# Direct stochastic theory of muon spin relaxation in a model for *trans*-polyacetylene

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A stochastic theory of muon spin relaxation in a model for muonium attached to *trans*-polyacetylene chains is given. The random walk of an unpaired electron provides a fluctuating hyperfine interaction with the muon. Since the correlation time of the stochastic process diverges, the standard NMR theory cannot be applied. The stochastic Liouville equation is solved, including spin flips of the electron. The resulting spin relaxation is nonexponential, and in reasonable agreement with the experimental data. The characteristic field dependence of one-dimensional diffusion is also contained in this theory.

## I. INTRODUCTION

This paper develops a direct stochastic theory of muon spin relaxation in a model for *trans*-polyacetylene. The underlying idea is that spin relaxation in this substance may be caused by one-dimensional diffusion of defects along the polyacetylene chains. The possible soliton nature of electronic defects in *trans*-polyacetylene has aroused much interest (for reviews see Refs. 1–3), and various experiments including muon spin relaxation were performed to study the dynamics of the supposed solitons. The emphasis of this paper, however, is not on the elucidation of the soliton properties of defects in real *trans*-polyacetylene. We are primarily concerned with a proper stochastic theory of spin relaxation by one-dimensional diffusion. Most of the spin relaxation experiments in the polyacetylenes have been analyzed by versions of the standard theory of magnetic resonance. The standard NMR theory[4,5] provides expressions for the longitudinal and transverse spin relaxation times. It presupposes the existence of a correlation time $\tau_c$ of the fluctuations that produce the relaxation, and assumes that this time is short compared to all other time scales. The correlation time for return to a given site by one-dimensional diffusion on an infinite chain diverges,[6] rendering thus one of the basic assumptions of the theory invalid.

We argue that in this situation a direct stochastic theory of spin relaxation is required, in the sense of the stochastic theories of Anderson,[7] and Kubo and Tomita.[8] In their pioneering work, these authors considered only very simple stochastic processes, in particular the Gauss-Markov process. As described below, one likely process causing muon spin relaxation in *trans*-polyacetylene is the fluctuating hyperfine interaction of the muon with a mobile defect, and the time dependence of the stochastic process is determined by one-dimensional diffusion.

The problem of relaxation of classical spin rotation by a defect which diffuses on a one-dimensional chain was already treated by Czech.[9] A stochastic theory of spin relaxation of muonium by switching between two values of the hyperfine interaction was made by Celio.[10] In this paper we are concerned with the influence of one-dimensional defect motion on the spin dynamics of muonium.

We study a very idealized model for muon spin relaxation in *trans*-polyacetylene. On the experimental side, one can say that the substance is not well characterized with regard to its microstructure. Also, the nature and the dynamics of the defects remain controversial. Compared to the soliton picture that has been elaborated in theoretical work (see, e.g., Refs. 1, 11, and 12), our model is quite simplified. At least here we can offer some arguments for justification of our assumptions. We believe it is worth developing such a theory for an idealized model, and comparing it with experiments on a concrete material.

## II. EXPERIMENTAL AND THEORETICAL BACKGROUND

### A. Muon-spin relaxation experiment

Experiments on muon spin relaxation ($\mu$SR) in the polyacetylenes were performed in the early 1980s by Ishida, Nagamine, and co-workers.[13–15] Thin films of *trans*- and *cis*-$(CH)_x$ were prepared by the so-called Shirakawa method[16] and exposed to muon beams at the Booster Meson Facility of the Meson Science Laboratory, University of Tokyo and at TRIUMF, Vancouver, Canada. The muons are stopped in the films, picking up an electron and forming muonium. The individual muonium atoms attach themselves to the carbon atoms of the polyacetylene chains by breaking a double bond and leaving an unpaired electron at a neighbor carbon atom. This electron forms a neutral spin-$\frac{1}{2}$ defect. A magnetic field $B$ is present parallel to the initial muon spin polarization. The asymmetry of the decay positrons in the forward and backward directions is measured as a function of time. For a general review on the $\mu$SR method

 

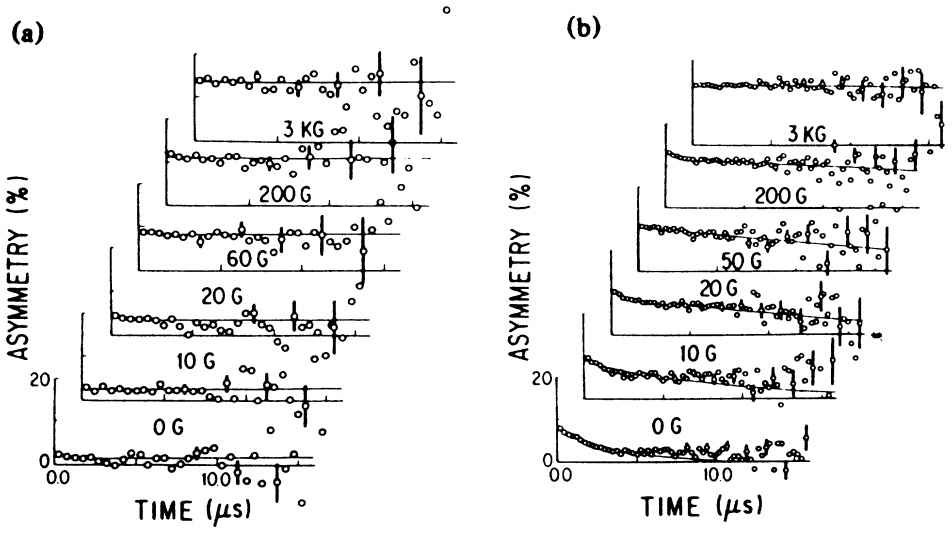


FIG. 1. Time spectra of decay positron asymmetry for $\mu^+$ in (a) *cis*-$(CH_x)$ and (b) *trans*-$(CH_x)$ at room temperature. This figure was adapted from Ref. 13.

see the book by Schenck,[17] for information on muonium see the review by Cox.[18]

The experimental results[13] for *cis*- and *trans*-$(CH)_x$ are reproduced in Fig. 1. Muon spin relaxation is observed in *trans*-$(CH)_x$, no relaxation is seen for the *cis* species. The magnetic-field dependence of the asymmetry for the *cis* species is consistent with the picture of a muonium atom attached to the $(CH)_x$ chain and a nearby immobile defect. Namely, the muonium atom forms a spin-paired double bond with the carbon, while the adjacent electron has a reduced hyperfine interaction with the muon. This situation is also well understood from radical chemistry.[19] It is natural to ascribe the relaxation observed in *trans*-$(CH)_x$ to the liberation and motion of the defects along the chains. The authors initially analyzed their experiments by assuming exponential decay and they determined a longitudinal relaxation rate $T_1^{-1}$. They referred to an expression for $T_1^{-1}$ derived by Devreux, Boucher, and Nechtschein[20] for the case of electronic motion,

$$T_1(\mu)^{-1} = \tfrac{1}{4} n_S [\tfrac{3}{5} d^2 f(\gamma_\mu B) + (a^2 + \tfrac{7}{5} d^2) f(\gamma_e B)] \quad . \quad (1)$$

Here $a$ and $d$ are the isotropic and the dipolar hyperfine coupling constants between the electron and the muon, respectively, $\gamma_e$ and $\gamma_\mu$ are the electron and the muon gyromagnetic ratios, respectively, and $n_S$ is the density of unpaired electrons per carbon atom. $f(\omega)$ is the spectral density function of the stochastic process leading to relaxation, evaluated at the respective Larmor frequencies. If spectral density functions for the process of one-dimensional diffusion are used, they behave, for smaller frequencies, as $\omega^{-1/2}$. The authors did indeed find a $B^{-1/2}$ behavior of their experimental $T_1^{-1}$, for $B \neq 0$. This observation constitutes a strong point in support of one-dimensional diffusion of the defect.

