Initial slips and transient effects in relaxation phenomena[a)]

B. C. Sanctuary

Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec H3A 2K6, Canada

R. F. Snider

Department of Chemistry, University of British Columbia, Vancouver V6T 1W5, Canada
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For a set of observables, it is shown how the solution of a master equation can approximate the solution of the generalized master quation at long times, but with an aproximate initial slip. The slip phenomena is discussed theoretically and then made more concrete by the exact and approximate solution of a simple but realistic system, namely the initial time dependence for the relaxation of a nuclear spin.

I. INTRODUCTION

The object of a relaxation theory is to describe how a system approaches, with increasing time t, its equilibrium state. There seem to be two superficially different ways of describing this phenomenon. One method is to consider the distribution function or density operator ρ for the system, the relevant projected part ρ_1 of ρ, and how the latter approaches its equilibrium value ρ_{1eq}. Exact dynamics leads to a generalized master equation (GME) for $\rho_1(t)$, following Zwanzig's[1] projection operator approach. The second approach is to consider the time dependence of the average $\langle B_\mu\rangle(t)$ of one or a set of several observables B_μ. These satisfy a set of coupled equations,[2] the generalized Langevin equations (GLE), having a memory kernel relating the past behavior of the $\langle B_\mu\rangle(t)$ to the present rate of change of these expectation values. This formulation is reviewed in Sec. II, where it is also stressed that, if the operator space spanned by the B_μ and the operator identity are used to define a projected space, then the GLE and GME are equivalent.

The object of this paper is to consider the implications of approximating the generalized master equation with a master equation (ME) (no memory), or equivalently, of approximating the generalized Langevin equation by the Langevin equation (LE). It is shown that the long time behaviors of their solutions are the same, provided that those singularities of the projected part of the resolvent of the evolution superoperator, that are closest to the real axis, are poles. As is well recognized, there are transient effects at small times. But what seems to have received little attention, is that if the solutions of the LE and GLE are to be identical at long times, that is, after the initial transients have died out, then the initial values for the two equations must be different. This initial slip phenomenon is solved for exactly (see Sec. III) and applied to a model of nuclear spin relaxation in Sec. IV.

II. REVIEW OF GENERAL RELAXATION THEORY

A. Phenomenological theory for one observable

For one observable B, linear response theory[3] equates the time rate of change $d\langle B\rangle/dt$ of its expectation value, at time t, to the past values $\langle B\rangle(t-s)$ of $\langle B\rangle$, through a memory kernel $K(s)$, thus

$$d\langle B\rangle(t)/dt = -\int_0^t K(s)\,[\langle B\rangle(t-s) - \langle B\rangle_{eq}]\,ds. \tag{1}$$

It is assumed in the remainder, that the observable B is defined in such a manner that its equilibrium average $\langle B\rangle_{eq}$ is zero.

A common assumption is that $K(s)$ decays to zero much more rapidly than $\langle B\rangle$ approaches $\langle B\rangle_{eq}=0$. This implies that the memory time τ_m of $K(s)$ is much shorter than the macroscopic relaxation time T. It is then reasonable to approximate the non-Markovian Eq. (1) with the Markovian equation

$$d\langle B\rangle(t)/dt = -T^{-1}\,\langle B\rangle(t)\,, \tag{2}$$

to be valid for times much longer than the memory time τ_m. Following this approach, the relaxation rate is given by

$$T^{-1} = \int_0^\infty K(s)\,ds. \tag{3}$$

An alternate formulation, is to formally solve Eq. (2) with an assumed initial value $\langle B\rangle(0)$ at zero time and then integrate again. The result is that

$$T = \int_0^\infty \langle B\rangle(t)\,dt\,[\langle B\rangle(0)]^{-1} \tag{4}$$

gives the relaxation time T as the area under the curve $\langle B\rangle(t)$. T is equal to the spectral density of B at zero frequency, compare Eq. (24) for the more general case of several observations.

Equations (3) and (4) give two ways of associating a relaxation time with the true dynamics of the system. While there are questions of convergence of the integrals, which are not discussed here, it is not at all clear that Eqs. (3) and (4) will give the same result, or that either of them will give the correct decay rate at long times. It is expected that Eqs. (2)–(4) will be approximately consistent if the time scales determined by T and τ_m are sufficiently different. This is equivalent to the assumption that the observable B is only weakly coupled to the other observables in the system. That this conclusion is valid, is argued in Sec. III for the general case, and exemplified by the NMR model calculation in Sec. IV.

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So far, the discussion has been phenomenological. Since the statistical mechanical formulas for one observable are special cases of those for several observables, it is the more general situation that is described in detail.

B. Statistical mechanics of several observable relaxation theory

It often happens that several observables are strongly coupled together by dynamics, but that this set of observables is only weakly coupled to the remaining degrees of freedom. The position and momentum of a molecule are examples. On the other hand, it may be that one observable is given an initial nonequilibrium value, but experimentally, a different quantity is observed. A relaxation theory that includes such a coupling requires the simultaneous study of both observables. Such considerations are the basis for the classification of observables as "relevant" or "irrelevant." Since non-Hermitian combinations of observables are useful for many theoretical discussions, e.g., the raising and lowering operators of angular momentum theory, the *relevant* observables B_μ will be allowed to be non-Hermitian. It is assumed however, that for any non-Hermitian observable B_μ that is considered relevant, its adjoint $B_\mu^\dagger$ is also considered relevant.

The expectation value $\langle B_\mu\rangle(t)$ of any (relevant) observable B_μ, is calculated according to the Heisenberg picture, by

$$\langle B_\mu\rangle(t) = \mathrm{Tr} B_\mu(t)\rho, \tag{5}$$

where $B_\mu(t)$ is the time dependent observable satisfying

$$i\partial B_\mu(t)/\partial t = -\mathcal{L} B_\mu(t), \tag{6}$$

subject to the initial condition $B_\mu(0) = B_\mu$. Here $\mathcal{L}$ is the commutator superoperator[4]

$$\mathcal{L}A \equiv \hbar^{-1}[\mathcal{H}, A] \equiv \hbar^{-1}(\mathcal{H}A - A\mathcal{H}), \tag{7}$$

or quantum Liouville operator,[5] which describes the time evolution of the system due to the many body Hamiltonian $\mathcal{H}$. Equation (6) can be formally solved

$$B_\mu(t) = \exp(i\mathcal{L}t) B_\mu, \tag{8}$$

which means that the behavior of $\langle B_\mu\rangle(t)$ is in principle obtained, provided that ρ is given.

