

Time evolution of the average energy of a relaxing molecule*

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Evolution equations for the average energy of a harmonic oscillator in interaction with a bath are derived and solved for two cases: (a) when the probability evolution obeys a master equation with a *true decay* representing a *sink-process* like radiative emission occurring simultaneously with vibrational relaxation, and (b) when the Markoffian approximation in the Heisenberg-equation analysis of relaxation is not made, allowing for short-time effects.

I. INTRODUCTION

Recent theoretical investigations of the vibrational relaxation of molecules, with or without other accompanying processes, have proceeded from master equations,¹⁻⁴ Heisenberg equations,⁵ or other starting points,⁶ and have often modeled the relaxing molecule as a harmonic oscillator. We have developed a general master-equation framework^{4b} capable of analyzing the *simultaneous* processes of radiative emission (or radiative absorption, or transfer) and relaxation, which is similar to some work of Freed and Heller,³ and we have reported some of its consequences in the context of initial Boltzmann distributions.^{4a} Here we derive evolution equations for the average energy, or alternatively the mean occupation number, of the harmonic oscillator, which display the effects of true sinks on the master-equation results (Sec. II) and of non-Markoffian terms on the Heisenberg-equation expressions (Sec. III).

Although the mean occupation number is a much more simplified entity relative to the complete state, it contains major physical information in the simple system of a harmonic oscillator, since, for instance, it is essentially identical to the average energy of the system. It has therefore received a good deal of attention in earlier analyses,^{1,5} and it will be the sole quantity of interest in this paper.

The evolution of the mean occupation number is known¹ when the probabilities of occupation of the oscillator states are taken to obey a closed master equation with nearest-neighbor rates: the Montroll-Shuler equation.¹ It is also known⁵ from the Heisenberg equations of motion that may be derived for the ladder operators of the oscillator under standard approximations and assumptions concerning the interaction with the bath. The two results are identical: the mean occupation number has a simple exponential decay from its initial to its thermalized value. This is a remarkable result since, for instance, the *probability* evolu-

tion from the master equation is extremely complicated and generally involves hypergeometric functions.

In this paper we study the effects of two *separate* generalizations of earlier analyses. In Sec. II we derive equations for the mean occupation number when a process involving a sink for the oscillator probability occurs simultaneously with the vibrational relaxation. The evolution is seen to lose its simplicity on account of the sink and to have an interesting structure. In Sec. III we return to the sink-less system but explore the consequences of relaxing the Markoffian approximation in the context of the Heisenberg-equation analysis⁵ of Nitzan and Jortner, and Nitzan and Silbey. The work described in Sec. II is relevant to those situations wherein the time scales of vibrational relaxation and an accompanying sink process, such as radiative or nonradiative decay or excitation transfer, are not disparately different. The work reported in Sec. IV is in the spirit of an earlier analysis⁷ by one of the authors in the context of Glauber's ferromagnet model⁸ and its relevance depends on the nature of the interaction of the molecule with the bath.⁹ Recently reported⁹ relaxation times appear, however, to be long enough to allow the *possibility* of observing non-Markoffian effects.

II. EVOLUTION FROM MASTER EQUATION WITH TRUE DECAY

Montroll and Shuler¹ proposed and solved the following master equation:

$$\frac{dP_m}{dt} = k[(m+1)P_{m+1} + me^{-\beta}P_{m-1} - \{m + (m+1)e^{-\beta}\}P_m], \quad (1)$$

where $P_m(t)$ is the probability that the m th level of the oscillator is occupied at time t , $\beta = \hbar\omega/k_B T$, ω and T are the oscillator frequency and temperature, respectively, and k is dependent

on the nature of the bath and its interaction with the oscillator. Vibration relaxation described thus does not entail a true decay of the probability: there being no sink (or source) in the system, it is globally conserved. In order to study relaxation in the presence of emission, transfer, or a similar process involving a true decay of the probability, the following extension^{3,4} of the Montroll-Shuler equation naturally suggests itself:

$$\frac{dP_m}{dt} + \alpha_m P_m = k[(m+1)P_{m+1} + me^{-\beta}P_{m-1} - \{m + (m+1)e^{-\beta}\}P_m]. \quad (2)$$