### B. Other relaxation experiments; structural information

First a brief summary will be given of experiments that indicate the existence of mobile defects in *trans*-$(CH)_x$. Further information can be found in reviews.[1–3] The experiments on dynamic nuclear polarization[21] (DNP) provide evidence that mobile defects exist in *trans*-$(CH)_x$ while they are immobile in the *cis* species. Further experiments[22,23] on DNP, nuclear magnetic resonance (NMR), and electron spin resonance (ESR) supported the existence of mobile defects in *trans*-$(CH)_x$, but they also showed the influence of trapping impurities. The picture of two different kinds of defects (mobile and trapped) in *trans*-$(CH)_x$ was introduced.[22,23] The analysis of these experiments, and other ESR experiments,[24,25] however, led to differences in the magnitude of the diffusion rates of the defects. One may conclude that the influence of trapping impurities in these experiments has not been unambiguously clarified. In another paper[26] the motional effects on the DNP spectra were studied in a simple model and the conclusion was that it is not necessary to adduce more than one kind of defect in *trans*-$(CH)_x$.

Other experiments, namely ENDOR[27] and multiple-quantum spin coherences[28] were interpreted as evidence for pinned defects both in *cis*- and *trans*-$(CH)_x$.

The conformation of the *trans*-$(CH)_x$ chains is also unclear. The polyacetylene films produced by the Shirakawa method show a fibril morphology.[16] It is not precisely known how the chains are arranged within these fibers. A more crystalline material is produced by the Durham route.[29] There are experimental indications that the *average* conjugation lengths of the *trans*-$(CH)_x$ chains are quite small, namely $n = 11-14$ in the Shirakawa material and $n = 30-40$ in the Durham material.[30] The conjugation length may be identified with the length of an ideal sequence of bond alternation.

In summary, the presently available polyacetylene is not well characterized and quite different from the idealized models. Although a majority of experiments indicate the existence of highly mobile defects, their existence has not been established beyond doubt. Also the influence of impurities and of the finite chain lengths has not yet been clarified.

### C. Theory of soliton motion

One usually associates the picture of a coherent motion with the notion of the soliton. Coherently moving solitons appear as solutions of the appropriate continuum models, e.g., in the model of Takayama, Lin-Liu, and Maki.[11] However, coherent motion does not occur for the supposed solitons in ideal *trans*-$(CH)_x$ chains. First, the discreteness of the chains requires a small activation energy for shifting the soliton one lattice unit. This energy has been estimated in the model of Su, Schrieffer, and Heeger (SSH) to be about 2 meV,[12] hence it would inhibit motion at low temperatures. Second, at finite temperatures the solitons interact with thermally excited phonons, and a stochastic motion of the soliton results. Already in the molecular-dynamics simulations of a discrete soliton model by Koehler *et al.*[31] a kind of Brownian motion of the domain walls was observed. The interaction of solitons in *trans*-$(CH)_x$ with phonons and its influence on mobility and diffusivity have been treated by various authors, see Ref. 32 for references. The diffusion coefficient, which results from the interaction with acoustic phonons, diverges for low temperatures as $T^{-1}$ if trapping effects are disregarded. Jeyadev and Conwell[32] were able to reproduce the approximate $T^2$ behavior observed in the NMR and ESR experiments by including trapping by impurities in an average way. For our purposes it is important to realize that the absorption and emission processes of thermal phonons effect an incoherent motion of the solitons in ideal chains of *trans*-polyacetylene. This may be summarized by the qualitative statement that the solitons perform Brownian motion at finite temperatures.

## III. THE STOCHASTIC MODEL

In this section we introduce the model that we formally analyze in the subsequent section. We assume that the defect is localized at the sites of a linear chain. In reality the electronic defect in *trans*-polyacetylene is delocalized. A delocalization of 14 lattice constants was found in the SSH model [the lattice constant $a$ is that of the undimerized $(CH)_x$ chain and the value given is twice the width parameter or extent $\xi$]. The self-consistent-field calculation of Boudreaux *et al.*[33] for finite *trans*-$(CH)_x$ gave a value of six lattice constants for the delocalization of the neutral spin-$\frac{1}{2}$ defect. The delocalization of the defect in the neighborhood of the attached muonium is not known at present.[34] We introduce a hopping picture where the localized defect makes a random walk on a half-sided linear chain with the transition rate $\gamma$ between neighboring sites, see Fig. 2. Thus we replace the Brownian motion of the extended defect by an effective hopping process of a localized defect. When is this replacement justified? One requirement is that the friction coefficient $\nu$, which describes the rate of decay of velocity correlations, is large compared to the transition rate $\gamma/2$ between the sites. The friction coefficient $\nu = (mB)^{-1}$, where $m$ is the effective mass and $B$ the mobility of the soliton. The mobility is related to the diffusion coefficient $D$ by the Einstein relation and for the random walk on the linear chain $D = \gamma d^2/2$ where $d$ is the effective hopping distance. The requirement can then be expressed as

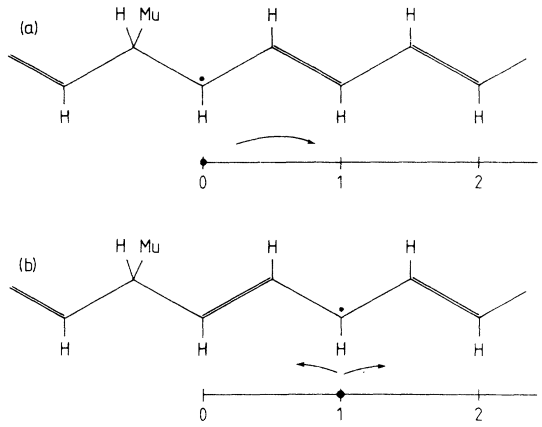


FIG. 2. Schematic representation of the *trans*-polyacetylene chain with an attached muonium and an unpaired electron, and of the random-walk model. (a) The defect is on the neighbor site of the muonium; (b) the defect has moved one unit.

$$\gamma^2 \ll \frac{4k_BT}{md^2}. \tag{2}$$

The criterion that the mean free path of thermal motion be small compared to the hopping distance leads to the same expression. For solitons in *trans*-$(CH)_x$ the effective mass is approximately six times the mass of an electron. Assuming a hopping distance $d = 3$ Å and room temperature the criterion (2) requires $\gamma \ll 10^{14}$ s$^{-1}$. The experimentally deduced diffusion rates are smaller than this value, hence we believe an effective hopping picture is justified.

We further assume that the hyperfine interaction is "on" when the defect is on the neighbor site (site 0) of the muonium, and that it is switched off when it is on the other sites. This is again a simplification, since the hyperfine interaction decays with the inverse third power of the distance. It is in vein with the effective hopping picture of a localized defect. In a more detailed description one should include both the extension of the defect and the range of the hyperfine interaction.

Finally, we introduce in our model the possibility of spin flips, with rate $\lambda$, when the defect is on other sites than site 0. This restriction is mainly for technical reasons in the treatment of the averaged time evolution. Our simplified model is then characterized by the parameters $\gamma$, the rate of transitions to adjacent sites, $\omega_0$, the hyperfine interaction at site 0, and $\lambda$, the spin-flip rate of the defect at the other sites.