Usually, it is not ρ that is initially given but rather only the average values $\langle B_\mu\rangle(0)$ of a certain set $\{B_\mu\}$ of observables. It is then necessary that ρ satisfy

$$\mathrm{Tr}\rho = 1; \quad \mathrm{Tr}\rho\mathcal{H} = E$$

and

$$\mathrm{Tr}\rho B_\mu = \langle B_\mu\rangle(0). \tag{9}$$

The first is a normalization condition, while the average energy requirement has been added for convenience and implies that at equilibrium, the distribution will be canonical. One way of specifying a unique ρ that satisfies Eqs. (9), is by appealing to information theory.[6] Thus the entropy $-k\mathrm{Tr}\rho\ln\rho$ is maximized subject to the constraints of Eq. (9). The density operator obtained in this manner is given by

$$\rho = Q_{\mathrm{tot}}^{-1} \exp\left[-\beta\mathcal{H} + \sum_\mu \lambda_\mu B_\mu\right], \tag{10}$$

with the (Lagrange) multipliers β and λ_μ adjusted to reproduce the constraints of Eq. (9). In the following, it is assumed that $\langle B_\mu\rangle(0)$ is very small, so that ρ can be expanded linearly in λ_μ as

$$\rho \simeq \rho_{\mathrm{eq}}\left[1 + \sum_\mu \lambda_\mu \tilde{B}_\mu\right]. \tag{11}$$

The equilibrium density operator is

$$\rho_{\mathrm{eq}} = Q^{-1}\exp(-\beta\mathcal{H}), \tag{12}$$

with partition function $Q = \mathrm{Tr}\exp(-\beta\mathcal{H})$. The tilde denotes the Kubo transform[7,8]

$$\tilde{A} \equiv \beta^{-1}\int_0^\beta \exp(\alpha\mathcal{H}) A \exp(-\alpha\mathcal{H})\, d\alpha$$

$$= (\beta\mathcal{L})^{-1}[\exp(\beta\mathcal{L}) - 1]A\,. \tag{13}$$

For the expansion [Eq. (11)] to be valid, it is necessary that the equilibrium values of B_μ vanish,

$$\langle B_\mu\rangle_{\mathrm{eq}} = \mathrm{Tr}\rho_{\mathrm{eq}} B_\mu = 0. \tag{14}$$

It is assumed that the observables are defined so that this convenient condition is satisfied.

It is more common[3] to derive Eq. (11) by adiabatically building up the constraints in Eqs. (9) as a linear response of the system to the perturbing, time dependent Hamiltonian

$$\mathcal{H}_1(t) = -\beta^{-1}\sum_\mu \lambda_\mu B_\mu \exp(\epsilon t)\,, \tag{15}$$

applied from $t = -\infty$ to $t = 0$ and then taking the limit $\epsilon \to 0+$.

Finally, in the linearized form, the λ_μ can be found by imposing the conditions of Eqs. (9); namely,

$$\sum_\mu \mathrm{Tr} B_\nu \rho_{\mathrm{eq}} \tilde{B}_\mu \lambda_\mu = \langle B_\nu\rangle(0), \tag{16}$$

and solving this resulting set of simultaneous linear equations. To this end, it is convenient to define the inner product

$$\langle\langle A \,|\, B\rangle\rangle \equiv \mathrm{Tr} A^\dagger \rho_{\mathrm{eq}} \tilde{B} = \mathrm{Tr}(\tilde{A})^\dagger \rho_{\mathrm{eq}} B. \tag{17}$$

Then, if the B_ν are orthonormal in the sense that

$$\langle\langle B_\nu \,|\, B_\nu\rangle\rangle \equiv \delta_{\mu\nu}\,, \tag{18}$$

it immediately follows that

$$\lambda_\mu^* = \langle B_\mu\rangle(0). \tag{19}$$

The time dependence of *any* observable B of the system then follows from Eqs. (5), (6), (11), and (19). In practice, this is usually one of the observables B_ν of the set whose values were known initially, thus

$$\langle B_\nu\rangle(t) = \mathrm{Tr} B_\nu(t)\rho$$

$$= \sum_\mu \mathrm{Tr}[\exp(i\mathcal{L}t) B_\nu]\rho_{\mathrm{eq}}(\tilde{B}_\mu^\dagger)\langle B_\mu\rangle(0)$$

$$= \sum_\mu \langle\langle \exp(i\mathcal{L}t) B_\nu^\dagger \,|\, B_\mu^\dagger\rangle\rangle \langle B_\mu\rangle(0). \tag{20}$$

Within the linear regime and the confines of the known data at zero time, this can be interpreted as the exact evolution of $\langle B_\nu\rangle(t)$.

The physical content of this set of equations is often analyzed with the help of their Fourier transforms

$$\langle \hat{B}_\nu\rangle(\omega) \equiv \lim_{\epsilon\to 0+}\int_0^\infty \exp[i(-\omega+i\epsilon)t]\,\langle B_\nu\rangle(t)\,dt$$

$$=\sum_\mu J_{\nu\mu}(\omega)\,\langle B_\mu\rangle(0), \tag{21}$$

and is contained in the matrix of spectral densities

$$J_{\nu\mu}(\omega)\equiv\int_0^\infty \exp[i(-\omega+i\epsilon)t]\,\mathrm{Tr}B_\nu(t)\,\rho_{\mathrm{eq}}(\tilde{B}_\mu^\dagger)\,dt$$

$$=i\,\langle\langle B_\nu^\dagger|\,(-\omega-\mathfrak{L}+i\epsilon)^{-1}\,|B_\mu^\dagger\rangle\rangle\ . \tag{22}$$