The solutions of Eq. (2) are trivial generalizations of those of Eq. (1) if α_m is m independent; and they are both important¹⁰ and can be obtained explicitly^{3,4} if α_m is linearly dependent on m . Here we take

$$\alpha_m = b + cm, \quad (3)$$

with b and c as constants. Equations (2) and (3) yield

$$\frac{1}{ke^{-\beta}} \frac{\partial G(z, t)}{\partial t} = (z-1)G(z, t) + \{z^2 - z(e^\beta + 1 + \delta) + e^\beta\} \frac{\partial G(z, t)}{\partial z} \quad (4)$$

for the Green's function

$$G(z, t) = \sum_{m=0}^{\infty} z^m P_m(t) e^{bt}, \quad (5)$$

with $\delta = e^\beta c/k$. The mean occupation number $\langle n(t) \rangle$ and the total probability $Q(t)$ are related to the Green's function through

$$\langle n(t) \rangle \equiv \sum_{n=0}^{\infty} n P_n(t) = e^{-bt} \left\{ \text{Lim}_{z \rightarrow 1} \frac{\partial G(z, t)}{\partial z} \right\} \equiv e^{-bt} G'(1, t), \quad (6a)$$

$$Q(t) \equiv \sum_{n=0}^{\infty} P_n(t) = e^{-bt} \left\{ \text{Lim}_{z \rightarrow 1} G(z, t) \right\} \equiv e^{-bt} G(1, t). \quad (6b)$$

Defining

$$G''(1, t) \equiv \text{Lim}_{z \rightarrow 1} \frac{\partial^2 G(z, t)}{\partial z^2}$$

and taking the limit $z \rightarrow 1$ of Eq. (4) before and after differentiation with respect to z , we obtain

$$\frac{dG(1, t)}{dt} + cG'(1, t) = 0 \quad (7a)$$

$$\frac{1}{ke^{-\beta}} \frac{dG'(1, t)}{dt} + (e^\beta - 1 + \delta)G'(1, t) + \delta G''(1, t) = G(1, t). \quad (7b)$$

Equations (7) are particular cases of a general hierarchy of equations that can be derived^{1b} for the moments of the probability by repeated differentiation of the Green's function. It is seen that the members of the hierarchy are interconnected and the equation for a given moment is, therefore, not closed, the evolution depending on a higher and a lower moment. From Eqs. (6) and (7) we have

$$\frac{dQ}{dt} + bQ + c\langle n(t) \rangle = 0, \quad (8a)$$

$$\frac{d\langle n \rangle}{dt} + \{b + k(1 - e^{-\beta})\} \langle n \rangle + c\langle n^2 \rangle = ke^{-\beta}Q, \quad (8b)$$

where use has been made of the relation

$$G''(1, t) = \langle n^2 \rangle - \langle n \rangle, \quad (9)$$

with

$$\langle n^2 \rangle \equiv \sum_{n=0}^{\infty} n^2 P_n(t).$$

Equations (8) possess an interesting structure: The total probability Q decays through the constant rate b and feeds the mean occupation number $\langle n \rangle$ through c , the coefficient of the linear term in α_m . Similarly $\langle n \rangle$ feeds the higher moment $\langle n^2 \rangle$ through c , gains from the lower moment $\langle n^2 \rangle$ through the "upward" rate $ke^{-\beta}$, and decays through $\{b + k(1 - e^{-\beta})\}$ which is the sum of b and the difference between the "downward" and "upward" rates of relaxation. These equations are reminiscent of the BBGKY hierarchy for reduced distribution functions and, in fact, constitute an example of mode-mode coupling.

Equations (8) do not allow explicit solutions for $\langle n(t) \rangle$ unless $Q(t)$ and $\langle n^2(t) \rangle$ are known *a priori*. It is possible, however, to close the equations for some particular initial probability distributions. Thus, for the case $P_r(0) = \delta_{r,m}$, on defining $\langle n \rangle_m$ and Q_m as the moment and the total probability for this distribution (initially localized on m), Eq. (8b), rewritten as

$$\frac{d\langle n \rangle_m}{dt} + \{b + k(1 - e^{-\beta})\} \langle n \rangle_m + c\langle n^2 \rangle_m = ke^{-\beta}Q_m \quad (8b')$$

is reduced to the closed equation

$$\frac{d\langle n \rangle_m}{dt} + \{b + c + k(1 - e^{-\beta})\} \langle n \rangle_m = \{ke^{-\beta} + B_m(t)\} Q_m, \quad (9)$$