## IV. STOCHASTIC TREATMENT OF AVERAGED TIME EVOLUTION

### A. Method

We calculate the polarization of the muon at time $t$ as the trace over the density matrix,

$$P(t) = tr\{\rho(t)\sigma_z\} \quad , \tag{3}$$

with the initial condition

$$\rho(0) = \tfrac{1}{4}[1 + P(0)\sigma_z] \tag{4}$$

corresponding to an electron that is either parallel or antiparallel to the muon spin, with probabilities $\frac{1}{2}$. The objective of this section is to evaluate the *averaged* time evolution operator $U(t)$ of the density matrix,

$$\rho(t) = U(t)\rho(0) \quad . \tag{5}$$

Here $U(t)$ is a so-called superoperator which acts on operators of the underlying Hilbert space.[35] We introduce the scalar product of the operators $a$ and $b$ in this operator space by the trace metric

$$(a, b) = tr\{a^+ b\} \quad , \tag{6}$$

where $a^+$ is the adjoint operator to $a$. If a complete set of state vectors $|k>$ is given, then we choose the shift operators

$$S_{kl} = |k><l| \tag{7}$$

as a basis of the operator space. In this way we can represent operators $a$ as vectors,

$$\mathbf{a} = (S_{kl}, a) = <k|a|l> \tag{8}$$

and superoperators $U$ as matrices,

$$\underline{U} = (S_{ij}, US_{kl}) = <ij|U|kl> \quad . \tag{9}$$

Hence we are able to calculate the polarization $P(t)$ by matrix multiplication:

$$P(t) = \boldsymbol{\sigma}_z^+ \cdot \underline{U}(t) \cdot \boldsymbol{\rho}(0) \quad . \tag{10}$$

### B. Time evolution

In this subsection we shall describe the time evolution of the electron spin and the muon spin in the case that the hyperfine interaction is either switched on or switched off, as described in Sec. III. If the hyperfine interaction is "on" then we assume that the Hamiltonian has the form

$$H = \frac{\hbar}{4}\omega_0 \sigma\tau - \frac{\hbar}{2}\omega_\mu \sigma_z + \frac{\hbar}{2}\omega_e \tau_z \equiv H_C + H_Z, \tag{11}$$

where $H_C$ corresponds to an isotropic muonium state and $H_Z$ contains the influence of the magnetic field along the $z$ axis. The quantities $\sigma$ and $\tau$ are the Pauli spin matrices for the muon and electron, respectively, and $\omega_\mu$,$\omega_e$ the associated Larmor frequencies. It is useful to define the frequencies

$$\omega_\pm = (\omega_e \pm \omega_\mu)/2 \tag{12}$$

and the specific magnetic field

$$x = 2\omega_+/\omega_0 \quad . \tag{13}$$

The Hamiltonian is easily diagonalized using the spin eigenfunctions

$$|\chi_\alpha> = |m_\alpha^\mu m_\alpha^e> \tag{14}$$

as a basis. Here $m_\alpha^\mu$ and $m_\alpha^e$ are the muon and electron magnetic quantum numbers:

$$\begin{aligned} &|\chi_1> = |++>, \quad |\chi_2> = |+->, \\ &|\chi_3> = |-+>, \quad |\chi_4> = |--> \quad . \end{aligned} \tag{15}$$

The eigenvalues $E_n$ of the Hamiltonian as well as the eigenvectors $|E_n>$ expressed in the basis $|\chi_\alpha>$ are given in Table I.

The time evolution of the density matrix is determined by

$$U_0(t) = \exp(iLt) \tag{16}$$

with the Liouville operator $L = -\frac{1}{\hbar}[H, \ldots]$. In dealing with the dynamics of the muonium we take the shift operators of the Hamiltonian $H$ as a basis of the 16-dimensional operator space

$$S_{kl} = |E_k><E_l| \quad . \tag{17}$$

They are the eigenoperators of the Liouville operator with the energy differences $\omega_{kl} = (E_k - E_l)/\hbar$ as eigenvalues. The time evolution operator is then diagonal in this representation,

$$(S_{kl}, U_0 S_{ij}) = \delta_{ik}\delta_{jl}\exp(i\omega_{ji}t) \quad . \tag{18}$$

When the hyperfine interaction is switched off, both spins are decoupled and are moving in the magnetic field according to the Liouville operator $L_Z$ associated with the Zeeman Hamiltonian $H_Z$. To include the possibility of spin flips of the electron we construct an averaged time evolution operator $U_1(t)$ using the pulse model of Clauser and Blume.[36]

In this model the system experiences pulses at time points $t_j$ that are distributed according to a Poisson process with event rate $\lambda$. The pulses effect transitions between different states of the system. We assume the Hamiltonian to have the form

TABLE I. Eigenfunctions and eigenvalues of the Hamiltonian Eq. (11). The coefficents are $c = \sqrt{1 + x/\sqrt{1+x^2}}/\sqrt{2}$ and $s = \sqrt{1-c^2}$.

| $i$ | $\mid E_i >$ | $E_i/\hbar$ |
|---|---|---|
| 1 | $\mid \chi_1 >$ | $\frac{\omega_0}{4} + \omega_-$ |
| 2 | $s \mid \chi_2 > + c \mid \chi_3 >$ | $-\frac{\omega_0}{4} + \sqrt{\frac{\omega_0^2}{4} + \omega_+^2}$ |
| 3 | $\mid \chi_4 >$ | $\frac{\omega_0}{4} - \omega_-$ |
| 4 | $c \mid \chi_2 > - s \mid \chi_3 >$ | $-\frac{\omega_0}{4} - \sqrt{\frac{\omega_0^2}{4} + \omega_+^2}$ |

$$H(t) = H_Z + \sum_j V_j \delta(t - t_j) \quad , \tag{19}$$

where the random interaction potentials $V_j$ are uncorrelated from one instant to the next. If one makes a decomposition into the number of pulse events and sums the corresponding series in the Laplace domain, the averaged time evolution operator is obtained as

$$\tilde{U}_1(u) = [u - iL_Z - \lambda(J_{\rm av} - E)]^{-1} \quad . \tag{20}$$

The tilde designates the Laplace transform. The pulse operator

$$J_{\rm av} = (\exp\{-(i/\hbar)[V_j, \ldots]\})_{\rm av} \tag{21}$$

is an average over the statistics of the random operators $V_j$. We imagine that the pulses effect rotations of the electronic spin about arbitrary directions $\phi$. Then the pulse operator is easily written down in the basis of the spin eigenfunctions $|\chi_\alpha>$: At first the muon spin is conserved under the action of the pulse operator

$$<\chi_\alpha\chi_\beta \mid J_{\rm av} \mid \chi_\gamma\chi_\delta>$$

$$= \delta_{m_\alpha^\mu m_\gamma^\mu}\delta_{m_\beta^\mu m_\delta^\mu} <m_\alpha^e m_\beta^e \mid J_{\rm av}^e \mid m_\gamma^e m_\delta^e> \quad . \tag{22}$$

Second, in the electronic subspace the pulse operator

$$J^e = \exp\{-(i/2)[\tau\phi, \ldots]\} \tag{23}$$

has to be averaged over the arbitrary directions $\phi$, as described by Dattagupta.[37] The matrix elements are given by

$$<m_\alpha^e m_\beta^e \mid J_{\rm av}^e \mid m_\gamma^e m_\delta^e> = \tfrac{1}{2}\delta_{\gamma\delta}\delta_{\alpha\beta} \quad . \tag{24}$$

Now the matrix $\tilde{U}_1(u)$ can be inverted explicitly and transformed back to the time domain; see Table II.

