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# Non-Markovian effects on vibrational energy relaxation in liquids

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We consider the non-Markovian effects on vibrational relaxation which can occur when the bath relaxation rate is comparable to or slower than the relaxation of the vibrational degrees of freedom. We carry out quantum mechanical simulations of a two level system strongly coupled to a bath of known statistical properties (either a Poisson or a Gaussian process) and show that the relaxation is surprisingly insensitive to the nature of the bath. Small oscillations in the relaxation are found for the Poisson simulation which maybe observable in high resolution picosecond experiments. We investigate both cumulant expansion and memory function descriptions of relaxation in the non-Markovian limit and show that neither approach provides quantitatively accurate results.

## I. INTRODUCTION

Most experimental and theoretical studies of vibrational energy relaxation in gases and liquids are based on a Markovian approximation, in which vibrational relaxation is assumed to take place slowly in comparison with the relaxation of other degrees of freedom such as rotations and translations. If this is the case, a molecule stays in a particular vibrational state long enough to lose its "memory" of how it reached that state so that its relaxation probability is independent of its past history. As a result, rate constants can be introduced for the rate of relaxation between different vibrational levels, and for a molecule coupled to a bath the relaxation of the population in any particular level can be expressed as a sum of exponentials.

This Markovian approximation is certainly valid for liquids of diatomic and triatomic molecules in which vibrational relaxation occurs on time scales ranging from nanoseconds<sup>1</sup> to seconds,<sup>2</sup> while translational and rotational relaxation occurs on a picosecond scale. However, recent experimental advances in picosecond spectroscopy<sup>3</sup> have allowed the direct study of liquids of larger molecules in which vibrational populations can change on a picosecond or even subpicosecond time scale. In these cases, the time scale separation assumption may not hold true, non-Markovian effects can appear, and a rate equation description will no longer be valid. To date no unambiguous experimental observations of non-Markovian effects have been made; however, it seems likely that with sufficient time resolution and for certain liquids they will be seen in the future. It is the purpose of this paper to investigate and predict the types of non-Markovian behavior that can occur.

There appear to be very few theoretical studies to date of non-Markovian effects on vibrational relaxation. Lin<sup>4</sup> showed that if the coupling between vibrational system and bath was carried to fourth order in perturbation theory memory effects began to appear. Rice and co-workers<sup>5</sup> have considered a Green's func-

tion description of vibrational relaxation and have shown that if the coupling of a level to the continuum varies rapidly enough with energy then nonexponential relaxation is predicted.

This paper has two basic purposes: first, to carry out exact quantum mechanical simulations of vibrational relaxation for a system strongly coupled to a bath with known statistical properties, and second, to develop approximate theories to describe the resulting non-Markovian relaxation. Two simulations have been carried out: In the first, the bath is modeled as a two state Poisson process, in which the coupling matrix elements jump at random intervals between two possible values; this is intended to roughly simulate the effects of hard repulsive binary collisions in liquids. In the second simulation, the bath is modeled as a Gaussian random process to imitate the relaxation behavior due to longer-ranged attractive interactions. One of the questions we will address is how sensitive the relaxation is to the stochastic properties of the bath. The simulation is described in Sec. II. In Sec. III, we present several approximate theories for non-Markovian relaxation based on cumulant expansion and memory function techniques, and compare them with the simulations. Section IV concludes with a brief discussion.

## II. SIMULATION

We model the vibrational degrees of freedom as a three level system involving a ground state and two closely spaced excited states. For the isolated molecule (in the absence of coupling to the bath), we take the ground state to have wave function  $\varphi_0$ , the first excited state to be  $\varphi_1$ , and the second one  $\varphi_2$ . We take  $\varphi_0$  to be far enough in energy from  $\varphi_1$  and  $\varphi_2$  that relaxation from the excited states to  $\varphi_0$  is negligible on the time scale of interest; thus, as far as relaxation is concerned, we have to deal only with a two level system. The Hamiltonian has the form

$$H = H_0 + H_B + V, \quad (1)$$

where  $H_0$  is the Hamiltonian for the vibrational degrees of freedom of the isolated molecule,  $H_B$  that for bath (rotational and translational) degrees of freedom,

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and  $V$  couples the two. Note that we do not assume in our simulation that the coupling is weak or  $V$  small. We take  $\hbar\omega_0$  to be the energy level difference between the zero-order states  $\varphi_1$  and  $\varphi_2$ . In our simulation, we will assume that the bath can be described as a high temperature, classical, stochastic driving force so that in the interaction representation the vibrational system evolves under a time dependent Hamiltonian

$$H(t) = H_0 + V(t), \quad (2)$$

where the stochastic properties of  $V$  will be specified later. Note that  $V$  is an operator in the system degrees of freedom so that all of its matrix elements  $V_{11}$ ,  $V_{22}$ , and  $V_{12} = V_{21}$  are stochastic functions of the time. Simulations could be carried out for quantum mechanical baths but are more complicated and will not be considered in the present paper.