where

$$B_m(t) = D(t) \{ (M - N)(M' - N') \}^{-2} \times [m^2 (NM' - MN')^2 + m \{ N^2 (M' - N')^2 + N'^2 (M - N)^2 + 2N'(M - N)(MN' - NM') \} + 2N'^2 (M - N)^2], \quad (10a)$$

$$D(t) = (\Gamma^+ - \Gamma^-) \exp[k e^{-\beta} (\Gamma^- - 1)t]. \quad (10b)$$

Here we have used the result^{3,4b}

$$G(z, t) = D(t) (M - zN)^m (M' - zN')^{-(m+1)} \quad (11)$$

and the symbols in Eqs. (10), (11) are given by

$$M = e^\beta N' = e^\beta (1 - e^{-\tau}), \quad (12a)$$

$$M' = \Gamma^+ - e^{-\tau} \Gamma^-, \quad (12b)$$

$$N = \Gamma^- - e^{-\tau} \Gamma^+, \quad (12c)$$

$$\Gamma^+ = \frac{1}{2}(e^\beta + 1 + \delta) + \left\{ \frac{1}{4}(e^\beta + 1 + \delta)^2 - e^\beta \right\}^{1/2}, \quad (12d)$$

$$\Gamma^- = \frac{1}{2}(e^\beta + 1 + \delta) - \left\{ \frac{1}{4}(e^\beta + 1 + \delta)^2 - e^\beta \right\}^{1/2}, \quad (12e)$$

$$\tau = (\Gamma^+ - \Gamma^-) k e^{-\beta} t. \quad (12f)$$

Simpler equations may be obtained from Eq. (9) for certain initial distributions by using

$$\langle n \rangle = \sum_r \langle n \rangle_r P_r(0), \quad (13a)$$

$$Q = \sum_r Q_r P_r(0). \quad (13b)$$

As an example we treat an initial Boltzmann distribution

$$P_r(0) = e^{-r\beta_0} (1 - e^{-\beta_0}), \quad (14)$$

at a nonenvironment temperature

$$T_0 \equiv \hbar\omega/k_B\beta_0 \neq \hbar\omega/k_B\beta = T.$$

On multiplying Eq. (9) by $(1 - e^{-\beta_0})e^{-m\beta_0}$, summing over m and utilizing the identity

$$\sum_{m=0}^{\infty} m^s e^{-\beta_0 m} Q_m = \frac{D(t)}{M' - N'} \frac{\partial^s \{ (1 - e^{-\beta_0 + \mu})^{-1} \}}{\partial (-\beta_0)^s}, \quad (15)$$

where $\mu = \ln[(M - N)/(M' - N')]$, we obtain

$$\frac{d\langle n \rangle}{dt} + \{ b + c + k(1 - e^{-\beta}) \} \langle n \rangle = k e^{-\beta} Q - 2c \frac{\langle n \rangle^2}{Q}. \quad (16)$$

Although nonlinear, this equation, along with Eq. (8a), describes the closed evolution of the pair Q and $\langle n \rangle$. Furthermore the two equations can be used to obtain an integro-differential equation for $\langle n \rangle$ alone. The solution of this equation, which may also be arrived at directly^{4b} from the Green's function pertinent to an initial Boltzmann distribution, is

$$\langle n(t) \rangle = Y(t) e^{-\beta(t)} \{ 1 - e^{-\beta(t)} \}^{-2}, \quad (17a)$$

$$\beta(t) = \ln \left(\frac{\Gamma^+ (1 - e^{-\beta_0} \Gamma^-) - e^{-\tau} \Gamma^- (1 - e^{-\beta_0} \Gamma^+)}{(1 - e^{-\beta_0} \Gamma^-) - e^{-\tau} (1 - e^{-\beta_0} \Gamma^+)} \right), \quad (17b)$$

$$Y(t) = (1 - e^{-\beta_0}) \{ \Gamma^+ (1 - e^{-\beta_0} \Gamma^-) - e^{-\tau} \Gamma^- (1 - e^{-\beta_0} \Gamma^+) \}^{-1} \{ \Gamma^+ - \Gamma^- \} \times \exp \{ -t [b + k e^{-\beta} (1 - \Gamma^-)] \}. \quad (17c)$$