The resulting time evolution operator is of course based on a very idealized picture of the interaction of the electronic spin with the polyacetylene chain. Nevertheless, it contains spin-lattice relaxation: If a pure spin state is given at time zero, the expectation value of the electronic spin decays exponentially with the decay constant $\lambda$, which we identify with the inverse spin-lattice relaxation time of the electron: $\lambda = 1/T_1^e$. To summarize, we use the relaxation operator $W = \lambda(J_{\rm av} - E)$ to describe the influence of the chain on the electronic spin, and the operator $U_1(t) = \exp[(iL_Z + W)t]$ for the time evolution of the spins, when the hyperfine interaction is "off."

### C. Average over random walk

The stochastic process of switching between the time evolution $U_0(t)$, when the unpaired electron is on the neighbor site of the muonium, and the time evolution $U_1(t)$, when the electron is on other sites, determines the averaged time evolution operator $U(t)$. The averaging that we shall perform in this subsection is similar to the procedure of Czech,[9] who solved the analogous problem for classical spin rotation.

We consider the random walk of the electron with hopping rate $\gamma$ on the half-sided linear chain. In the following frequencies and inverse times will always be measured in units of $\gamma$. First we have to describe the statistics of the

TABLE II. Time evolution operator $U_1$ in the spin basis

$$\left(S_{\chi_\alpha\chi_\beta} \, , \, U_1(t)\, S_{\chi_\gamma\chi_\delta}\right) = \begin{pmatrix} U_1^{(a)} & 0 \\ 0 & U_1^{(b)} \end{pmatrix}.$$

We tabulated the matrices $U_1^{(a)}$, $U_1^{(b)}$ and used the abbreviations $p \equiv p(t) = 1/2\,[1 + \exp(-\lambda t)]$ , $q \equiv q(t) = 1 - p(t)$ , $\alpha \equiv \alpha(t) = \exp(-\lambda t)$.

| $U_1^{(a)}$ | 11 | 12 | 13 | 14 | 21 | 22 | 23 | 24 |
|---|---|---|---|---|---|---|---|---|
| 11 | $p$ | | | | | $q$ | | |
| 12 | | $e^{-i\omega_e t}\alpha$ | | | | | | |
| 13 | | | $e^{i\omega_\mu t}p$ | | | | | $e^{i\omega_\mu t}q$ |
| 14 | | | | $e^{-i2\omega_- t}\alpha$ | | | | |
| 21 | | | | | $e^{i\omega_e t}\alpha$ | | | |
| 22 | $q$ | | | | | $p$ | | |
| 23 | | | | | | | $e^{i2\omega_+ t}\alpha$ | |
| 24 | | | $e^{i\omega_\mu t}q$ | | | | | $e^{i\omega_\mu t}p$ |

| $U_1^{(b)}$ | 31 | 32 | 33 | 34 | 41 | 42 | 43 | 44 |
|---|---|---|---|---|---|---|---|---|
| 31 | $e^{-i\omega_\mu t}p$ | | | | | $e^{-i\omega_\mu t}q$ | | |
| 32 | | $e^{-i2\omega_+ t}\alpha$ | | | | | | |
| 33 | | | $p$ | | | | | $q$ |
| 34 | | | | $e^{-i\omega_e t}\alpha$ | | | | |
| 41 | | | | | $e^{i2\omega_- t}\alpha$ | | | |
| 42 | $e^{-i\omega_\mu t}q$ | | | | | $e^{-i\omega_\mu t}p$ | | |
| 43 | | | | | | | $e^{i\omega_e t}\alpha$ | |
| 44 | | | $q$ | | | | | $p$ |

visits at the origin ($r = 0$) :

(i) $F(t)$ is the probability density of the first return to the origin at time $t$ when the electron starts at it at $t = 0$. The corresponding survival probability

$$N(t) = 1 - \int_0^t F(t')dt' \tag{25}$$

is the probability that the electron does not reach the origin until time $t$. The Laplace transform of $F$ is given by[9]

$$\tilde{F}(u) = u + 1 - \sqrt{u(u+2)} \ . \tag{26}$$

(ii) For the continuous-time random walk the statistics of the time the electron spends at the origin is given by

$$\psi(t) = \gamma_0 \exp(-\gamma_0 t) \ , \tag{27}$$

where $\psi(t)$ is the probability density that the electron makes a transition at time $t$ from the origin to the neighbor site. Evidently,

$$\phi(t) = \exp(-\gamma_0 t) \tag{28}$$

is the probability that no such transition occurs until time $t$. We assume that all transition rates on the chain are equal. Because the electron can only jump to the single neighbor site $r = 1$, the transition rate at the origin is, with our normalization,

$$\gamma_0 = \tfrac{1}{2} \ . \tag{29}$$

To calculate the averaged time evolution operator it is useful to classify the random walk according to the number $n$ of visits at the origin and also according to whether the last $n$th visit (a) still continues at time $t$ or not (b):

$$U(t) = \sum_{n=1}^{\infty} [\tau_n^a(t) + \tau_n^b(t)] \ . \tag{30}$$

For instance, the electron that hops away once and comes back to the origin until time $t$, contributes

$$\tau_2^{(a)}(t) = \int_0^t dt_2 \phi(t - t_2) U_0(t - t_2) \times \int_0^{t_2} dt_1 F(t_2 - t_1) U_1(t_2 - t_1) \psi(t_1) U_0(t_1) \ . \tag{31}$$

The $n$th contributions to the processes (a) and (b) are $(2n-1)$ convolution integrals, which are given in the Laplace domain by simple multiplications :

$$\tilde{\tau}_n^{(a)}(u) = \widetilde{\phi U_0}(u) \left[ \widetilde{F U_1}(u) \widetilde{\psi U_0}(u) \right]^{n-1} \ , \tag{32}$$

$$\tilde{\tau}_n^{(b)}(u) = \widetilde{N U_1}(u) \widetilde{\psi U_0}(u) \left[ \widetilde{F U_1}(u) \widetilde{\psi U_0}(u) \right]^{n-1} \ . \tag{33}$$

The sum (30) of these contributions yields the final result for the averaged time evolution operator in the Laplace domain:

$$\tilde{U}(u) = \left[ \widetilde{\phi U_0}(u) + \widetilde{N U_1}(u) \widetilde{\psi U_0}(u) \right] \times \left[ E - \widetilde{F U_1}(u) \widetilde{\psi U_0}(u) \right]^{-1} \ . \tag{34}$$

### D. Evaluation

Now we combine the results of the preceding subsections to evaluate the depolarization of the muon,

$$\tilde{P}(u) = \left( \sigma_z \ , \ \tilde{U}(u) \rho(0) \right) \ , \tag{35}$$

where $\tilde{U}(u)$ is given by (34). We utilize the damping theorem for Laplace transformation in handling the probabilities $\phi$, $\psi$, and $F$; we utilize the fact that the muon spin is conserved under the action of $U_1$,

$$\sigma_z^{\dagger} \ U_1(t) = \sigma_z^{\dagger} \ E \quad , \tag{36}$$

and Eq. (25) to eliminate $\tilde{N}$

$$\tilde{N}(u) = \frac{1}{u} \left( 1 - \tilde{F}(u) \right) \quad , \tag{37}$$

to obtain the following trace

$$\tilde{P}(u) = \frac{1}{u} \left[ u + \gamma_0 \left( 1 - \tilde{F}(u) \right) \right] \times \mathrm{Tr} \left\{ \sigma_z^{\dagger} \ \tilde{U}_0(u + \gamma_0) \times \left[ E - \gamma_0 \widetilde{F U_1}(u) \tilde{U}_0(u + \gamma_0) \right]^{-1} \rho(0) \right\} \ . \tag{38}$$

