Spin-lattice relaxation of polymers: The memory-function formalism

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An alternative and general formalism for the frequency dependence of the spin-lattice relaxation time T_1 of polymer liquids is derived on the basis of memory functions of polymer theories. As examples the original Rouse model [J. Chem. Phys. **21**, 1272 (1953)] and the renormalized Rouse model by Schweizer [J. Chem. Phys. **91**, 5802 (1989)] are considered. The results fit well the experimental data obtained for polydimethylsiloxane (PDMS) melts and solutions by the field-cycling technique. The Rouse model fits solutions and low-molecular-weight melts. The renormalized Rouse model explains the peculiar $\nu^{0.25}$ dispersion of the spin-lattice relaxation time observed with PDMS melts at molecular weights $M_w \gg M_c$.

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INTRODUCTION

Chain dynamics in polymer melts and concentrated solutions has attracted considerable attention in recent years. Many theoretical approaches have been published on this subject [1–6]. The discussion of the theories is, however, still rather controversial [7]. It mainly refers to experimental data of rheology [8], mechanical relaxation [9], diffusion [10], neutron spin-echo spectroscopy [11], and other techniques. Molecular-dynamics simulations [12] also play a central role in this context.

A particularly direct access to the features of chain dynamics in terms of the spectral density $I(\omega)$ and the dipolar orientation correlation function $G(t)$ is provided by field-cycling NMR relaxation spectroscopy which permits the record of the frequency dependence of the spin-lattice relaxation rate over many decades [13–17]. The difficulty up to now was that polymer theories usually do not refer to orientation correlation functions of dipolar couplings so that the comparison with field-cycling NMR relaxation data needs some additional formalism.

On the other hand, polymer theories are often based on memory functions. Here we are particularly thinking of Schweizer's *ab initio* theory [5,6], and other memory-function formalisms [3,4]. The predominant purpose of the present work is to establish a relation linking the memory function of polymer theories with the spin-lattice relaxation rate. Such a formalism was hitherto merely considered for low-molecular liquids [18].

Furthermore, a series of experimental field-cycling NMR relaxation data will be presented and compared with the memory-function formalism of spin-lattice relaxation. Schweizer's results will be briefly discussed on this basis.

MEMORY-FUNCTION FORMALISM OF SPIN-LATTICE RELAXATION IN POLYMERS

The time scale of the fluctuations within a Kuhn segment is characterized by the segment correlation time [2]

$\tau_s = b^2 \zeta / (k_B T)$ where k_B is Boltzmann's constant, T the absolute temperature, b the length of a Kuhn segment, and ζ the friction coefficient of a Kuhn segment. The longest chain relaxation time is given by $\tau_R = N^2 \tau_s / (3\pi^2)$, called "Rouse relaxation time." N is the number of Kuhn segments per chain.

Let us now consider the time range $\tau_s \ll t \ll \tau_R$ in which the polymer chain dynamics can be described by the generalized Langevin equation

$$\zeta \left[\frac{\partial \mathbf{r}_n(t)}{\partial t} + \int_0^t d\tau \, \Gamma(t-\tau) \frac{\partial \mathbf{r}_n(\tau)}{\partial \tau} \right]$$
$$= -\frac{3k_B T}{b^2} \frac{\partial^2 \mathbf{r}_n(t)}{\partial n^2} + \mathbf{F}_n(t) , \quad (1)$$

with $\mathbf{r}_n(t)$ the position of the nth Kuhn segment of a "tagged" chain at time t, $\Gamma(t-\tau)$ the memory function, and $\mathbf{F}_n(t)$ the stochastic force acting on the Kuhn segment number n at time t. The memory function has the quality of a correlation function of the random forces exerted by the matrix chains on a representative segment of the tagged chain. Hydrodynamic and excluded-volume interactions are not considered. This means that we are restricting ourselves to melts and concentrated solutions.