At any given time  $t$ , the Hamiltonian  $H(t)$  can be diagonalized to give the two level system ground state  $\psi_1(t)$  and excited state  $\psi_2(t)$ . Because of the strong mixing from  $V(t)$ ,  $\psi_1$  and  $\psi_2$  involve both  $\varphi_1$  and  $\varphi_2$ . If we have an ensemble of molecules in a bath with different local values for  $V(t)$ , the two zero-order states will mix to form two broadened vibrational states. There are two types of excitation which we could consider. In the first, coherent broad-band excitation could be used to excite a coherent superposition of the two excited states, giving rise to quantum beats and oscillations at the difference frequency. In the second, stimulated Raman scattering<sup>3</sup> could be used to excite only one of the two bands (the one with higher gain). We consider only the second type of excitation, so that we take the initially excited state to be  $\psi(t=0) = \psi_2(t=0)$ . In other words, the system is initially placed in the excited state of the Hamiltonian  $H(t)$  at time  $t=0$ . We will eventually average over the possible values for  $V(t)$  at  $t=0$ .

One potentially significant approximation which we have made should be noted. We have assumed that the interaction with the exciting light is strong enough and of short enough duration that the system is prepared in a true eigenstate at  $t=0$ . A more exact calculation would require a convolution over the time profile of the exciting pulse.

The subsequent time evolution of the quantum  $\psi(t)$  involves the full Hamiltonian  $H(t)$  and can be written

$$\psi(t) = \exp_0 \left[ i \int_0^t dt' H(t') \right] \psi_2(t=0), \quad (3)$$

where  $\exp_0$  is a time ordered exponential and  $H$  is an operator in the system degrees of freedom. Detection in most cases is carried out<sup>1-3</sup> by monitoring the time evolution of the spontaneous anti-Stokes Raman spectrum; ideally, we would like to calculate the evolution of the full spectrum  $I(\omega)$  as a function of the time elapsed after excitation, in which case we would expect to see the spectrum evolve from one with a single peak around  $\psi_2$  into a two peaked spectrum at equilibrium. In practice, this full calculation would be quite lengthy, so we monitor instead only the total intensity of the anti-Stokes Raman spectrum. We assume for sim-

plicity that only one of the zero order states  $\varphi_1$  and  $\varphi_2$  is directly coupled through a nonzero matrix element of the polarizability  $\alpha_{02}$ ;  $\alpha_{01}$  is taken to be zero. This choice is simply a matter of convenience; it would be equally easy to calculate the time evolution of the Raman scattering for  $\alpha_{01}$  nonzero. The total intensity as a function of time is then given by

$$I(t) \propto |\alpha_{02}|^2 \langle |\langle \varphi_2 | \psi(t) \rangle|^2 \rangle, \quad (4)$$

where the outer brackets refer to a statistical average over the states of the bath and the inner brackets to a projection of  $\psi(t)$  onto  $\varphi_2$ , where  $\psi(t)$  is given by Eq. (3). We can define a population evolution function by

$$P(t) = \langle |\langle \varphi_2 | \psi(t) \rangle|^2 \rangle. \quad (5)$$

At long times  $P(t)$  will reach the equilibrium value of  $P(\infty)$ . It is convenient to define a normalized correlation  $C(t)$  through

$$C(t) = [P(t) - P(\infty)] / [P(0) - P(\infty)] = \frac{\Delta P(t)}{\Delta P(0)}. \quad (6)$$

$C(t)$  decreases from 1 to 0 as  $t$  ranges from 0 to  $\infty$ .

To calculate the ensemble averages, we have carried out a series of  $N$  realizations for a particular stochastic process. For each realization  $k$ ,  $H_k(t)$  is obtained through a random number generator and from it the exact wave function  $\psi(t)$  is found at each time.  $P(t)$  is then obtained by projecting it onto  $\varphi_2$ , squaring, and then averaging over the different realizations  $k$ :

$$P(t) = \frac{1}{N} \sum_{k=1}^N |\langle \varphi_2 | \exp \left[ i \int_0^t dt' H_k(t') \right] | \psi_2^0 \rangle|^2. \quad (7)$$

If  $H_k(t)$  is constant for some interval of time and  $\psi(t)$  is known of the beginning of the interval, then it is straightforward to calculate  $\psi$  at all times during the interval. (This is done simply by finding the eigenfunctions of  $H_k$  during the interval, expressing the initial  $\psi$  in terms of them, and then propagating them forward in time under the influence of this constant  $H_k$ .) We can approximate a time dependent  $H(t)$  as a piecewise constant operator to arbitrary accuracy by taking the time intervals short enough so that the exact evolution of  $\psi(t)$  can then be calculated for each realization  $H_k$ .