We calculate the trace in the basis $S_{E_i E_j}$, where $U_0$ is diagonal. Hence the time evolution operator $U_1$, which was determined in the spin basis, must be represented in this basis; this can be done by a basis transformation. Furthermore the matrix algebra has to be carried out. Because of the longitudinal geometry it is sufficent to consider the 6-dim subspace, which is spanned by the following shift operators:

$$\left\{ S_{E_1 E_1} \ , S_{E_2 E_2} \ , S_{E_2 E_4} \ , S_{E_3 E_3} \ , S_{E_4 E_2} \ , S_{E_4 E_4} \right\} \ . \tag{39}$$

The algebra was performed with the help of symbolic formula manipulation by REDUCE. The final expression for the decay of the polarization (in the Laplace domain) is

$$\tilde{P}(u) = \frac{(\Lambda - 1 - 2u)}{u} \frac{X}{Y}(u) \quad , \tag{40}$$

where

$$X = 2u\{(\Lambda_+ + \Lambda_0 - 2)\Lambda_- + (\Lambda_0 - 2)\Lambda_+ - 2\Lambda_0 - 2\omega_0^2 + 4\omega_{24}^2 + 3\}$$
$$+4i\omega_0 x(2u - \Lambda_0 + 1)(\Lambda_- - \Lambda_+) - 4u^2(\Lambda_- + \Lambda_+ + \Lambda_0 - 3) - \omega_0^2(\Lambda_- + \Lambda_+ - 4\Lambda_0 + 2)$$
$$-(\Lambda_+ - 1)(\Lambda_0 - 1)\Lambda_- + 4\omega_{24}^2 - (4\omega_{24}^2 + 1)\Lambda_0 + (\Lambda_0 - 1)\Lambda_+ + 8u^3 + 1 \quad , \tag{41}$$

$$Y = 2u\{(\Lambda_0 + \Lambda - 2)\Lambda_+ + (\Lambda - 2)\Lambda_0 - 2\Lambda + 3\}\Lambda_- + 2u\{(\Lambda - 2)\Lambda_0 - 2\Lambda + 3\}\Lambda_+$$
$$+2u\{-(2\Lambda - 4\omega_{24}^2 - 3)\Lambda_0 + (4\omega_{24}^2 + 3)\Lambda - 8\omega_{24}^2 - 4\} + 2u\{2\omega_0^2(\Lambda_- + \Lambda_+ - \Lambda_0 - \Lambda)\}$$
$$+\omega_0^2\{(\Lambda_- + \Lambda_+)(\Lambda_0 + \Lambda - 2) - 2(2\Lambda - 1)\Lambda_0 + 2\Lambda\} - 4u^2\{(\Lambda_0 + \Lambda - 3)\Lambda_+ + (\Lambda_0 + \Lambda_+ + \Lambda - 3)\Lambda_-\}$$
$$-4u^2\{(\Lambda - 3)\Lambda_0 - 3\Lambda + 4\omega_{24}^2 + 6\} - 4i\omega_0 x(2u - \Lambda_0 + 1)(\Lambda_- - \Lambda_+)(2u - \Lambda + 1)$$
$$+8u^3(\Lambda_- + \Lambda_+ + \Lambda_0 + \Lambda - 4) - (\Lambda_+ - 1)(\Lambda_0 - 1)(\Lambda - 1)\Lambda_- + (\Lambda_0 - 1)(\Lambda - 1)\Lambda_+$$
$$-(\Lambda - 1)(4\omega_{24}^2 + 1)\Lambda_0 + (4\omega_{24}^2 + 1)\Lambda - 16u^4 - 4\omega_{24}^2 - 1 \quad . \tag{42}$$

We used the following abbreviations for the return probability:

$$\Lambda = \tilde{F}(u),$$
$$\Lambda_0 = \tilde{F}(u + \lambda),$$
$$\Lambda_+ = \tilde{F}(u + \lambda + i2\omega_+), \tag{43}$$
$$\Lambda_- = \tilde{F}(u + \lambda - i2\omega_+).$$

We obtain explicit results by numerical Laplace inversion, see the next section.

## V. DISCUSSION AND ASYMPTOTIC THEORY

We will now look at the result Eq. (40) for the polarization. As discussed in Sec. II B experiments indicate transition rates $\gamma$ of the unpaired electron of the order of $10^{12}$–$10^{13}$ $s^{-1}$. The other rates of the system are much smaller than $\gamma$: the hyperfine interaction is bounded by its vacuum value, the Larmor frequencies are small (otherwise complete decoupling of the muon and electron spin would result), and also the electronic spin-flip rate is much smaller than $\gamma$. Consequently, we shall develop asymptotic expressions for the spin relaxation. We will first discuss the zero-field case.

### A. Zero-field case

A considerable simplification of the result (40) is obtained for the case $B = 0$. The polarization is then given in the Laplace domain by

$$\tilde{P}(u) = \frac{1}{u}\left(1 - \frac{2\omega_0^2 G_\lambda}{2\omega_0^2(G_\lambda + G) + G_\lambda^2 G}\right), \tag{44}$$

where the following auxiliary functions are used:

$$G = G(u) \equiv 2u + 1 - \tilde{F}(u) \quad ,$$
$$G_\lambda = G_\lambda(u) \equiv 2u + 1 - \tilde{F}(u + \lambda) \tag{45}$$

As stated in Sec. IV C we use scaled units; i.e., all frequencies and the Laplace variable are expressed in units of $\gamma$ and times in units of $\gamma^{-1}$. The dependence of the depolarization on the spin-flip rate $\lambda$ for fixed $\omega_0$ is shown in Fig. 3. For zero flip rate, the polarization decays to a plateau value of $\frac{1}{2}$. This is in agreement with the result for the residual polarization of free muonium in zero field. For small $\lambda$, the plateau value decays and with increasing $\lambda$, the initial decay of the plateau becomes slower.

The dependence of the depolarization on the transition rate $\gamma$ is exhibited in Fig. 4. In this figure, the original parameters $\omega_0$ and $\lambda$ are kept fixed, i.e., the scaled parameters vary with $\gamma^{-1}$. It is seen that the depolarization is strongly reduced by increasing the transition rate $\gamma$, and its behavior becomes simpler than that for smaller values. For large $\gamma$ it is possible to perform an asymptotic expansion, and its result has already been included in this figure. The two small parameters are $u$ and $\lambda$ and the auxiliary functions (46) behave asymptotically as

$$G \to \sqrt{2u}, \qquad G_\lambda \to \sqrt{2(u + \lambda)} \quad . \tag{46}$$

In the case of $\lambda/u \ll 1$, i.e., in the case of small spin-flip rate of the electron compared to the experimental inverse time scale, the asymptotic behavior of the polarization is

$$\tilde{P}(u) \to \frac{1}{u}\left(1 - \frac{\omega_0^2}{2\omega_0^2 + u}\right) \quad , \tag{47}$$

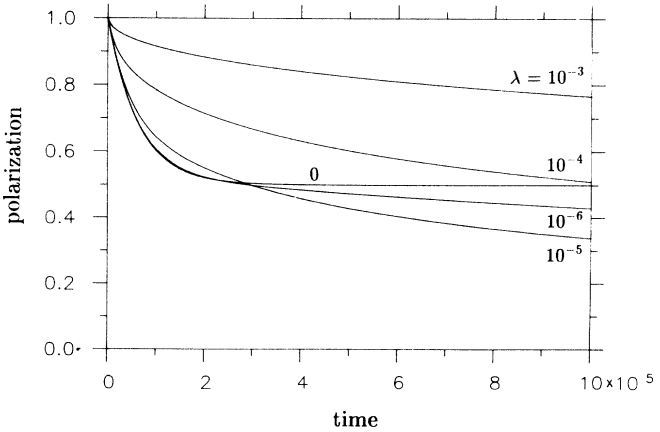


FIG. 3. Zero-field depolarization, Eq. (44), for different values of the pulse rate $\lambda$. The value of the hyperfine constant $\omega_0/2\pi$ is $4.5 \times 10^{-4}$.

