Journal of Statistical Physics, Vol. 5, No. 3, 1972

Decay of Correlations in Spin Systems

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Received August 9, 1971

We investigate the decay of initial correlations in a spin system where each spin relaxes independently by an intramolecular mechanism. The equation of motion for the spin density matrix is assumed to be the Redfield equation, which is of the form of a quantum mechanical master equation. Our analysis of this problem is based on the techniques of Shuler, Oppenheim, and co-workers, who have studied the decay of correlations in systems which can be described by classical stochastic master equations. We find that the off-diagonal elements of the reduced spin density matrices approach their equilibrium values faster than the diagonal elements. The Ursell functions, which are a measure of the correlations in the system, decay to their zero equilibrium values faster than the spin density matrix except for the furthest off-diagonal elements. Far off-diagonal matrix elements of the spin density matrix approach equilibrium at the same rate as the Ursell functions, which is the important difference between the quantum mechanical model studied here and the classical models studied earlier.

KEY WORDS: Spin correlations; dynamics of correlations; Redfield equation; quantum mechanical master equation.

1. INTRODUCTION

The problem of the decay of initial correlations in transport theory has received relatively little attention. An important exception is the work of Shuler, Oppenheim, and co-workers,[1–3] who have considered the relaxation of initial correlations in a number of model systems which can be treated analytically in complete detail. Our purpose here is to apply the techniques of these workers to spin relaxation. We investigate the decay of initial correla-

Supported in part by the National Science Foundation.

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822/5/3-1

tions in an N-spin system under conditions where the spins relax independently, by intramolecular coupling to a heat bath. The equation of motion we adopt for the N-spin density matrix is the Redfield equation,[4] which is known to give an excellent description of spin relaxation in fluid systems.

The model we study is of interest because it describes the relaxation of a quantum mechanical system in weak interaction with a bath. In contrast, the models previously studied[1-3] deal with classical systems which can be characterized in terms of probabilities. The problem of spin relaxation is one of many examples where one encounters a so-called quantum mechanical master equation. This equation describes the time evolution of the elements of the density matrix by coupled first-order differential equations with constant, perhaps complex, coefficients. Although we shall use the language of spin relaxation, our results are applicable to a wide class of relaxation problems. Comparison of the results obtained here with the earlier work[1] indicates the difference to be expected in the decay of correlations in classical and quantum systems.

2. THE REDFIELD EQUATION FOR NONINTERACTING SPINS

The system we consider consists of N spins weakly coupled to a large heat bath. The Hamiltonian for the system can be written

$$H = H_z + H_L + H' = H_0 + H' \tag{1}$$

where H_z is the Hamiltonian for the spin subsystem, H_L is the bath Hamiltonian, and H' is the interaction between the spins and the bath responsible for the relaxation.

The spin density matrix is assumed to satisfy the Redfield equation:

$$(\partial/\partial t)\langle\alpha \mid \sigma(t)\mid \alpha'\rangle = -i\omega_{\alpha\alpha'}\langle\alpha \mid \sigma(t)\mid \alpha'\rangle + \sum_{\beta\beta'} R_{\alpha\alpha'\beta\beta'}\langle\beta \mid \sigma(t)\mid \beta'\rangle \tag{2}$$

In Eq. (2), σ is the spin density matrix of the N-spin subsystem; $\mid \alpha\rangle$, $\mid \beta\rangle$, etc. are spin states; $\omega_{\alpha\alpha'} = (E_\alpha - E_{\alpha'})/\hbar$, where E_α is the energy of the spin state $\mid \alpha\rangle$; and $R_{\alpha\alpha'\beta\beta'}$ is a tetradic usually referred to as the "relaxation matrix." Here and in the following, we compress the notation by denoting $\alpha = (\alpha_1, ..., \alpha_N)$ and $\beta = (\beta_1, ..., \beta_N)$, where α_i or β_i designate the substates of the ith spin.

The Redfield equation can be simplified by transforming to the interaction representation. The spin density matrix in the interaction representation σ^* is defined by

$$\sigma^*(t) = e^{(i/\hbar)H_0 t}\sigma(t)\, e^{-(i/\hbar)H_0 t} \tag{3}$$

The Redfield equation for $\sigma^*(t)$ is

$$(\partial/\partial t)\langle\alpha \mid \sigma^*(t)\mid \alpha'\rangle = \sum_{\beta\beta'} \{\exp[i(\omega_{\alpha\alpha'} - \omega_{\beta\beta'})t]\}\, R_{\alpha\alpha'\beta\beta'}\langle\beta \mid \sigma^*(t)\mid \beta'\rangle \quad (4)$$

In almost all cases of physical interest, the elements of R vanish unless there is energy conservation. We may quite generally assume that

$$R_{\alpha\alpha'\beta\beta'} = 0 \qquad \text{if} \quad \omega_{\beta\beta'} \neq \omega_{\alpha\alpha'} \quad (5)$$

so that the sum in Eq. (4) is effectively restricted to those states for which $\omega_{\beta\beta'} = \omega_{\alpha\alpha'}$. With this assumption, Eq. (4) may be expressed in operator form as

$$\partial\sigma^*(t)/\partial t = R : \sigma^*(t) \quad (6)$$

The restriction to energy-conserving transitions, expressed in Eq. (5), may be relaxed, but for simplicity, we shall not consider this case here.

