate the diffusive and relaxation damping. The SSE amplitude $A(0)$ is measured at zero magnetic-field and then the quantity $\tilde{A}(g) = A(g)/A(0)$, called the SSE diffusive damping amplitude, is calculated for a specified magnetic-field gradient $A(g)$.

It is easily seen from (1) that the diffusive SSE damping satisfies the equation

$$\tilde{A}(g)=\frac{1}{N_s}\sum_k\langle\exp\{i(\varphi_{2k}-\varphi_{1k})\}\rangle. \tag{3}$$

This quantity is in effect the incoherent dynamic Van Hove factor (see, e.g., Ref. 4) of the system and contains information on the spatial displacements of the system spins. The parameter $\gamma\delta g$ is the analog of the wave vector and a reciprocal measure of the spatial resolution of the experiment.

The described theoretical basis for relations (1) and (3), however, oversimplifies the real kinetics of the spin system. The point is that relation (1) takes into account only the following processes:

1) spin–spin relaxation, which affects $A(g)$ between the first and second and after the third RF pulse;

2) spin–lattice relaxation, which decreases the amplitude $A(g)$ between the second and third RF pulses;

3) spatial displacements of the spins between the first and third RF pulses.

Flip-flop processes that cause spin diffusion are also possible, and the magnetic-field gradients can influence the spin relaxation.

Allowance for these processes may seem at first glance inessential for the following reasons. The characteristic times for performing the experiment are $\tau_1 \approx 10^{-3}$ s, $\delta < \tau_1$, $\tau_2 \approx 10^{-1}$–1 s and the characteristic relaxation times are $T_2 \approx 10^{-3}$–10^{-2} s, $T_1 \approx 10^{-1}$–1 s (see Ref. 3). The characteristic flip-flop times are $T_2 \lesssim \tau_f \lesssim T_1$, i.e., $\tau_f \approx 0.1$–1 s. Within these times the nuclei in liquid-phase systems are displaced by a distance $r(\tau_f) \approx 10^2$–10^4 Å. Flip-flop processes induce exchange of magnetic polarization between spins that approach one another. This leads to additional displacements of magnetic polarization (of the spin diffusion). Flip-flop processes, however, are caused by short-range dipole–dipole interactions. Additional magnetic-polarization displacements due to flip-flop processes are therefore of the order of $a_0 \approx 1$–2 Å, i.e., of the distance between nearest neighboring magnetic nuclei. It might seem thus that allowance for the effects in question can lead only to corrections of order $[a_0/r(\tau_f)]^2 \ll 1$ to the measured macromolecule self-diffusion coefficients.

An influence of pulsed magnetic-field gradients on spin relaxation, on the other hand, is at first glance possible only during the time δ of action of the magnetic-field gradient. It is customary to attempt to make this time $\delta < \tau_1 \ll \tau_2$ as short as possible. One can also naturally expect the corresponding corrections to be small.

The action of the aforementioned factors can nonetheless be predominant. The point is that the macromolecule terminal relaxation time T_r depends strongly on the molecular mass, $T_r \sim N^3$, where N is the number of Kuhn segments in the macromolecule (see Refs. 5–8). This means that for macromolecules of sufficiently large mass we have $T_r \gg \tau_f$, so that the time of stochastiation of the spatial spreading of the nonequilibrium magnetization in the sample will not be T_r by τ_f, which leads indeed to a qualitatively different behavior. The ensuing questions are in fact the subject of the present article.

2. AMPLITUDE OF STIMULATED SPIN ECHO WITH PULSED MAGNETIC-FIELD GRADIENTS

We choose the Hamiltonian of the spin subsystem in the form

$$\hat{H}=\hat{H}_0+\hat{H}_{dd}+\hat{H}_{rf}+\hat{H}_g, \tag{4}$$

where $\hat{H}_0 = \Sigma_n \hbar\omega_n \hat{I}_n^z$ is the Hamiltonian of the Zeeman interaction of the spins with the constant magnetic field, ω_n is the frequency of the Larmor precession of the nth spin, the summation is over all the spins of the system,

$$\hat{H}_{dd}=\sum_{n<m}\gamma^2\hbar^2\left(\frac{\hat{\mathbf{I}}_k\hat{\mathbf{I}}_m}{r_{nm}^{\ 3}(t)}-3\frac{(\mathbf{r}_{nm}(t)\hat{\mathbf{I}}_k)\,(\mathbf{r}_{nm}(t)\hat{\mathbf{I}}_m)}{r_{nm}^{\ 5}(t)}\right)$$

is the dipole–dipole interaction operator of the system spins, $\mathbf{r}_{nm}(t)$ is the vector joining the spins numbered n and m at the instant of time t, $\hat{\mathbf{I}}_n$ is the spin-vector operator,

$$\hat{H}_{rf}=\sum_n \frac{\pi}{2}\hbar\hat{I}_n^{x}[\delta(t)+\delta(t-\tau_1)+\delta(t-\tau_1-\tau_2)]$$

is the Hamiltonian of the 90-degree RF momenta that rotate the spin system through an angle $\pi/2$ around the x axis,

$$\hat{H}_g=\sum_n \hbar\gamma_g z_n(tI_n^{z}[\delta(t)+\delta(t-\tau_1-\tau_2)]$$

is the Hamiltonian of the magnetic-field-gradient pulses along the z axis, and $z_n(t)$ is the spatial coordinate of the nth spin at the instant of time t.