We have proved earlier^{4a} that an initial Boltzmann distribution maintains its Boltzmann form throughout the decay process and that $\hbar\omega/k_B\beta(t)$ can be viewed as a time-dependent temperature. This is seen from the form of Eq. (17a). The evolution equation for the dimensionless inverse temperature $\beta(t)$ may be obtained from Eq. (17b), or otherwise, as

$$- \frac{1}{k e^{-\beta}} \frac{d\beta(t)}{dt} = -\delta + 4 e^{\beta/2} [\sinh \frac{1}{2} \beta(t)] \times [\sinh \frac{1}{2} \{\beta(t) - \beta\}]. \quad (18)$$

As we pointed out earlier,^{4a} $T(0)$ equals the temperature characterizing the initial distribution, but $T(\infty)$ is less than the environment temperature. This interesting result which is relevant to the Stepanov problem,¹¹ is also reflected in the evolution of the quantity $\chi(t) \equiv (e^{\beta(t)} - 1)^{-1}$, which we have plotted in Fig. 1. This quantity gives the moment $\langle n(t) \rangle$ when multiplied by a normalizing factor and the decay term $Y(t)$, equals the moment in the absence of the sink, and may thus be called the quasimoment. The equation obeyed

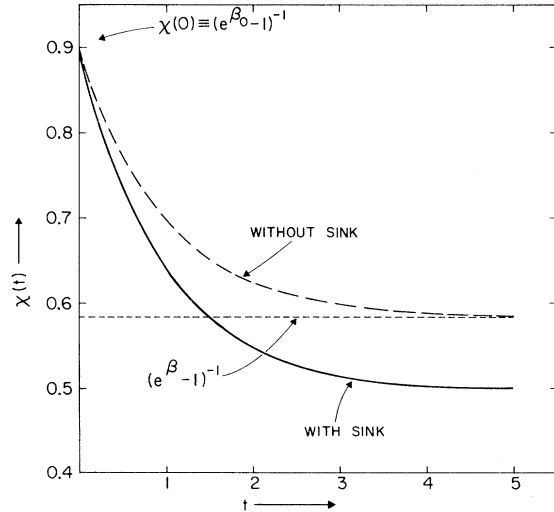


FIG. 1. Quasimoment $\chi(t) \equiv (e^{\beta(t)} - 1)^{-1}$ in the presence and absence of the sink process plotted as a function of time t in units of $k e^{-\beta} (\Gamma^+ - \Gamma^-)$. Parameter values are arbitrary: $c = 0.2$, $\hbar\omega/k_B T_0 = \beta_0 = 0.75$, and $\hbar\omega/k_B T = \beta = 1.0$.

by this quasimoment follows from Eqs. (17);

$$\frac{1}{k e^{-\beta}} \frac{d\chi(t)}{dt} = [1 + (1 - e^{-\beta})\chi(t)] - \delta\chi(t)[1 + \chi(t)]. \quad (19)$$

The effect of the sink process on the evolution of the average energy of the relaxing oscillator (molecule) may be studied from Eqs. (8) and (16)–(19). A level-independent sink term ($c=0$) imposes a simple exponential time dependence on the total probability $Q(t)$ [see Eq. (8a)] and the effect on the average energy is also straightforward [see Eq. (8b)]. A level-dependent sink-term “opens” the equation for $Q(t)$, connects $\langle n(t) \rangle$ to $\langle n^2(t) \rangle$ and complicates the evolution. Closing the evolution in the manner of Eq. (9) does not result in significant simplification because the terms $B_m(t)$, although known, are quite complex. Specific initial conditions do simplify the evolution as in the initial Boltzmann case: Eq. (16). We note that the nonlinear term in this equation, as well as in Eq. (19) is proportional to c , which characterizes the level dependence of the sink term. The effect of the sink is particularly transparent in Eqs. (16) and (19). Figure 1 compares the solutions of (19) with and without the sink term, for arbitrary values of the parameters.

