



Vibrational relaxation of a molecule in strong interaction with a reservoir: Nonmonotonic temperature dependence

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ABSTRACT

This theoretical study of the vibrational relaxation of a molecule in interaction with a reservoir uncovers a noteworthy temperature (T) dependence of the time evolution of the relaxation. Its rate increases with T in one interval but decreases in another. The feature arises not for a weak molecule-reservoir interaction but only for coupling strong enough to require polaronic dressing transformations. Our treatment, based on a recent generalization of the well-known Montroll–Shuler equation for relaxation and an explicit calculation of bath correlations from the microscopically specified Hamiltonian, could provide an alternative explanation of an “inverted” T -dependence of relaxation in an experimental report by Fayer and collaborators on $W(\text{CO})_6$ dissolved in CHCl_3 .

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1. Introduction

Vibrational relaxation of a molecule embedded in a bath (reservoir) from an initial state to which it is excited is of interest [1–7] for practical purposes in chemical physics as well as for fundamental reasons in statistical mechanics. We investigate this process here by representing the molecule as a harmonic oscillator of frequency Ω in interaction with phonons produced by the complex motions of the reservoir. Two cases are studied: weak linear interaction which involves the absorption or emission of single phonons [5,7], and strong linear interaction which, after the well-known polaronic transformation [8–10] is carried out to diagonalize the Hamiltonian partially in the standard manner and to perform a perturbation calculation in the remainder, introduces multiphonon processes in the transformed Hamiltonian. Our study uncovers no surprises in the first (single-phonon, weak coupling) case but noteworthy features in the second (multiphonon arising from strong coupling). These features include nonmonotonic behavior in the relaxation both in the time evolution and the temperature dependence of the rates of relaxation.

The tool that we use for our theoretical investigation is a generalized master equation (GME) derived by extending the methodology of Zwanzig [11] to include coarse-graining [12,13]. The form of the GME for P_M , the probability that the molecular oscillator is in its M th state at time t , is [13]

$$\frac{1}{\kappa} \frac{dP_M}{dt} = \int_0^t ds \left\{ \phi_-(t-s) [(M+1)P_{M+1}(s) - MP_M(s)] - \phi_+(t-s) [(M+1)P_M(s) - MP_{M-1}(s)] \right\}, \quad (1)$$

where κ is the relaxation rate, and the observable we focus on is the energy, $E(t) = \hbar\Omega \langle (M+1/2) \rangle$. The origin of the nonmonotonic relaxation is in the memories $\phi_{\pm}(t)$ which we calculate here explicitly from the specified microscopic interaction.

2. Calculation of the bath correlation functions

We consider two forms of the Hamiltonian, signifying respectively weak and strong interaction with the reservoir. Both interactions involve a weak perturbative force exerted by the bath on the molecule as in the prescription of Landau and Teller [14] incorporated in the original relaxation theory [1]. In one case, a weighted sum of bath displacements is proportional to the force. In the other, the force is displacement-independent but the bath has an additional effect in that it modulates the frequency of the molecular oscillator. This effect is strong, i.e., not amenable to a perturbative treatment. Specifying these features of the interaction, while unnecessary in the original analysis of vibrational relaxation [1,14], is critical here because we derive a GME capable of a short-time description with much more detail. The effect of the original Landau–Teller assumptions is recovered in appropriate limits. With the definition

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$$V_B = \sum_q g_q \hbar \omega_q (b_q + b_q^\dagger), \quad (2)$$

the first case (weak coupling) has the Hamiltonian

$$\mathcal{H} = \hbar \Omega (a^\dagger a + 1/2) + \sum_q \hbar \omega_q (b_q^\dagger b_q + 1/2) + V_B (a + a^\dagger). \quad (3)$$

Here a 's describe the relaxing molecule, b_q 's describe bath phonons of frequency ω_q and wavevector q , and g_q 's are the dimensionless coupling constants determining the interaction strength. Because the latter are taken to be small for this weak-coupling case, the calculational procedure can use a perturbation in orders of the third term of Eq. (3). The second case we consider (strong coupling) is

$$\mathcal{H} = \hbar \Omega (a^\dagger a + 1/2) + \sum_q \hbar \omega_q (b_q^\dagger b_q + 1/2) + V_B a^\dagger a + u(a + a^\dagger). \quad (4)$$