Note that the RF and gradient pulses are assumed to be much shorter than the times T_1 and T_2, and also that the gradient pulses act on the system after the first and second RF pulses.

We describe the state of the spin system with the aid of a density matrix $\hat{\rho}(t)$ satisfying the evolution equation

$$i\hbar\frac{\partial}{\partial t}\hat{\rho}(t)=[\hat{H};\hat{\rho}]. \tag{5}$$

The initial state of the nonrenormalized density matrix takes in the high-temperature approximation the form

$$\rho_0=I-\beta\hat{H}_0, \tag{6}$$

where $\beta = (kT)^{-1}$ is the reciprocal temperature.

The functions $\mathbf{r}_{nm}(t)$ that describe the relative spatial spin displacements and are contained in (4) and (5) will be treated as stationary random processes with known correlation functions. Note that this approach and relation (6) are standard and well-corroborated approximations in NMR theory (see, e.g., Refs. 1, 2, and 9).

The measured evolution of the system's macroscopic magnetic moment is proportional to the mean value of the macroscopic spin component:

$$\langle \hat{I}^+(t)\rangle=\mathrm{Sp}[\hat{I}^+\hat{\rho}(t)], \tag{7}$$

where $\hat{I}^+ = \Sigma_n(\hat{I}_n^x + i\hat{I}_n^y)$ and $\hat{\rho}(t)$ is the solution of Eq. (5) with initial condition (6).

In view of the presence of multiparticle interactions in the operator $\hat{H}_{dd}$, no exact solution of Eq. (5) is known. The standard means of theoretically analyzing expressions of type (7) in such situations is perturbation theory in the operator $\hat{H}_{dd}$, while the action of the operators $\hat{H}_{rf}$ and $\hat{H}_g$ can be taken into account exactly with no particular difficulty. The unwieldy form of the operator $\hat{H}_{dd}$, however, complicates greatly the calculations of the higher-order terms of the perturbation-theory series. As a rule, therefore, only the first nonzero moment of the perturbation-theory series, corresponding to second order in the operator $\hat{H}_{dd}$, lends itself to an effective theoretical analysis. For a number of physical situations, for example for low-viscosity liquids, for which the short-correlation-time approximation can be used, higher orders of perturbation theory reduce to second order. In these cases the second-order perturbation theory results describe adequately the spin-system dynamics.

A feature of polymer systems is the existence of a correlation-time spectrum. The terminal relaxation time, as noted above, increases monotonically with the molecular mass. Even in this case, however, one can hope that the physical effects reflected in second-order perturbation theory in the operator $\hat{H}_{dd}$ describe correctly the real situations at least qualitatively. For quantities determined by local motions of the macromolecules, with times $\tau_0 \approx 10^{-10}$–10^{-8} s, however, the short-correlation-time approximation is certainly valid. One can count here also on a qualitative agreement.

Omitting the details of the unwieldy and standard calculations, we write for the stimulated-echo amplitude normalized to the total number of spins in the system and calculated to second-order perturbation theory in the operator $\hat{H}_{dd}$:

$$\begin{aligned}A(g)=&\sum_n\langle\exp\{i(\varphi_{2n}-\varphi_{1n})\}\rangle\\&\times(1-P_{fn}(\tau_2)-2P_{2n}{}'(\tau_1)-P_{1n}{}'(\tau_2))\\&+\sum_{n\neq m}\langle\exp[i(\varphi_{2n}-\varphi_{1m})]\rangle[P_{fnm}(\tau_2)-2P''_{2nm}(\tau_1)-P''_{1nm}(\tau_2)],\end{aligned} \tag{8}$$

where $P_{fn}(\tau_2)$ is the probability of a flip–flop transition of the magnetic polarization from the nth spin of the system to any other in a time τ_2, $2P'_{2nm}(\tau_1)$ is that part of the contribution to the spin–spin relaxation probability which is connected with the dipole–dipole interactions, $P'_{1nm}(\tau_2)$ is the analogous contribution to the probability of the spin–lattice relaxation, and $P_{fnm}(\tau_2)$ is the probability of a flip-flop between the nth and mth spins.

The following natural relations are obtained for the total probabilities of the above processes:

$$
\begin{aligned}
&P_{fn}(\tau_2)=\sum_m P_{fnm}(\tau_2),\\
&P_{1n}(\tau_2)=P_{1n}'(\tau_2)+\sum_m P_{1nm}''(\tau_2),\\
&P_{2n}(\tau_1)=P_{2n}'(\tau_1)+\sum_m P_{2nm}''(\tau_1),
\end{aligned}
\tag{9}
$$

where $P_{1n}(\tau_2)$ is the total probability of spin–lattice relaxation of the nth spin between the second and third RF pulses; $2p_{2n}(\tau_1)$ is the total probability of the spin–spin relaxation between the first and third and after the third RF pulses.