It is expected that the $\langle B_\mu\rangle(t)$ will decay in time to their equilibrium (zero) values. Such decay is usually assumed to be exponential or more generally, a combination of exponentials. Equivalently, the set $\langle B_\mu\rangle(t)$ should satisfy the set of Markovian equations

$$\frac{\partial\langle B_\nu\rangle(t)}{\partial t}=-\sum_\mu(\mathfrak{T}^{-1})_{\nu\mu}\langle B_\mu\rangle(t)\ , \tag{23}$$

with a relaxation time matrix $\mathfrak{T}$. In analogy to Eq. (4), one method of associating a relaxation time matrix with the exact dynamics of the system, is to equate $\mathfrak{T}$ to the matrix of spectral densities,

$$\mathfrak{T}_{\nu\mu}=J_{\nu\mu}(0)\ . \tag{24}$$

It is stressed that Eq. (20) describes the exact dynamics of the system while Eq. (23) is approximate. A question of fundamental importance is then, in what sense does Eq. (23) give a reasonable approximation to the exact dynamics. Presumably, if the relevant set of observables $\{B_\mu\}$ are only weakly coupled to the remainder of the system, then Eq. (23) may give a fair representation of the time dependence of the $\langle B_\mu\rangle(t)$. Again, this should be valid for long times, when transient effects have had time to decay. The validity of Eq. (23) in this regime is discussed in Sec. III. It is shown there, that the presence of initial transients requires that Eq. (23) be solved, not with the true initial values of $\langle B_\mu\rangle(0)$, but with *effective* initial values, related to $\langle B_\mu\rangle(0)$ by a slip matrix $S_{\nu\mu}$. To carry out this analysis, it is convenient to make connections with other formalisms of general relaxation theory. This is done in the next two subsections.

C. Generalized master equation

Zwanzig[1] separated the time dependent density operator into relevant and irrelevant parts. This is accomplished by a projection superoperator (tetradic operator) $\mathcal{P}_s$. In the present case, it is the set of observables B_μ that are relevant. Thus the relevant projector for states (subscript s) should involve the operator subspace spanned by the B_μ. To be a density operator this needs to be multiplied by the equilibrium density operator ρ_{eq}, and for technical reasons, a Kubo transform must be taken.[9] Moreover, normalization should be preserved. With these considerations, together with the assumed orthonormality of the B_μ as expressed in Eqs. (17) and (18), the state projector is defined as (χ is any trace class operator)

$$\mathcal{P}_s\,\chi\equiv\rho_{\mathrm{eq}}\left[\mathrm{Tr}\chi+\sum_\mu\tilde{B}_\mu\,\mathrm{Tr}B_\mu^\dagger\,\chi\right]. \tag{25}$$

If χ is a density operator, then $\mathrm{Tr}\chi=1$, and this normalization is preserved by this projection operator.

While Eqs. (5)–(8) represent the time dependence of the observables according to the Heisenberg picture, it is equivalent to write Eq. (5) in the Schrödinger picture; namely,

$$\langle B_\mu\rangle(t)=\mathrm{Tr}B_\mu\,\rho(t)=\mathrm{Tr}B_\mu\,e^{-i\mathfrak{L}t}\,\rho, \tag{26}$$

with $\rho(t)$ satisfying the von Neumann (or quantum Liouville) equation

$$i\partial\rho(t)/\partial t=\mathfrak{L}\rho(t). \tag{27}$$

It is then a standard derivation,[1] to obtain the GME for the relevant part $\rho_1\equiv\mathcal{P}_s\rho$ of ρ as

$$\frac{\partial\rho_1}{\partial t}=-i\mathcal{P}_s\mathfrak{L}\mathcal{P}_s\rho_1-\int_0^t K_s(t')\rho_1(t-t')\,dt', \tag{28}$$

with memory kernel

$$K_s(t')=\mathcal{P}_s\mathfrak{L}(1-\mathcal{P}_s)\exp[-i(1-\mathcal{P}_s)\mathfrak{L}(1-\mathcal{P}_s)t']$$

$$\times(1-\mathcal{P}_s)\mathfrak{L}\mathcal{P}_s\ . \tag{29}$$

This also uses the initial data, that

$$\rho_1(0)=\rho(0)=\rho_{\mathrm{eq}}\left[1+\sum_\mu\tilde{B}_\mu\,\langle B_\mu\rangle^*(0)\right], \tag{30}$$

a combination of Eqs. (11) and (19). The GME (28) is simpler than the von Neumann Eq. (27) in the sense that the former involves fewer degrees of freedom. On the other hand, the GME is non-Markovian, having a memory kernel, which considerably complicates the time dependence, while the von Neumann equation is Markovian.

D. Generalized Langevin equation

Mori[2] applied the projection operator technique to the observables themselves, specifically to the set of dynamical Eqs. (6) in the Heisenberg picture. Now the projection superoperator $\mathcal{P}$ is to be onto the (subspace spanned by the) relevant observables themselves, in contradistinction to $\mathcal{P}_s$ which projects onto the relevant density operator. On using the inner product defined in Eq. (17) and the assumed orthonormality of the B_μ, Eq. (18), the appropriate projection is defined as

$$\mathcal{P}A\equiv\sum_\mu B_\mu\,\langle\langle B_\mu|A\rangle\rangle\ , \tag{31}$$

for any observable A. It is clear that $\mathcal{P}$ is idempotent and self-adjoint with respect to the inner product, Eq. (17). The relation between $\mathcal{P}_s$ and $\mathcal{P}$ is as follows: If ρ is expressed as $\rho_{\mathrm{eq}}\tilde{A}$, which can always be done,[9] then

$$\mathcal{P}_s\rho=\rho_{\mathrm{eq}}(\mathrm{Tr}\rho+\widetilde{\mathcal{P}A}). \tag{32}$$

Thus the differences reside in: (i) a general factor of

ρ_{eq}; (ii) the normalization of ρ preserved by the addition of an explicit term $\mathrm{Tr}\rho$; and (iii) by the presence of the Kubo transform, Eq. (13).

Rather than applying $\mathcal{P}$ to the dynamical Eqs. (6), it is equivalent to begin with the spectral densities $J_{\nu\mu}(\omega)$ and to recognize that these are matrix elements of the *relevant part* of the resolvent $(-\omega - \mathcal{L} + i\epsilon)^{-1}$. It is a straightforward problem of resolvent algebra to prove that this relevant part can be written in the form[1]

$$\mathcal{P}(-\omega - \mathcal{L} + i\epsilon)^{-1}\mathcal{P} = (-\omega - \mathcal{P}\mathcal{L}\mathcal{P} + i\hat{K}(\omega) + i\epsilon)^{-1}\mathcal{P}, \quad (33)$$

where

$$\hat{K}(\omega) = i\mathcal{P}\mathcal{L}(1-\mathcal{P})[-\omega - (1-\mathcal{P})\mathcal{L}(1-\mathcal{P}) + i\epsilon]^{-1} \times (1-\mathcal{P})\mathcal{L}\mathcal{P}. \quad (34)$$

The inverse on the right hand side of Eq. (33) looks like a resolvent, but is not, since the superoperator $\mathcal{P}\mathcal{L}\mathcal{P} - i\hat{K}(\omega)$ is frequency dependent.