III. EVOLUTION FROM HEISENBERG EQUATIONS AND CUMULANT TECHNIQUES

Nitzan and Jortner⁵ studied vibrational relaxation by developing Heisenberg equations of motion for the ladder operators a and a^\dagger which lower or raise the oscillator state. With harmonic oscillators representing the bath and using the rotating-wave and the random-phase approximations, they obtained

$$a(t) = u(t)a + \sum_{\nu} v_{\nu}(t)B_{\nu}, \quad (20)$$

where B_{ν} is a bath operator and $u(t)$ and $v_{\nu}(t)$ are c -number functions given by

$$\tilde{u}(\epsilon) = [\epsilon + i\omega + \tilde{\eta}(\epsilon)]^{-1} \quad (21)$$

$$\tilde{v}_{\nu}(\epsilon) = -iG_{\nu}(\epsilon + i\omega_{\nu})^{-1}\tilde{u}(\epsilon). \quad (22)$$

ω_{ν} 's are frequencies (or combinations of them) of the bath oscillators, G_{ν} is an interaction matrix element and the function $\eta(t)$, given by

$$\eta(t) = \sum_{\nu} |G_{\nu}|^2 e^{-i\omega_{\nu}t} \quad (23)$$

plays the role of a “memory function.”¹² Here ϵ is the Laplace variable and tildes denote Laplace transforms. A further approximation¹³ on the evolution of the number operator $a^\dagger a$, obtained

as a consequence of Eq. (20), then gives for the evolution of the mean occupation number

$$\langle n(t) \rangle = \langle n(0) \rangle |u(t)|^2 + \langle n(\infty) \rangle [1 - |u(t)|^2]. \quad (24)$$

The analysis in Ref. 5 obtains

$$u(t) = e^{-(i\omega + \gamma)t} \quad (25)$$

for substitution in Eq. (24) and thus essentially makes the “Markoffian” approximation in Eq. (21) whereby the Laplace transform $\tilde{\eta}(\epsilon)$ is replaced by its value $\tilde{\eta}(-i\omega) = \gamma$ at $\epsilon = -i\omega$. While this may be an excellent approximation for a given system, it depends on its validity on width properties of the density of states and of the interaction G_{ν} . Our interest here lies in studying the consequences of *relaxing* that approximation. Since $u(0) = 1$ it is clear that $u(t)$ is given in general by

$$\frac{du(t)}{dt} + i\omega u(t) + \int_0^t dt' \eta(t-t')u(t') = 0, \quad (26)$$

and the deviation of the solution of Eq. (26) from Eq. (25) corresponds to the difference between the last term in Eq. (26) and $[\int_0^{\infty} dt' \eta(t')e^{i\omega t'}]u(t)$. This deviation would be absent if $\eta(t) = \gamma\delta(t)$, and this would correspond to $|G_{\nu}|^2\rho_{\nu}$, the product of $|G_{\nu}|^2$ and the density of states ρ_{ν} , being independent of ω_{ν} . Generally the form of this function determines $\eta(t)$ through the Fourier transform

$$\eta(t) = \int d\omega' \rho(\omega') |G(\omega')|^2 e^{-i\omega' t}, \quad (23')$$

which is Eq. (23) rewritten in the integral form with $\rho_{\nu} \rightarrow \rho(\omega')$, $G_{\nu} \rightarrow G(\omega')$, etc. Here $\rho(\omega')$ will be a smooth function only in the continuum limit and the integral spans the frequency range of the bath oscillators.

For the particular model consisting of a (displaced) Lorentzian dependence of $|G_{\nu}|^2\rho_{\nu}$ on ω_{ν}

$$|G_{\nu}|^2\rho_{\nu} = (\gamma\lambda^2/\pi)[\lambda^2 + (\omega - \omega_{\nu})^2]^{-1} \quad (27)$$

Eq. (23), gives¹⁴

$$\eta(t) = \gamma\lambda e^{-(\lambda+i\omega)t}, \quad (28)$$

which, on substitution in Eq. (26), yields

$$u(t) = e^{-(\lambda/2+i\omega)t}(2\xi)^{-1}(\lambda \sinh \xi t + 2\xi \cosh \xi t), \quad (29a)$$

$$\xi = \frac{1}{2}(\lambda^2 - 4\gamma\lambda)^{1/2}. \quad (29b)$$

Equations (29) and (24) then give

$$\langle n(t) \rangle = \langle n(\infty) \rangle + [\langle n(0) \rangle - \langle n(\infty) \rangle] (1/4 |\xi|^2) \times e^{-\lambda t} |(\lambda \sinh \xi t + 2\xi \cosh \xi t)|^2. \quad (30)$$

This time dependence of the moment $\langle n \rangle$ is more general than that in Ref. 5 and reduces to it: (i)

in the limit $\lambda \rightarrow \infty$, and also (ii) as $t \rightarrow \infty$ at finite λ 's. Equations (30) and (24) have been plotted in Fig. 2 with arbitrary parameter values. Our Eq. (30) contains short-time information not present in Eq. (24), and its form depends as shown on the specific frequency dependence of the interaction matrix elements, and the density of states. This information is, however, obviously unimportant if λ is very large for a given system since in that case solutions of Eq. (30) coincide with those of Eq. (24) after *very* short times.