To understand expression (8) better, we compare it with the "classical" expression (9) expanded in a Taylor series:

$$
A(g)=\sum_n \langle \exp[i(\varphi_{2n}-\varphi_{1n})]\rangle\left(1-\frac{2\tau_1}{T_2}-\frac{\tau_2}{T_1}+\ldots\right), \tag{10}
$$

Comparing (8) with (10) at zero magnetic-field gradient, i.e., $\varphi_{1n}=\varphi_{2n}=0$, and taking (9) into account we find readily the correspondence

$$
\begin{aligned}
&2P_{2n}(\tau_1)\to 2\tau_1/T_2,\\
&P_{1n}(\tau_2)\to \tau_1/T_1.
\end{aligned}
\tag{11}
$$

Expression (8), which is accurate to second-order perturbation theory, differs from its "classical" analog (10) in two respects: 1) by the presence of terms proportional to $P_{fn}(\tau_2)$ and $P_{fnm}(\tau_2)$, which are connected with the influence of the flip-flop processes on the amplitude $A(g)$; 2) by the splitting of the probabilities of the relaxation processes [see (8)–(11)] into partial probabilities of type P' and P''. This splitting is due to the influence of the gradient magnetic-field pulses on the relaxation processes and leads to defactoring of the spin-echo amplitude.

The qualitative cause of the indicated effects is the following. The spatial inhomogeneity of the system's magnetic field along the z axis, which sets in after the second RF pulse, is equalized in the presence of dipole–dipole interactions not only on account of spatial displacements of the spins themselves, but also on account of spin-polarization exchange induced by flip-flop processes. Note that this takes place only in the interval between the second and third RF pulses, when the system's magnetic moment is oriented on the average along the z axis. At other instants of time the spin-flop processes contribute only to the spin–lattice-relaxation processes, as taken phenomenologically into account in (1).

As to the probabilities of the relaxation transitions, the point is that the dipole–dipole interactions are two-particle, while the relaxation transition itself is of quantum character, as indicated for example in Eqs. (12) and (13) that follow. Typical relaxation times are $T_1\approx 10^{-1}$–1 s and $T_2\approx 10^{-2}$–10^{-3} s. Therefore spins numbered n and m, which underwent mutual relaxation transitions, were separated at the initial instant from one another by distances of the order of the molecule paths traversed during the times T_1 and T_2. In the absence of magnetic-field gradients the mutual orientations of the spins are determined only by Gibbs statistics. In the presence of a gradient, spins located at different points of space are rotated through different angles about the z axis. The Gibbs statistics is violated, as is manifested by the defactoring of the spin-echo amplitude.

Expression (8) for the amplitude $A(g)$, as already noted, was obtained in second-order perturbation theory in the operator $\hat{H}_{dd}$. Its physical meaning, however, is very simple. It is clear therefore that the next higher orders of perturbation theory will lead only to more exact equations for the probabilities $P_{fn}(\tau_2)$, $P_{fnm}(\tau_2)$, $P_{in}'(\tau_1)$, etc. in the right-hand side of (8), but the structure of this relation will not change further.

We call attention also to the difference between the influences of the relaxation and flip-flop-processes on the spin-echo amplitude. This influence is manifested by different signs in front of $P_{fnm}(\tau_2)$ and in front of $P_{2nm}''(\tau_1)$ and $P_{nm}''(\tau_2)$ in relation (8). The point is that flip-flop processes induce during the time τ_2 a spin diffusion, whereas relaxation processes decrease the total number of spins that form the spin-echo signal.

The expressions for probabilities of type P_2 in second-order perturbation theory turned out to be

$$
\begin{aligned}
P_{2n}'(\tau_1)={}&\frac{3}{8}I(I+1)\gamma^4\hbar^2\sum_m\int_{-\tau_1}^{\tau_1}(\tau_1-|\tau|)\left[\frac{5}{9}L_{nm}^{zz}(\tau)\right.\\
&\left.+6L_{nm}^{z+}(\tau)\exp(i\omega_0\tau)+L_{nm}^{++}(\tau)\exp(2i\omega_0\tau)\right]d\tau,\\
P_{2nm}''(\tau_1)={}&\frac{3}{8}I(I+1)\gamma^4\hbar^2\int_{-\tau_1}^{\tau_1}(\tau_1-|\tau|)\\
&\times\left[\frac{4}{9}L_{nm}^{zz}(\tau)+4L_{nm}^{z+}(\tau)\exp(i\omega_0\tau)\right]d\tau,
\end{aligned}
\tag{12}
$$

where

$$
\begin{aligned}
L_{nm}^{zz}(\tau)={}&\left\langle\frac{1-3\cos^2\theta_{nm}(\tau)}{r_{nm}^3(\tau)}\,\frac{1-3\cos^2\theta_{nm}(0)}{r_{nm}^3(0)}\right\rangle,\\
L_{nm}^{z+}(\tau)={}&\left\langle\frac{\sin\theta_{nm}(\tau)\cos\theta_{nm}(\tau)\exp[-i\varphi_{nm}(\tau)]}{r_{nm}^3(\tau)}\right.\\
&\left.\times\frac{\sin\theta_{nm}(0)\cos\theta_{nm}(0)\exp[i\varphi_{nm}(0)]}{r_{nm}^3(0)}\right\rangle,\\
L_{nm}^{++}(\tau)={}&\left\langle\frac{\sin^2\theta_{nm}(\tau)\exp[2i\varphi_{nm}(\tau)]}{r_{nm}^3(\tau)}\right.\\
&\left.\times\frac{\sin^2\theta_{nm}(0)\exp[-2i\varphi_{nm}(0)]}{r_{nm}^3(0)}\right\rangle
\end{aligned}
$$

