Journal of Statistical Physics, Vol. 67, Nos. 1/2, 1992

Exact Time Correlation Function for a Nonlinearly Coupled Vibrational System

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Received April 18, 1991; final November 26, 1991

The time correlation function $\chi(t) = \mathrm{Re}\langle [c(t), c^{\dagger}(0)] \rangle$, which is related to the dipole spectrum and is the main focus of quantum molecular time scale generalized Langevin equation theory, is calculated for the Hamiltonian system in which a single oscillator is coupled by a nonlinear Davydov term to a chain of oscillators comprising a phonon heat bath. An exact expression for $\chi(t)$ is obtained. At long times we find that the time correlation function decays as a small power law at $T = 0\mathrm{K}$, but switches to exponential decay at higher temperature. This is a new result and bears on the long-standing issue of the existence of long-time tails.

KEY WORDS: Time correlation function; long-time tail; nonlinear; generalized Langevin equation.

1. INTRODUCTION

The role of time correlation functions (TCF) as a formal tool in statistical mechanics is fundamental.[1] It is therefore of interest to examine their properties and behavior, especially for Hamiltonian systems, which can serve as archetypical models. Generally speaking, except for linear systems, which can be solved straightforwardly, such studies must be carried out computationally, since only a very few nonlinear Hamiltonian systems can be solved analytically. Analytic solutions, when they can be obtained, serve as important benchmarks to calibrate computational studies and to improve our understanding of TCFs.

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0022-4715/92/0400-0331$06.50/0

One nonlinear Hamiltonian system for which an exact solution exists is the single-oscillator Davydov Hamiltonian[2] given by[3]

$$H = \hbar\omega_0 \left(c^\dagger c + \frac{1}{2} \right) + \sum_{k=-N}^{N} \hbar\omega_k \left(a_k^\dagger a_k + \frac{1}{2} \right) - (2c^\dagger c + 1) \sum_{k=-N}^{N} \hbar\sigma_k (a_k + a_k^\dagger) \tag{1}$$

where

$$\omega_k = \omega_a \left| \sin \frac{\pi k}{2N+1} \right| \tag{2}$$

with ω_a the maximum frequency of an acoustic phonon band and

$$\sigma_k = \frac{2\bar{\chi}}{\hbar} \operatorname{sgn} k \cos \frac{\pi k}{2N+1} \left\{ \frac{|\sin[\pi k/(2N+1)]|}{2N+1} \right\}^{1/2} \tag{3}$$

with $\bar{\chi}$ the nonlinear coupling parameter; sgn k is the sign $(+1$ or $-1)$ of the index k. The annihilation (creation) operators c $(c^\dagger)$ and a_k $(a_k^\dagger)$ represent the single-oscillator and the phonon modes respectively. The oscillator frequency of the single oscillator is given by ω_0. The phonon chain is $2N+1$ units long with labels from $-N$ to N with the single oscillator situated at site 0. In the final results N is taken to be indefinitely large. The Hamiltonian in Eq. (1) represents a single oscillator, which we call the vibron, coupled nonlinearly to a harmonic phonon bath. It will be recognized as a displaced harmonic oscillator which can be exactly diagonalized.[4–6] In this paper we carry out this diagonalization and then for the first time explicitly calculate the time correlation function $\bar{\chi}(t)$ of the vibron quantum oscillator given in Eq. (4). We obtain the unexpected result that an impulse given to the system at $t=0$ decays at moderate temperatures as a small inverse power of time for many cycles before finally entering into exponential decay.

As has been discussed elsewhere,[3] Eq. (1) is a modified version of the Takeno Hamiltonian,[7] which is based on physically real models of nonlinearly interacting vibrational systems in pseudo-one-dimensional solids. For the case of a single vibron oscillator, the Takeno Hamiltonian can be written in the form

$$H = \hbar\omega_0 \left(c^\dagger c + \frac{1}{2} \right) + \sum_{k=-N}^{N} \hbar\omega_k \left(a_k^\dagger a_k + \frac{1}{2} \right) + (c^\dagger - c)^2 \sum_{k=-N}^{N} \hbar\sigma_k (a_k + a_k^\dagger)$$

This Hamiltonian has no known exact solutions. The Hamiltonian of Eq. (1) is obtained by retaining in the interaction term only terms in $c^{\dagger}c$ and $cc^{\dagger}$. This has the effect of making the perturbation acting on the vibron oscillator diagonal in the eigenstates of $\hbar\omega_0(c^{\dagger}c + 1/2)$ and conserving the number of quanta in the vibron oscillator, which is the feature that makes the problem exactly soluble. The Davydov Hamiltonian in Eq. (1) is therefore physically distinct from the Takeno Hamiltonian. It can nevertheless be derived from a real physical model only slightly different from the model underlying the Takeno Hamiltonian.[8] Because it can be solved exactly, the Davydov Hamiltonian is a valuable prototype model.