The c -number u which describes the constant force exerted by the reservoir on the molecular oscillator is weak but V_B in this case is not because the coupling constants g_q are taken to be large. The term proportional to V_B cannot be treated in this second case perturbatively. The large interaction strength necessitates the standard polaronic transformation [8–10] from the bare operators a , b , to their dressed versions A , B . The transformation, as is well known [8–10], corresponds to a shift of the equilibrium position of the bath oscillators and converts Eq. (4) into

$$\mathcal{H} = \left(\hbar \Omega - \sum_q g_q^2 \hbar \omega_q \right) A^\dagger A + \sum_q \hbar \omega_q (B_q^\dagger B_q + 1/2) + u \left[A e^{\sum_q g_q (B_q - B_q^\dagger)} + A^\dagger e^{-\sum_q g_q (B_q - B_q^\dagger)} \right]. \quad (5)$$

The smallness of u makes the new interaction (third term) in Eq. (5) weak enough to justify perturbation. The transformed Hamiltonian is *multiphonon* in the bath (B_q , B_q^\dagger appear in the exponent). One then obtains [13], after the usual initial random phase assumption [11] is made,

$$\frac{dP_M(t)}{dt} = \sum_N (\mathcal{W}_{MN} * P_N - \mathcal{W}_{NM} * P_M), \quad (6)$$

where M , N denote the molecular energy states, and $*$ represents a convolution, i.e., $a * b = \int_0^t ds a(t-s)b(s)$. The separability of the interaction allows the memory functions to be given as:

$$\mathcal{W}_{MN}(t) = C \left[e^{i\Omega_{MN}t} \mathcal{B}(t) + e^{-i\Omega_{MN}t} \mathcal{B}^*(t) \right], \quad (7)$$

where C is $(1/\hbar^2) [\delta_{N+1,M}(N+1) + \delta_{N-1,M}N]$. Generally, Ω_{MN} is the frequency defined by the energy difference between the system energy levels M and N , and is here $\pm\Omega$ if M and N are neighboring energy states. In a perturbative treatment involving powers of the interaction the memories vanish if $M - N \neq \pm 1$.

Crucial in Eq. (7), the thermal bath correlation function $\mathcal{B}(t)$ equals $\text{Tr} (e^{-\beta H_B} V_i e^{iH_B t/\hbar} V_i e^{-iH_B t/\hbar}) / \text{Tr} (e^{-\beta H_B})$, where H_B is the Hamiltonian of the bath alone, V_i is the interaction, and $\beta = 1/k_B T$ with k_B the Boltzmann constant. For the weak-coupling case, the interaction V_i is V_B in Eq. (2), and leads to

$$\mathcal{B}(t) = \sum_q g_q^2 \hbar^2 \omega_q^2 [\coth(\beta \hbar \omega_q / 2) \cos \omega_q t + i \sin \omega_q t]. \quad (8)$$

For the strong-coupling case, V_i is not V_B but replaced by the third term in Eq. (5), and leads to a result quite different from Eq. (8):

$$\mathcal{B}(t) = u^2 e^{-\sum_q g_q^2 \coth(\beta \hbar \omega_q / 2)} \times e^{\sum_q g_q^2 \hbar (\omega_q) (e^{\beta \hbar \omega_q} e^{i\omega_q t} + e^{-i\omega_q t})}. \quad (9)$$

To perform the summation over the reservoir modes q implicit in $\mathcal{B}(t)$, we use the simplification of optical phonons with peak frequency ω_0 and small dispersion $\sigma \ll \omega_0$, and an average coupling constant g . We can then write Eqs. (8) and (9), respectively for the two interactions, as

$$\mathcal{B}(t) = g^2 \hbar^2 \omega_0^2 [\coth(\beta \hbar \omega_0 / 2) \cos \omega_0 t + i \sin \omega_0 t] f(t), \quad (10a)$$

$$\mathcal{B}(t) = u^2 e^{-g^2 \coth(\beta \hbar \omega_0 / 2) (1 - \cos \omega_0 t)} e^{ig^2 \sin \omega_0 t} f(t). \quad (10b)$$