($\omega_0\approx\omega_n\approx\omega_m$ is the resonance frequency) are dipole–dipole correlation functions in standard notation (see, e.g., Refs. 1, 2, and 9).

Similar expressions are obtained also for probabilities of type P_1:

$$
\begin{aligned}
P_{1n}'(\tau_2)={}&\frac{3}{4}I(I+1)\gamma^4\hbar^2\int_{-\tau_2}^{\tau_2}\sum_m(\tau_2-|\tau|)\\
&\times\left[2L_{nm}^{+z}(\tau)\exp(i\omega_0\tau)\right.
\end{aligned}
$$

$$+\frac{1}{2}L_{nm}^{++}(\tau)\exp(2i\omega_0\tau)\Big]d\tau,$$

$$P''_{1nm}(\tau_2)=\frac{3}{8}I(I+1)\gamma^4\hbar^2\int_{-\tau_2}^{\tau_2}(\tau_2-|\tau|)L_{nm}^{++}(\tau)\exp(2i\omega_0\tau)d\tau. \quad (13)$$

The expression for the probability of a flip-flop transition from the nth spin to any other turned out to be:

$$P_{fn}(\tau_2)=\frac{1}{24}I(I+1)\gamma^4\hbar^2 \times\sum_m\int_{-\tau_2}^{\tau_2}(\tau_2-|\tau|)L_{nm}^{zz}(\tau)\exp(2i\omega_{nm}\tau)d\tau, \quad (14)$$

where $\omega_{nm}=\omega_n-\omega_m$.

It will be seen from what follows that particular interest attaches to flip-flop transitions between spins of different molecules. In these cases the dipole correlation functions $L_{nm}^{zz}(\tau)$ attenuate within short times $\tau_0\approx10^{-10}-10^{-8}$ s, so that it is possible to determine correctly with the aid of (14) the average time τ_f of a spin-flop transition to any other spin of a neighboring macromolecule:

$$\tau_f^{-1}=\frac{1}{24}I(I+1)\gamma^4\hbar^2\sum_m\int_{-\infty}^{\infty}L_{nm}^{zz}(\tau)\exp(i\omega_{nm}\tau)d\tau. \quad (15)$$

Using (8), we calculate the amplitude of the diffuse scattering of a spin-echo signal:

$$\tilde{A}(g)=A(g)/A(0)=\tilde{A}_{sp}(g)+\tilde{A}_{df}(g), \quad (16)$$

where

$$\tilde{A}_{sp}(g)=\sum_n[\langle\exp[i(\varphi_{2n}-\varphi_{1n})]\rangle[1-P_{fn}(\tau_2)] +\sum_m\langle\exp[i(\varphi_{2m}-\varphi_{1n})]\rangle P_{fnm}(\tau_2)$$

is the contribution of the influence of spin-flop processes and

$$A_{df}=\sum_{n\neq m}(\langle\exp[i(\varphi_{2n}-\varphi_{1n})]\rangle-\langle\exp[i(\varphi_{2m}-\varphi_{1n})]\rangle) \times[2P''_{2nm}(\tau_1)+P''_{1nm}(\tau_2)]$$

is the contribution of the effect of pulsed magnetic-field gradients on the rates of the relaxation processes.

It is appropriate to note that at the presently attainable values of the gradient g we have $\gamma\delta g a_0\ll1$, where $a_0\approx1$ Å. For neighboring spins of one and the same macromolecule the phase shifts $\varphi_{1n}\approx\varphi_{1m}$ and their contributions can be left out of (16) when summing over the interspin interactions.

For short times τ_1 and τ_2 the second term of (16) is small, since relation (11) leads to the estimate

$$P_{nm}''(\tau_1;\tau_2)\equiv2P''_{2nm}(\tau_1)+P''_{1nm}(\tau_2)\approx\frac{\alpha}{N_s}\left(\frac{2\tau_1}{T_2}+\frac{\tau_2}{T_1}\right), \quad (17)$$

where α is the fraction of the contribution of the intermolecular dipole–dipole interactions to the probability of relaxation processes, with $\alpha\approx0.1$–0.25 in typical situations; N_s is the total number of spins. With increase of the duration of the experiments, $\tau_1\gtrsim T_1$, this factor reaches saturation and may turn out to be substantial: $P''_{nm}(\tau_1;\tau_2)\approx\alpha/N_s$. The same holds also for the time τ_2, which must however be related to spin–spin relaxation time T_2. Since $T_1\gg T_2$ in concentrated polymer systems (see Ref. 3), it is possible to determine satisfactorily two different characteristic times:

1. The aforementioned time τ_f which is determined by (15) and amounts to $\tau_f\approx\alpha^{-1}T_2$.

2. The characteristic time $\tau_{df}\simeq\alpha^{-1}T_1$ of defactoring of the spin-echo signal, defined as the typical time for saturation of the parameter $P''_{nm}(\tau_1;\tau_2)$. Recall that in experiment attempts are made to choose τ_2 as small as possible is fixed, or else an extrapolation to zero is used.