The two state Poisson bath is particularly easy to simulate. In this model, the bath jumps between two states (which we will call + and -) at an average rate  $b/2$ . The probability that a jump will occur within a time  $t$  is given for a Poisson process by  $(2/b) \exp(-bt/2)$ . For simplicity, we take the average residence times in the + and - states to be equal, although it would be straightforward to generalize this. The coupling Hamiltonian matrix elements then jump between the two sets of values  $(V_{11}^+, V_{22}^+, V_{12}^+ = V_{21}^+)$  and  $(V_{11}^-, V_{22}^-, V_{12}^- = V_{21}^-)$ . Since the Hamiltonian is rigorously piecewise constant,  $\psi(t)$  is straightforward to generate. For each realization, we use a random number generator to obtain a series of times at which the bath changes states; we also choose at random whether it starts out in the + or - state.  $\psi(t)$  is calculated exactly at a series of times, projected onto  $\varphi_2$ , squared and then averaged

with the other  $N$  runs. We obtained good statistics after only a few thousand runs.

The Gaussian bath is only a bit more complicated to simulate. For a Gaussian process the matrix elements  $V_{ij}(t)$  change continuously so it is necessary to approximate them as piecewise constant in time. This gives a series of values of  $V_{ij}^n$  for each time step  $n$ . For a Gaussian process, we must take

$$V_{ij}^{n+1} = \exp(-bh) V_{ij}^n + \omega_{ij}^n, \quad (8)$$

where  $h$  is the time interval between step  $n$  and step  $n+1$ ,  $b$  is the time constant characteristic of the Gaussian process, and  $\omega_{ij}^n$  is a Gaussian random variable with mean square given by

$$\langle (\omega_{ij}^n)^2 \rangle = [1 - \exp(-2bh)] (V_{ij}^0)^2, \quad (9)$$

where  $V_{ij}^0$  defines the strength of the fluctuations in  $V_{ij}$ . In the limit  $h \rightarrow 0$  this describes a true Gaussian process; we carry out our simulations with values of  $h$  which are finite but small enough so that spurious effects are absent. A realization is obtained by generating a random series of values for  $\omega_{ij}^n$  with a Gaussian distribution<sup>6</sup>: from this  $V_{ij}^n$  is calculated and  $\psi(t_n)$ .  $P(t)$  is obtained by averaging over several thousand such realizations.

These simulations are of course much faster than full classical molecular dynamics simulations since they involve the quantum evolution of only a single molecule in a stochastic bath rather than the evolution of a large number of interacting molecules. A full molecular dynamics calculation would be more complicated but still feasible.

In the first pair of simulations the diagonal elements  $V_{11}$  and  $V_{22}$  were set to zero. In the Poisson case we chose

$$V_{12}^{\pm} = V_{21}^{\pm} = \pm V, \quad (10)$$

where  $V$  is the coupling strength of the potential, while in the Gaussian case we took  $V_{12}^0 = V_{21}^0 = V$ . We worked in dimensionless units in which  $b$ ,  $V$ , and  $t^{-1}$  are mea-

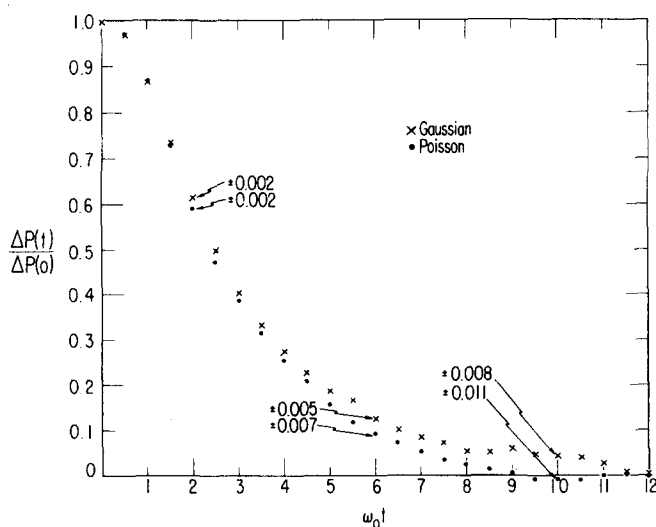


FIG. 1. Simulation results for  $V_{12} = 0.5$ ,  $V_{11} = V_{22} = 0$ ,  $b = 2.0$ .