In matrix form, the operator equation (6) resembles a master equation generalized to matrices, but the tetradic R is not a transition matrix. The terms of type $R_{\alpha\alpha\beta\beta}$ can be interpreted as transition rates, but the terms of type $R_{\alpha\alpha'\beta\beta'}$, where $\alpha \neq \alpha'$ or $\beta \neq \beta'$, cannot be so interpreted and need not be real.

The relaxation matrix has the following important properties:

$$\sum_{\alpha} R_{\alpha\alpha\beta\beta'} = 0 \quad (7)$$

$$R : \sigma^{\text{eq}} = 0 \quad (8)$$

where σ^{eq} is the equilibrium spin density matrix:

$$\langle\alpha \mid \sigma^{\text{eq}} \mid \alpha'\rangle = \sigma^{\text{eq}}_{\alpha\alpha'} = \delta_{\alpha\alpha'}\, e^{-\hbar\omega_\alpha/kT} \Big/ \sum_{\beta} e^{-\hbar\omega_\beta/kT} \quad (9)$$

Also note that

$$\text{Tr}^{(N)}\, \sigma^*(t) = 1 \quad (10)$$

Reduced spin density matrices can be defined by

$$\langle\alpha_1 \cdots \alpha_n \mid \sigma^*_{(n)}(t)\mid \alpha_1' \cdots \alpha_n'\rangle = \sum_{\alpha_{n+1}} \cdots \sum_{\alpha_N} \langle\alpha_1 \cdots \alpha_N \mid \sigma^*(t)\mid \alpha_1' \cdots \alpha_n'\alpha_{n+1} \cdots \alpha_N\rangle \quad (11)$$

or in operator form,

$$\sigma^*_{(n)}(t) = \text{Tr}^{(N-n)}\, \sigma^*(t) \quad (12)$$

where $\sigma^*_{(n)}(t)$ is the reduced n-spin spin density matrix (in the interaction representation).

The following properties follow directly from the definition of the reduced spin density matrices (11) and (10):

$$\sum_{\alpha_j}\sum_{\alpha_j'}\delta_{\alpha_j\alpha_j'}\langle\alpha_1\cdots\alpha_n\,|\,\sigma^*_{(n)}(t)|\,\alpha_1'\cdots\alpha_n'\rangle$$

$$=\langle\alpha_1\cdots\alpha_{j-1}\alpha_{j+1}\cdots\alpha_n\,|\,\sigma^*_{(n-1)}(t)|\,\alpha_1'\cdots\alpha'_{j-1}\alpha'_{j+1}\cdots\alpha_n'\rangle$$

$$\text{for}\quad j=1,\ldots,n \tag{13}$$

$$\mathrm{Tr}^{(n)}\,\sigma^*_{(n)}(t)=1 \tag{14}$$

A reduced spin density matrix which is not a product of one-particle matrices is said to be correlated. The reduced spin density matrix is uncorrelated if it can be written as the product of one-particle density matrices. The degree of correlation is conveniently studied by means of the Ursell (or correlation) functions, which are defined in analogy to those of Ref. 1 as

$$u^*_{(n)}(t)=[\sigma^*_{(n)}(t)]_c \tag{15}$$

where $[\cdots]_c$ denotes the "connected average." Ursell functions (here really Ursell operators) have the following properties[1]:

(1) $u^*_{(n)}(t)=0$ if any subset containing m of the n-spins is uncorrelated with the remaining n-m spins,

$$(2)\quad u^{\mathrm{eq}}_{(n)}=0,\quad n\geqslant 2,\qquad \text{since}\quad \sigma^{\mathrm{eq}}_{(n)}=\prod_{i=1}^{n}\sigma_i^{\mathrm{eq}} \tag{16}$$

$$(3)\quad \sum_{\alpha_j\alpha_j'}\delta_{\alpha_j\alpha_j'}\langle\alpha_1\cdots\alpha_n\,|\,u^*_{(n)}(t)|\,\alpha_1'\cdots\alpha_n'\rangle=0,\quad n\geqslant 2,\ j=1,2,\ldots,n \tag{17}$$

Since $u^*_{(n)}(t)$ is non-zero only if correlations exist between all n spins, the Ursell functions are a measure of the correlations in the spin system.