Equation (24) when rewritten as

$$\frac{d\langle n \rangle}{dt} = -B\langle n \rangle + C \quad (31)$$

where B and C are γ and $\gamma\langle n(\infty) \rangle$, respectively, has the same form as Eq. (23) of Nitzan and Silbey^{5b} except that in the latter B and C are generally t -dependent quantities. This time dependence also originates in the frequency dependence of $|G_\nu|^2 \rho_\nu$ and can be computed explicitly for our model. Thus, the expressions^{5b}

$$B(t) = \int_0^\infty d\omega' \rho(\omega') |G(\omega')|^2 \frac{\sin[(\omega' - \omega)t]}{\omega' - \omega}, \quad (32a)$$

$$C(t) = \int_0^\infty d\omega' \rho(\omega') |G(\omega')|^2 \frac{1}{e^{\beta\hbar\omega'} - 1} \frac{\sin[(\omega' - \omega)t]}{\omega' - \omega} \quad (32b)$$

reduce, for the above model, to

$$B(t) = \gamma(1 - e^{-\lambda t}), \quad (33a)$$

$$C(t) = \gamma\langle n(\infty) \rangle(1 - e^{-\lambda t}), \quad (33b)$$

where certain contributions which can be made negligible in some limits of the parameter values have been omitted for simplicity.¹⁶ The solution of Eq. (31), with B and C given by Eqs. (33), represents the short-time description of relaxation as described not by non-Markoffian equations [as in Eq. (30)] but by the cumulant expansion technique¹⁵ used in Ref. 5(b). The resultant moment expression

$$\langle n(t) \rangle = \langle n(\infty) \rangle + [\langle n(0) \rangle - \langle n(\infty) \rangle] \times e^{-\gamma t} \exp[(\gamma/\lambda)(1 - e^{-\lambda t})] \quad (34)$$

involves the Gumbel distribution and it is displayed in Fig. 2.

IV. CONCLUSION

We have studied the evolution of the average energy of a molecule in interaction with a bath under two *separate* generalizations of existing theory: (i) In Sec. II the master equation (1) was extended [Eq. (2)] to include the effect of a true sink (or source) corresponding to a simultaneously

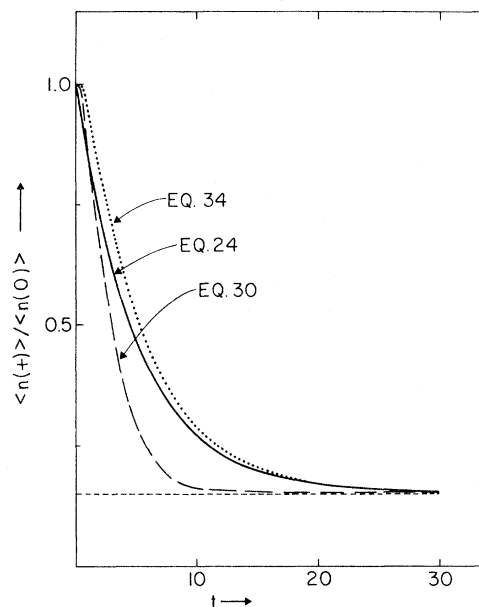


FIG. 2. Mean occupation number $\langle n(t) \rangle$ as given by the Markoffian result [Eq. (24) and our generalizations, Eqs. (30) and (34)]. Parameter values are arbitrary: $\lambda=1$, $\gamma=0.2$, and $\hbar\omega/k_B T=2.0$. The dashed line is $\langle n(\infty) \rangle / \langle n(0) \rangle$.

occurring process like emission or transfer and leading to nonconservation of the total probability. Equations for the average energy were derived and shown to contain "mode-mode coupling" terms in general. It was shown that simpler closed equations could result for particular initial distributions and the case of initial Boltzmann distributions at temperatures different from the environment temperature was studied. Figure 1 compares this analysis with the results of the ordinary master equation (1). (ii) In Sec. III short-time details in the evolution of the average energy were studied in two ways: through *non-local* equations in time in the spirit of Ref. 7 and through *local* equations with time-dependent coefficients, in the spirit of Ref. 5(b). Figure 2 provides a comparison of both results with the simple exponential evolution^{1,5a} of the average energy.