The Davydov Hamiltonian is also widely used as an approximation to the Takeno Hamiltonian[7] for situations where the vibron oscillator frequency ω_0 is much greater than the highest frequencies in the phonon band. For such cases the terms in the Takeno Hamiltonian in $c^{\dagger}c^{\dagger}$ and cc are neglected because they have the effect of introducing unimportant terms with frequencies near $2\omega_0$. This approximation is generally known as the rotating wave approximation.[9,10]

The TCF of interest for the Hamiltonian system in Eq. (1) is given by

$$\dot{\chi}(t) = \tfrac{1}{2}\langle [c(0), c^{\dagger}(t)] + [c(t), c^{\dagger}(0)] \rangle \tag{4}$$

where the quantum statistical average $\langle \cdots \rangle$ is taken to be the canonical ensemble. This particular form arises naturally in a quantum version of molecular time-scale generalized Langevin equation (MTGLE) theory.[11-16] Furthermore, the cosine Fourier transform of the TCF given by

$$\rho(\omega) = \frac{2}{\pi} \int_0^{\infty} dt\, \dot{\chi}(t) \cos \omega t \tag{5}$$

has been shown elsewhere[14] to be related to the dipole spectrum of the single oscillator and thus serves as a means of establishing the location and line shape of spectral lines and their temperature dependence. In this paper the eigenvalues and eigenstates of the Hamiltonian in Eq. (1) are used to find an exact expression for $\dot{\chi}(t)$.

In studying the properties of the TCF in Eq. (4) we will be interested in its behavior at both short and long times. The long-time behavior is of interest since the question of a long-time tail arises.[17,18] This issue has been reviewed and new insights provided by R. F. Fox in a seminal paper.[19] The exact asymptotic (long-time) behavior we find for this system is especially important in that a power law decay is found at absolute zero which switches over to a power law decay at intermediate times and exponential decay at long times for finite temperatures.

The organization of this paper is as follows: in Section 2 we develop an exact solution for $\dot{\chi}(t)$. Section 3 presents a derivation of the short-time form, while Section 4 presents the long-time form. Section 5 contains some concluding remarks.

2. DERIVATION OF EXACT SOLUTION

Diagonalization of Hamiltonians similar to the one in Eq. (1) and subsequent analysis of their time-dependent properties has been discussed in a number of papers.[4–6] Our focus here is to calculate and describe the time evolution of the particular TCF given in Eq. (4). We first carry out a canonical transformation using the definitions

$$U = \exp\left[(2c^\dagger c + 1) \sum_{k=-N}^{N} \frac{\sigma_k}{\omega_k}(a_k^\dagger - a_k)\right] \tag{6}$$

$$D = UcU^\dagger \tag{7}$$

and

$$B_k = Ua_k U^\dagger \tag{8}$$

These definitions lead directly to the transformed Hamiltonian

$$H = H_B + H_D \tag{9}$$

where

$$H_B = \sum_{k=-N}^{N} \hbar\omega_k\left(B_k^\dagger B_k + \frac{1}{2}\right) \tag{10}$$

$$H_D = \hbar\omega_0\left(D^\dagger D + \frac{1}{2}\right) - \hbar\eta(2D^\dagger D + 1)^2 \tag{11}$$

and

$$\eta = \sum_{k=-N}^{N} \frac{\sigma_k^2}{\omega_k} = \frac{2\bar{\chi}^2}{\hbar^2\omega_a} \tag{12}$$

The latter result for the parameter η is obtained by substitution of Eqs. (2) and (3) into the sum, converting the sum to an integral as N goes to infinity, and performing the integration. The transformation defined by Eq. (6) can be explicitly carried out to achieve the well-known result[4–6]

$$D(t) = e^{-S(t)}c(t) \tag{13}$$

or

$$c(t)=e^{S(t)}D(t) \tag{14}$$

where

$$S(t)=2\sum_{k=-N}^{N}\frac{\sigma_k}{\omega_k}(B_k^\dagger(t)-B_k(t)) \tag{15}$$