We now make the further assumption that the spins do not interact with each other, but only with the bath. Then, the relaxation tetradic R is a sum of single-spin terms

$$R_{\alpha\alpha'\beta\beta'}=\sum_{i=1}^{N}(R_i)_{\alpha_i\alpha_i'\beta_i\beta_i'}\prod_{\substack{j=1\\ j\neq i}}^{N}\delta_{\alpha_j\beta_j}\delta_{\alpha_j'\beta_j'} \tag{18}$$

where $\alpha=(\alpha_1,\ldots,\alpha_N)$, etc., and R_i is the relaxation tetradic for the ith spin. The single-spin relaxation tetradic has properties analogous to Eqs. (5), (7), and (8).

With this assumption, the reduced spin density matrices satisfy reduced Redfield equations

$$(\partial/\partial t)\langle\alpha_{(n)} \mid \sigma^*_{(n)}(t)\mid \alpha'_{(n)}\rangle = \sum_{\beta_{(n)}\beta'_{(n)}} \sum_{i=1}^{n} (R_i)_{\alpha_i\alpha_i'\beta_i\beta_i'}$$

$$\times \prod_{\substack{j=1\\ j\neq i}}^{n} \delta_{\alpha_j\beta_j}\delta_{\alpha_j'\beta_j'}\langle\beta_{(n)} \mid \sigma^*_{(n)}(t)\mid \beta'_{(n)}\rangle \tag{19}$$

Here, as before, we compress the notation by denoting $\alpha_{(n)} = (\alpha_1, ..., \alpha_n)$, $\beta_{(n)} = (\beta_1, ..., \beta_n)$, etc.

The Ursell functions satisfy the same equation[1]:

$$(\partial/\partial t)\langle\alpha_{(n)} \mid u^*_{(n)}(t)\mid \alpha'_{(n)}\rangle = \sum_{\beta_{(n)}\beta'_{(n)}} \sum_{i=1}^{n} (R_i)_{\alpha_i\alpha_i'\beta_i\beta_i'}$$

$$\times \prod_{\substack{j=1\\ j\neq i}}^{n} \delta_{\alpha_j\beta_j}\delta_{\alpha_j'\beta_j'}\langle\beta_{(n)} \mid u^*_{(n)}(t)\mid \beta'_{(n)}\rangle \tag{20}$$

The two equations may be written in operator form as

$$(\partial/\partial t)\sigma^*_{(n)}(t) = R_{(n)} : \sigma^*_{(n)}(t) \tag{21}$$

$$(\partial/\partial t)u^*_{(n)}(t) = R_{(n)} : u^*_{(n)}(t) \tag{22}$$

where

$$[R_{(n)}]_{\alpha_{(n)}\alpha'_{(n)}\beta_{(n)}\beta'_{(n)}} = \sum_{i=1}^{n} (R_i)_{\alpha_i\alpha_i'\beta_i\beta_i'} \prod_{\substack{j=1\\ j\neq i}}^{n} \delta_{\alpha_j\beta_j}\delta_{\alpha_j'\beta_j'} \tag{23}$$

3. EIGENVALUE ANALYSIS OF THE RELAXATION OF $\sigma^*_{(n)}(t)$ AND $u^*_{(n)}(t)$

We may solve Eqs. (21) and (22) formally to obtain

$$\sigma^*_{(n)}(t) = e^{R_{(n)}t} : \sigma^*_{(n)}(0) = \prod_{i=1}^{n} e^{R_i t} : \sigma^*_{(n)}(0) \tag{24}$$

$$u^*_{(n)}(t) = e^{R_{(n)}t} : u^*_{(n)}(0) = \prod_{i=1}^{n} e^{R_i t} : u^*_{(n)}(0) \tag{25}$$

Note that since the propagator $e^{R(n)t}$ factors, it is only necessary to consider the single-particle equation

$$\sigma_1^*(t) = e^{R_1 t}\sigma_1^*(0) \tag{26}$$

in order to solve the general equations (24) and (25). Furthermore, if the initial spin density matrix were uncorrelated, the complete spin relaxation would be described by single-particle equations of the form of Eq. (26).