In the formula for the spectral densities [Eq. (22)] the projector $\mathcal{P}$ can be inserted on either side of the resolvent. Thus $J(\omega)$ is (as a matrix) just the matrix inverse of $-\omega - \mathcal{P}\mathcal{L}\mathcal{P} + i\hat{K}(\omega)$ or, elementwise

$$[J(\omega)^{-1}]_{\nu\mu} = i\omega\delta_{\nu\mu} + i\mathcal{L}_{\nu\mu} + \hat{K}_{\nu\mu}(\omega). \quad (35)$$

Here $\mathcal{L}_{\nu\mu}$ and $\hat{K}_{\nu\mu}(\omega)$ are matrix elements of $\mathcal{L}$ and $\hat{K}(\omega)$: namely,

$$\mathcal{L}_{\nu\mu} \equiv \langle\langle B_\nu^\dagger | \mathcal{L} | B_\mu^\dagger \rangle\rangle = -\langle\langle B_\nu | \mathcal{L} | B_\mu \rangle\rangle^* , \quad (36)$$

and the memory function matrix

$$\hat{K}_{\nu\mu}(\omega) \equiv \langle\langle B_\nu^\dagger | \hat{K}(\omega) | B_\mu^\dagger \rangle\rangle . \quad (37)$$

It is a property of the Liouville superoperator that, if the set $\{B_\mu\}$ consists of only one observable B, the $\mathcal{L}$ term vanishes. This implies for one observable, that only memory effects occur, and in the associated Markovian approximation, only exponential decay occurs.

The inverse Fourier transform of Eq. (21) together with the expression [Eq. (35)] for $J(\omega)^{-1}$ gives the generalized Langevin equation (GLE)[10]

$$\frac{\partial\langle B_\nu\rangle}{\partial t}(t) = -i\sum_\mu \mathcal{L}_{\nu\mu}\langle B_\mu\rangle(t) - \sum_\mu \int_0^t K_{\nu\mu}(s) \times \langle B\rangle_\mu(t-s)\,ds, \quad (38)$$

where a matrix element of the memory kernel is

$$K_{\nu\mu}(s) \equiv (2\pi)^{-1}\int_{-\infty}^{\infty} \exp(i\omega s)\hat{K}_{\nu\mu}(\omega)\,d\omega. \quad (39)$$

If it so happens that the set $\{B_\mu\}$ is linearly closed under the action of $\mathcal{L}$ (that is, $\mathcal{L}B_\mu$ is a linear combination of the B_ν), then $K = 0$ and Eq. (38) is just the matrix representation of the von Neumann equation [compare[10] Eq. (6)]. In essence, for $\mathcal{P} \neq 1$, the von Neumann equation [Eq. (6)] is simplified by a reduction in dimensionality but becomes more complicated in that the (exact) equation is no longer Markovian.

The GLE (38) could also have been obtained directly from Eq. (6) by the projection method, which is Mori's approach.[2] Just as the observable and state projectors are related [Eq. (32)] so are the memory kernels $K(t)$ and $K_s(t)$. This involves the identity, that if $\chi = \rho_{eq}\tilde{A}$, then

$$(1-\mathcal{P}_s)\mathcal{L}(1-\mathcal{P}_s)\chi = \rho_{eq}\widetilde{(1-\mathcal{P})\mathcal{L}(1-\mathcal{P})A} \quad (40)$$

and results in the relation

$$K_s(t)\chi = \rho_{eq}\widetilde{K(t)A} . \quad (41)$$

From this it follows that the GME based on the projector $\mathcal{P}_s$ is completely equivalent to the GLE based on the projector $\mathcal{P}$. Stated otherwise and in reference to Eqs. (26), (28), and (38), the GLE is just a matrix representation of the GME.

In concluding this subsection, it is noted that $\hat{K}(\omega)$ is defined in Eq. (34) for real frequencies ω. This definition can also be used for complex frequencies in the lower half of the complex ω plane since $\hat{K}(\omega)$ is holomorphic there. Assuming that the real part of *any* diagonal matrix element of $\hat{K}(\omega)$ is positive in the lower-half plane, an analytic continuation of $\hat{K}(\omega)$ across the real axis is possible and provided that the real (Hermitian) part of $\hat{K}(\omega)$ does not vanish *on* the real axis, it follows that the zeros of $-\omega - \mathcal{L} + i\hat{K}(\omega)$ occur off the real axis and in the upper-half of the complex ω plane. With this proviso, the vector $\langle B\rangle(t)$ decays to equilibrium.

III. LONG TIME BEHAVIOR

The standard method[1-3] of approximating the GLE is to assume that the memory kernel $K(s)$ decays rapidly to zero, on a memory time (τ_m) scale. Then for experimental times on a scale large compared to τ_m, the GLE reduces to the Markovian equation (23). This implies that there is a separation of time scales, that is, some of the time dependence is slow, which is accounted for by Eq. (23), while the rapid time dependence appears as transients that decay to zero. It is a necessary requirement for this approximation to work, that all of the slow time dependence is included in Eq. (23). Alternately, this means that the set of relevant observables is chosen large enough (and appropriately enough) that all the slow decay rates are included in $\mathfrak{T}$, and none in $K(s)$. It is assumed that the set of B_μ has been chosen so that this separation does occur. A further constraint, is that the experimental times are small compared to the Poincaré recurrence time of the system, otherwise the Markovian decay equations are not valid, as is very clearly illustrated by Zwanzig's example.[1]

It is now necessary to select out the slowly decaying part of the $\langle B_\nu\rangle(t)$. Rather than examine the GLE [Eq. (38)] it is equivalent to look for those singularities of the spectral matrix $J(\omega)$ [Eq. (22)] which lie closest to the real axis.