The structure of Eq. (14) permits us to obtain the explicit time dependence of $c(t)$. We first note that $B_k(t)$ and $D(t)$ can be found in explicit form from the transformed Hamiltonian as

$$B_k(t)=e^{-i\omega_k t}B_k(0) \tag{16}$$

and

$$D(t)=\exp\{-i\omega_0 t+i8\eta[D^\dagger(0)\,D(0)+1]\,t\}\,D(0) \tag{17}$$

The explicit time dependence of $c(t)$ is found by substituting Eq. (16) and its adjoint and Eq. (17) into Eq. (14) to obtain

$$c(t)=e^{S(t)}\exp\{-i\omega_0 t+i8\eta[D^\dagger(0)\,D(0)+1]\,t\}\,D(0) \tag{18}$$

where $S(t)$ is now given explicitly by

$$S(t)=2\sum_{k=-N}^{N}\frac{\sigma_k}{\omega_k}(B_k^\dagger(0)\,e^{i\omega_k t}-B_k(0)\,e^{-i\omega_k t}) \tag{19}$$

We next proceed to compute the time correlation function $\dot{\chi}(t)$. Since the transformation defined by Eq. (6) is unitary and the Hamiltonian is separable, we have

$$\langle c(t)\,c^\dagger(0)\rangle=\langle e^{S(t)}e^{-S(0)}\rangle_B\,\langle D(t)\,D^\dagger(0)\rangle_D \tag{20}$$

where

$$\langle e^{S(t)}e^{-S(0)}\rangle_B=\frac{1}{Q_B}\,\mathrm{Tr}_B\,e^{-\beta H_B}e^{S(t)}e^{-S(0)} \tag{21}$$

$$Q_B=\mathrm{Tr}_B\,e^{-\beta H_B}=\prod_{k=-N}^{N}\frac{e^{-\beta\hbar\omega_k/2}}{1-e^{-\beta\hbar\omega_k}} \tag{22}$$

$$\langle D(t)\,D^\dagger(0)\rangle_D=\frac{1}{Q_D}\sum_{n=0}^{n_{\max}}e^{-\beta E_n}\langle n\,|D(t)\,D^\dagger(0)|\,n\rangle \tag{23}$$

$$Q_D=\sum_{n=0}^{n_{\max}}e^{-\beta E_n} \tag{24}$$

and

$$E_n = \hbar\omega_0\left(n + \frac{1}{2}\right) - \hbar\eta(2n+1)^2 \tag{25}$$

A number of points need to be made here. First, the trace operation in Eqs. (21) and (22) is over the harmonic oscillator states associated with the $2N+1$ independent oscillators labeled by the index k. The sums in Eqs. (23) and (24) are over the harmonic oscillator states associated with the Hamiltonian H_D. We note from Eq. (11) that H_D is diagonalized by harmonic oscillator states but with a shifted energy given by Eq. (25). However, it is necessary to truncate the number of states in Eqs. (23) and (24) since the unphysical polynomial interaction implied in Eq. (1) leads to large negative energies for large n.[20] The energy E_n given by Eq. (25) reaches a maximum for

$$\Delta E_n = E_{n+1} - E_n = 0 \tag{26}$$

which requires that

$$n_{\max} + 1 = \frac{\omega_0}{8\eta} \tag{27}$$

For typical values used later in Eq. (53), $\omega_0/8\eta = 0.25 \times 10^4$. The expectation value of $(n+1)$, on the other hand, is given approximately by

$$\langle n+1 \rangle = \left[1 - \exp\left(-\frac{\hbar\omega_0}{kT}\right)\right]^{-1}$$

which for $T = 300$ K is typically less than 10. Thus, for temperatures up to room temperature the eigenvalue spectrum given by Eq. (25) can be truncated at its maximum value with insignificant numerical error.

In the Appendix, we show that the ensemble average in Eq. (21) is given by

$$\langle e^{S(t)} e^{-S(0)} \rangle_B = \exp\left[-4i \sum_k \frac{\sigma_k^2}{\omega_k^2} \sin\omega_k t + 4 \sum_k \frac{\sigma_k^2}{\omega_k^2} \times (\cos\omega_k t - 1) \coth\left(\frac{\beta\hbar\omega_a}{2}\right)\right] \tag{28}$$

The ensemble average in Eq. (23) is easily computed by substitution of Eq. (17) to give

$$\langle D(t)\, D^\dagger(0) \rangle_D = \frac{1}{Q_D} \sum_{n=0}^{n_{\max}} e^{-\beta E_n} e^{-i\omega_0 t + i8\eta(n+1)t}(n+1) \tag{29}$$