The relaxation of the single spin density matrix is conveniently described in terms of the eigenmatrices of the tetradic R_1. Let $\{A_j\}$ and $\{B_j\}$ be, respectively, the sets of right and left eigenmatrices of R_1 with eigenvalues $\{\lambda_j\}$; then

$$\sum_{\beta_1\beta_1'} R^1_{\alpha_1\alpha_1'\beta_1\beta_1'}\langle\beta_1 \mid A_j \mid \beta_1'\rangle = \lambda_j\langle\alpha_1 \mid A_j \mid \alpha_1'\rangle \tag{27}$$

$$\sum_{\alpha_1\alpha_1'} \langle\alpha_1 \mid B_j \mid \alpha_1'\rangle R^1_{\alpha_1\alpha_1'\beta_1\beta_1'} = \lambda_j\langle\beta_1 \mid B_j \mid \beta_1'\rangle \tag{28}$$

or in operator form

$$R_1 : A_j = \lambda_j A_j \tag{27a}$$

$$B_j : R_1 = \lambda_j B_j \tag{28a}$$

For energy conserving transitions it can be shown that the property of "detailed balance,"

$$R_{\alpha\alpha'\beta\beta'} = e^{-\hbar\omega_{\alpha\beta}/kT}R^*_{\beta\beta'\alpha\alpha'}$$

is satisfied, from which it follows that the λ_j are real and nonpositive. Further, the eigenmatrices can be made "orthonormal" in the following sense:

$$B_j : A_k = \sum_{\alpha_1\alpha_1'} \langle\alpha_1 \mid B_j \mid \alpha_1'\rangle\langle\alpha_1 \mid A_k \mid \alpha_1'\rangle = \delta_{jk} \tag{29}$$

It follows from Eqs. (7) and (8) that

$$A_0 = \sigma_1^{\text{eq}} \tag{30}$$

$$B_0 = I \quad \text{(identity)} \tag{31}$$

where we have arbitrarily designated the right- and left-hand eigenmatrices corresponding to zero eigenvalue as A_0 and B_0, respectively. If it is assumed that there is only one equilbrium density matrix, then the eigenvalues can be arranged so that

$$\lambda_0 = 0 > \lambda_1 \geqslant \lambda_2 \geqslant \cdots \geqslant \lambda_{4s(s+1)} \tag{32}$$

where s is the spin of the particle.

The sets of eigenmatrices are complete, so if we use Eq. (29), $\sigma_1^*(t)$ can be expanded as

$$\sigma_1^*(t) = \sum_j [B_j : \sigma_1^*(t)]\, A_j \tag{33}$$

From Eqs. (26) and (28), it follows that

$$\sigma_1^*(t) = \sum_j [B_j : e^{R_1 t} : \sigma_1^*(0)]\, A_j = \sum_j e^{\lambda_j t} [B_j : \sigma_1^*(0)]\, A_j \tag{34}$$

If we express Eqs. (26) and (34) in terms of matrix elements and compare them, we find that the propagator $e^{R_1 t}$ has matrix elements:

$$(e^{R_1 t})_{\alpha_1\alpha_1'\beta_1\beta_1'} = \sum_j \langle \alpha_1 \mid A_j \mid \alpha_1' \rangle \langle \beta_1 \mid B_j \mid \beta_1' \rangle\, e^{\lambda_j t} \tag{35}$$

The term with $\lambda = 0$ may be separated out, so that

$$(e^{R_1 t})_{\alpha_1\alpha_1'\beta_1\beta_1'} = \delta_{\beta_1\beta_1'}\sigma^{\mathrm{eq}}_{\alpha_1\alpha_1'} + \sum_{j>0} \langle \alpha_1 \mid A_j \mid \alpha_1' \rangle \langle \beta_1 \mid B_j \mid \beta_1' \rangle\, e^{\lambda_j t} \tag{36}$$

where we have used Eqs. (30) and (31). Since σ^{eq} is diagonal, Eq. (36) takes the form

$$(e^{R_1 t})_{\alpha_1\alpha_1'\beta_1\beta_1'} = \delta_{\alpha_1\alpha_1'}\delta_{\beta_1\beta_1'}\sigma^{\mathrm{eq}}_{\alpha_1\alpha_1} + \phi_{\alpha_1\alpha_1'\beta_1\beta_1'}(t) \tag{37}$$

with

$$\phi_{\alpha_1\alpha_1'\beta_1\beta_1'}(t) = \sum_{j>0} \langle \alpha_1 \mid A_j \mid \alpha_1' \rangle \langle \beta_1 \mid B_j \mid \beta_1' \rangle\, e^{\lambda_j t} \tag{38}$$

The function $\phi(t)$ asymptotically behaves as

$$\phi_{\alpha_1\alpha_1'\beta_1\beta_1'}(t) \sim e^{\lambda_{\max} t} \to 0 \qquad \text{as} \quad t \to \infty \tag{39}$$

Here, $\lambda_{\max}$ is the largest nonzero eigenvalue for which

$$\langle \alpha_1 \mid A_j \mid \alpha_1' \rangle \langle \beta_1 \mid B_j \mid \beta_1' \rangle \neq 0$$

The particular eigenvalue may depend on α_1, α_1', β_1, β_1'.