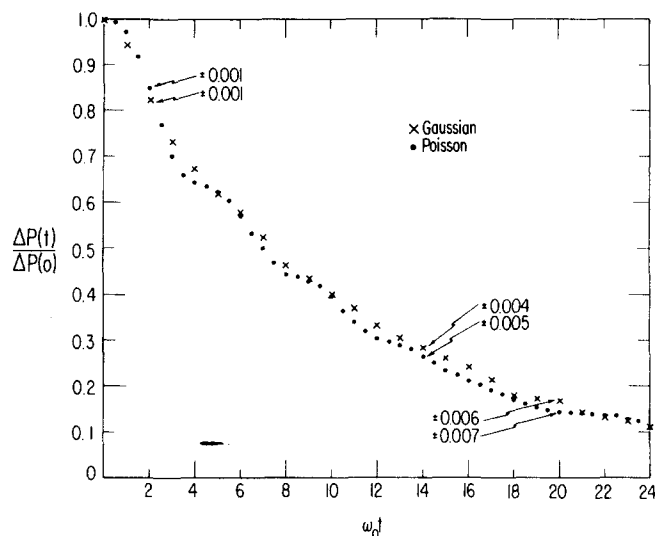


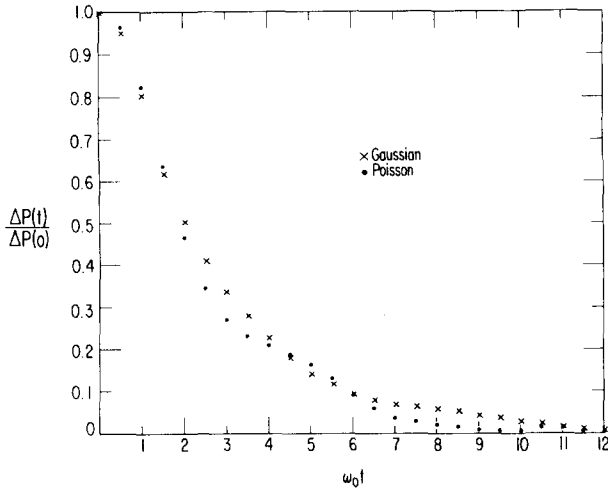
FIG. 2. Simulation results for  $V_{12} = 0.5$ ,  $V_{11} = V_{22} = 0$ ,  $b = 0.2$ .

sured in units of  $\omega_0$ , the frequency difference between states  $\varphi_1$  and  $\varphi_2$  in the isolated molecule. The Markovian limit corresponds to taking  $b$  large or  $V$  small. We chose  $V = 0.5$  and  $b = 2.0$  (see Fig. 1) or  $0.2$  (Fig. 2). As an example of "real" units, if the zero-order splitting were  $30 \text{ cm}^{-1}$ , this would imply root mean square fluctuations of  $V$  of  $15 \text{ cm}^{-1}$ , a bath relaxation time of  $0.08$  or  $0.8 \text{ psec}$ , and a time unit of  $0.17 \text{ psec}$ . The results shown in Figs. 1 and 2 reveal perhaps the most surprising result of this study: The gross details of both models (relaxation rate, for instance) are much the same, even though the Poisson and Gaussian models correspond to very different bath properties. Figure 1, which corresponds to a larger value of  $b$ , shows the simple decay expected at or near the Markovian limit, while in Fig. 2 the Poisson simulations show pronounced oscillations. That these oscillations are real and not a statistical artifact is shown by the error estimates on the figures, which were obtained by a calculation of the variance of  $\Delta P(t)/\Delta P(0)$  over the  $N$  realizations of each random process. The oscillation period is  $2\pi/\Delta\omega$ , where  $\Delta\omega$  is the frequency difference between the eigenstates of the full Hamiltonian. No detectable oscillations were found in the Gaussian simulation.

We performed a second simulation with  $V_{22} = V_{12}$  in order to test the effect of diagonal matrix element fluctuations on relaxation; the same values of  $V$  and  $b$  were used. In Figs. 3 and 4 are shown the results for  $b = 2.0$  and  $0.2$ . The differences between Poisson and Gaussian baths are somewhat larger, and the Poisson oscillations are enhanced. In this case, the frequency difference between  $\psi_2^*$  and  $\psi_1^*$  is not the same as that between  $\psi_2$  and  $\psi_1$ ; it is the larger of these two frequencies that characterizes the Poisson oscillations.