From Eqs. (20), (28), and (29) and their complex conjugates it is a simple matter to determine $\dot{\chi}(t)$, which we write as

$$\dot{\chi}(t) = e(t)\, f(t) \tag{30}$$

where

$$f(t) = \frac{1}{Q_D} \sum_{n=0}^{n_{\max}} e^{-\beta E_n} \left\{ (n+1) \cos\left\{ [\omega_0 - 8\eta(n+1)]\, t + 4 \sum_k \frac{\sigma_k^2}{\omega_k^2} \sin \omega_k t \right\} \right.$$
$$\left. - n \cos\left[(\omega_0 - 8\eta n)\, t - 4 \sum_k \frac{\sigma_k^2}{\omega_k^2} \sin \omega_k t \right] \right\} \tag{31}$$

and

$$e(t) = \exp\left[4 \sum_k \frac{\sigma_k^2}{\omega_k^2} (\cos \omega_k t - 1) \coth\left(\frac{\hbar \beta \omega_k}{2} \right) \right] \tag{32}$$

The exact solution given by Eq. (30) provides us with a rather straightforward analytic form which can be used to study the behavior of the time correlation function $\dot{\chi}(t)$.

To obtain a more explicit form of Eq. (30), we make use of the definitions of ω_k and σ_k in Eqs. (2) and (3).[2,3] Examination of Eq. (30) shows that only two functions need to be computed; namely, $e(t)$ in Eq. (32) and

$$g(t) = 4 \sum_{k=-N}^{N} \frac{\sigma_k^2}{\omega_k^2} \sin \omega_k t \tag{33}$$

To determine $g(t)$, we substitute Eqs. (2) and (3) into Eq. (33) and let $N \to \infty$, to obtain

$$g(t) = \frac{32\bar{\chi}^2}{\pi \hbar^2 \omega_a^2} \int_0^{\pi/2} dy \frac{\cos^2 y}{\sin y} \sin(\omega_a t \sin y)$$
$$= \frac{16\bar{\chi}^2}{\hbar^2 \omega_a^2} \int_0^{\omega_a t} dx \frac{J_1(x)}{x} \tag{34}$$

where a standard integral representation for the Bessel function $J_1(x)$ is used. Substituting Eq. (12), we have

$$g(t) = \frac{8\eta}{\omega_a} \int_0^{\omega_a t} dx \frac{J_1(x)}{x} \tag{35}$$

so that

$$f(t) = \frac{1}{Q_D} \sum_{n=0}^{n_{\max}} e^{-\beta E_n} \{ (n+1) \cos\{ [\omega_0 - 8\eta(n+1)]\, t + g(t) \}$$
$$- n \cos[(\omega_0 - 8\eta n)\, t - g(t)] \} \tag{36}$$

By a similar argument, the function $e(t)$ can be written as

$$e(t)=\exp\left[-\frac{64\bar{\chi}^2}{\pi\hbar^2\omega_a^2}\int_0^1 dy\frac{1}{y}(1-y^2)^{1/2}\sin^2\frac{\omega_a t y}{2}\coth\left(\frac{\beta\hbar\omega_a y}{2}\right)\right] \tag{37}$$

We have not achieved a further reduction of this integral. Since Eqs. (35) and (37) are both one-dimensional integrals, it is a simple matter to calculate them numerically, using, for example, Simpson's rule. Thus, we have achieved through Eqs. (30), (35), and (37) an exact solution for the Davydov time correlation function in Eq. (4) which can easily be computed for arbitrary choice of the defining parameters. In the next sections we further extend the analytic analysis and develop both short- and long-time forms.

3. TIME CORRELATION FUNCTION AT SHORT TIMES

We begin by examining $g(t)$ in Eq. (33). We have, after expansion of the sine function, that

$$g(t)\cong 4t\sum_k \frac{\sigma_k^2}{\omega_k}=4\eta t \tag{38}$$

for t small, using Eq. (12). Similarly, the function $e(t)$ in Eq. (32) reduces to

$$e(t)\cong\exp\left[-2t^2\sum_k \sigma_k^2\coth\left(\frac{\beta\hbar\omega_k}{2}\right)\right] \tag{39}$$

at small t so that

$$\begin{aligned}\dot{\chi}(t)\cong{}&\exp\left[-2t^2\sum_k \sigma_k^2\coth\left(\frac{\beta\hbar\omega_k}{2}\right)\right]\\&\times\frac{1}{Q_D}\sum_{n=0}^{n_{\max}} e^{-\beta E_n}\cos[\omega_0-4\eta(2n+1)]\,t\end{aligned} \tag{40}$$

which can then be further expanded to give

$$\dot{\chi}(t)\cong 1-\frac{1}{2}\left[(\omega_0-4\eta\langle 2n+1\rangle_D)^2+4\sum_k\sigma_k^2\coth\left(\frac{\beta\hbar\omega_k}{2}\right)\right]t^2 \tag{41}$$