In the continuum limit, n can be taken as a variable. Equation (1) can then be rewritten by the aid of the Rouse normal coordinates,

$$\mathbf{x}_p(t) \equiv \frac{1}{N} \int_0^N dn \cos\left[\frac{\pi p n}{N} \right] \mathbf{r}_n(t)$$
$$(p = 0, 1, 2, \ldots, N-1) \quad (2)$$

as

$$\zeta \left[\frac{\partial \mathbf{x}_p(t)}{\partial t} + \int_0^t d\tau \, \Gamma(t-\tau) \frac{\partial \mathbf{x}_p(\tau)}{\partial \tau} \right]$$
$$= -\frac{p^2 \zeta}{\tau_R} \mathbf{x}_p(t) + \mathbf{F}_p(t) . \quad (3)$$

With the time autocorrelation functions of the normal coordinates, $c_p(t) = \langle \mathbf{x}_p(t) \cdot \mathbf{x}_p(0) \rangle$, we obtain

$$\frac{\partial c_p(t)}{\partial t} + \int_0^t d\tau\, \Gamma(t-\tau)\frac{\partial c_p(\tau)}{\partial \tau} = -\frac{p^2}{\tau_R}c_p(t) \ . \tag{4}$$

The chain tangent vector at the nth segment, $\mathbf{b}_n$, is given by the derivative of the inverse transform of Eq. (2),

$$\mathbf{r}_n = \mathbf{x}_0 + 2\sum_{p=1}^{N-1} \mathbf{x}_p \cos\left[\frac{\pi p n}{N}\right] \ , \tag{5}$$

that is,

$$\mathbf{b}_n(t) = \frac{\partial}{\partial n}\mathbf{r}_n(t) = -\frac{2\pi}{N}\sum_{p=1}^{N-1} p\,\mathbf{x}_p \sin\left[\frac{\pi p n}{N}\right] \ . \tag{6}$$

The time autocorrelation function of the tangent vectors is then

$$\langle \mathbf{b}_n(t) \cdot \mathbf{b}_n(0) \rangle = \frac{4\pi^2}{N^2}\sum_{p=1}^{N-1} p^2 \langle \mathbf{x}_p(t) \cdot \mathbf{x}_p(0)\rangle \sin^2\left[\frac{\pi p n}{N}\right]$$

$$\approx \frac{2\pi^2}{N^2}\sum_{p=1}^{N} p^2 \langle \mathbf{x}_p(t) \cdot \mathbf{x}_p(0)\rangle \ , \tag{7}$$

where we have replaced the $\sin^2$ term by its average $1/2$ and $N-1$ by N. Hence

$$\langle \mathbf{b}_n(t) \cdot \mathbf{b}_n(0) \rangle = \frac{2\pi^2}{N^2}\sum_{p=1}^{N} p^2 c_p(t) \ . \tag{8}$$

The Fourier-Laplace transform of this correlation function is

$$\hat{J}(\omega) = \int_0^\infty e^{i\omega t}\langle \mathbf{b}_n(t)\cdot\mathbf{b}_n(0)\rangle dt = \frac{2\pi^2}{N^2}\sum_{p=1}^{N} p^2 \hat{c}_p(\omega) \ , \tag{9}$$

where $\hat{c}_p(\omega) = \int_0^\infty c_p(t)e^{i\omega t}dt$. The Fourier-Laplace transform of Eq. (4),

$$-i\omega\hat{c}_p(\omega) - \hat{c}_p(0) + \hat{\Gamma}(\omega)[-i\omega\hat{c}_p(\omega) - \hat{c}_p(0)]$$
$$= -\frac{p^2}{\tau_R}\hat{c}_p(\omega) \ , \tag{10}$$

has the solution

$$\hat{c}_p(\omega) = \frac{c_p(0)}{\dfrac{p^2}{\tau_R[1+\hat{\Gamma}(\omega)]} - i\omega} \ , \tag{11}$$

where $c_p(0) = \langle \mathbf{x}_p(0)\cdot\mathbf{x}_p(0)\rangle = Nb^2/(2\pi^2 p^2)$ and $\hat{\Gamma}(\omega) = \int_0^\infty \Gamma(t)e^{i\omega t}dt$. Equation (9) thus can be written as