### III. THEORY

Let us define  $|\varphi_1(t)\rangle$  and  $|\varphi_2(t)\rangle$  as the time dependent wave function of a system that starts out in the state  $\varphi_1$  or  $\varphi_2$  at  $t = 0$  and subsequently evolves in time under the influence of the full Hamiltonian. Then

FIG. 3. Simulation results for  $V_{12} = V_{22} = 0.5$ ,  $V_{11} = 0$ ,  $b = 2.0$ .

$$|\psi_2(t)\rangle = C_1 |\varphi_1(t)\rangle + C_2 |\varphi_2(t)\rangle, \quad (11)$$

where  $C_1$  and  $C_2$  depend on the initial state of the bath over which one must eventually average. Then

$$\begin{aligned} |\langle \varphi_2 | \psi_2(t) \rangle|^2 &= C_1^2 |\langle \varphi_2 | \varphi_1(t) \rangle|^2 + C_2^2 |\langle \varphi_2 | \varphi_2(t) \rangle|^2 \\ &\quad + C_1 C_2 [\langle \varphi_2 | \varphi_1(t) \rangle \langle \varphi_2(t) | \varphi_2 \rangle \\ &\quad + \langle \varphi_2 | \varphi_2(t) \rangle \langle \varphi_1(t) | \varphi_2 \rangle]. \end{aligned} \quad (12)$$

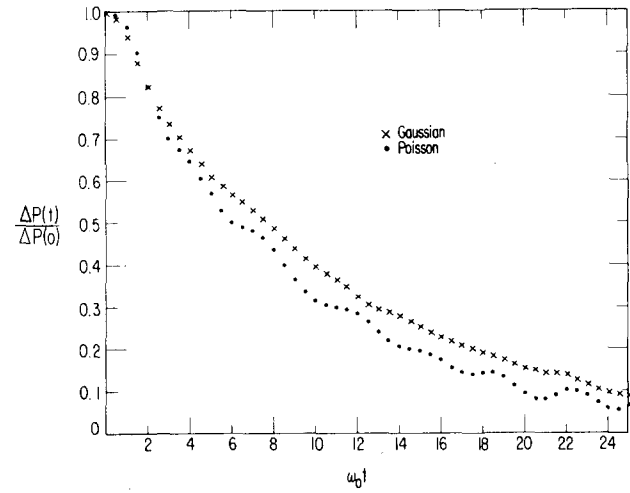
If we assume that the average in Eq. (12) can be separated into an average over the initial state and one over the subsequent bath evolution (the relaxation of this assumption will be discussed in the next section) and if we define<sup>7</sup> on operator  $G_{ij}$  by

$$G_{ij}(t) \equiv \langle |\varphi_i(t)\rangle \langle \varphi_j(t)| \rangle, \quad (13)$$

where the outer brackets refer to an average over the bath evolution, then the population relaxation of Eq. (12) which we seek to calculate is given by the  $2 \times 2$  matrix element of

$$\overline{C_1^2 G_{11}(t)} + \overline{C_2^2 G_{22}(t)} + \overline{C_1 C_2 [G_{21}(t) + G_{12}(t)]}. \quad (14)$$

At long times, states  $\varphi_1$  and  $\varphi_2$  are equally likely to be populated (for a classical bath) so the asymptotic value will be  $1/2$ . We therefore have

FIG. 4. Simulation results for  $V_{12} = V_{22} = 0.5$ ,  $V_{11} = 0$ ,  $b = 0.2$ .

$$\begin{aligned} \frac{\Delta P(t)}{\Delta P(0)} &= (\overline{C_1^2} - \frac{1}{2})^{-1} [\overline{C_1^2} \langle \varphi_2 | G_{11}(t) | \varphi_2 \rangle + \overline{C_2^2} \langle \varphi_2 | G_{22}(t) | \varphi_2 \rangle \\ &\quad + \overline{C_1 C_2} \langle \varphi_2 | G_{21}(t) + G_{12}(t) | \varphi_2 \rangle - \frac{1}{2}]. \end{aligned} \quad (15)$$

We now discuss several approximate ways of calculating the time evolution of the operators  $G_{ij}(t)$ . All of them involve a knowledge of the correlation function of  $V_{ij}(t)$ ; it is straightforward to show that for both the Poisson and Gaussian processes

$$\langle V_{ij}(t) V_{ij}(0) \rangle = V^2 \exp(-bt). \quad (16)$$

The two processes differ in their higher-order correlation functions, but our hope is that since the simulation results are so similar the relaxation will be insensitive to correlation functions of higher than second order. We will discuss both cumulant expansion and projection operator techniques. It has been shown<sup>8</sup> for *dephasing* of a two level system that these approaches differ only in their assumptions about which higher-order correlations to retain; it is possible therefore that they can provide a reasonable description of non-Markovian relaxation.