The function $f(t)$ is determined primarily via a Fourier transform applied to the shape of the phonon band in Eq. (8), but also by other disordered sources not taken explicitly into account in the statement of the Hamiltonian. For Eq. (9), the introduction of disordered sources is unavoidable [9] since linear interactions cannot broaden zero-phonon lines [15]. The procedure we follow [8,9] has been given earlier and discussed [9,16] and is compatible with the derivation of a GME in the presence of disorder [17]. The most convenient representation of $f(t)$ is the exponential $e^{-\alpha t}$; an alternative, valid for the weak-coupling case, is a Gaussian with width σ . We take the exponential in the following. This leads to memories

$$\kappa \phi_{\pm}(t) = 2g^2 \omega_0^2 \left[\coth(\beta \hbar \omega_0 / 2) \cos \omega_0 t \cos \Omega t \mp \sin \omega_0 t \sin \Omega t \right] e^{-\alpha t}, \quad (11a)$$

$$\kappa \phi_{\pm}(t) = 2(u/\hbar)^2 e^{-g^2 \coth(\beta \hbar \omega_0 / 2) (1 - \cos \omega_0 t)} \times \cos \left[g^2 \sin(\omega_0 t) \pm \Omega t \right] e^{-\alpha t}, \quad (11b)$$

for the two cases, respectively.

3. Noteworthy features in the relaxation

An efficient way of investigating the molecular relaxation process is to follow the recent Kenkre–Chase generalization [13] of the Bethe–Teller result [18] for the vibrational energy $E(t)$ of the molecule, which is the first moment of the probabilities in the GME, Eq. (6),

$$E(t) = E(0)\eta(t) + E_{th} \int_0^t ds \xi(t-s) [1 - \eta(s)], \quad (12)$$

using the $\phi_{\pm}(t)$ that we have calculated here from specified Hamiltonians. Here $E(0)$ is the initial energy of the system, $E_{th} = (\hbar \Omega / 2) \coth(\beta \hbar \Omega / 2)$ is its thermal value, and $\eta(t)$ and $\xi(t)$ have, as their respective transforms (ϵ is the Laplace variable and tildes denote transforms),

$$\tilde{\eta}(\epsilon) = \frac{1}{\epsilon + \kappa \tilde{\phi}_D(\epsilon)}, \quad \tilde{\xi}(\epsilon) = \frac{\tilde{\phi}_S(\epsilon)}{\tilde{\phi}_D(\epsilon)} \tanh\left(\frac{\beta \hbar \Omega}{2}\right). \quad (13)$$

Here, $\phi_S(t)$ and $\phi_D(t)$ are, respectively, the sum and difference of $\phi_-(t)$ and $\phi_+(t)$. Thus, $\phi_v = \phi_- \pm \phi_+$. In the strong interaction regime, the microscopic memories have the form

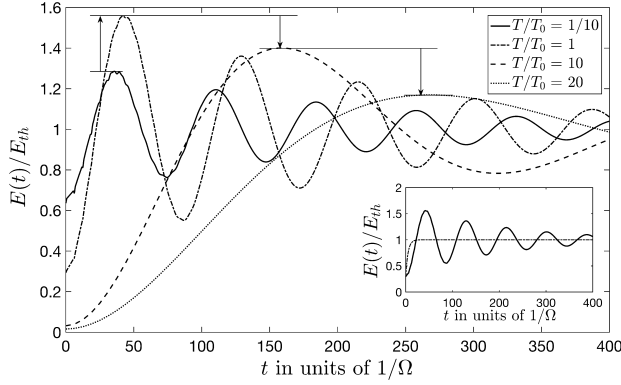


Fig. 1. Nonmonotonic temperature dependence of the molecular energy for the strong-coupling case shown via the time evolution of the energy $E(t)$ scaled to its thermal value E_{th} . Here the molecular frequency Ω equals the peak frequency of the bath phonons ω_0 , $g = 2$, and $\alpha/\Omega = 0.01$. We plot $E(t)$ for varying T/T_0 where $T_0 = \hbar\omega_0/k_B$ (see legend). A nonmonotonic T -dependence is observed as T increases, first a rise and then a drop (see arrows). The inset shows the difference between the incoherent limit (Montroll–Shuler, see text) (dash-dot line) and our GME predictions (solid line) for one representative case, $T/T_0 = 1$.