If there are M different B_ν's, then $\mathfrak{T}$ (being time independent) can incorporate at most M first order poles of $J(\omega)$, other types of singularities being ruled out by the *assumed* time independence of $\mathfrak{T}$ and consequent exponential decay of the $\langle B_\nu\rangle(t)$. Thus it is assumed that $J(\omega)$ can be approximated by ($m \leq M$)

$$J(\omega) \simeq -i\sum_{\alpha=1}^{m} (\omega - \bar{\omega}_\alpha)^{-1} J^{(\alpha)} , \quad (42)$$

where $J^{(\alpha)}$ is the (matrix) residue of $iJ(\omega)$ at the pole[11]

$\bar{\omega}_\alpha$. It is important that m be chosen large enough so that the range of $\sum_\alpha J^{(\alpha)}$ is M dimensional. A simple but physically realistic example illustrating these ideas is given in Sec. IV.

The matrix $\mathfrak{T}^{-1}$ can be expressed as a linear combination of the $\bar{\omega}_\alpha$ but the numerical coefficients can be complicated if $m>1$. First consider the case $m=1$. Then all the $\langle B_\nu\rangle(t)$ decay at the same rate $-i\bar{\omega}_1$. The inverse Fourier transform of Eq. (21) with a one term approximation for $J(\omega)$ [Eq. (42)] is then

$$\langle B_\nu\rangle(t) = \exp(i\bar{\omega}_1 t)\sum_\mu J^{(1)}_{\nu\mu}\langle B_\mu\rangle(0)$$

$$\equiv \exp(i\bar{\omega}_1 t)\langle B_\nu\rangle_{\text{eff}}(0). \tag{43}$$

The matrix $\mathfrak{T}^{-1}$ is thus $-i\bar{\omega}_1$ times the identity matrix but the effective initial value $\langle B_\nu\rangle_{\text{eff}}(0)$ of $\langle B_\nu\rangle(t)$ has been modified from the true initial value $\langle B_\nu\rangle(0)$. Since Eq. (43) is valid only at long times, this *slip*[12] is due to the decay of the transients.

For $m>1$, the long time behavior of the observables is given by

$$\langle B_\nu\rangle(t) = \sum_{\alpha,\mu}\exp(i\bar{\omega}_\alpha t)J^{(\alpha)}_{\nu\mu}\langle B_\mu\rangle(0). \tag{44}$$

This can always be written in the form

$$\langle B_\nu\rangle(t) = \sum_\lambda [\exp(-t\,\mathfrak{T}^{-1})]_{\nu\lambda}\langle B_\lambda\rangle_{\text{eff}}(0), \tag{45}$$

so that it can be recognized as the solution of Eq. (23) with effective initial values. But for the general case, it is not an obvious manipulation to rewrite Eq. (44) in the form of Eq. (45).

The natural interpretation of Eq. (44) is that the αth component of the relevant observable subspace has a complex eigenfrequency $\bar{\omega}_\alpha$. If this is the case, then the relaxation rate matrix $\mathfrak{T}^{-1}$ would be written

$$\mathfrak{T}^{-1} = \sum_\alpha (-i\bar{\omega}_\alpha)\mathcal{P}^{(\alpha)}\ , \tag{46}$$

where $\mathcal{P}^{(\alpha)}$ is the projector on the αth component. This requires that the $\mathcal{P}^{(\alpha)}$ be orthogonal in the sense that

$$\mathcal{P}^{(\alpha)}\mathcal{P}^{(\beta)} = \delta_{\alpha\beta}\mathcal{P}^{(\alpha)}\ . \tag{47}$$

Then on equating Eqs. (44) and (45), it is seen that the $\mathcal{P}^{(\alpha)}$ must also satisfy

$$\sum_\lambda \mathcal{P}^{(\alpha)}_{\nu\lambda}\langle B_\lambda\rangle_{\text{eff}}(0) = \sum_\mu J^{(\alpha)}_{\nu\mu}\langle B_\mu\rangle(0). \tag{48}$$

If $\mathfrak{T}$ and the $\mathcal{P}^{(\alpha)}$'s are to be independent of the initial data, the $\langle B_\mu\rangle(0)$, then the matrix of residues $J^{(\alpha)}$ must factor according to

$$J^{(\alpha)} = \mathcal{P}^{(\alpha)}S, \tag{49}$$

where S is the (α independent) slip matrix. Moreover, the $\mathcal{P}^{(\alpha)}$ must span the relevant subspace, so summing Eq. (49) implies that

$$\sum_\alpha J^{(\alpha)} = \sum_\alpha \mathcal{P}^{(\alpha)}S = S\ , \tag{50}$$

and S is uniquely determined. Finally, the effective initial data is given by

$$\langle B_\lambda\rangle_{\text{eff}}(0) = \sum_\mu S_{\lambda\mu}\langle B_\mu\rangle(0) = \sum_{\alpha,\mu} J^{(\alpha)}_{\lambda\mu}\langle B_\mu\rangle(0). \tag{51}$$

If the $J^{(\alpha)}$ do not factor according to Eq. (49), or equivalently, that $J^{(\alpha)}S^{-1}$ is not an orthogonal projector satisfying Eq. (47), then it is still possible to forcibly satisfy Eq. (48). Since the range of $S\equiv\sum_\alpha J^{(\alpha)}$ is M dimensional, that is, spans the whole of the relevant subspace, it is possible to subdivide any $J^{(\alpha)}$ whose range is more than one dimensional, to give M linearly independent $J^{(\alpha)}$'s, some of which may have the same $\bar{\omega}_\alpha$. But now the matrix

$$X_{\nu\alpha} \equiv \sum_\mu J^{(\alpha)}_{\nu\mu}\langle B_\mu\rangle(0) \tag{52}$$

is square and assumed nonsingular. The projectors $\mathcal{P}^{(\alpha)}$ are now defined as

$$\mathcal{P}^{(\alpha)}_{\nu\mu} \equiv X_{\nu\alpha}(X^{-1})_{\alpha\mu}\ . \tag{53}$$

These satisfy Eqs. (47) and (48) with effective initial data determined by Eq. (51). But the projectors, and thus also $\mathfrak{T}$, depend on the initial data, which appears necessary but unpleasant. Thus it can be seen that the general behavior at long times [Eq. (44)] can be written in the form of Eq. (45), which appears as the solution of the Markovian Eq. (23) but with effective initial values.