#### A. Cumulant expansion

An equation of motion for the operator  $G_{ki}(t)$  was derived by us in Ref. 7 using cumulant expansion techniques. It is

$$\begin{aligned} \frac{d}{dt} G_{ki}(t) &= i\omega_{ki} G_{ki}(t) - \sum_{j,l} \int_0^t d\tau [e^{i\omega_{kl}\tau} \langle V_{ji}(\tau) V_{lk} \rangle G_{ji}(t) \\ &\quad - e^{i\omega_{kl}\tau} \langle V_{lk} V_{ji}(\tau) \rangle G_{ij}(t) - e^{i\omega_{jl}\tau} \langle V_{ik}(\tau) V_{lj} \rangle G_{ij}(t) + e^{i\omega_{jl}\tau} \langle V_{lj} V_{ik}(\tau) \rangle G_{ki}(t)]. \end{aligned} \quad (17)$$

For simplicity we look at the case  $\langle V \rangle = 0$  and  $V_{22} = V_{11} = 0$  (corresponding to Figs. 1 and 2). In this case it is straightforward to show that

$$\langle 2 | G_{12}(t) | 2 \rangle = \langle 2 | G_{21}(t) | 2 \rangle = 0 \quad (18)$$

and

$$\langle 2 | G_{11}(t) + G_{22}(t) | 2 \rangle = 1 \quad (19)$$

for all times. Therefore,

$$\frac{\Delta P(t)}{\Delta P(0)} = 2 [\langle 2 | G_{22}(t) | 2 \rangle - \frac{1}{2}] \quad (20)$$

for this case and ( $\omega_{12}=1$ )

$$\langle 2 | \dot{G}_{22}(t) | 2 \rangle = \left[ -4 \int_0^t dt_1 \langle V_{12}(t_1) V_{21} \rangle \cos t_1 \right] \langle 2 | G_{22}(t) | 2 \rangle + 2 \int_0^t dt_1 \langle V_{12}(t_1) V_{21} \rangle \cos t_1. \quad (21)$$

After inserting Eq. (16) we can solve this linear differential equation to obtain

$$\frac{\Delta P(t)}{\Delta P(0)} = \exp \left\{ -\frac{4V^2 b t}{1+b^2} - \frac{4V^2}{(1+b^2)^2} [(b^2-1) \cos t - 2b \sin t] e^{-bt} + \frac{4V^2}{(1+b^2)^2} (b^2-1) \right\}. \quad (22)$$

## B. Memory function formalism

To arrive at a description of the relaxation process in terms of memory functions, we start with the identity<sup>9</sup>

$$\dot{e}^{iLt} = i e^{i(1-P)L} (1-P)L + i e^{i(1-P)L} PL - \int_0^t d\tau e^{i(t-\tau)L} PL e^{i\tau(1-P)L} (1-P)L. \quad (23)$$

Here  $L$  is the full Liouville operator

$$LX = [H_0 + H_B + V, X], \quad (24)$$

where  $X$  is an arbitrary operator.  $P$  is any projection operator and must satisfy the condition

$$P^2 X = PX. \quad (25)$$

We choose in the present case  $PX = \langle X \rangle$ , where the average is with respect to the bath Hamiltonian. Again  $\langle V \rangle$  is assumed zero. Multiplying Eq. (23) by  $|\varphi_k\rangle\langle\varphi_l|$  and averaging over the bath yields

$$\begin{aligned} \dot{G}_{kl}(t) = & iP e^{i(1-P)L} (1-P)L |\varphi_k\rangle\langle\varphi_l| \\ & + iP e^{i(1-P)L} PL |\varphi_k\rangle\langle\varphi_l| \\ & - \int_0^t d\tau P e^{i(t-\tau)L} PL e^{i\tau(1-P)L} (1-P)L |\varphi_k\rangle\langle\varphi_l|. \end{aligned} \quad (26)$$

The first term is zero since

$$P(1-P)X = 0. \quad (27)$$

The second term is  $i\omega_{kl} G_{kl}(t)$  since

$$\langle V_{ij} \rangle = 0 = PV_{ij} \quad (28)$$

and

$$\omega_{kl} = \langle k | H_0 | k \rangle - \langle l | H_0 | l \rangle. \quad (29)$$

To evaluate the last term note that

$$(1-P)LX = (1-P)[H_0, X] + (1-P)[V, X] \quad (30)$$

if  $X$  involves the isolated molecule wave functions only. Since

$$PL_0X = L_0PX \quad (31)$$

and

$$P[V, X] = PV^X X = 0, \quad (32)$$

the last term can be written as

$$\begin{aligned} \int_0^t d\tau K(t, \tau) &= \int_0^t d\tau P e^{i(t-\tau)L} P V^X e^{i\tau(1-P)L} V^X |\varphi_k\rangle\langle\varphi_l| \\ &\approx \int_0^t d\tau P e^{i(t-\tau)L} P V^X \bar{V}^X(\tau) |\varphi_k\rangle\langle\varphi_l| e^{i\omega_{kl}\tau} \\ &= \int_0^t d\tau \langle e^{i(t-\tau)L} \langle V^X \bar{V}^X(\tau) \rangle |\varphi_k\rangle\langle\varphi_l| \rangle e^{i\omega_{kl}\tau}, \end{aligned} \quad (33)$$