$$\hat{J}(\omega) = \frac{b^2}{N}\sum_{p=1}^{N} \frac{1}{\dfrac{p^2}{\tau_R[1+\hat{\Gamma}(\omega)]} - i\omega}$$

$$\approx \frac{b^2}{N\omega}\int_1^N \frac{1}{\dfrac{p^2}{\omega\tau_R[1+\hat{\Gamma}(\omega)]} - i}\,dp$$

$$= K\frac{b^2}{2N}\left[\frac{\tau_R[1+\hat{\Gamma}(\omega)]}{\omega}\right]^{1/2} \ , \tag{12}$$

where

$$K = \int_{1/[\omega\tau_R(1+\hat{\Gamma})]}^{N^2/[\omega\tau_R(1+\hat{\Gamma})]} \frac{1}{y^{3/2} - iy^{1/2}}\,dy \ .$$

In the limit $\tau_R^{-1} \ll \omega|1+\hat{\Gamma}| \ll \tau_s^{-1}$, K can be approximated by

$$K \approx \int_0^\infty \frac{1}{y^{3/2} - iy^{1/2}}\,dy = \pi e^{i\pi/4}$$

so that it can be considered as a frequency-independent constant. Equation (12) thus can be approximated by

$$\hat{J}(\omega) = \frac{e^{i\pi/4}}{2\sqrt{3}}b^2\tau_s^{1/2}\left[\frac{1+\hat{\Gamma}(\omega)}{\omega}\right]^{1/2} \ . \tag{13}$$

From Eq. (9) it follows that the correlation function of the tangent vectors is given by

$$\langle \mathbf{b}_n(t)\cdot\mathbf{b}_n(0)\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty} \hat{J}'(\omega)e^{-i\omega t}d\omega \ , \tag{14}$$

where

$$\hat{J}'(\omega) = 2\,\mathrm{Re}\{\lim_{\epsilon\to 0+}\hat{J}(\omega+i\epsilon)\}$$
$$= \frac{b^2\tau_s^{1/2}}{\sqrt{3}}\lim_{\epsilon\to 0+}\mathrm{Re}\left\{\left[\frac{1+\hat{\Gamma}(\omega+i\epsilon)}{\omega+i\epsilon}\right]^{1/2}e^{i\pi/4}\right\} \ .$$

The dipolar coupling Hamiltonian of two interacting nuclear spins $\mathbf{I}_1$ and $\mathbf{I}_2$ is given by $\mathcal{H}_d = \mathbf{I}_1\cdot\tilde{D}\cdot\mathbf{I}_2$, where $\tilde{D}$ is the dipolar coupling tensor with the elements $\tilde{D}_{\alpha\beta} = (\gamma^2/r_{12}^3)\hbar(\delta_{\alpha\beta} - 3\epsilon_n^\alpha\epsilon_n^\beta)$. α and β indicate the Cartesian space coordinates x,y,z. ϵ_n^α and ϵ_n^β are the components of the unit vector $\boldsymbol{\epsilon}_n = \mathbf{r}_{12}/r_{12}$, where $\mathbf{r}_{12}$ is the internuclear distance vector of two representative spins $\mathbf{I}_1$ and $\mathbf{I}_2$ sitting on the nth Kuhn segment of the tagged chain. γ is the gyromagnetic ratio, $\hbar$ is Planck's constant divided by 2π, and $\delta_{\alpha\beta}$ is the Kronecker symbol.