$$\kappa\phi_\nu(t) = (2u/\hbar)^2 e^{-g^2 \coth(\beta\hbar\omega_0/2)(1-\cos\omega_0 t)} \times \Lambda(g^2 \sin\omega_0 t) \Lambda(\Omega t) e^{-\alpha t}, \quad (14)$$

where if $\nu = S$ the function $\Lambda(x)$ is $\cos(x)$ and if $\nu = D$ it is $\sin(x)$. In the weak interaction case,

$$\kappa\phi_\nu(t) = 2g^2\omega_0^2 \Upsilon(\omega_0) \Lambda(\omega_0 t) \Lambda(\Omega t) e^{-\alpha t}, \quad (15)$$

where the function $\Upsilon(\omega_0)$ is $\coth(\beta\hbar\omega_0/2)$ if $\nu = S$ and 1 if $\nu = D$.

The time-dependent energy in Eq. (12), with the substitution of Eq. (14), shows striking behavior displayed in Fig. 1 for the strong-coupling (multiphonon) interaction. As the temperature is increased, nonmonotonic behavior in the energy is exhibited for different T intervals. As the arrows show, the peaks of the time-dependent $E(t)$ increase as T increases at first, but decrease as T increases further. In the inset in Fig. 1, for one illustrative T , we display the oscillatory $E(t)$ our GME predicts along with the non-oscillatory evolution [1,18] predicted by the incoherent Master equation. That difference between the exponential rise from the incoherence-based treatment of ref. [1] and the oscillations from the coherent GME treatment of ref. [13] is not our focus. What we stress here is, rather, represented by the reversal of the arrow directions in the main Fig. 1.

No such nonmonotonicity effect is seen for the weak-interaction case (with the \mathcal{H} of Eq. (3) or the $\mathcal{B}(t)$ of Eq. (10a)). This is clear in Fig. 2 which is the counterpart of Fig. 1 for the weak-coupling case. The peaks in the main figure show only a monotonic variation as T is increased.

To make the effect additionally clear, we show Fig. 3 in which we plot the rate of relaxation κ obtained by integrating the expressions in Eqs. (11) from $t = 0$ to ∞ . The strong-coupling case (solid line) from Eq. (11b) exhibits nonmonotonicity in T . Whether the rate increases or decreases with T is determined by the T -interval in which observations are made. The weak-coupling case (dashed line) by contrast shows a monotonic increase. We note in passing that the expressions for the relaxation rate that we have derived in the present paper, while similar to ones encountered in the theory of mobility of photo-injected holes in naphthalene [16], differ in some essential features. While the phonons analyzed in ref. [16] only modulate the energy of the moving quasi-particle (charge carrier), here they help the quasi-particle (the vibrational excitation) bridge the energy gap between adjacent states in addition to modulating the energy.

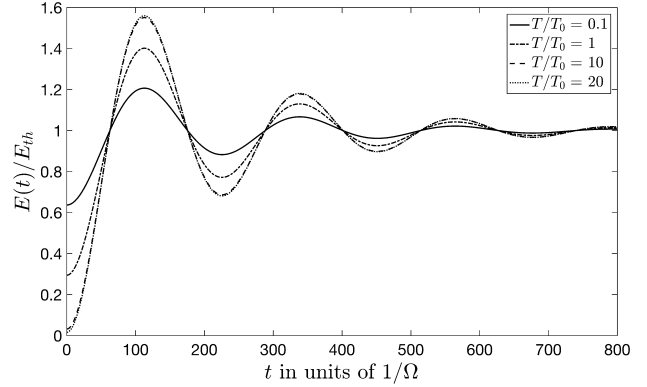


Fig. 2. Absence of nonmonotonicity in the time evolution of the energy in the weak-coupling case. Here $g = 0.02$, but $\omega_0 = \Omega$ and $\alpha/\Omega = 0.01$ as in Fig. 1. As T is increased, the energy rises above the incoherent limit value, with oscillations decaying faster to E_{th} . The frequency of oscillation of $E(t)$ appears to remain unchanged. The amplitude increases monotonically with increasing T for all T 's considered in the plot.

