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Phonon thermal baths: A treatment in terms of reduced models

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We describe a general procedure for building up reduced heatbaths simulating a many-body system of coupled harmonic oscillators. Finite lifetimes of phonons can be taken into account by the appropriate generalization of the Mori formalism that provides the tool for modeling the real phonon reservoir. The related Fokker-Planck equation is also discussed.

I. INTRODUCTION

The classical subject of the lattice dynamics of solids is an active and rapidly developing field of investigation[1,2], no longer focused[3] on the harmonic approximation. The statistical properties of a system of coupled oscillators have also been widely investigated.[2-4] Since a number of properties of interest can be calculated exactly, this many-body system constitutes a natural candidate to test and apply new theoretical techniques. The problem of building up reduced heatbaths to simulate actual solids has recently received increasing attention[5,6] because of its important implications. So far, however, the attempts have been confined to harmonic crystals mainly in the Debye approximation. The purpose of this paper is to provide a systematic and simple procedure for replacing a true phonon reservoir including anharmonic effects with an equivalent one with a few degrees of freedom. This purpose is achieved by appropriate generalization and application of the Mori memory-function formalism.[7]

It is well known that the Mori formalism has been successfully applied to a large variety of phenomena concerning relaxation. For example Lado *et al.*[8] used a procedure of the Mori type for building up a general approach to the line-shape problem in nuclear-magnetic-resonance spectra. This work contains elements of considerable interest. In particular Lado *et al.*[8] pointed out a close relationship between the Mori procedure and the "classical moment problem" of mathematical analysis.[9] They expressed the Laplace transform of the correlation function $\langle A \mid A(t) \rangle$ (A is the variable of interest) by a continued fraction expansion. The parameters of this continued fraction are then expressed in terms of the spectral moments $\langle A \mid (iL)^n \mid A \rangle / \langle A \mid A \rangle$ where L is the dynamical operator driving the variable of interest $\mid A \rangle$ according to the law[10]

$$\frac{d}{dt} \mid A \rangle = iL \mid A \rangle \ . \tag{1}$$

Their results completely agree with Dupuis's findings.[11] However, Dupuis by using mathematical arguments did obtain a continued fraction whatever the nature of L is. On the contrary, the Mori theory[7] is strongly based on the assumption that L is Hermitian. This ambiguous feature is completely clarified by the present work. We shall show, in fact, that the Mori approach can be extended to the case of dynamical operators without definite symmetry properties. Schneider[12] in his effort to generalize the Mori theory confined his attention on pseudosymmetric dynamical operators.

Our point of view is closely related to that of Ref. 13 and to the recent theoretical developments of the Mori school,[14,15] which in turn generalize the procedure derived by De Raedt *et al.*[16] in the context of studies on the classical Heisenberg chain. In this recent work,[15] in fact, the Mori school recognizes the importance of studying the time evolution of the flux variables. This is indeed the kind of time evolution to be studied for building up the Fokker-Planck equation driving the phonon operators of interest, considered as stochastic variables.

Our strategy is as follows. In Sec. II, we give a brief survey of the generalized Mori theory, which is our basic tool for describing phonon baths in the presence of anharmonic effects. The parameters of

the Mori chain are evaluated with the help of the Dupuis algorithm, which allows a routine calculation of the quantities of interest. In Sec. III we provide for the first time a systematic procedure for replacing a real-phonon thermal bath with an equivalent one with a few degrees of freedom. In Sec. IV we illustrate operatively our procedure by applying it to the specific case of the Einstein and Debye models. In Sec. V we further exploit the complementary aspects between the generalized Mori theory and the Dupuis algorithm. Whereas the latter makes it possible to get a fast computational approach, the former enables us to replace the quantum-mechanical Liouvillian driving the thermal bath with a quite useful mathematical tool, i.e., the Fokker-Planck operator.

II. THE GENERALIZED MORI THEORY AND THE DUPUIS ALGORITHM

In this section we give a brief account of the theoretical tools which are needed for modeling harmonic or anharmonic phonon baths. The novelty of this section is given by the general relationship, here established for the first time, between the Mori theory and the computational algorithm[8,9,11] (referred to as the Dupuis algorithm from the author[11] who first gave a detailed account of it). For the benefit of the reader, throughout this paper we use familiar notations borrowed from the quantum-mechanical formalism.