The result of having initial transients decay out is to modify the initial data for the long time behavior (Markovian regime) of the system. This is usually not discussed in relation to the theory of the GME or of the GLE. In fact, the generalized equations are used most often in weak coupling situations, in which case $\hat{K}(\omega)$ is small. The zeros of $J(\omega)^{-1}$ [poles of $J(\omega)$] occur when there is an operator A_α and a frequency $\bar{\omega}_\alpha$ such that

$$J(\bar{\omega}_\alpha)^{-1}A_\alpha = i\mathcal{P}\mathcal{L}\mathcal{P}A_\alpha + i\bar{\omega}_\alpha A_\alpha + \hat{K}(\bar{\omega}_\alpha)A_\alpha = 0, \tag{54}$$

compare Balescu.[11] If $\hat{K}(\omega)$ is small, it acts as a perturbation so that the A_α are to zeroth order the eigenvectors of $\mathcal{P}\mathcal{L}\mathcal{P}$ and the poles are to first order in $\hat{K}$,

$$\bar{\omega}_\alpha \cong \bar{\omega}^{(0)}_\alpha + \bar{\omega}^{(1)}_\alpha = [-\langle\langle A_\alpha|\mathcal{P}\mathcal{L}\mathcal{P}|A_\alpha\rangle\rangle$$
$$+ i\langle\langle A_\alpha|\hat{K}(\bar{\omega}^{(0)}_\alpha)A_\alpha\rangle\rangle]\langle\langle A_\alpha|A_\alpha\rangle\rangle^{-1}. \tag{55}$$

Since $\mathcal{P}\mathcal{L}\mathcal{P}$ is self-adjoint, the decay rate is the real part of the matrix element of $\hat{K}(\bar{\omega}^{(0)}_\alpha)$. Ignoring the oscillatory effects which are absent if there is only one relevant observable ($\bar{\omega}^{(0)}_\alpha = 0$), this decay rate is the same as Eq. (3). If $J(0)$ is calculated in the same approximation, *for one observable* and thus vanishing $\mathcal{P}\mathcal{L}\mathcal{P}$, then

$$J(0) = \hat{K}(0)^{-1}\ , \tag{56}$$

compare Eqs. (4) and (24). Thus, either of Eqs. (3) or (4) give the same decay rate in the weak coupling limit.

In contrast, if there are several relevant observables and strong mechanical coupling between them (a nonvanishing $\mathcal{P}\mathcal{L}\mathcal{P}$), then Eq. (24) can give only a first approximation to $\mathfrak{T}$, with $\hat{K}(\bar{\omega}^{(0)}_\alpha)$ replaced by $\hat{K}(0)$, while the matrix generalization of Eq. (3) gives only an approximate decay rate and completely ignores the oscillatory effects. Finally, if $\hat{K}(\omega)$ is *not* small, then

neither Eqs. (3), (4), nor (24) can be counted on to give approximate decay rates. It is stressed that the long time behavior is correctly given by the relaxation matrix calculated by Eq. (46). Thus it is in general necessary to solve for the $\bar{\omega}_\alpha$ via Eq. (54) rather than use approximations as in Eqs. (3), (4), and (24). The simple model discussed in the next section illustrates these ideas.

IV. INITIAL SLIP EFFECTS IN NUCLEAR MAGNETIZATION

The initial slip phenomenon is exemplified by the gas phase magnetic relaxation of a nuclear spin of $\frac{1}{2}$. The relaxation mechanism is restricted to be via the spin rotation intramolecular coupling with the nuclear spin being coupled to one rotational state of magnitude J. Collisions lead to reorientation of the rotational vector, but have no effect on the nuclear states. This model has been treated in detail earlier[13–15] and it has been shown that the time dependence of the transverse component of the nuclear spin polarization, $b_1(t) \equiv -i(2)^{3/2}\langle I_+\rangle$ is given by

$$db_1(t)/dt = i\omega_I b_1(t) - \int_0^t dt' K_\perp(t-t') b_1(t'), \tag{57}$$

with the initial condition that $b_1(0) = 1$. The kernel $K_\perp(t)$ is given by[14,15]

$$K_\perp(t) = (\tfrac{1}{3})c^2 J(J+1)\exp(-t/\tau')\{\exp(i\omega_J t) + \exp(i\omega_I t)\}, \tag{58}$$

where c is the spin rotation coupling strength; $\tau' > 0$ is the rotational correlation time, and ω_I, ω_J, respectively, are the nuclear and rotational Larmour precession frequencies. τ' is also interpretable as the memory time τ_m for the memory kernel $K_\perp(t)$. Equation (58) is an approximation to the true memory kernel. This has been obtained by averaging over the translational degrees of freedom of the molecules to arrive at an effective collision rate τ'^{-1}. For this reason, Eqs. (34) and (58) should not be compared.

Equation (57) is a special case of Eq. (38) in which the kernel is diagonal. From the point of view of the general formalism, the relevant space is three dimensional, related to the three spin operators I_+, I_-, and I_z. It is then an aspect of rotational invariance, that the three equations decouple, Eq. (57) being one of the set.

Equation (57) can be solved in the same manner as described in Sec. III. But it can also be solved exactly, so that a comparison of approximate and exact results can be made. The Fourier transform of Eq. (57) gives

$$\hat{b}_1(\omega) = J_{11}(\omega)\, b_1(0), \tag{59}$$

where

$$J_{11}(\omega) = [i\omega - i\omega_I + \hat{K}(\omega)]^{-1} = \frac{[1+i(\omega-\omega_I)\tau'][1+i(\omega-\omega_J)\tau']}{i(\omega-\omega_I)[1+i(\omega-\omega_I)\tau'][1+i(\omega-\omega_J)\tau'] + \frac{1}{3}c^2 J(J+1)\tau'[2+i(2\omega-\omega_I-\omega_J)\tau']}. \tag{60}$$

It is seen that the denominator is cubic in ω so that the exact solution of Eq. (57) involves three exponentials.