This is in agreement with MTGLE theory,[11-16] which gives for short times

$$\dot{\chi}(t)\cong 1-\tfrac{1}{2}\omega_{e0}^2 t^2 \tag{42}$$

where

$$\omega_{e0}^2=\langle[\dot{c}(0),\dot{c}^\dagger(0)]\rangle \tag{43}$$

4. TIME CORRELATION FUNCTION AT LONGER TIMES

We first examine $g(t)$ in Eq. (34). For long times we approximate $g(t)$ as

$$g(t) \cong \frac{16\bar{\chi}^2}{\hbar^2\omega_a^2} \int_0^\infty dx \frac{J_1(x)}{x} \tag{44}$$

since the integrand goes to zero at large values of x. The integral is found to be equal to 1, so that

$$g(t) \cong \frac{16\bar{\chi}^2}{\hbar^2\omega_a^2} = \frac{8\eta}{\omega_a} \tag{45}$$

at long times.

We next focus on the exponential in Eq. (37). The argument of the exponential can be broken up into a contribution independent of temperature and a part which becomes nonzero only as temperature increases from $T = 0\text{K}$. This is accomplished by rewriting the hyperbolic cotangent factor in the form

$$\coth\left(\frac{\beta\hbar\omega_a y}{2}\right) = 1 + \left[\coth\left(\frac{\beta\hbar\omega_a y}{2}\right) - 1\right] \tag{46}$$

Note that the temperature-dependent factor in brackets goes to zero at $T = 0\text{K}$. Focusing first on the temperature-independent part, we have

$$-\frac{64\bar{\chi}^2}{\pi\hbar^2\omega_a^2} \int_0^1 dy \frac{(1-y^2)^{1/2}}{y} \sin^2\frac{\omega_a t y}{2} = -\frac{8\eta}{\omega_a} \int_0^{\omega_a t} dx \frac{\mathscr{H}_1(x)}{x} \tag{47}$$

where $\mathscr{H}_1(x)$ is the Struve function.[21] One can show by a variety of arguments, including numerical integration via computer, that

$$\lim_{t\to\infty} \left[\int_0^{\omega_a t} dx \frac{\mathscr{H}_1(x)}{x} - \frac{2}{\pi} \ln \omega_a t\right] = 0.172118 \tag{48}$$

Thus, the long-time form for the exponential factor in Eq. (37) at $T = 0\text{K}$ is

$$e(t) \cong (\omega_a t)^{-16\eta/\pi\omega_a} \exp\left[-\frac{8\eta}{\omega_a}(0.172118)\right] \tag{49}$$

Combining Eqs. (30), (45), and (49) at $T = 0\,\text{K}$, we have

$$\chi(t) \cong \frac{\exp[-(8\eta/\omega_a)(0.172118)]}{(\omega_a t)^{16\eta/\pi\omega_a}} \cos\left[(\omega_0 - 8\eta)\,t + \frac{8\eta}{\omega_a}\right] \tag{50}$$

We find that the exact quantum time correlation function $\dot{\chi}(t)$ at $T=0$ K has a long-time tail or power law decay. We believe this result to be a new and previously unknown example of a long-time tail.

We turn next to the contribution of the second temperature-dependent term in Eq. (46) to the exponential factor in Eq. (37). We have that

$$-\frac{64\bar{\chi}^2}{\pi\hbar^2\omega_a^2}\int_0^1 dy\,\frac{(1-y^2)^{1/2}}{y}\sin^2\frac{\omega_a t y}{2}\left[\coth\left(\frac{\beta\hbar\omega_a y}{2}\right)-1\right]$$
$$=-\frac{128\bar{\chi}^2}{\pi\hbar^2\omega_a^2}\int_0^1 dy\,\frac{(1-y^2)^{1/2}}{y(e^{\beta\hbar\omega_a y}-1)}\sin^2\frac{\omega_a t y}{2} \tag{51}$$

At not too high a temperature the principal contributions to the integral come at small y, so we drop the square root term and extend the upper limit to infinity. Thus,

$$-\frac{128\bar{\chi}^2}{\pi\hbar^2\omega_a^2}\int_0^1 dy\,\frac{(1-y^2)^{1/2}}{y(e^{\beta\hbar\omega_a y}-1)}\sin^2\frac{\omega_a t y}{2}$$
$$\cong -\frac{128\bar{\chi}^2}{\pi\hbar^2\omega_a^2}\int_0^\infty dy\,\frac{\sin^2(\omega_a t y/2)}{y(e^{\beta\hbar\omega_a y}-1)}$$
$$=-\frac{16\eta}{\pi\omega_a}\left[\frac{\pi t}{\hbar\beta}+\ln\left(\frac{1-\exp(-2\pi t/\hbar\beta)}{2\pi t/\hbar\beta}\right)\right] \tag{52}$$