If all the spins are identical, we can substitute Eq. (37) in Eq. (24) and obtain (in terms of matrix elements)

$$\langle \alpha_1 \cdots \alpha_n \mid \sigma^*_{(n)}(t) \mid \alpha_1' \cdots \alpha_n' \rangle$$

$$= \sum_{\substack{\beta_1 \cdots \beta_n \\ \beta_1' \cdots \beta_n'}} \prod_{i=1}^{n} [\delta_{\alpha_i\alpha_i'}\delta_{\beta_i\beta_i'}\sigma^{\mathrm{eq}}_{\alpha_i\alpha_i} + \phi_{\alpha_i\alpha_i'\beta_i\beta_i'}(t)] \langle \beta_1 \cdots \beta_n \mid \sigma^*_{(n)}(t) \mid \beta_1' \cdots \beta_n' \rangle \tag{40}$$

We now expand the product and use Equations (13) and (14) to obtain

$$\begin{aligned}
&\langle \alpha_1 \cdots \alpha_n \mid \sigma^*_{(n)}(t) \mid \alpha_1' \cdots \alpha_n' \rangle - \prod_{i=1}^{n} \delta_{\alpha_i\alpha_i'} \sigma^{\mathrm{eq}}_{\alpha_i\alpha_i} \\
&\quad = \sum_{j=1}^{n} \prod_{\substack{i=1 \\ i\neq j}}^{n} \delta_{\alpha_i\alpha_i'} \sigma^{\mathrm{eq}}_{\alpha_i\alpha_i} \sum_{\beta_j\beta_j'} \phi_{\alpha_j\alpha_j'\beta_j\beta_j'}(t) \langle \beta_j \mid \sigma_j^*(0) \mid \beta_j' \rangle \\
&\quad + \sum_{\substack{j=1 \\ j\neq k}}^{n} \sum_{\substack{k=1 \\ i\neq j, i\neq k}}^{n} \prod_{i=1}^{n} \delta_{\alpha_i\alpha_i'} \sigma^{\mathrm{eq}}_{\alpha_i\alpha_i} \\
&\quad \times \sum_{\substack{\beta_j\beta_j' \\ \beta_k\beta_k'}} \phi_{\alpha_j\alpha_j'\beta_j\beta_j'}(t) \phi_{\alpha_k\alpha_k'\beta_k\beta_k'}(t) \langle \beta_j\beta_k \mid \sigma^*_{(2)}(0) \mid \beta_j'\beta_k' \rangle \\
&\quad + \cdots + \sum_{\substack{\beta_1\cdots\beta_n \\ \beta_1'\cdots\beta_n'}} \prod_{i=1}^{n} \phi_{\alpha_i\alpha_i'\beta_i\beta_i'}(t) \langle \beta_1 \cdots \beta_n \mid \sigma^*_{(n)}(0) \mid \beta_1' \cdots \beta_n' \rangle
\end{aligned} \tag{41}$$

This is the exact solution for $\sigma^*_{(n)}(t)$, but we are interested in the asymptotic behavior. Since the $\phi(t)$ go to zero asymptotically, the asymptotic behavior of $\sigma^*_{(n)}(t)$ is governed by the first nonzero term on the right-hand side of Eq. (41). Note that the first term contains a product of $n-1$ Kronecker deltas and will be zero if more than one $\alpha_i \neq \alpha_i'$; the second term contains a product of $n-2$ Kronecker deltas and will be zero if more than two $\alpha_i \neq \alpha_i'$, etc. Hence for the diagonal elements, the asymptotic behavior is[2]

$$\begin{aligned}
&\langle \alpha_1 \cdots \alpha_n \mid \sigma^*_{(n)}(t) \mid \alpha_1 \cdots \alpha_n \rangle - \prod_{i=1}^{n} \sigma^{\mathrm{eq}}_{\alpha_i\alpha_i} \\
&\quad \sim \sum_{j=1}^{n} \prod_{\substack{i=1 \\ i\neq j}}^{n} \sigma^{\mathrm{eq}}_{\alpha_i\alpha_i} \sum_{\beta_i\beta_j'} \phi_{\alpha_j\alpha_j\beta_j\beta_j'} \langle \beta_j \mid \sigma_j^*(0) \mid \beta_j' \rangle \\
&\quad \sim \phi(t)
\end{aligned} \tag{42}$$

For the off-diagonal elements, assume that m of the α_i, say $\alpha_1, \ldots, \alpha_m$, have $\alpha_i \neq \alpha_i'$, while $\alpha_i = \alpha_i'$ for the remaining $n-m$ spins; then, the asymptotic behavior is

$$\begin{aligned}
&\langle \alpha_1 \cdots \alpha_n \mid \sigma^*_{(n)}(t) \mid \alpha_1' \cdots \alpha_n' \rangle \\
&\quad \sim \sum_{i=m+1}^{n} \sigma^{\mathrm{eq}}_{\alpha_i\alpha_i} \sum_{\substack{\beta_1\cdots\beta_m \\ \beta_1'\cdots\beta_m'}} \prod_{j=1}^{m} \phi_{\alpha\,\alpha_j'\beta_j\beta_j'}(t) \langle \beta_1 \cdots \beta_m \mid \sigma^*_{(m)}(0) \mid \beta_1' \cdots \beta_m' \rangle \\
&\quad \sim \phi^m(t)
\end{aligned} \tag{43}$$

[2] There are pathological cases where the $\sigma^*_{(n)}(0)$ are chosen so that all the sums in Eqs. (42) or (43) are zero and the relaxation is of higher order.