In the long-time limit $t \gg \tau_s$, intermolecular and intersegmental spin couplings can be neglected so that only interactions of spins having fixed distances $r_{12} \approx \text{const}$ are relevant. The correlation function of dipole-dipole coupling therefore can be identified with the orientation correlation function of the spin system and can be expressed by a linear combination of the form

$$\langle \mathcal{H}_d(t)\mathcal{H}_d(0)\rangle \propto \sum_{\alpha,\beta} c_{\alpha,\beta}\langle \epsilon_n^\alpha(t)\epsilon_n^\alpha(0)\epsilon_n^\beta(t)\epsilon_n^\beta(0)\rangle \tag{15}$$

with constant coefficients $c_{\alpha,\beta}$. Moreover, in the limit $t \gg \tau_s$ the effective internuclear unit vector $\boldsymbol{\epsilon}_n$ and the chain tangent vector $\mathbf{b}_n$ tend to be aligned along the same direction so that

$$\langle \epsilon_n^\alpha(t)\epsilon_n^\alpha(0)\epsilon_n^\beta(t)\epsilon_n^\beta(0)\rangle \approx \frac{1}{b^4}\langle b_n^\alpha(t)b_n^\alpha(0)b_n^\beta(t)b_n^\beta(0)\rangle \ . \tag{16}$$

Using Eq. (5) we obtain

$$b_n^\alpha(t) = \frac{\partial}{\partial n}r_n^\alpha(t) = -\frac{2\pi}{N}\sum_{p=1}^{N} p x_p^\alpha(t)\sin\left[\frac{\pi p n}{N}\right] \tag{17}$$

so that

$$\langle b_n^\alpha(t)b_n^\alpha(0)b_n^\beta(t)b_n^\beta(0)\rangle = \left[\frac{2\pi}{N}\right]^4 \sum_{p_1,p_2,p_3,p_4=1}^{N} p_1p_2p_3p_4\langle x_{p_1}^\alpha(t)x_{p_2}^\alpha(0)x_{p_3}^\beta(t)x_{p_4}^\beta(0)\rangle$$

$$\times \sin\left[\frac{\pi p_1 n}{N}\right]\sin\left[\frac{\pi p_2 n}{N}\right]\sin\left[\frac{\pi p_3 n}{N}\right]\sin\left[\frac{\pi p_4 n}{N}\right] . \qquad (18)$$

The fluctuations of the normal modes are independent from one another [see Eq. (2)]. The components of the vectors x_p are also uncorrelated. The cross terms in the above correlation function therefore vanish, so that only autocorrelation terms remain:

$$\langle b_n^\alpha(t)b_n^\alpha(0)b_n^\beta(t)b_n^\beta(0)\rangle = \left[\frac{2\pi}{N}\right]^4 \sum_{p_1,p_2=1}^{N} p_1^2 p_2^2 \langle x_{p_1}^\alpha(t)x_{p_1}^\alpha(0)\rangle\langle x_{p_2}^\beta(t)x_{p_2}^\beta(0)\rangle \sin^2\left[\frac{\pi p_1 n}{N}\right]\sin^2\left[\frac{\pi p_2 n}{N}\right]$$

$$= \left[\frac{2\pi}{N}\right]^4 \left\{\sum_{p=1}^{N} p^2\langle x_p^\alpha(t)x_p^\alpha(0)\rangle \sin^2\left[\frac{\pi pn}{N}\right]\right\}^2 = \langle b_n^\alpha(t)b_n^\alpha(0)\rangle^2 . \qquad (19)$$

Combining Eqs. (15), (16), and (19) gives

$$\langle \mathcal{H}_d(t)\mathcal{H}_d(0)\rangle \propto \langle \mathbf{b}_n(t)\cdot\mathbf{b}_n(0)\rangle^2 . \qquad (20)$$

This and Eq. (14) lead to the proportionality of the spin-lattice relaxation rate

$$\frac{1}{T_1} \propto \int_{-\infty}^{\infty} \langle \mathcal{H}_d(t)\mathcal{H}_d(0)\rangle e^{-i\omega t}dt$$

$$\propto \frac{1}{2\pi}\int_{-\infty}^{\infty} \hat{J}'(\omega')\hat{J}'(\omega-\omega')d\omega'$$

$$\propto \int_{-\infty}^{\infty} \text{Re}\left\{\left[\frac{1+\hat{\Gamma}(\omega')}{\omega'}\right]^{1/2}\right\}$$

$$\times \text{Re}\left\{\left[\frac{1+\hat{\Gamma}(\omega-\omega')}{\omega-\omega'}\right]^{1/2}\right\}d\omega' . \qquad (21)$$