The final integration in Eq. (52) was obtained from a standard source.[22] Combining the $T=0$ K result in Eq. (48) with Eq. (52), we have for $e(t)$ at long times and $T>0$ K that

$$e(t)=\exp\left(-\frac{8\eta}{\omega_a}\left\{0.172118+\frac{2}{\pi}\ln\frac{\hbar\omega_a\beta}{2\pi}+\frac{2}{\pi}\ln\right.\right.$$
$$\left.\left.\times\left[1-\exp\left(-\frac{2\pi t}{\hbar\beta}\right)\right]+\frac{2t}{\hbar\beta}\right\}\right) \tag{53}$$

We have tested this approximate long-time form against the exact solution in Eq. (37) for a variety of parameter choices and find excellent agreement. As an example, we show in Figs. 1 and 2 plots of $\ln e(t)$ for Eqs. (37) and (53) at very short (Fig. 1) and at long times (Fig. 2). The parameter values are $\hbar\omega_0=30\text{ cm}^{-1}$, $\hbar\omega_a=60\text{ cm}^{-1}$, $\bar{\chi}=0.3\text{ cm}^{-1}$, and $T=50$ K. This particular choice of parameters is described elsewhere.[3] The agreement is manifest.

An approximate closed form for the D-space sum in Eq. (36) can be obtained using the result for $g(t)$ in Eq. (45). We begin by dropping the n^2

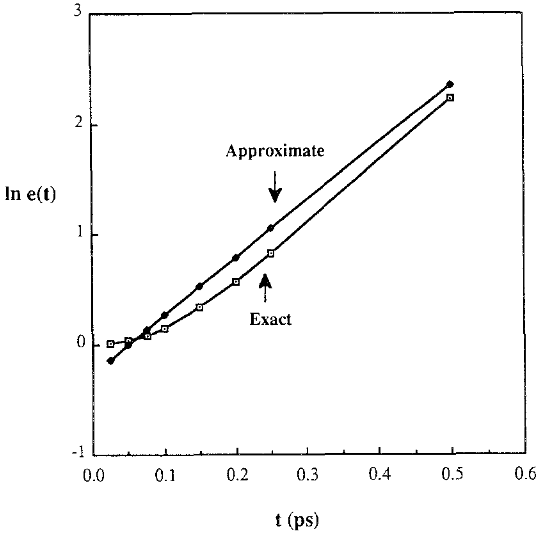

Fig. 1. Comparison of exact exponential factor with approximate analytic long-time form at short times.

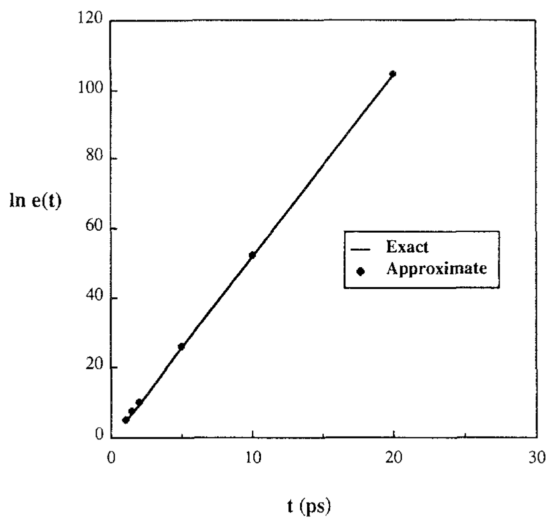

Fig. 2. Comparison of exact exponential factor with approximate analytic long-time form at long times.

term in Eq. (25) for E_n. We denote the approximate energy by E_n^a and obtain

$$E_n^a = \hbar\omega_1 n + \frac{\hbar\omega_0}{2} - \hbar\eta \tag{54}$$

where

$$\omega_1 = \omega_0 - 4\eta \tag{55}$$

Noting that

$$E_n^a = E_{n+1}^a - \hbar\omega_1 \tag{56}$$

we have, letting $n_{\max}$ become indefinitely large,

$$f(t) \cong \frac{1}{Q_D} \sum_{n=0}^{\infty} e^{-\beta E_n^a} \Bigg((n+1) \cos \left\{ [\omega_0 - 8\eta(n+1)]\, t + \frac{8\eta}{\omega_a} \right\} - n \cos \left[(\omega_0 - 8\eta n) t - \frac{8\eta}{\omega_a} \right] \Bigg) \tag{57}$$

and then resetting the index n in the first term,

$$f(t) \cong \frac{1}{Q_D^a} \sum_{n=1}^{\infty} e^{-\beta E_n^a} n \left\{ e^{\beta\hbar\omega_1} \cos \left[(\omega_0 - 8\eta n)\, t + \frac{8\eta}{\omega_a} \right] - \cos \left[(\omega_0 - 8\eta n)\, t - \frac{8\eta}{\omega_a} \right] \right\} \tag{58}$$