The behavior of the Ursell function is obtained in the same manner from Eqs. (25) and (37),

$$\langle \alpha_1 \cdots \alpha_n \mid u^*_{(n)}(t) \mid \alpha_1' \cdots \alpha_n' \rangle$$

$$= \sum_{\substack{\beta_1 \cdots \beta_n \\ \beta_1' \cdots \beta_n'}} \prod_{i=1}^{n} [\delta_{\alpha_i \alpha_i'} \delta_{\beta_i \beta_i'} \sigma^{\mathrm{eq}}_{\alpha_i \alpha_i} + \phi_{\alpha_i \alpha_i' \beta_i \beta_i'}(t)] \langle \beta_1 \cdots \beta_n \mid u^*_{(n)}(0) \mid \beta_1' \cdots \beta_n' \rangle$$

$$= \prod_{i=1}^{n} \delta_{\alpha_i \alpha_i'} \sigma^{\mathrm{eq}}_{\alpha_i \alpha_i} \sum_{\substack{\beta_1 \cdots \beta_n \\ \beta_1' \cdots \beta_n'}} \prod_{i=1}^{n} \delta_{\beta_i \beta_i'} \langle \beta_1 \cdots \beta_n \mid u^*_{(n)}(0) \mid \beta_1' \cdots \beta_n' \rangle$$

$$+ \sum_{j=1}^{n} \prod_{\substack{i=1 \\ i \neq j}}^{n} \delta_{\alpha_i \alpha_i'} \sigma^{\mathrm{eq}}_{\alpha_i \alpha_i} \sum_{\beta_j \beta_j'} \phi_{\alpha_j \alpha_j' \beta_j \beta_j'}(t)$$

$$\times \sum_{\substack{\beta_1 \cdots \beta_{j-1} \beta_{j+1} \cdots \beta_n \\ \beta_1' \cdots \beta_{j-1}' \beta_{j+1}' \cdots \beta_n'}} \prod_{\substack{i=1 \\ i \neq j}}^{n} \delta_{\beta_i \beta_i'} \langle \beta_1 \cdots \beta_n \mid u^*_{(n)}(0) \mid \beta_1' \cdots \beta_n' \rangle$$

$$+ \cdots + \sum_{\substack{\beta_1 \cdots \beta_n \\ \beta_1' \cdots \beta_n'}} \prod_{i=1}^{n} \phi_{\alpha_i \alpha_i' \beta_i \beta_i'}(t) \langle \beta_1 \cdots \beta_n \mid u^*_{(n)}(0) \mid \beta_1' \cdots \beta_n' \rangle \tag{44}$$

But by the sum rule given in Eq. (17), all the sums except the last are zero, hence

$$\langle \alpha_1 \cdots \alpha_n \mid u^*_{(n)}(t) \mid \alpha_1' \cdots \alpha_n' \rangle$$

$$= \sum_{\substack{\beta_1 \cdots \beta_n \\ \beta_1' \cdots \beta_n'}} \prod_{i=1}^{n} \phi_{\alpha_i \alpha_i' \beta_i \beta_i'}(t) \langle \beta_1 \cdots \beta_n \mid u^*_{(n)}(0) \mid \beta_1' \cdots \beta_n' \rangle \tag{45}$$

so that

$$\langle \alpha_1 \cdots \alpha_n \mid u^*_{(n)}(t) \mid \alpha_1' \cdots \alpha_n' \rangle \sim \phi^n(t) \tag{46}$$

In summary we find the asymptotic behavior of this model to be as follows:

$$\langle \alpha_1 \cdots \alpha_n \mid \sigma^*_{(n)}(t) \mid \alpha_1 \cdots \alpha_n \rangle \to \prod_{i=1}^{n} \sigma^{\mathrm{eq}}_{\alpha_i \alpha_i} \qquad \text{as} \quad \phi(t) \tag{47}$$

$$\langle \alpha_1 \cdots \alpha_n \mid \sigma^*_{(n)}(t) \mid \alpha_1' \cdots \alpha_n' \rangle \to 0 \qquad \text{as} \quad \phi^m(t) \tag{48}$$

where m is the number of spins i for which $\alpha_i \neq \alpha_i'$, $1 \leqslant m \leqslant n$;

$$\langle \alpha_1 \cdots \alpha_n \mid u^*_{(n)}(t) \mid \alpha_1' \cdots \alpha_n' \rangle \to 0 \qquad \text{as} \quad \phi^n(t) \tag{49}$$

for both diagonal and off-diagonal elements.