which is exact to second order in  $V$  and

$$\bar{V}(\tau) = e^{iL_0\tau} V \quad (34)$$

where

$$L_0X = [H_0 + H_B, X]. \quad (35)$$

Performing the required commutations leads to

$$\begin{aligned} K(t, \tau) = & \sum_{i,j} [\langle V_{ji} V_{ik}(\tau) \rangle G_{ji}(t-\tau) e^{i\omega_{ji}\tau} - \langle V_{ik}(\tau) V_{ij} \rangle G_{ij}(t-\tau) e^{i\omega_{ij}\tau} \\ & - \langle V_{jk} V_{il}(\tau) \rangle G_{ji}(t-\tau) e^{i\omega_{kl}\tau} + \langle V_{il}(\tau) V_{ij} \rangle G_{kj}(t-\tau) e^{i\omega_{kl}\tau} ]. \end{aligned} \quad (36)$$

Again for  $k \neq l$  and  $V_{11} = V_{22} = 0$ ,

$$\langle 2 | G_{21}(t) | 2 \rangle = \langle 2 | G_{12}(t) | 2 \rangle = 0 \quad (37)$$

for all times. For the classical case where

$$\langle V V(t) \rangle = \langle V(t) V \rangle \quad (38)$$

we have ( $\omega_{12}=1$ )

$$\begin{aligned} \langle 2 | \dot{G}_{22}(t) | 2 \rangle &= -4 \int_0^t dt_1 \langle V_{12} V_{21}(t_1) \rangle \cos t_1 \langle 2 | G_{22}(t-t_1) | 2 \rangle + 2 \int_0^t dt_1 \langle V_{12} V_{21}(t_1) \rangle \cos t_1 \\ &= \int_0^t dt_1 f(t_1) \langle 2 | G_{22}(t-t_1) | 2 \rangle + \int_0^t dt_1 \frac{f(t_1)}{2}. \end{aligned} \quad (39)$$

Using the required form for  $\langle V_{12} V_{21}(t) \rangle$ , a Laplace transform results in

$$\frac{\Delta \hat{P}(s)}{\Delta P(0)} = \{s[s+b]^2 + 1\} + 4V^2(s+b)^{-1}[(s+b)^2 + 1] \quad (40)$$

or

$$\frac{\Delta P(t)}{\Delta P(0)} = A e^{-z_1 t} + B e^{-z_2 t} + C e^{-z_3 t} \quad (41)$$

where  $z_1, z_2, z_3$  are the roots of the denominator of Eq. (40) and  $A, B, C$  the corresponding residues.

### C. Conventional rate laws

The usual rate expressions can be obtained from the cumulant expansion by letting  $t \rightarrow \infty$  in the integral and in the memory function approach by letting  $s \rightarrow 0$  in the transformed memory kernel

$$\hat{f}(s) \rightarrow \hat{f}(0). \quad (42)$$

Either way yields

$$\frac{\Delta P(t)}{\Delta P(0)} = \exp\left(-\frac{4V^2 b t}{1+b^2}\right). \quad (43)$$

### D. Comparison with simulations

Figures 5 and 6 show the comparison of the simulations with the various theories for the case where only off-diagonal terms are present ( $V = 0.5$ , and  $b = 2.0$  or  $0.2$ ). For the larger value of  $b$  (Fig. 5) all the theories give good results, especially in the long time regime, with the cumulant expansion perhaps slightly better than the others. Figure 6 shows, however, that when  $b$  is smaller and non-Markovian effects are larger none of the approximate theories is successful. The envelope of the memory function formalism follows the simulations reasonably well, and its oscillations match those of the Poisson simulation, but their amplitude is much too large. It is clear that none of these simple theories provides an adequate description of non-Markovian effects on relaxation.

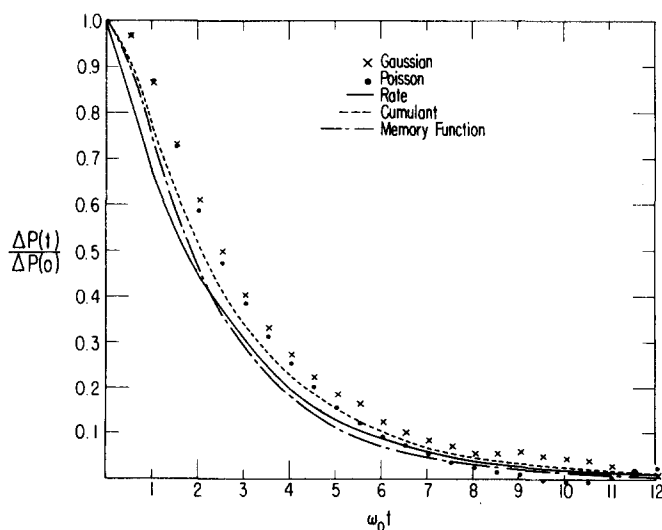


FIG. 5. Comparison of theories with simulation for  $V_{12} = 0.5$ ,  $V_{11} = V_{22} = 0$ ,  $b = 2.0$ .