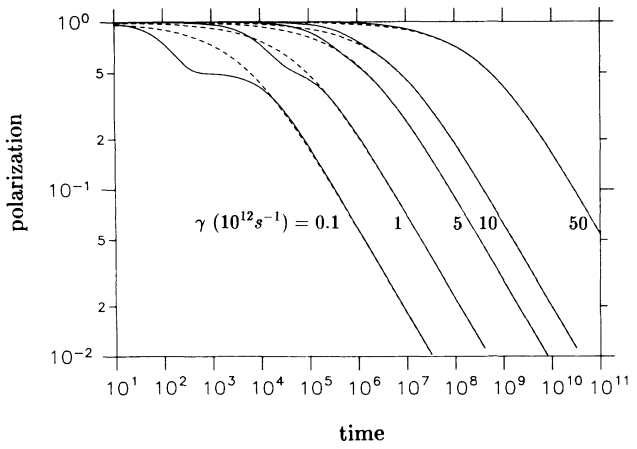


FIG. 4. Zero-field depolarization, Eq. (44), for different values of the hopping rate $\gamma$. The hyperfine constant $\omega_0/2\pi = 10^9\ \mathrm{s}^{-1}$ and the pulse rate $\lambda = 10^7\ \mathrm{s}^{-1}$ are kept fixed. Dashed line: asymptotic decay with $\phi(\Gamma_0 t)$, Eq. (52).

or, in the time domain,

$$P(t) \to \tfrac{1}{2} + \tfrac{1}{2}\exp(-2\omega_0^2 t). \tag{48}$$

This result reproduces the exponential decay to the plateau value of Fig. 3 for vanishing pulse rates.

For large ratio $\lambda/u \gg 1$ or large spin-flip rate with respect to the inverse of the experimental time scale, the asymptotic polarization is given by

$$\tilde{P}(u) \to \frac{1}{\sqrt{u}}\left(\frac{1}{\sqrt{\Gamma_0}+\sqrt{u}}\right) \quad , \tag{49}$$

with the parameter $\Gamma_0$,

$$\Gamma_0 = \frac{\omega_0^4 \lambda}{(\omega_0^2+\lambda)^2} \quad . \tag{50}$$

In the time domain

$$P(t) \to \phi(\Gamma_0 t), \tag{51}$$

where we have introduced the relaxation function

$$\phi(T) = \exp(T)\mathrm{erfc}(\sqrt{T}) \tag{52}$$

and erfc signifies the complementary error function.

It is of interest to display the dependence of the polarization on time for small and large arguments,

$$P(t) \overset{\Gamma_0 t \ll 1}{\longrightarrow} 1 - 2\sqrt{\frac{\Gamma_0 t}{\pi}}\ , \qquad P(t) \overset{\Gamma_0 t \gg 1}{\longrightarrow} \frac{1}{\sqrt{\pi \Gamma_0 t}} \quad . \tag{53}$$

Thus, for nonvanishing spin-flip rates this theory yields a power-law decay of the polarization for large times, not exponential decay, as assumed in the original analysis of the experiments. This power-law decay is a consequence of the revisiting effects of the unpaired electron at the origin by one-dimensional random walk.

### B. Finite magnetic fields

The polarization $P$ depends on the magnetic field via the electronic Larmor frequency $\omega_e$, if one considers that $2\omega_+ \approx \omega_e$. The behavior of the polarization with the electronic Larmor frequency, at a fixed time point, is shown in Fig. 5 for different values of the coupling strength $\omega_0$ and fixed pulse rates $\lambda$, and in Fig. 6 for different values of $\lambda$ and fixed $\omega_0$. When a very strong magnetic field acts on the system, with $\omega_e \gg \omega_0$, the muon spin is effectively decoupled from the electron spin and remains polarized. For very small fields $\omega_e \ll \omega_0$ and $\omega_e \ll \lambda$ the results of the preceding subsection apply. Hence we consider intermediate fields with $\lambda \ll \omega_e$. The transition rate $\gamma$ is again regarded as the large parameter, and in scaled units $\omega_e \ll 1$ and $\lambda \ll 1$. We have the following two cases:

(i) The case $\lambda/u \gg 1$, i.e., the mean time between electron spin flips is short compared to the experimental time scale. In this case the asymptotic evaluation of (40) yields

$$\tilde{P}(u) \to \frac{1}{\sqrt{u}}\left(\frac{1}{\sqrt{\Gamma}+\sqrt{u}}\right) \quad , \tag{54}$$

with the parameter

$$\frac{1}{\sqrt{\Gamma}} = \frac{1}{\sqrt{\lambda}} + \frac{\sqrt{2}}{\omega_0^2}\left(\sqrt{\omega_e} + 2\omega_e^{3/2}\right) + 2\sqrt{2}\frac{\sqrt{1+(\omega_0/\omega_e)^2}}{\sqrt{1+(\omega_0/\omega_e)^2}-1}. \tag{55}$$

Since (54) is of the same form as (49), $P(t)$ in the time domain is given by the relaxation function $\phi$ (52), with the argument $T = \Gamma t$. For moderate values of the mag-

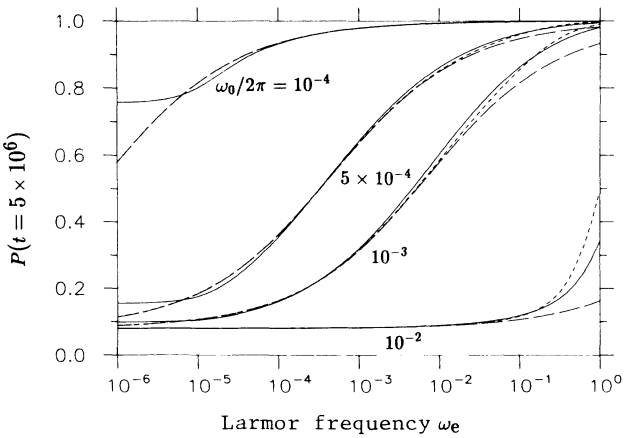


FIG. 5. Depolarization, Eq. (40), as a function of the electronic Larmor frequency for different values of the hyperfine frequency $\omega_0$, at fixed time $t = 5 \times 10^6$ and fixed pulse rate $\lambda = 10^{-5}$. (- - - - -) relaxation function $\phi(\Gamma t)$ with $\Gamma$ from Eq. (55); (— . — .— .) line with $\Gamma$ from Eq. (56).