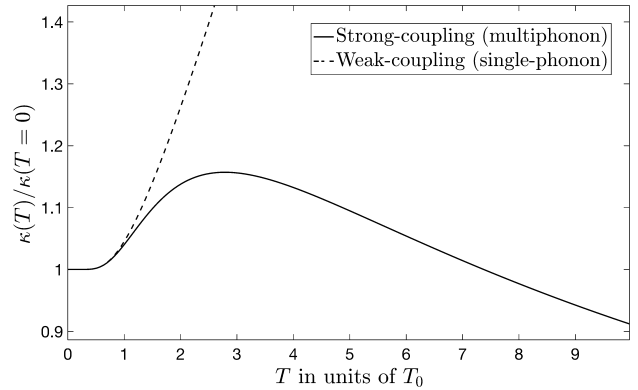


Fig. 3. Temperature dependence of the relaxation rate $\kappa(T)$ plotted with respect to T in units of T_0 . In the strong-coupling case (solid line) a nonmonotonic T dependence is observed: the rate rises with increasing T and then decreases as T increases further. The behavior for the weak coupling case (dashed line) is, by contrast, monotonic. Parameter values are as in the main Figs. 1 and 2, respectively.

Eq. (12) in its incoherent (Montroll–Shuler) form can be written as

$$\frac{E(t) - E_{th}}{E(0) - E_{th}} = e^{-\kappa(1 - e^{-\beta\hbar\Omega})t}. \quad (16)$$

Although our generalization in ref. [13] reflected in Eq. (12) results in a non-exponential t -dependence of the left hand side of Eq. (16), its Laplace transform can be always expressed as

$$\frac{1}{\epsilon + \tilde{\zeta}(\epsilon)}$$

where ζ represents a memory decay rate governing the relaxation behavior of the oscillator. We find that a plot of $\tilde{\zeta}(0) = \int_0^\infty \zeta(t)dt$, which corresponds to, but is a non-Markoffian generalization of, the incoherent rate $\kappa(1 - e^{-\beta\hbar\Omega})$, shows multiple oscillations with increasing temperature. We do not display these oscillations graphically here; they and details of the underlying analysis may be found elsewhere [19].

Another interesting feature that we have observed here is the periodic kinks observed along the main oscillation which dissipate as time progresses (see Fig. 4). These kinks are related to revivals known in spin-boson [20] systems and can be said to arise

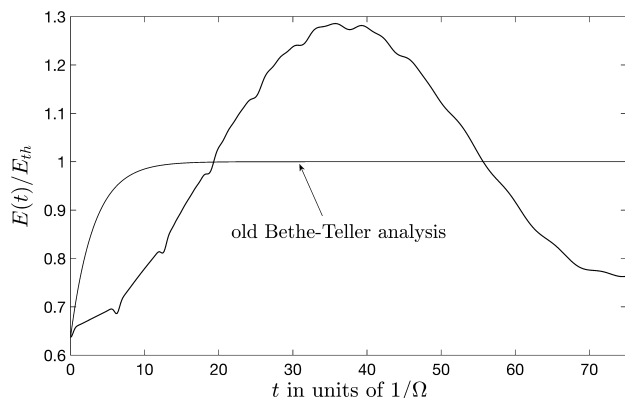


Fig. 4. Kinks associated with microscopic revivals seen clearly at very low T in the time evolution $E(t)$ scaled to its thermal value E_{th} . Parameters are as in Fig. 1. The kinks are seen superimposed on the oscillatory relaxation of the energy, disappearing as time progresses. For comparison we show the nonoscillatory exponential rise of $E(t)$ to its thermal (Bethe–Teller) value predicted by the old Montroll–Shuler analysis. This is precisely Eq. (16) and corresponds to a delta-function memory in the GME, Eq. (6). Our predicted curve with kinks also saturates to the same thermal value (not visible in the plot).

from the competition between the periods inside each of the two cosines in the memories in Eq. (11b).