Introducing a new variable $y=\omega'/\omega$ finally leads to

$$\frac{1}{T_1} \propto \int_{-\infty}^{\infty} \text{Re}\left\{\left[\frac{1+\hat{\Gamma}(\omega y)}{|y|}\right]^{1/2}\right\}$$

$$\times \text{Re}\left\{\left[\frac{1+\hat{\Gamma}(\omega[1-y])}{|1-y|}\right]^{1/2}\right\}dy . \qquad (22)$$

APPLICATION TO THE ORIGINAL ROUSE MODEL

In the original Rouse model [19] we have $\Gamma(t)\equiv 0$. In this model, the upper frequency limit is $\omega=1/\tau_s$ per *definitionem*. From Eq. (21), the relaxation rate thus is

$$\frac{1}{T_1} \propto \int_{-1/\tau_s}^{1/\tau_s} \left[\frac{1}{|\omega-\omega'||\omega'|}\right]^{1/2} d\omega' \approx \ln\left[\frac{1}{\omega\tau_s}\right] , \qquad (23)$$

where the approximation refers to the limit $\omega\tau_s \ll 1$. This result coincides with the formula obtained by Khazanovich [20] using a different formalism.

Figures 1 and 2 show a comparison with experimental spin-lattice relaxation data [16,17] of polydimethylsiloxane (PDMS) melts and solutions measured with the field-cycling technique [21]. With solutions at low concentrations and with melts below the critical molecular weight,

i.e., $M_w \ll M_c$, the data can be described by Eq. (23) for the original Rouse model. This corresponds to the expected behavior of "unentangled" polymer chains [2].

APPLICATION TO POWER-LAW MEMORY FUNCTIONS

Several polymer theories such as those recently presented by Schweizer [5,6] lead to memory functions of the type $\Gamma(t)\propto t^{-\kappa}$ where $0<\kappa<1$. Thus

$$\hat{\Gamma}(\omega) \propto \int_0^\infty t^{-\kappa}e^{-i\omega t}dt \propto \omega^{-(1-\kappa)} . \qquad (24)$$

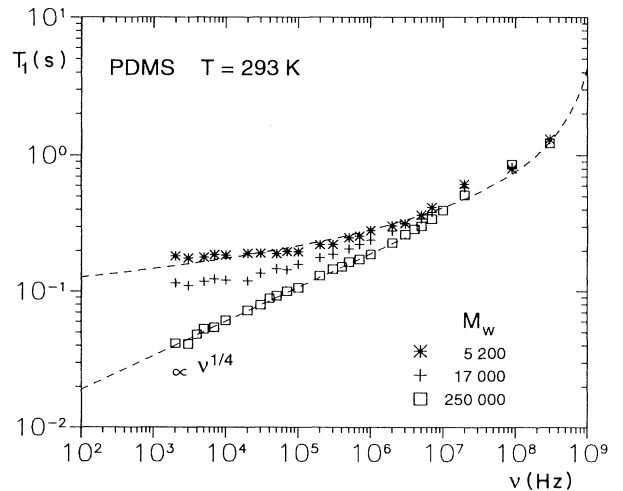For frequencies low enough to justify the limit $\hat{\Gamma}(\omega)\gg 1$ we obtain from Eq. (22)