Note added in proof. It has recently come to our attention that some calculations involving a true decay term appended to the Montroll-Shuler equation have appeared earlier in P. M. Matthews, I. I. Shapiro, and D. L. Falkoff, Phys. Rev. **120**, 1 (1960).

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⁴(a) V. Seshadri and V. M. Kenkre, *Phys. Lett.* **56A**, 75 (1976); (b) V. M. Kenkre and V. Seshadri (unpublished).

⁵(a) A. Nitzan and J. Jortner, *Molec. Phys.* **25**, 713 (1973); (b) A. Nitzan and R. J. Silbey, *J. Chem. Phys.* **40**, 70 (1974).

⁶See, e.g., S. Fischer, *J. Chem. Phys.* **53**, 3195 (1970).

⁷V. M. Kenkre, *Phys. Rev. B* **11**, 3406 (1975).

⁸R. J. Glauber, *J. Math. Phys.* **4**, 294 (1963); J. C. Goldstein and M. O. Scully, *Phys. Rev. B* **7**, 1084 (1973).

⁹As has been shown in Sec. III, the effects explored therein exist in principle but may or may not be negligible in *magnitude*. Their description may be important for some systems but unnecessary for others. The latter appears to be the case in the experiments of H. Dubost, L. Abouaf-Marguin, and F. Legay [*Phys. Rev. Lett.* **29**, 145 (1972)], but deviations from "exponential behavior" have been observed for instance by D. S. Tinti and G. W. Robinson [*J. Chem. Phys.* **49**, 3229 (1968)] and C. J. Werkhoven, T. Deinum, J. Langelaar, R. P. H. Rettschnick, and J. D. W. Van Voorst [*Chem. Phys. Lett.* **18**, 171 (1973)]. We have not explored in this paper the subject of non-exponential evolution (in the sense of a sum of many exponentials) that can result from perfectly Markoffian

master equations.

¹⁰We have shown in Ref. 4b that Eq. (3) is a consequence of the Franck-Condon principle when the decay process is radiative emission.

¹¹B. I. Stepanov, *Dokl. Akad. Nauk SSSR* **112**, 839 (1957) [*Sov. Phys. Dokl.* **2**, 81 (1957)]; R. L. Van Metter and R. S. Knox, *Chem. Phys.* **12**, 333 (1976).

¹²Our presentation, although slightly different from that of Ref. 5, is equivalent to it, except for our neglect of the level shift, which is very small in most instances.

¹³The approximation makes it possible to write a part of $\langle u(t) \rangle$ involving $v_\nu(t)$'s in terms of $|u(t)|^2$. It involves system properties different from those used to evaluate $|u(t)|^2$, and we shall not discuss it in this paper.

¹⁴For mathematical convenience we extend the limits in Eq. (23), to $-\infty$ and $+\infty$. This is not justified in general.

¹⁵R. Kubo, *J. Phys. Soc. Jpn.* **17**, 1100 (1962).

¹⁶Among the terms neglected in Eq. (33b) there are, a persistent oscillation $[-\lambda^2\gamma/\beta\omega(\lambda^2+\omega^2)]\cos\omega t$ with zero average and an infinite series

$$\operatorname{Im}\left(2i\frac{\lambda^2\gamma}{\beta}\sum_{k=1}^{\infty}\frac{e^{it\Omega_k}}{\Omega_k(\lambda^2+\Omega_k^2)}\right),$$

where $\Omega_k = (2ik\pi/\beta) - \omega$ and k is an integer. Neglecting the terms is justified in the limit $\omega \gg \lambda$, and the persistent oscillation is reminiscent of the behavior of a light impurity in a chain of harmonic oscillators [see, e.g., R. Cukier, *Physica* **61**, 321 (1972)]. Numerical computation of the neglected terms is straightforward since the series converges rapidly.