Since $\omega_0\approx\omega_n\approx\omega_m\gg\omega_{nm}\approx0$, it can be seen from (14) and from the estimates above that $\tau_f\ll\tau_{df}$. At any rate, this inequality is always valid for sufficiently strong external fields that lengthen τ_{df} and do not affect τ_f. Therefore each of the contributions $\tilde{A}_{sp}(g)$ and $\tilde{A}_{df}(g)$ in (16) can in principle be measured separately.

3. SPIN DIFFUSION IN POLYMER MELTS

The second term of (16) can be neglected for a diffusion time $t_D=\tau_1+\tau_2\ll\tau_{df}$. As a rule $\delta\ll t_D$ and, taking (2) into account, the amplitude of the diffusion damping can be written in the form

$$\tilde{A}(g)\approx\tilde{A}_{sp}(g)=\sum_n[\langle\exp\{i\gamma\delta g(\mathbf{r}_n(t_D)-\mathbf{r}_n(0))\}\rangle(1-P_{fn}(\tau_2)) +\sum_m\langle\exp\{i\gamma\delta g(\mathbf{r}_m(t_D)-\mathbf{r}_n(0))\}\rangle P_{fnm}(\tau_2)]. \quad (18)$$

This expression describes spin diffusion. The first term describes the motion of the spin polarization together with the nth spin of the system, whereas the second is connected with polarization exchange between the nth and mth protons of the system in a time τ_2.

Expression (18) can be made much more compact by introducing, for convenience, the concept of effective quasiparticles that carry spin polarizations, so to speak spin excitons. These quasiparticles appear in the system after the action of the first gradient pulse and are carried by the spins of the system. The factor $1-P_{fn}(\tau_2)$ in (18) is equal to the probability that a particle created on the nth spin remains on it for a time τ_2. After a time τ_f on the average, in the time interval between the action of the second and third RF pulses, the quasiparticles hop over to one of the nearest spins of the system. The factor $P_{fnm}(\tau_2)$ is equal to the probability of observing at the instant τ_2, on an mth spin, a spin exciton created on a spin numbered n.

Spin-relaxation processes actually decrease the total number of quasiparticles in the system, while the second gradient pulse measured the path traveled by the quasiparticle.

It is useful to understand clearly how the quasiparticles introduced above are similar to and differ from the magnons of magnetically ordered media. Magnons are due to bulk spin–spin interactions. They describe the deviation of a spin system from the quantum-mechanical ground state. In our case, however, the quasiparticles are due to interaction with an external magnetic field (gradient pulse of a magnetic field) and describe the deviation of the spin system from thermodynamic equilibrium. Figuratively speaking, the quasiparticles in question resemble magnons to the same extent that motion of particles of a real system are similar to phonons of solids.

It is easily seen from an analysis of the structure of (18) that in terms of the spatial variables of the quasiparticles the spin-echo amplitude can be represented by an expression formally equivalent to (3):

$$\mathcal{A}_{sp}(g)=\sum_{s}\langle\exp\{i\gamma\delta g[\mathbf{r}_s(t_D)-\mathbf{r}_s(0)]\}\rangle_s, \tag{19}$$

where the summation is over all the system quasiparticles that contribute to the echo amplitude; $\langle\ldots\rangle_s$ denotes, in contrast to (3), averaging over all the random quasiparticle trajectories, and not of the system spins; $r_s(t)$ is the radius vector of the sth quasiparticle.

Assume a diffusion time $t_D \gg \tau_f$. Since the motion of different macromolecules is not correlated, Eq. (19) takes the well-known diffusive asymptotic form (see, e.g., Ref. 4):

$$\mathcal{A}_{sp}(g)=\exp(-\gamma^2 g^2\delta^2 t_D D_{sp}), \tag{20}$$

where D_{sp} is the spin-diffusion coefficient, in other words the quasiparticle self-diffusive coefficient.

Each quasiparticle is displaced together with the spins in the time τ_f to a distance $r(\tau_f)$; it makes next another jump, due to flip-flop, to a distance on the order of $a_0 \approx 1$–3 Å.

To calculate the spin-diffusion coefficient we expand the relations (19) and (20) in Taylor series. Comparing the series terms quadratic in g, we get

$$D_{sp}=\frac{1}{6\tau_f}(\langle r^2(\tau_f)\rangle+a_0^2), \tag{21}$$

where $\langle r^2(\tau_f)\rangle$ is the rms displacement of the macromolecule spins in the time τ_f.