FIG. 1. Proton spin-lattice relaxation time T_1 of PDMS melts vs the Larmor frequency $\nu=\omega/(2\pi)$. For experimental details see Ref. [16]. The critical molecular weight is $M_c=19\,000$. The dashed lines correspond to the theory for the original Rouse model and the renormalized Rouse model. The value of the segmental correlation time fitted to the $M_w=5200$ data by the aid of the Rouse expression equation 23 is $\tau_s=9.8\times 10^{-11}s$.
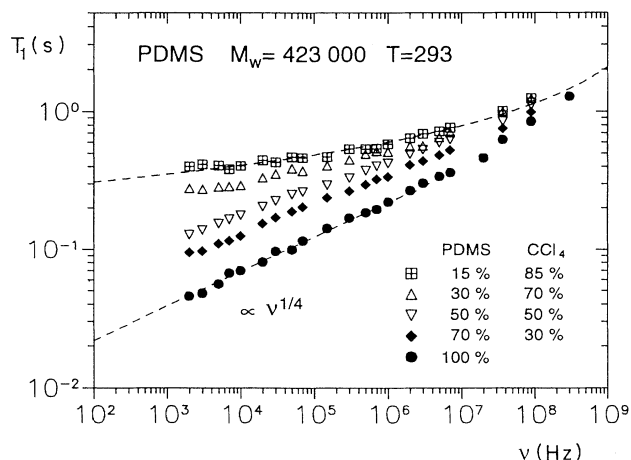
FIG. 2. Proton spin-lattice relaxation time T_1 of PDMS solutions in CCl_4 vs the Larmor frequency $\nu = \omega/(2\pi)$. For experimental details see Ref. [16]. The dashed lines correspond to the theory for the original Rouse model and the renormalized Rouse model. The value of the segmental correlation time fitted to the data for a polymer concentration of 15% (by weight) using the Rouse expression equation 23 is $\tau_s = 9.7 \times 10^{-12} s$.

$$\frac{1}{T_1} \propto \int_{-\infty}^{\infty} \left\{ \frac{[\omega(1-y)]^{-(1-\kappa)}}{|1-y|} \frac{(\omega y)^{-(1-\kappa)}}{|y|} \right\}^{1/2} dy$$

$$\propto \omega^{-(1-\kappa)} , \tag{25}$$

i.e., the frequency dependences of T_1^{-1} and $\hat{\Gamma}$ are equal in this limit.

With the renormalized Rouse model [5] the memory function decays according to the power law $\Gamma(t) \propto t^{-3/4}$, i.e., $\kappa = 3/4$. The dispersion of the spin-lattice relaxation time therefore is expected to follow $T_1 \propto \omega^{1/4}$.

This peculiar power law was verified experimentally with PDMS and other polymer melts with molecular weights $M_w \gg M_c$. Representative data sets are shown in Figs. 1 and 2. Thus the original Rouse model can be dis-

tinguished experimentally from the renormalized Rouse model by the very different frequency dependence of the spin-lattice relaxation time.

DISCUSSION

A formalism has been presented generally linking the dispersion of spin-lattice relaxation with the memory functions of polymer theories [Eqs. (22) and (25)]. As first examples we have considered the original Rouse model and the renormalized Rouse model by Schweizer. The results fit well to experimental data obtained for PDMS melts and solutions by the field-cycling technique. The original Rouse model fits to solutions and low-molecular melts. The renormalized Rouse model explains the peculiar $\nu^{0.25}$ dispersion of the spin-lattice relaxation time of PDMS melts at molecular weights $M_w \gg M_c$.

A further example of memory-function formalisms for polymers is the polymeric mode-coupling theory by Schweizer [6]. The time dependence of the memory function derived on this basis, $\Gamma(t) \propto t^{-9/16}$, leads to a power law $T_1 \propto \nu^{7/16}$ in the limit of very low frequencies, i.e., below a certain characteristic rate. The corresponding treatment and the comparison with experimental data suggesting a corresponding dynamical regime will be published elsewhere.

The theories so far mentioned are restricted to the time scale assumed in the present study, i.e., $\tau_s \ll t \ll \tau_R$. Beyond this regime at longer times, the equation of motion, Eq. (1), must be assumed in a more general form [22]. In particular, the memory function will depend on the normal modes as discussed in Refs. [5] and [6], for instance. T_1 (as well as the transverse relaxation time) then is expected to become intrinsically molecular mass dependent as it was observed [15,16] not too far above M_c. At such extremely long times Kawasaki's criticism [23] of Schweizer's approach may also be relevant, i.e., the limit of reptational dynamics should be effective.

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