Given a variable of interest A, consider the standard equation of motion

$$\frac{d}{dt}A = iLA \ . \tag{2}$$

After properly defining a scalar product among operators,[7] we can adopt the quantum-mechanical formalism, to which Eq. (1) is related. The standard Mori theory is based on the assumption that L is Hermitian with respect to the scalar product, i.e.,

$$\langle A \mid L \mid B \rangle = \langle B \mid L \mid A \rangle^* \ . \tag{3}$$

In order to treat anharmonicities we shall simulate their influence on the normal modes by suitable operators local in time, which destroy the Hermitian nature of the Liouvillian L. As a consequence, a major care of this section is devoted to avoiding the Hermitian assumption.

Without using the property of Eq. (3), Dupuis[11] showed that the Laplace transform of the correlation function,

$$\Phi(t) = \frac{\langle A \mid \exp(iLt) \mid A \rangle}{\langle A \mid A \rangle} \ , \tag{4}$$

can be written as follows,

$$\hat{\Phi}(z) = \cfrac{1}{z - a_0 - \cfrac{b_1^2}{z - a_1 - \cfrac{b_2^2}{z - a_2 - \cdots}}} \ . \tag{5}$$

The parameters a_i and b_i of this continued fraction are defined as

$$a_n = \frac{D_{n-1}}{D_n} \mathcal{F}[\lambda P_n(\lambda) P_n(\lambda)] \ ,$$

$$b_0 = 0, \quad b_n^2 = \frac{D_n D_{n-2}}{D_n}, \quad D_{-1} = 1 \ .$$

The orthogonal set of polynomials $P_n(\lambda)$ is given by

$$P_0(\lambda) = 1 \ ,$$

$$P_n(\lambda) = \frac{1}{D_{n-1}} \begin{vmatrix} s_0 & s_1 & \cdots & s_n \\ s_1 & s_2 & \cdots & s_{n+1} \\ \vdots & \vdots & \ddots & \vdots \\ s_{n-1} & s_n & \cdots & s_{2n-1} \\ 1 & \lambda & \cdots & \lambda^n \end{vmatrix} \ ,$$

The symbols D_n denote the Hankel determinants

$$D_n \equiv \begin{vmatrix} s_0 & s_1 & \cdots & s_n \\ s_1 & s_2 & \cdots & s_{n+1} \\ \vdots & \vdots & \ddots & \vdots \\ s_n & s_{n+1} & \cdots & s_{2n} \end{vmatrix} \ ,$$

where s_n are the spectral moments

$$s_n \equiv \frac{\langle A \mid (iL)^n \mid A \rangle}{\langle A \mid A \rangle} \ .$$

The symbol $\mathcal{F}$ denotes a scalar product for polynomials defined by

$$\mathcal{F}(\alpha_0 + \alpha_1 \lambda + \alpha_2 \lambda^2 + \cdots) = \alpha_0 s_0 + \alpha_1 s_1 + \alpha_2 s_2 + \cdots \ .$$

By using this general algorithm it is straightforward to build up the continued fraction of Eq. (5) in terms of the moments s_n. Dupuis[11] could not entirely exploit the generality of his approach, in that he was obliged to make the Hermitian assumption on L for establishing a relationship between his and Mori's approach. We can establish a

wider connection simply by noticing that Mori's approach can be extended to the case of a non-Hermitian Liouvillian. Such an interesting result can be obtained by building up the following sequence of biorthogonal variables[17]

$$
\begin{aligned}
&|f_0\rangle = A \ , \\
&P_0 = |f_0\rangle\langle f_0|f_0\rangle^{-1}\langle f_0| \ , \\
&|f_1\rangle = (1-P_0)iL\,|f_0\rangle \ , \\
&\langle \tilde{f}_1| = \langle f_0|iL(1-P_0) \ , \\
&P_1 = |f_1\rangle\langle \tilde{f}_1|f_1\rangle^{-1}\langle \tilde{f}_1| \ , \\
&|f_2\rangle = \langle 1-P_1)(1-P_0)iL\,|f_1\rangle \ , \\
&\langle \tilde{f}_2| = \langle \tilde{f}_1|iL(1-P_0)(1-P_1) \ , \\
&P_2 = |f_2\rangle\langle \tilde{f}_2|f_2\rangle^{-1}\langle \tilde{f}_2| \ ,
\end{aligned}
\tag{6}
$$

etc. By a straightforward extension of the standard Mori approach,[7] we then obtain

$$
\hat{\Phi}_0(z) = \cfrac{1}{z-\lambda_0+\cfrac{\Delta_1^2}{z-\lambda_1+\cfrac{\Delta_2^2}{z-\lambda_2+\cdots}}} \ , \tag{7}
$$

where

$$
\lambda_i \equiv \langle \tilde{f}_i|iL\,|f_i\rangle / \langle \tilde{f}_i|f_i\rangle \ , \tag{8a}
$$

$$
\Delta_i^2 \equiv -\langle \tilde{f}_i|f_i\rangle / \langle \tilde{f}_{i-1}|f_{i-1}\rangle \ . \tag{8b}
$$