In liquids, solutions, and melts we have $r(\tau_f) \gtrsim 10^2$ Å for typical values $\tau_f \approx 0.1$–1 s. The additional displacement $a_0 \approx 1$–3 Å of the quasiparticle during the flip-flop time can therefore be neglected.

In solids, on the other hand, the situation is reversed. Here $r(\tau_f) \approx 0.01$ Å is of the order of the atom-oscillation amplitude; therefore $a_0 \gg r(\tau_f)$. Expression (15) for τ_f for solids also requires some modification, since the short-correlation-times approximation is inapplicable (see, e.g., Ref. 2).

From (15) we obtain the estimate

$$\tau_f^{-1}\approx\frac{1}{12}I(I+1)\gamma^4\hbar^2 z\varphi\tau_c/r_0^6, \tag{22}$$

where $r_0 \approx a_0 \approx 1$–3 Å is the shortest distance to the spins of the "foreign" macromolecule, $\tau_c \approx 10^{-9}$–10^{-7} s is the time of "intermolecular" correlation, z is the possible number of nearest neighboring spins, something of the type of the coordinate number, and φ is the bulk density of the macromolecules. It is clear hence that the time τ_f is independent of the molecular mass of the macromolecules.

One can separate in polymer systems the following characteristic times of macromolecule motion (see Refs. 3 and 5–8):

1) Tube replenishing time $T_r \approx \tau_0 N^3/N_e$, where $\tau_0 \approx 10^{-9}$ s is the segmental-motion time and $N_e \approx 25$–30 is the number of Kuhn segments in a macromolecule of critical molecular mass.

2) Rouse-relaxation time $T_R \approx \tau_0 N^2$.

3) Time $T_e \approx \tau_0 N_e^2$ to reach the entangled-motion regime.

The rms displacement of the macromolecule segments, and hence of the spins, has the following time dependence:[5–8]

$$\langle r^2(t)\rangle=\begin{cases} 6D_p t, & t\gg T_r,\\ l^2(N_e t/N\tau_0)^{1/2}, & T_r\gg t\gg T_R,\\ l^2 N_e^{1/2}(t/\tau_0)^{1/4}, & T_R\gg t\gg T_e,\\ l^2(t/\tau_0)^{1/4}, & T_e\gg t\gg \tau_0, \end{cases} \tag{23}$$

where $D_p \cong l^2 N_e/\tau_0 N^2$ is the macromolecule diffusion coefficient and l is the Kuhn-segment length.

Depending on the relation between the time τ_f and the times T_r, T_R, and T_e we can separate the following four cases:

A. Slow flip-flop processes, i.e., $\tau_f \gg T_R$

In this case we obtain with the aid of (21) and (23) the following expression for the spin-diffusion coefficient:

$$D_{sp}=D_p+\frac{1}{6}\frac{a_0^2}{\tau_f}\approx D_p. \tag{24}$$

It can be seen that the spin-diffusion and self-diffusion coefficients of macromolecules are practically equal. Allowance for the spin-flop processes leads only to the small correction $a_0^2/6\tau_f$. Note that this takes place for all polymer melts with sufficiently small molecular masses measured in Kuhn-segment units:

$$N\ll N_{cr}{}^{*}\approx N_e^{1/3}(\tau_f/\tau_0)^{1/3}\approx 10^3. \tag{25}$$

B. Intermediate flip-flop processes, i.e., $T_r \gg \tau_f \gg T_R$

The spin-diffusion coefficient calculated similar to the preceding case turns out to be

$$D_{sp}\approx l^2(N_e/N\tau_f\tau_0)^{1/2}. \tag{26}$$

The spin-diffusion coefficient is larger than the macromolecule-diffusion coefficient and is characterized by a weaker molecular-mass dependence $D_{sp} \simeq N^{-1/2}$ and by a weak temperature dependence, since the temperature dependences of the times τ_0 and τ_f are reciprocals of one another.

The time T_R gives rise naturally to one more critical molecular mass:

$$N_{cr}{}^{**}\simeq(\tau_f/\tau_0)^{1/2}\simeq 10^4-10^5. \tag{27}$$

It is clear from the foregoing that the situation in question obtains for intermediate molecular masses $N_{cr}^{*} < N < N_{cr}^{**}$.

C. Fast flip-flop processes, i.e., $T_R \gg \tau_f \gg T_e$

Using (21) and (23) we obtain

$$D_{sp}\approx l^2 N_e^{1/2}/(\tau_0\tau_f)^{1/4}. \tag{28}$$

Just as in the preceding case we have $D_{sp} \gg D_p$, but the spin-diffusion coefficient is independent of the molecular mass and D_{sp} can decrease with rise of temperature. The latter is due to thermal averaging of dipole–dipole interactions which cannot be offset in this case by the increased translational mobility of the macromolecules.

D. Ultrafast flip-flop processes, i.e., $T_e\gg\tau_f$

This situation can apparently not be realized, at any rate in macromolecule melts.