At long times the factor $\pm 8\eta/\omega_a$ in Eq. (58) can be dropped to yield

$$f(t) = \frac{e^{\beta\hbar\omega_1} - 1}{Q_D^a} \sum_{n=1}^{\infty} e^{-\beta E_n^a} n [\cos(\omega_0 - 8\eta n)\, t] \tag{59}$$

The partition function can be evaluated and we have

$$Q_D^a = \sum_{n=0}^{\infty} e^{-\beta E_n^a} = \frac{\exp[-\beta(\hbar\omega_0/2 - \hbar\eta)]}{1 - e^{-\beta\hbar\omega_1}} \tag{60}$$

Substituting Eq. (60) into Eq. (59) yields

$$\begin{aligned} f(t) &= (e^{\beta\hbar\omega_1} - 1)(1 - e^{-\beta\hbar\omega_1}) \sum_{n=1}^{\infty} e^{-\beta\hbar\omega_1 n} n \{\cos(\omega_0 - 8\eta n)\, t\} \\ &= \mathrm{Re}(e^{\beta\hbar\omega_1} - 1)(1 - e^{-\beta\hbar\omega_1}) \frac{\exp(i\omega_0 t - \beta\hbar\omega_1 - i8\eta t)}{[1 - \exp(-\beta\hbar\omega_1 - i8\eta t)]^2} \end{aligned} \tag{61}$$

Rearrangement of Eq. (61) by some straightforward but tedious manipulations yields

$$f(t)=\frac{2\cos(\omega_0 t-2\tan^{-1}\{[2n(\omega_1)+1]\tan 4\eta t\})}{1+[2n(\omega_1)+1]^2+\{1-[2n(\omega_1)+1]^2\}\cos 8\eta t} \tag{62}$$

where

$$n(\omega_1)=\frac{1}{e^{\beta\hbar\omega_1}-1} \tag{63}$$

Although it is an approximate form, we have found Eq. (62) to be extremely useful in another context.[3] To achieve a final approximate long-time expression for $\dot{\chi}(t)$, we combine Eqs. (53) and (62) to obtain

$$\begin{aligned}\dot{\chi}(t)\cong\exp\Bigg(&-\frac{8\eta}{\omega_a}\bigg\{0.172118+\frac{2}{\pi}\ln\frac{\hbar\omega_a\beta}{2\pi}\\&+\frac{2}{\pi}\ln\left[1-\exp\left(-\frac{2\pi t}{\hbar\beta}\right)\right]+\frac{2t}{\hbar\beta}\bigg\}\Bigg)\\&\times\frac{2\cos(\omega_0 t-2\tan^{-1}\{[2n(\omega_1)+1]\tan 4\eta t\})}{1+[2n(\omega_1)+1]^2+\{1-[2n(\omega_1)+1]^2\}\cos 8\eta t}\end{aligned} \tag{64}$$

In examining the exponential contribution $e(t)$ from Eq. (53) to Eq. (64) we find there are several time regimes. For $2\pi t\gg\hbar\beta$ we find

$$e(t)=\exp\left(-\frac{16\eta}{\hbar\omega_a\beta}t\right) \tag{65}$$

which displays exponential decay for $T>0$ K. For $2\pi t\ll\hbar\beta$, but beyond initial transients, we find

$$e(t)=\exp\left[-\frac{8\eta}{\omega_a}\left(0.172118+\frac{2}{\pi}\ln\omega_a t\right)\right] \tag{66}$$

Equation (64) therefore shows that for $t\ll\hbar/2\pi kT$, $\dot{\chi}(t)$ decays as a small power of time in agreement with Eq. (50), but that for $t\gg\hbar/2\pi kT$, $\dot{\chi}(t)$ decays exponentially. Thus, for very low temperatures there is a long period of small power law decay followed by exponential decay.

5. CONCLUSION

We have examined a time correlation function for a nonlinear condensed matter Hamiltonian whose spectral density is related to the dipole spectrum. The Hamiltonian, which couples a single oscillator nonlinearly to a chain of oscillators, can be diagonalized. Using the diagonalization results, we have obtained an exact expression for the TCF. Using this expression, we have obtained exactly the long-time behavior and shown that the TCF decays as a power law at $T=0$ K. At somewhat higher temperatures there is an extended period of time during which the TCF decays as a power law followed finally by exponential decay. We believe this behavior to be a new result which adds to our understanding of time correlation functions.