Finally, we mention a “half-Markoffian” approximation [17,21] we have developed [19] which is able to describe, with excellent accuracy *both* the short-time and the long-time evolution of the energy $E(t)$ but not the intermediate oscillations that only the convolutions of Eq. (12) can give. We do not discuss this analysis here but display the interpolation formula we have obtained,

$$E(t) = \hbar\Omega/2 + [E(0) - \hbar\Omega/2] e^{-\int_0^t \mathcal{I}_D(t') dt'} + \hbar\Omega \int_0^t dt' \mathcal{I}_+(t') e^{-\int_{t'}^t \mathcal{I}_D(s) ds}, \quad (17)$$

where $\mathcal{I}_v(t) = \int_0^t \kappa \phi_v(s) ds$. We also provide its results graphically in Fig. 5. Our interpolation formula yields the approach of the molecular energy to its thermal equilibrium E_{th} perfectly at long times (as does the exact solution at longer times although this is not apparent from the figure). Fig. 5 shows that our formula reproduces faithfully the kinks at very short times as well.

4. Conclusions

Of several distinct motivations for our theory (including the study of the approach to thermal equilibrium of complex systems), one is (see the abstract) experiments [5,7] on what may be termed inverted T -dependence of relaxation rates (e.g., on $W(\text{CO})_6$). The phenomenon is interesting because it appears counterintuitive. Our present analysis provides one possibility as its source: polaronic processes arising from strong coupling to phonons. This source is quite unrelated to that invoked by other authors earlier: the T -dependence of the density of states of *liquid* phonons of the solvent. The source we suggest here as an alternative, is similar to that shown [16] to give rise to the observed T -dependence of the mobility of photo-injected holes in aromatic hydrocarbon crystals [22]. It stems from oppositely trending effects of virtual phonons and appears to be at least as natural and physical as the T -dependence of the liquid phonon density of states of solvents.

The focus in this Letter being only on the *qualitative* features of the nonmonotonicity phenomenon we have described, for this work we have neither sought specific molecules in given environments nor examined quantitative values of the coupling constant,

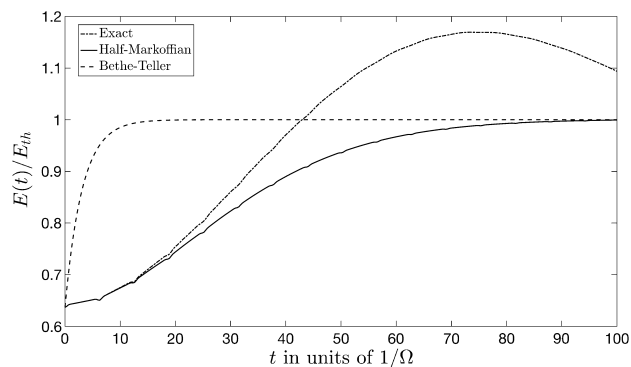


Fig. 5. Excellent agreement at *both* short and long times (but not for intermediate times) of our “half-Markoffian” approximation leading to the interpolation formula.

molecular frequency and bath parameters. It is our intention to extend the analysis in those directions as well as to employ more realistic models involving several vibrations in addition to a phonon band [5,7]. Our predicted graphs here are shown in t expressed in units of $1/\Omega$ and T expressed in units of $\hbar\omega_0/k_B$. We have considered extreme values of the interaction strength, $g = 0.02$ and 2 , respectively. Features we see in Figs. 1–3 appear to suggest that the effects predicted should be measurable on these scales. By changing various parameters such as α within reasonable limits, we have assured ourselves that the qualitative aspects of our predictions remain valid. Inclusion of further numerical detail, while unnecessary at this stage, will be straightforward when explicit experiments are under investigation.¹

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¹ Realizing that a harmonic oscillator model may be less accurate a representation of the relaxing molecule than an anharmonic one, and that a two-level system provides an adequate representation of the latter given the large energy difference, we have also carried out an analysis for a nonresonant dimer and found precisely the same results as reported here [19].

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