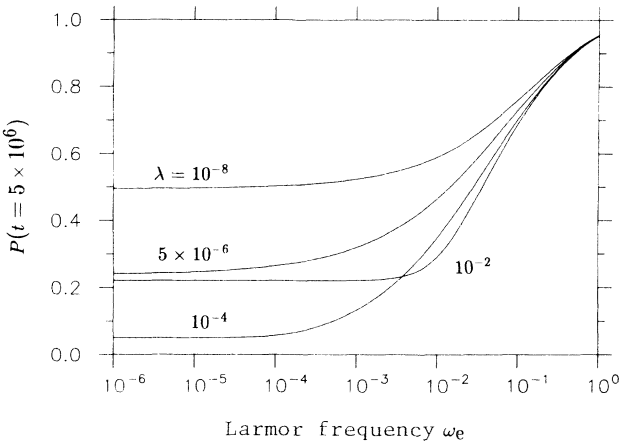


FIG. 6. Magnetic field dependence of the depolarization, Eq. (40), for different pulse rates $\lambda$; $t = 5 \times 10^6$ , $\omega_0 = 10^{-2}$ fixed.

netic field the parameter $\Gamma$ is given by

$$\Gamma = \frac{\omega_0^4 \lambda}{(\omega_0^2 + \sqrt{2\omega_e \lambda})^2} , \tag{56}$$

which approaches

$$\Gamma \to \Gamma_B = \frac{\omega_0^4}{2\omega_e} \tag{57}$$

for transition rates very large compared to the hyperfine frequency. Note that $\Gamma_B$ is proportional to $B^{-1}$.

(ii) $\lambda/u \ll 1$. In this case the state $|m_\mu = +, m_e = +>$ is effectively not mixed into other states, and the asymptotic expansion for moderate fields leads to

$$P(t) \to \tfrac{1}{2} + \tfrac{1}{2}\phi(4\Gamma_B t). \tag{58}$$

The behavior of $P(t)$ for short and long times follows from the behavior of the relaxation function $\phi(t)$. Its behavior has already been given in the preceding subsection, cf. Eq. (53), only new parameters $\Gamma$ or $\Gamma_B$ have to be inserted into the formulas. The main conclusion remains valid, namely, the long-time decay of the polarization is proportional to $t^{-1/2}$.

## VI. COMPARISON WITH EXPERIMENT

### A. Fit of experimental data

We now examine how our theory describes the experimental results on muon spin relaxation in *trans*-polyacetylene. For this purpose we made fits of the experimental data of Ref. 15 by our theory. The time interval of the experiments is 10–15 $\mu$s and the time resolution of the order of 0.1 $\mu$s. We assume that the asymptotic theory of the last section is applicable. It will be confirmed self-consistently that the transition rate $\gamma$ of the unpaired electron is indeed large. In the zero-field case we have as

TABLE III. Fit parameter $\gamma$ for different magnetic fields and temperatures.

| $B$ (G) | $\gamma$ ($10^{12}$ s$^{-1}$) | | |
|---|---|---|---|
| | 293 K | 288 K | 29 K |
| 10 | 1.2 | 1.6 | 0.7 |
| 20 | 1.5 | 1.5 | 1.6 |
| 50 | 1.3 | 1.0 | 1.9 |

parameters $\gamma$, $\omega_0$, and $\lambda$, cf. (50). In the finite-field case we assume that $\lambda \ll \omega_e$; this is the case for the published ESR value of $\lambda$ for fields above 10 G. The transition rate $\gamma$ is in fact so large that the simplified expression $\Gamma_B$ instead of $\Gamma$ can be used, cf. (57). We have examined this point consistently by using both the complete and the approximate expression. The parameters $\Gamma_0$ for the zero-field case, and $\Gamma_B$ for $B \neq 0$ depend on the combination $\omega_0^2/\gamma$. This means that we cannot determine $\omega_0$ and $\gamma$ independently when $\Gamma_B$ is to be used for the finite-field case. We assumed that $\omega_0/2\pi = 4.5 \times 10^8$ s$^{-1}$; this value is approximately $\frac{1}{10}$ of the vacuum value. Similar reductions have been observed for separated muons and electrons in organic substances.[19] There remains $\gamma$ as the free parameter for $B \neq 0$ and the free parameters $\gamma$ and $\lambda$ for $B = 0$. We made first fits of the individual relaxation data at different fields $B = 10$, 20, and 50 G. The resulting $\gamma$ values are given in Table III. Then we made fits of the data at $B = 0$ using the mean values of $\gamma$ at the corresponding temperatures, and determined $\lambda$. The resulting $\lambda$ values are given in Table IV.

Figure 7(a) shows the data together with the fit curves at $T = 293$ K and Fig. 7(b) the data together with the fit at $T = 29$ K. The fit of the data by our theory is fair at $B = 0$ and good at finite fields. One possible reason for the reduced quality of the fit at $B = 0$ is the neglect of the dipolar coupling of the muon to the surrounding protons in our theory. This interaction becomes decoupled by the application of fields of the order of 10 G and larger.

One major problem is that the transition rate $\gamma$ found at 29 K is practically the same as the one at room temperature. This problem is not specific to the theory developed here. However, it is related to the applicability of the model that we use, or, in other words, to the precise origin of the muon spin relaxation in *trans*-$(CH)_x$. We shall return to this question in the conclusion.

### B. Field dependence of slope

A strong point of the original analysis of the experiments[13] was the observation that the apparent spin-lattice relaxation rate $T_1^{-1}$ is proportional to $B^{-1/2}$;

TABLE IV. Fit parameter $\lambda$ for different temperatures at zero magnetic field.

| | 293 K | 288 K | 29 K |
|---|---|---|---|
| $\lambda$ ($10^7$ s$^{-1}$) | 6 | 7 | 2 |

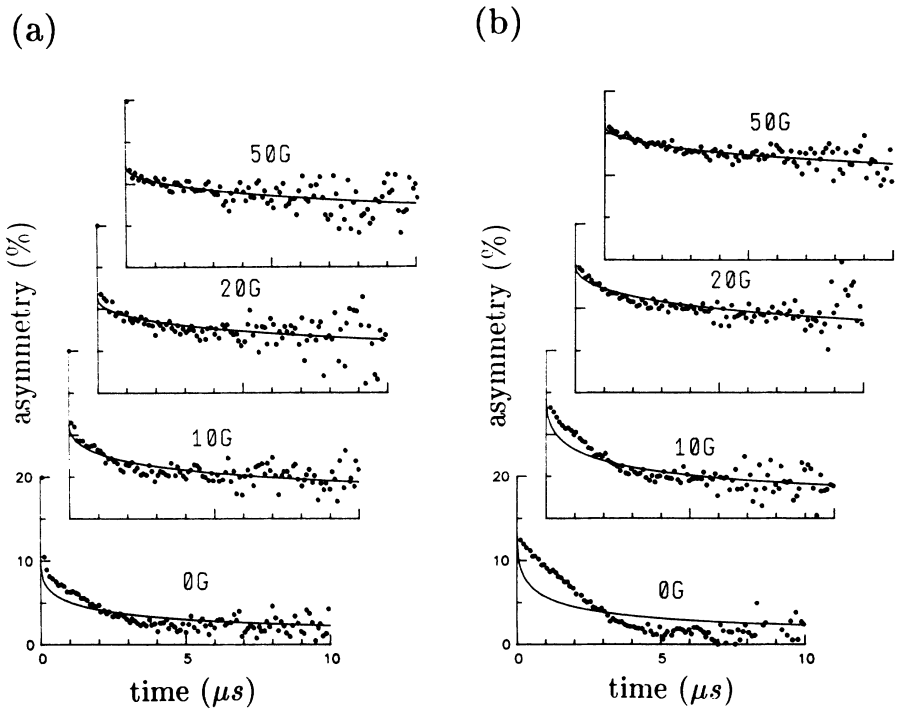


FIG. 7. Asymmetry of the decay positrons as a function of time (a) at $T = 293$ K and (b) at $T = 29$ K for several magnetic fields. Points, experimental data from Ref. 15; lines, fit by the relaxation function $\phi$.

this was taken as evidence for relaxation through one-dimensional motion. Similar conclusions were drawn in other mainly NMR experiments on one-dimensional systems.[38] The stochastic theory of relaxation resulted in a more complicated than exponential relaxation function. Does it contain the same features as obtained in the simple analysis? To examine this question we calculated from the theoretical expression Eq. (40) values at fixed time points (up to 15 $\mu$s with time intervals of 1 $\mu$s). These points were treated in the same manner as the experimental data in Ref. 13, i.e., they were fitted by a single exponential relaxation function. The resulting apparent decay rate is plotted in Fig. 8 as a function of the magnetic field; a $B^{-1/2}$ behavior is recognized over several decades of the field. There are deviations at very small and very large $B$ values. Hence the more elaborate theory contains this feature, in a range of $B$ values.