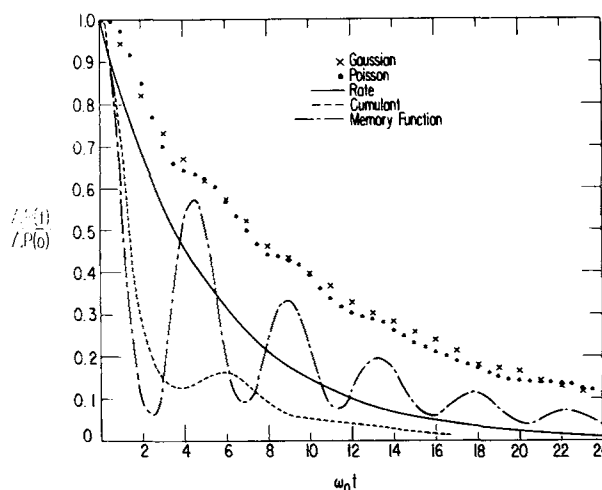


FIG. 6. Comparison of theories with simulation for  $V_{12} = 0.5$ ,  $V_{11} = V_{22} = 0$ ,  $b = 0.2$ .

## IV. DISCUSSION

Since the truncation of a cumulant expansion at second order is exact for a Gaussian process, one might expect the approach of Sec. III. A to provide a good description of the relaxation in that case; its failure indicates the importance of the other approximation made in Sec. III, namely, the separability of the dynamical averaging from the static average over bath states at  $t = 0$ . This can be seen from another point of view by examining the limit  $b \rightarrow 0$ . In this limit, in which the bath state does not change, the molecule will remain in the initial state forever and  $\Delta P(t)/\Delta P(0)$  will simply be unity. Use of Eq. (22), however, incorrectly predicts oscillations in this function. The reason is that in separating the averages one discards knowledge about the initial state of the bath; in a slowly relaxing bath the dynamical evolution is dependent on the initial state, so that unphysical oscillations result.

To avoid this problem, we have generalized the cumulant expansion as follows: For a given initial bath state  $V_0$ , we calculated the first two cumulants as constrained averages subject to the condition  $V_0$ :

$$\langle V(t) \rangle_{V_0} \text{ and } \langle V(t) V(t_1) \rangle_{V_0} - \langle V(t) \rangle_{V_0} \langle V(t_1) \rangle_{V_0}. \quad (44)$$

These are no longer stationary correlation functions. We then used these in a generalized version of Eq. (47) and obtained three coupled linear differential equations. These were solved numerically and  $\Delta P(t)/\Delta P(0)$  calculated, and only then were the initial conditions averaged over. This approach has certain desirable features: As  $b \rightarrow \infty$ , it gives the correct Markovian limit, and as  $b \rightarrow 0$  it gives the correct non-relaxing limit (in contrast to the unphysical oscillations arising from the simple cumulant approach). For intermediate values of  $b$ , however, the numerical results (for the Poisson bath) were poor, giving too slow a relaxation and oscillations that were too pronounced. This potentially promising approach to the problem of initial conditions therefore gives disappointing results.

Some basic theoretical problems remain: first, to account for the similarity of the results for the Poisson

and Gaussian baths, and second to account for the presence but small amplitude of the oscillations in the Poisson bath. These are questions which any comprehensive theory of strongly coupled systems must resolve.

The simulations we have carried out are novel in that they combine a classical stochastic simulation of the bath with a fully quantum mechanical treatment of the vibrational degrees of freedom. The techniques could be extended to study more realistic bath models (obtained for example from full molecular dynamics simulations) or to more general vibrational level structures such as three level systems. As such they provide a promising method for the study of non-Markovian effects on relaxation.

A final question is whether the oscillations which appear in some of the simulations will be experimentally observable. It is clear from the figures that this will pose substantial problems in time and signal resolution which may be difficult to overcome. The fact that they appear primarily in the Poisson case suggests that they may be a "ringing" phenomenon like that which arises from the sudden change of an external potential. In this case, one would expect to see oscil-

lations only in cases where the bath jumps relatively rapidly between well-defined states.

## ACKNOWLEDGMENT

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