It is evident that Mori's parameters λ_i and Δ_i^2 can be identified with Dupuis's parameters a_i and $-b_i^2$, respectively. We can thus write

$$
\lambda_i = \frac{D_{i-1}}{D_i}\mathcal{F}[\lambda P_i(\lambda)P_i(\lambda)] \ , \tag{9a}
$$

$$
\Delta_i^2 = -\frac{D_i D_{i-2}}{D_{i-1}^2} \ . \tag{9b}
$$

The Dupuis expressions (9a) and (9b) for λ_i^2 and Δ_i^2 are much more convenient from a computational point of view than the corresponding Mori expressions (8a) and (8b). We have now available all the tools required for a thorough treatment of phonon baths.

III. MODELING OF PHONON BATHS IN THE GENERAL CASE

In recent years it has become almost standard procedure to investigate (theoretically or experimentally) not only the phonon dispersion curves but also the phonon lifetimes due to anharmonic effects.[2,3] In a number of cases the phonon lifetimes are quite important, in that some phonons vibrate not more than ten times, or even less before decaying.

To keep our problem to the essential, we consider for simplicity a solid with one atom of mass M per unit cell. In the harmonic approximation, the nuclear motion is described by the Hamiltonian

$$
H_0 = \sum_{\vec{q}j} \hbar\omega_{\vec{q}j}(a^\dagger_{\vec{q}j}a_{\vec{q}j} + \tfrac{1}{2}) \ , \tag{10}
$$

where $a^\dagger_{\vec{q}j}$ and $a_{\vec{q}j}$ are the creation and annihilation operators for the phonon of wave vector $\vec{q}$, branch index j, and frequency $\omega_{\vec{q}j}$. In our case of a simple lattice with N unit cells, j takes only three values, while $\vec{q}$ runs over the N allowed values in the first Brillouin zone.

When the crystal is in thermal equilibrium, the only nonvanishing scalar products between creation and annihilation operators are those of the type $\langle a_{\vec{q}j}|a_{\vec{q}j}\rangle$ and $\langle a^\dagger_{\vec{q}j}|a^\dagger_{\vec{q}j}\rangle$. In the classical limit of temperatures much higher than the Debye temperature, we have

$$
\begin{aligned}
\langle a_{\vec{q}j}|a_{\vec{q}j}\rangle &= \frac{1}{e^{\hbar\omega_{\vec{q}j}/\kappa_B T}-1} \\
&\simeq \frac{k_B T}{\hbar\omega_{\vec{q}j}} \simeq \langle a^\dagger_{\vec{q}j}|a^\dagger_{\vec{q}j}\rangle \ .
\end{aligned}
\tag{11}
$$

The equations of motion of the operators $a_{\vec{q}j}$ and $a^\dagger_{\vec{q}j}$ driven by the Liouvillian L_0 corresponding to the Hamiltonian H_0 are

$$
\begin{aligned}
&\frac{d}{dt}a_{\vec{q}j} = iL_0 a_{\vec{q}j} = -i\omega_{\vec{q}j}a_{\vec{q}j} \ , \\
&\frac{d}{dt}a^\dagger_{\vec{q}j} = iL_0 a^\dagger_{\vec{q}j} = i\omega_{\vec{q}j}a^\dagger_{\vec{q}j} \ .
\end{aligned}
\tag{12}
$$

When anharmonic effects are taken into account, we expect a (small) renormalization of the phonon dispersion curves and a damping parameter $\Gamma_{\vec{q}j}$ to be added in the equation of motion of the operators $a_{\vec{q}j}$ and $a^\dagger_{\vec{q}j}$. The effective Liouvillian L becomes

$$
\begin{aligned}
&iLa_{\vec{q}j} \equiv (-i\omega_{\vec{q}j} - \Gamma_{\vec{q}j})a_{\vec{q}j} \ , \\
&iLa^\dagger_{\vec{q}j} \equiv (i\omega_{\vec{q}j} - \Gamma_{\vec{q}j})a^\dagger_{\vec{q}j} \ .
\end{aligned}
\tag{13}
$$