A. Exact solution

The spectral density $J_{11}(\omega)$ [Eq. (60)] can in principle be written *exactly* as a sum of three simple pole terms in the manner of Eq. (42). As a consequence, the *exact* solution of Eq. (57) has the form

$$b_1(t) = \sum_{\alpha=1}^{3} \exp(i\bar{\omega}_\alpha t) J_{11}^{(\alpha)}\, b_1(0). \tag{61}$$

The roots of the denominator cannot be expressed explicitly in reasonable form, rather the exact solution is obtained numerically.[14] For H_2 gas the parameters are $c = 0.115$ MHz, $\tau' p = 8\times10^{-8}$ sec torr, and $J = 1$. Nuclear Larmour frequencies of 61 and 35 MHz were used,[14] but at low densities when $(\omega_I - \omega_J)\tau' \gg 1$, the results are independent of $\omega_I - \omega_J$ and the choice of Larmour frequency.

From the point of view of the general theory discussed in the earlier sections, the observable I_+ and its expectation value $b_1(t)$ is *one* observable, so it is expected that its decay will be governed at long times by *one* exponential. That is, the Markovian approximation Eqs. (2) and (23), is one dimensional and the deviations from Markovian behavior appear as a nonexponential time decay. On the other hand, the problem is strictly not one dimensional, but really three dimensional, involving I_- and I_z as well as I_+. It is for this reason that a natural oscillation frequency ω_I appears in the equation for $b_1(t)$, while rotational invariance decouples the three observables and makes the problem appear here as a one-dimensional problem for a non-Hermitian observable. Thus there is a natural oscillatory behavior $\exp(i\omega_I t)$ for $b_1(t)$. Over and above this, the numerical solution of Eq. (57) displays apparent exponential decay at long times, for densities corresponding to pressures above 0.02 torr. Below this density, oscillatory motion sets in. These aspects are treated in detail in Ref. 14.

The short initial time dependence of $b_1(t)\exp(-i\omega_I t)$ is not exponential except at much higher densities ($p > 1$ torr). The exact solution for $\mathrm{Re}[b_1(t)]$ for $t < 0.01$ msec is given in Fig. 1 for pressures down to 0.01 torr. It is clear from these curves that if the long time exponential decay is extrapolated back to $t = 0$, that the initial condition $b_1(0) = 1$ is not reproduced. The difference between $b_1(0) = 1$ and the extrapolated value is the initial slip.

An alternative way of representing the slip is to plot the initial time dependence of $-Re[\ln(b_1(t)]$. This is

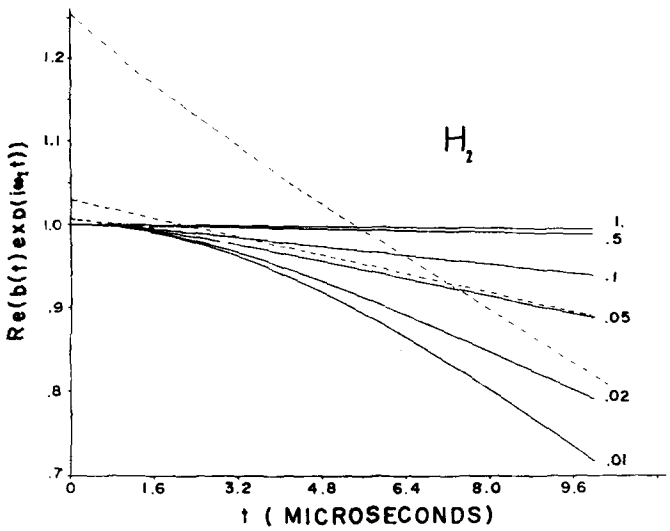

FIG. 1. Short-time behavior of $Re\,[b_1(t)\exp(-i\omega_I t)\,]$. The solid curves give the exact solutions at different densities, while the dashed lines give the extrapolation from long times to zero time.

given in Fig. 2 for the same densities as in Fig. 1. Clearly the long time dependence is linear but this breaks down at small time. Again the long time extrapolation does not pass through the origin, although the exact solution, subject to $\ln[b_1(0)]=0$ must.

B. Weak coupling solution

The perturbative solution for small c (in comparison to τ'^{-1}) has been treated earlier.[13,14] The poles of the spectral density are located approximately, in the regime where $(\omega_J-\omega_J)\tau'\gg 1$, according to

$$-i(\bar{\omega}_1-\omega_I)=\tfrac{1}{3}c^2J(J+1)\tau'\equiv 1/T_2\,, \tag{62}$$

$$-i(\bar{\omega}_2-\omega_I)=\tau'^{-1}-\tfrac{1}{3}c^2J(J+1)\tau'\,, \tag{63}$$

and

$$-i(\bar{\omega}_3-\omega_J)=\tau'^{-1}\,. \tag{64}$$

For $c^2\tau'^2\ll 1$ there is only one slowly decaying term, the first one. This corresponds then to exponential decay and a Markovian equation governing the time dependence at long times, that is

$$\exp(-i\omega_I t)\,b_1(t)=\exp(-t/T_2)J_{11}^{(1)}b_1(0)$$
$$=\exp(-t/T_2)b_1(0)_{\rm eff}\,. \tag{65}$$

As stressed earlier, this example is one dimensional, corresponding to only one relevant observable. Thus only one pole of the spectral density is expected to be near the imaginary axis and this is what is found. The residue $J_{11}^{(1)}$ for this term is then the initial slip (matrix)

$$S=J_{11}^{(1)}\cong 1+\tfrac{1}{3}c^2J(J+1)\tau'^2+\tfrac{1}{3}c^4J^2(J+1)^2\tau'^4+\cdots\,. \tag{66}$$

If, for example, $\frac{1}{3}c^2J(J+1)\tau'^2=1/14$, then surely this gives a sufficient difference in decay rates [Eqs. (62) vs Eqs. (63) and (64)] so that over a long period of time, only one exponential is important. Yet the slip is 1.25, which means that the effective initial value $b_1(0)_{\rm eff}$ for the Markovian equation, is significantly different from the true initial value $b_1(0)=1$. This is demonstrated in Fig. 1, corresponding to pressures of about 0.02 torr. The time axis is taken only to 10 μsec so that the higher pressure extrapolations are evident. The 0.02 torr extrapolated (dashed) curve joins the true curve (solid) at larger times off the figure.

Below 0.02 torr, the three decay rates become comparable and a weak coupling solution is no longer valid. Thus for the 0.01 torr curve in Figs. 1 and 2, it is not possible to extrapolate from a single long-time decay to zero time, since the decay is not exponential. This is discussed in Ref. 14 and is reviewed in Sec. IV.C.