The $B^{-1/2}$ behavior of the slope of an exponential decay can be directly deduced by considering the slope of $y \equiv \ln P(t)$, when the approximate relaxation function (52) is used for $P(t)$,

$$-\frac{dy}{dt} = \Gamma[(\pi\Gamma t)^{-1/2}P^{-1}(t) - 1] \ . \tag{59}$$

For small argument $\Gamma t$ the negative slope of $y$ is given by

$$-\frac{dy}{dt} \approx \left(\frac{\Gamma}{\pi t}\right)^{1/2} \ . \tag{60}$$

If $\Gamma$ is identified with $\Gamma_B$ of (57), the proportionality of the slope with $B^{-1/2}$ follows. The quantity $\Gamma_B$ becomes small with increasing $B$, hence the argument $\Gamma t$ of (59) is indeed small for larger $B$.

In the second experimental paper[14] a detailed analysis of the time-dependent polarization was made. The authors first calculated the contributions of the dipolar interactions between the muon and the protons and subtracted it from the data. Then they determined a time-dependent relaxation rate $T_1^{-1}(t)$ in windows of finite widths of 1 $\mu$s (first data point) and 2 $\mu$s (other

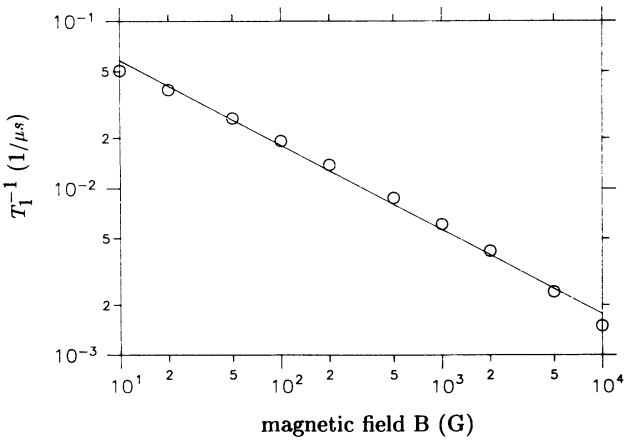


FIG. 8. The apparent decay rate $T_1^{-1}$ vs external magnetic field. The data points (open spheres) are obtained by an exponential fit of the polarization function (40) at fixed time points, with $\gamma = 1.3 \times 10^{12}$ s$^{-1}$, $\lambda = 7 \times 10^7$ s$^{-1}$, and $\omega_0/2\pi = 4.5 \times 10^8$ s$^{-1}$. The fitted curve through these data points is $T_1^{-1} = 0.19B^{-0.51}$ $\mu$s$^{-1}$.

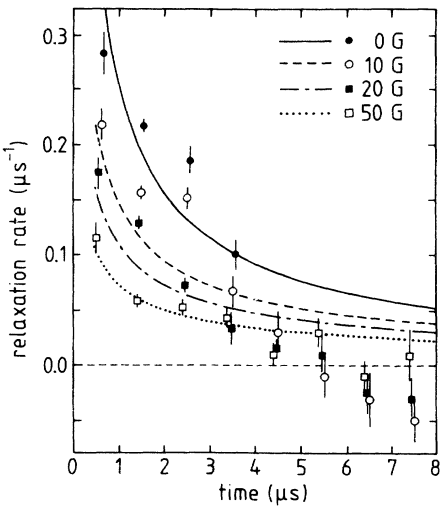


FIG. 9. Effective relaxation rate as a function of time, for several magnetic fields. This figure has experimental points adapted from Ref. 14, where the contribution of the dipolar interaction with the protons is already subtracted. The lines represent Eq. (59).

points). Their results are reproduced in Fig. 9. We have added to this figure our theoretical slope Eq. (59), for the different magnetic fields, where average parameters $\lambda$ and $\gamma$ have been used. The theoretical curves reproduce the qualitative behavior of the experimental points. Although there is considerable scatter in the data, we are quite satisfied by this agreement.

## VII. CONCLUSION

In this paper we have developed a stochastic theory of spin relaxation for a simple model of muonium in *trans*-polyacetylene, where the hyperfine interaction is modulated by the random walk of the unpaired electron. The model already represents a quantum-mechanical situation, although the state space is restricted to the singlet and triplet states. A stochastic theory of spin relaxation is necessary in those cases where the correlation time $\tau_c$ of the fluctuations acting on the spin is large or infinite. In the system considered here $\tau_c$ is infinite because the stochastic process is governed by the one-dimensional random walk of the defect. The basic assumption of the standard NMR theory, namely the existence of a short correlation time, is then violated. In contrast to the single-exponential decay predicted by the standard NMR theory, we found more complicated behavior, for instance nonexponential relaxation, and a power-law decay of the spin polarization at long times, in suitable parameter ranges.

The results of our theory could be applied to the muon spin relaxation experiments on *trans*-polyacetylene, and the parameters were in reasonable agreement with other experimental determinations. Since our theory contains the $B^{-1/2}$ behavior of the slope of the logarithmic polarization, it corroborates the previous conclusions concerning the one-dimensional nature of the defect motion. In addition, we obtain an apparent time dependence of this slope in qualitative agreement with experiment. We emphasize that we need not invoke additional dynamical processes, such as interchain diffusion, to obtain such a time dependence.

It should be kept in mind that we considered a highly idealized model of defect motion in *trans*-polyacetylene. We disregarded the finiteness of the real *trans*-$(CH)_x$ chains. Also, our model may be too crude to describe the actual dynamics of the defect which arise from muonium in *trans*-$(CH)_x$. E.g., soliton properties of the defects were neglected, and we could not contribute to the elucidation of their nature.

There are various possibilities to improve the description given here. For instance, the finiteness of the chains could be taken into account by using in Eq. (26) the suitable probability densities $F(t)$ for the first return to the origin. Also the finite extension of the defects could be included. Such theoretical efforts seem only then warranted when better characterized material becomes available. In any case, we believe that the direct stochastic theory developed here is the appropriate description of spin relaxation caused by one-dimensional defect motion.

Finally, we point out that also the inclusion of the quantum-mechanical aspects is necessary to obtain a proper description of the spin relaxation of muonium in the model for *trans*-polyacetylene. Our derivations indicate that a correct description is achieved by considering the quantum-mechanical evolution as modulated by the stochastic process, whereas a treatment which neglects the off-diagonal elements of the density matrix is not appropriate.[39,40]

## ACKNOWLEDGMENTS

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