The off-diagonal elements of the spin density matrix decay faster than the diagonal elements and decay increasingly rapidly the further off-diagonal the element is. The Ursell functions decay faster than the spin density matrix, except for the furthest off-diagonal elements, for which the rates are the same.

The diagonal and first off-diagonal elements ($m = 1$) both decay asymptotically as $\phi(t)$, but since different matrix elements of $\phi(t)$ are involved, the actual rates may be different.

4. EXAMPLE

We consider here a simple system of noninteracting spin-1/2 particles which illustrates all the features of the general case discussed in the last section. We assume that the interaction between a single spin and the bath has the form

$$H' = F_z S_z + F_+ S_+ + F_- S_- \tag{50}$$

where the S_q are spin operators and the F_q are lattice operators, with

$$F_\pm = \tfrac{1}{2}(F_x \mp iF_y) \tag{51}$$

The elements of the one-spin relaxation matrix $R'_{\alpha_1\alpha_1'\beta_1\beta_1'}$ can be calculated explicitly in terms of the F_q as[4]

R_1

α_1	α_1' \ β_1	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$
	β_1'	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$
$\frac{1}{2}$	$\frac{1}{2}$	$-2a$	$2\mu a$	0	0
$-\frac{1}{2}$	$-\frac{1}{2}$	$2a$	$-2\mu a$	0	0
$\frac{1}{2}$	$-\frac{1}{2}$	0	0	$-b-(1+\mu)a$	0
$-\frac{1}{2}$	$\frac{1}{2}$	0	0	0	$-b-(1+\mu)a$

(52)

In Eq. (52),

$$\mu = e^{-\hbar\omega/kT} \tag{53}$$

where ω is the Larmor frequency for the spins,

$$a = \int_{-\infty}^{\infty} dt\, e^{-i\omega t}\langle F_+F_-(t)\rangle_L \tag{54}$$

$$b = \int_{-\infty}^{\infty} dt\, \langle F_zF_z(t)\rangle_L \tag{55}$$

In Eqs. (54) and (55), the lattice correlations are considered real and even functions of time; $\langle\cdots\rangle_L$ denotes an average over the lattice variables. The quantities a and b are real and nonnegative.

The four eigenvalues of R_1 are

$$\lambda_0 = 0, \qquad \lambda_1 = -2(1+\mu)a, \qquad \lambda_2 = \lambda_3 = -b-(1+\mu)a \tag{56}$$

The eigenvalues are all real and nonpositive. The order is arbitrary since there is no *a priori* way to decide whether λ_1 or λ_2 is the larger. However, for a model of isotropic, exponential relaxation of the lattice operators, with correlation time τ,

$$a = \tfrac{1}{2}\langle F^2\rangle\,\tau/(1+\omega^2\tau^2) \qquad b = \langle F^2\rangle\tau \tag{57}$$

so that $b \geqslant 2a$ and hence $|\lambda_2| \geqslant |\lambda_1|$.

A complete set of eigenmatrices for R_1 is

$$\begin{aligned} A_0 &= [1/(1+\mu)]\begin{pmatrix}\mu & 0\\ 0 & 1\end{pmatrix} & B_0 &= \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\\ A_1 &= [1/(1+\mu)]\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} & B_1 &= \begin{pmatrix}1 & 0\\ 0 & -\mu\end{pmatrix}\\ A_2 &= \begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix} & B_2 &= \begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}\\ A_3 &= \begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix} & B_3 &= \begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix} \end{aligned} \tag{58}$$

We may now use Eq. (38) to obtain the elements of $\phi(t)$:

$$\begin{aligned} \phi_{1/2,1/2,1/2,1/2}(t) &= [1/(1+\mu)]\, e^{\lambda_1 t}\\ \phi_{1/2,1/2,-1/2,-1/2}(t) &= [-\mu/(1+\mu)]\, e^{\lambda_1 t}\\ \phi_{-1/2,-1/2,1/2,1/2}(t) &= -[1/(1+\mu)]\, e^{\lambda_1 t}\\ \phi_{-1/2,-1/2,-1/2,-1/2}(t) &= [\mu/(1+\mu)]\, e^{\lambda_1 t}\\ \phi_{1/2,-1/2,1/2,-1/2}(t) &= e^{\lambda_2 t}\\ \phi_{-1/2,1/2,-1/2,1/2}(t) &= e^{\lambda_3 t} = e^{\lambda_2 t} \end{aligned} \tag{59}$$

For our purposes, the basic result is that

$$\phi_{\alpha_1\alpha_1'\beta_1\beta_1'}(t) \sim \begin{cases} e^{\lambda_1 t} & \text{if} \quad \alpha_1 = \alpha_1' \\ e^{\lambda_2 t} & \text{if} \quad \alpha_1 \neq \alpha_1' \end{cases} \tag{60}$$

if β_1 and β_1' are such that $\phi(t)$ does not vanish.