Of course the imposed initial condition: namely, $b_1(0)=1$ must be satisfied in the exact solution and this is seen from the values of $J_{11}^{(2)}$ and $J_{11}^{(3)}$; namely,

$$J_{11}^{(2)}\cong-\tfrac{1}{3}c^2J(J+1)\tau'^2-\tfrac{1}{3}c^4J^2(J+1)^2\tau'^4+\cdots\,, \tag{67}$$

and

$$J_{11}^{(3)}\cong\tfrac{1}{3}c^2J(J+1)\,(\omega_I-\omega_J)^{-2}\cong 0. \tag{68}$$

Hence the sum is unity [cf. Eq. (61)]

$$\sum_i J_{11}^{(i)}=1. \tag{69}$$

Again it is stressed that the present problem is one dimensional, so the slip is given by *one* residue; namely, Eq. (66). It is evident that the initial slip comes from the neglect of initial transients which in this case arise from the $\bar{\omega}_2$ and $\bar{\omega}_3$ contributions.

C. Strong coupling solutions

When the density is low, the collision rate τ'^{-1} becomes small and the dimensionless coupling ratio $\frac{1}{3}c^2J(J+1)\tau'^2$ becomes large. In this case the memory kernel is not a small effect on the free motion and in consequence, a Markovian approximation to Eq. (57) is not expected to be valid. This is the behavior that is found. At low densities the poles of the spectral density are given approximately by

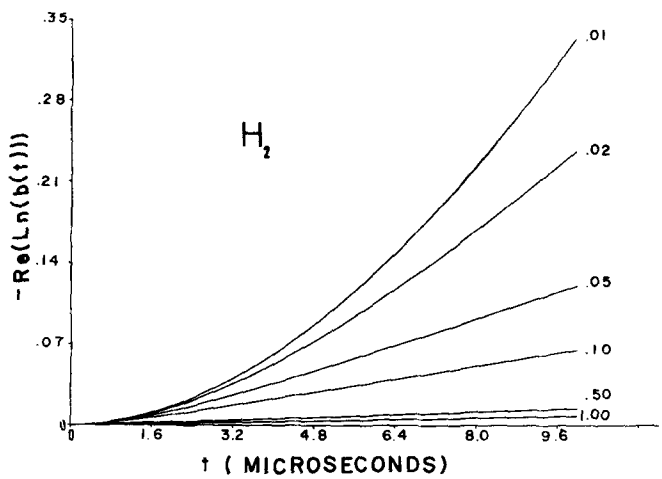

FIG. 2. Short-time behavior of $-Re[\ln(b_1(t)]$ at the same densities as in Fig. (1).

$$\bar{\omega}_1 \cong \omega_I + \delta + \tfrac{1}{2} i\tau'^{-1} \ , \tag{70}$$

$$\bar{\omega}_2 \cong \omega_I - \delta + \tfrac{1}{2} i\tau'^{-1} \ , \tag{71}$$

and

$$\bar{\omega}_3 \cong \omega_J + i\tau'^{-1} \ , \tag{72}$$

where the dynamical shift δ is[14]

$$\delta \cong [\tfrac{1}{3} J(J+1)]^{1/2} c. \tag{73}$$

All three decay rates are approximately equal so that no one exponential dominates the time dependence. The associated residues are

$$J_{11}^{(1)} \cong \tfrac{1}{2} - i(4\delta\tau')^{-1} \ , \tag{74}$$

$$J_{11}^{(2)} \cong \tfrac{1}{2} + i(4\delta\tau')^{-1} \ , \tag{75}$$

and

$$J_{11}^{(3)} \cong \tfrac{1}{3} c^2 J(J+1)\,(\omega_I - \omega_J)^{-2} \cong 0. \tag{76}$$

The solution of the GLE (57) is thus approximated by

$$b_1(t) \cong \exp[(i\omega_I - \tfrac{1}{2}\tau'^{-1})t][\cos(\delta t) + \tfrac{1}{2}(\delta\tau')^{-1} \times \sin(\delta t)]\, b_1(0). \tag{77}$$

Besides the natural oscillation, the motion is damped and oscillatory with a frequency determined by the dynamical shift δ. In no way is Eq. (77) the solution of a *one-dimensional* Langevin equation of the type Eq. (23). The strong coupling implies that there are two motions going on simultaneously, described by the complex frequencies $\bar{\omega}_1$ and $\bar{\omega}_2$ and these decay at the same rate, compare the discussion in Ref. 14.

V. DISCUSSION

The solutions of the GLE and of the associated LE have been compared. It has been argued that these should be equal at long times, provided there is a sufficient difference between the memory (correlation) time and the relaxation time. But to have equal values for the physical observables at long times, the initial value assigned to an observable must be different when solving the LE. This initial slip is due to the decay of transients described by the GLE but not described by the LE. These ideas are illustrated by a simple case of spin relaxation.

The particular example chosen (Sec. IV) is outside the range of experimental observation, but is mathematically simple and conceptually important in light of recent discussions of the same system.[14,15] Observation of other initial transient effects in the plots of correlation functions can be seen in the literature. For example, the dipolar and Raman correlation functions computed by O'Dell and Berne[16] and by Gordon[17] using m and J diffusion models, have curvature in their plots for small times.

Gordon,[18] has examined the small time regime by an asymptotic expansion of the correlation function in time. He explains the initial time dependence in terms of moments of the frequency spectrum from which interesting conclusions can be drawn. In contrast to Gordon's work, we concentrate on the time dependence of the normal modes of the system, rather than the moments. The curvature of the correlation function at small time is therefore interpreted as the rapid decay of initial transients before the slower decay and oscillatory behavior dominates.

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[10] Note that if B_ν is an eigenfunction of $\mathcal{L}$ with eigenvalue ω_ν, then

$$\mathcal{L}_{\nu\mu} = -\omega_\nu \delta_{\nu\mu} \text{ and } \partial(B_\nu)(t)/\partial t = i\omega_\nu (B_\nu)(t),$$

as it should according to the Heisenberg picture for the time evolution of an observable. That is, the signs, adjoints, etc., are consistent with pure dynamical evolution. In particular, the minus sign in $\mathcal{L}_{\nu\mu} = -\omega_\nu \delta_{\nu\mu}$ appears because $\mathcal{L}$ is the time evolution operator in the Schrödinger picture (acting on states or density operators), while B_ν is an observable and the Heisenberg picture is appropriate.

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