The spin-diffusion coefficient would equal in this case:

$$D_{sp}\approx l^2/(\tau_0\tau_f)^{1/2}. \tag{29}$$

Just as in the case of fast flip-flop processes,the spin-diffusion coefficient is independent of the molecular mass of the macromolecules, while the temperature dependence is similar to that in the case of intermediate flip-flop processes.

To conclude this section, we note that the results can be generalized by the dynamic-scaling method to include macromolecule solutions (see Ref. 10).

4. EFFECTS OF DEFACTORING OF SPIN-ECHO AMPLITUDE

For a diffusion time $t_D\gtrsim\tau_{df}$, an important role is assumed in (16) by the second term, which we shall call, to be specific, the defactoring amplitude. It follows hence from relations (16) and (17) that

$$\tilde{A}_{df}(g)=\sum_{n\neq m}P_{nm}''(\tau_1;\tau_2)[\langle\exp\{i\gamma\delta\mathbf{g}(\mathbf{r}_n(t_D)-\mathbf{r}_n(0))\}\rangle -\langle\exp\{i\gamma\delta\mathbf{g}(\mathbf{r}_m(t_D)-\mathbf{r}_n(0))\}\rangle]. \tag{30}$$

The probability factor $P''_{nm}(\tau_1;\tau_2)$, as already noted, increases monotonically with time and reaches saturation at $t_D\approx\tau_{df}$. Each exponential of (30) decreases with time. The first exponential describes spatial displacements of individual macromolecules. The second, cross-exponential, describes relative displacements of the polymer chains whose spins have induced mutual relaxation transitions.

The amplitude $\tilde{A}_{sp}(g)$ also has a similar structure, but with a basic difference. The two exponentials in the amplitude $\tilde{A}_{sp}(g)$, which describes spin diffusion, have different weights. In fact, $1-P_{nf}(\tau_2)$ is the probability that a spin numbered n will not experience even a single flip-flop transition by the instant τ_2. Clearly,

$$\lim_{\tau_2\to\infty}[1-P_{fn}(\tau_2)]=0.$$

The relative role of the second exponential in (18), on the other hand, increases with time. The physical cause is migration of the spin polarization over different macromolecules.

The exponentials in question have in the amplitude $\tilde{A}_{df}(g)$ opposite signs but weights of equal modulus. The cause is the influence of the pulsed magnetic field gradients on the spin-relaxation rate.

We denote by t' the time when the spins numbered n and m underwent mutual relaxation transitions. The cross-exponential can then be written in the form

$$\langle\exp\{i\gamma\delta\mathbf{g}[\mathbf{r}_m(t_D)-\mathbf{r}_n(0)]\}\rangle =\langle\exp\{i\gamma\delta\mathbf{g}[\mathbf{r}_m(t_D)-\mathbf{r}_m(t')+\mathbf{r}_m(t')-\mathbf{r}_n(0)]\}\rangle. \tag{31}$$

The dipole–dipole interactions are short-range, so that one of the radius vectors $\mathbf{r}_m(t')$ can be replaced in (31) by $\mathbf{r}_n(t')$. In fact, $|\mathbf{r}_{nm}(t')|\approx 1\,\text{Å}\ll|\mathbf{r}(t')-\mathbf{r}(0)|\approx 10^2$–$10^4\,\text{Å}$. Next, recognizing that the motions of different molecules are not correlated (see Refs. 5–8) we can "factor out" relation (31):

$$\langle\exp\{i\gamma\delta\mathbf{g}[\mathbf{r}_m(t_D)-\mathbf{r}_n(0)]\}\rangle=\langle\exp\{i\gamma\delta\mathbf{g}[\mathbf{r}_m(t_D)-\mathbf{r}_m(t')]\}\rangle \times\langle\exp\{i\gamma\delta\mathbf{g}[\mathbf{r}_n(t')-\mathbf{r}_n(0)]\}\rangle. \tag{32}$$

In the case of macromolecules of low molecular mass, i.e., such that $T_2\ll\tau_{df}\sim t'$, the motion of the individual macromolecules is likewise fully stochasticized. Consequently, the first exponential of (30) can also be factored out similar to (32):

$$\langle\exp\{i\gamma\delta\mathbf{g}[\mathbf{r}_n(t_D)-\mathbf{r}_n(0)]\}\rangle=\langle\exp\{i\gamma\delta\mathbf{g}[\mathbf{r}_n(t_D)-\mathbf{r}_n(t')]\}\rangle \times\langle\exp\{i\gamma\delta\mathbf{g}[\mathbf{r}_n(t')-\mathbf{r}_n(0)]\}\rangle. \tag{33}$$

Substituting (32) and (33) in (30) we find that for systems with sufficiently small molecular masses the defactoring amplitude $\tilde{A}_{df}(g)$ is zero accurate to quantities of order $\exp(-\gamma^2g^2\delta^2a_0^2)\approx\exp(-10^4)$. Note that this situation is similar to the case of slow flip-flop processes, discussed above in connection with spin diffusion.