The asymptotic behavior of the diagonal elements of the spin density matrix is given by Eq. (42). Only elements $\phi_{\alpha_i\alpha_i'\beta_i\beta_i'}(t)$ for which $\alpha_i = \alpha_i'$ appear, and hence

$$\langle \alpha_1 \cdots \alpha_n \mid \sigma_{(n)}^*(t) \mid \alpha_1 \cdots \alpha_n \rangle - \prod_{i=1}^{n} \sigma_{\alpha_i\alpha_i}^{\text{eq}} \sim e^{\lambda_1 t} \tag{61}$$

The off-diagonal elements of $\sigma_{(n)}^*(t)$ have asymptotic behavior given by Eq. (43). The elements $\phi_{\alpha_i\alpha_i'\beta_i\beta_i'}(t)$ which appear here all have $\alpha_i \neq \alpha_i'$, and hence

$$\langle \alpha_1 \cdots \alpha_n \mid \sigma_{(n)}^*(t) \mid \alpha_1' \cdots \alpha_n' \rangle \sim e^{m\lambda_2 t} \tag{62}$$

where m is the number of spins i for which $\alpha_i \neq \alpha_i'$, $1 \leqslant m \leqslant n$.

The time behavior of the Ursell functions is given by Eq. (45) for both diagonal and off-diagonal elements. We find that

$$\langle \alpha_1 \cdots \alpha_n \mid u_{(n)}^*(t) \mid \alpha_1' \cdots \alpha_n' \rangle \sim e^{m\lambda_2 t} e^{(n-m)\lambda_1 t} \tag{63}$$

where m is the number of spins i for which $\alpha_i \neq \alpha_i'$, $0 \leqslant m \leqslant n$.

The Ursell functions decay faster than the spin density matrix except for the furthest off-diagonal element ($m = n$), where both decay as $e^{n\lambda_2 t}$.

The diagonal and first off-diagonal ($m = 1$) elements of the density matrix decay as $e^{\lambda_1 t}$ and $e^{\lambda_2 t}$, respectively. For a model of isotropic, exponential decay of the lattice operators, $|\lambda_2| \geqslant |\lambda_1|$, and hence all the off-diagonal elements decay faster than the diagonal elements.

5. CONCLUDING REMARKS

In the quantum mechanical model of spin relaxation considered here, one must be concerned with both diagonal and off-diagonal elements of the system density matrix. We have shown that, in general, the off-diagonal elements of the reduced spin density matrix approach equilibrium much faster than the diagonal elements. We have also shown that the initial correlations, as measured by Ursell functions, go to zero more rapidly with time than the reduced spin density matrix approaches its equilibrium value. For the diagonal elements, our results agree exactly with those found by Oppenheim *et al.*[1] for the classical probability master equation model. The essential modification in the quantum mechanical case arises in consideration of the off-

diagonal elements of the density matrix, which decay to their zero equilibrium value at a variable asymptotic rate depending on the location relative to the diagonal. At the extreme, the off-diagonal element will decay as rapidly as the initial correlation. These results may be expected to hold for all systems where the particles relax independently, and where the relaxation is adequately described by a quantum mechanical master equation.

It would be interesting to extend our considerations to quantum mechanical systems where there are intermolecular interactions between spins as well as interaction with a lattice.[3] Traditionally, the case of intermolecular relaxation of spins in fluid systems had been handled on the basis of a two-spin density matrix.[6] The reduction of the N-spin Redfield equation (2) to a two-spin Redfield equation when intermolecular interactions are present has not been rigorously accomplished, to our knowledge. The treatment of such a case would require an analysis of the decay of initial correlations similar to that undertaken here. Our results suggest that difficulties may arise in treating the furthest off-diagonal elements of the two-spin reduced density matrix.

One may raise the question about the practical possibility of measuring the decay of correlations in actual NMR experiments. In general, we do not believe that this is possible, because, to an excellent degree of approximation, the initial nonequilibrium states established in experiments are *not* correlated. For example, the famous 90° pulse instantaneously rotates the equilibrium z component of the magnetization into the x, y phase. Thus the initial nonequilibrium density matrix is

$$\sigma(0) = \exp(\beta\gamma H_0 M_x) = \prod_{i=1}^{N} \exp(\beta w_0 S_x^{(i)}) = \prod_{i=1}^{N} \sigma_i(0) \tag{64}$$

which is of the form of an uncorrelated initial condition.

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[3] Techniques recently introduced by Bedeaux *et al.*[5] may profitably be used to investigate this question.