APPENDIX

From Eq. (19) one finds that

$$[S(t), -S(0)] = -4 \sum_k \frac{\sigma_k^2}{\omega_k^2} (e^{i\omega_k t} - e^{-i\omega_k t}) \tag{A.1}$$

Using the operator relation

$$e^A e^B = e^{A+B} e^{[A,B]/2} \tag{A.2}$$

and Eq. (21) yields

$$\langle e^{S(t)} e^{-S(0)} \rangle_B = \exp\left[-2 \sum_k \frac{\sigma_k^2}{\omega_k^2} (e^{i\omega_k t} - e^{-i\omega_k t}) \right] \frac{1}{Q_B} \times \sum_{\{n\}=0}^{\infty} \exp\left[-\beta\hbar \sum_k \omega_k \left(n_k + \frac{1}{2} \right) \right] M\{n\} \tag{A.3}$$

where

$$M\{n\} = \langle \{n\} | \exp\left\{ 2 \sum_k \frac{\sigma_k}{\omega_k} [(e^{i\omega_k t} - 1) B_k^\dagger(0) + (1 - e^{-i\omega_k t}) B_k(0)] \right\} | \{n\} \rangle \tag{A.4}$$

and

$$\{n\} = n_{-N}, n_{-N+1}, \ldots, n_{N-1}, n_N \tag{A.5}$$

Focusing on $M\{n\}$ and using Eq. (A.2) again yields

$$M\{n\} = \exp\left[-2 \sum_k \frac{\sigma_k}{\omega_k} (e^{i\omega_k t} - 1)(1 - e^{-i\omega_k t}) \right] \times \langle \{n\} | \exp\left[\sum_k \mu_k B_k(0) \right] \exp\left[\sum_k \nu_k B_k^\dagger(0) \right] | \{n\} \rangle \tag{A.6}$$

where

$$\mu_k = 2\frac{\sigma_k}{\omega_k}(1 - e^{-i\omega_k t}) \tag{A.7a}$$

and

$$\nu_k = 2\frac{\sigma_k}{\omega_k}(e^{i\omega_k t} - 1) \tag{A.7b}$$

The matrix elements in Eq. (A.6) can be rewritten as

$$\begin{aligned}\langle\{n\}|\exp\left[\sum_k \mu_k B_k(0)\right]\exp\left[\sum_k \nu_k B_k^\dagger(0)\right]|\{n\}\rangle \\ = \prod_{k=-N}^{N} \langle n_k|\, e^{\mu_k B_k(0)} e^{\nu_k B_k^\dagger(0)}\, |n_k\rangle\end{aligned} \tag{A.8}$$

which is easily shown to be equal to

$$\prod_{k=-N}^{N}\sum_{\lambda=0}^{\infty}\frac{(\mu_k\nu_k)^\lambda}{(\lambda!)^2}\frac{(n_k+\lambda)!}{n_k!}$$

Thus,

$$\begin{aligned}&\langle e^{S(t)}e^{-S(0)}\rangle_B \\ &= \exp\left[4\sum_k \frac{\sigma_k^2}{\omega_k^2}(1 - e^{i\omega_k t})\right] \\ &\times \prod_{k=-N}^{N}\frac{1 - e^{-\beta\hbar\omega_k}}{e^{-\beta\hbar\omega_k/2}}\sum_{n_k=0}^{\infty}\exp\left[-\beta\hbar\omega_k\left(n_k + \frac{1}{2}\right)\right] \\ &\times \sum_{\lambda=0}^{\infty}\frac{(\mu_k\nu_k)^\lambda}{(\lambda!)^2}\frac{(n_k+\lambda)!}{n_k!}\end{aligned} \tag{A.9}$$

Using the fact that

$$\left(\frac{1}{1-x}\right)^{n+1} = \sum_{\lambda=0}^{\infty}\frac{x^\lambda (n+\lambda)!}{n!\,\lambda!} \tag{A.10}$$

we obtain, after carrying out the λ and n_k summations in Eq. (A.9), that

$$\begin{aligned}\langle e^{S(t)}e^{-S(0)}\rangle_B = \exp\Bigg[&-4i\sum_k \frac{\sigma_k^2}{\omega_k^2}\sin\omega_k t \\ &+ 4\sum_k \frac{\sigma_k^2}{\omega_k^2}(\cos\omega_k t - 1)\coth\left(\frac{\beta\hbar\omega_a}{2}\right)\Bigg]\end{aligned} \tag{A.11}$$

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