For macromolecules with large molecular mass, i.e., $T_f\gg\tau_{df}$, the cross-exponential decreases, as seen from (32), with a diffusion coefficient of order D_{sp}:

$$\langle\exp\{i\gamma\delta\mathbf{g}[\mathbf{r}_m(t_D)-\mathbf{r}_n(0)]\}\rangle=\exp(-\gamma^2\delta^2g^2D_{df}t_D), \tag{34}$$

where

$$D_{df}\approx\frac{\langle r^2(\tau_{df})\rangle}{6\tau_{df}}\sim D_{sp}.$$

The first exponential of (30) describes the displacements of the macromolecules themselves. In the case considered $\langle[\mathbf{r}_n(t_D)-\mathbf{r}_n(0)]^2\rangle\ll 6D_{df}t_D$. It therefore decreases significantly more slowly than the cross-exponential. The latter makes is possible to take in (30) only the first exponential into account:

$$\tilde{A}_{df}(g)=\sum_{n,m}P_{nm}''(\tau_1;\tau_2)\langle\exp\{i\gamma\delta\mathbf{g}[\mathbf{r}_n(t_D)-\mathbf{r}_n(0)]\}\rangle. \tag{35}$$

Summing over m and assuming all spins to be relaxionally equivalent, we transform (35) into

$$\tilde{A}_{df}(g)=P''(\tau_1;\tau_2)\sum_n\langle\exp\{i\gamma\delta\mathbf{g}[\mathbf{r}_n(t_D)-\mathbf{r}_n(0)]\}\rangle, \tag{36}$$

where

$$P''(\tau_1;\tau_2)=\sum_m P_{nm}(\tau_1;\tau_2).$$

It follows from the properties of $P''_{nm}(\tau_1;\tau_2)$ discussed in Sec. 2 that at times $t_D\gtrsim\tau_{df}$ the value of $P''(\tau_1;\tau_2)\approx\alpha$ reaches saturation.

The diffuse-damping amplitude $\tilde{A}(g)$ [see (16)] contains, besides the amplitude $\tilde{A}_{df}(g)$, a contribution from the spin-diffusion amplitude $\tilde{A}_{sp}(g)$. As already noted, its contribution for times $t_D>\tau_{df}$ is of the order of the contribution of the cross-exponential to $\tilde{A}_{df}(g)$, i.e., negligibly small. Therefore

$$\tilde{A}(g)\approx\tilde{A}_{df}(g)\approx\alpha\sum_n\langle\exp\{i\gamma\delta\mathbf{g}(\mathbf{r}_n(t_D)-\mathbf{r}_n(0)]\}\rangle, \tag{37}$$

and the spin-echo amplitude for diffusion times $t_D\gtrsim\tau_{df}$ again contains information about the true macromolecule displacements, and not about the spin diffusion, as was the case for times $\tau_f\ll t_D\ll\tau_{df}$. The measured diffusion coefficient will therefore be equal to the self-diffusion coefficient of the macromolecules.

5. DISCUSSION OF RESULTS

The amplitude $\widetilde{A}(g)$ of the diffusion damping of the stimulated spin echo signal was shown to be equal to the sum of two amplitudes, the spin-diffusion amplitude $\widetilde{A}_{sp}(g)$ and the defactoring amplitude $\widetilde{A}_{df}(g)$. The amplitude $\widetilde{A}_{sp}(g)$ reflects the influence of the flip-flop processes in the spin system on the spin-echo signal and describes the spin diffusion. The amplitude $\widetilde{A}_{df}(g)$ is connected with the influence of pulsed magnetic-field gradients on the rates of the relaxation processes. Each of these amplitudes gives rise to characteristic times: the average time τ_f of the flip-flop processes and the characteristic defactoring time τ_{df} of the spin-echo amplitude.

For liquid-phase systems of sufficiently low molecular mass [see (25)] our expression (16) for the amplitude $\widetilde{A}(g)$ is equivalent to the universally known expression (3). For polymer systems with close enough molecular masses the situation is the following:

1) For diffusion times $t_D \ll \tau_f$ the spin-echo amplitude, just as (3), contains information on the spatial displacements of the macromolecules.

2) For diffusion times $\tau_f \ll t_D \ll \tau_{df}$ the amplitude $\widetilde{A}(g)$ describes spin diffusion. The spin-diffusion coefficient D_{sp} differs here substantially from the macromolecule spin-diffusion coefficients D_p, see relations (26), (28), and (29).

3) For diffusion times $t_D \gg \tau_{df}$ the amplitude $\widetilde{A}(g)$ again becomes equivalent to (3) and describes diffusion of the macromolecules.

The most important physical quantities, which are the objects of radiospectroscopic research into polymer systems, are the relaxation times T_1 and T_2 and the macromolecule self diffusion coefficient D_p. The present results point to a possibility of adding to this list the spin-diffusion coefficient, which contains for polymer sufficient of sufficiently large mass additional information on the molecular processes in the system.

To conclude, we point out a report[11] of anomalous behavior of the diffusion coefficient in anomalous lattices, measured by the spin-echo method. Note that the anomalies described in Ref. 11 agree qualitatively with the notions developed in the present paper concerning spin diffusion.

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