Thus,

$$
\begin{aligned}
&a_{\vec{q}j}(t) = a_{\vec{q}j}e^{(-i\omega_{\vec{q}j}-\Gamma_{\vec{q}j})t} \ , \\
&a^\dagger_{\vec{q}j}(t) = a^\dagger_{\vec{q}j}e^{(i\omega_{\vec{q}j}-\Gamma_{\vec{q}j})t} \ ,
\end{aligned}
\tag{14}
$$

and the correlation functions for phonon annihila-

tion and creation operators are $e^{-i\omega_{\vec{q}j}t-\Gamma_{\vec{q}j}t}$ and $e^{i\omega_{\vec{q}j}-\Gamma_{\vec{q}j}t}$, respectively.

Throughout this paper we are interested in the autocorrelation function of the displacement of a generic atom belonging to the solid. The procedure here outlined can straightforwardly be extended to the other variables of interest (such as "the interaction modes" of the work of Takagahara *et al.*[18] on second-order optical processes).

The displacement $\vec{u}_n$ of the atom in the generical cell $\vec{\tau}_n$ (without loss of generality we keep $\vec{\tau}_n=0$) can always be expanded in normal modes[19]

$$\vec{u}_n=\frac{1}{\sqrt{N}}\sum_{\vec{q}j}\vec{e}_{\vec{q}j}\left[\frac{\hbar}{2M\omega_{\vec{q}j}}\right]^{1/2}(a_{\vec{q}j}+a^{\dagger}_{\vec{q}j}) , \tag{15}$$

where the polarization vectors $\vec{e}_{\vec{q}j}$ (assumed to be real for simplicity) satisfy the orthogonality conditions $\vec{e}_{\vec{q}j}\cdot\vec{e}_{\vec{q}j'}=\delta_{jj'}$. We consider as our variable of interest the component u_{nx} of the atomic displacement along, say, the x axis:

$$u_{nx}\equiv f_0=\frac{1}{\sqrt{N}}\sum_{\vec{q}j}e_{x\vec{q}j}\left[\frac{\hbar}{2M}\omega_{\vec{q}j}\right]^{1/2}\times(a_{\vec{q}j}+a^{\dagger}_{\vec{q}j}) . \tag{16}$$

Let us evaluate the normalization factor:

$$\langle f_0\,|\,f_0\rangle=\frac{1}{N}\sum_{\vec{q}j}e^2_{x\vec{q}j}\frac{\hbar}{2M\omega_{\vec{q}j}}\times\langle a_{\vec{q}j}+a^{\dagger}_{\vec{q}j}\,|\,a_{\vec{q}j}+a^{\dagger}_{\vec{q}j}\rangle . \tag{17}$$

To eliminate inessential difficulties, we assume that the crystal has cubic symmetry. This enables us to replace the polarization vectors in Eq. (17) with the $\frac{1}{3}$ factor. Using Eq. (11) we have

$$\langle f_0\,|\,f_0\rangle=\frac{1}{3N}\sum_{\vec{q}j}\frac{\hbar}{2M\omega_{\vec{q}j}}(\langle a_{\vec{q}j}\,|\,a_{\vec{q}j}\rangle+\langle a^{\dagger}_{\vec{q}j}\,|\,a^{\dagger}_{\vec{q}j}\rangle)=\frac{k_BT}{M}\frac{1}{3N}\sum_{\vec{q}j}\frac{1}{\omega^2_{\vec{q}j}}=\frac{k_BT}{M}\left\langle\frac{1}{\omega^2_{\vec{q}j}}\right\rangle , \tag{18}$$

where the symbol $\langle\ \rangle$ is a shorthand notation to denote the average on the phonon branches and on the Brillouin zone.

If we define the adiabatic frequency as

$$\frac{1}{\omega_a^2}=\left\langle\frac{1}{\omega^2_{\vec{q}j}}\right\rangle , \tag{19}$$

we can write Eq. (18) in the compact form

$$\langle f_0\,|\,f_0\rangle=\frac{k_BT}{M\omega_a^2} . \tag{20}$$

The calculation of the moments is also straightforward. Using Eqs. (11), (13), (16), and (20) we have

$$s_m=\frac{\langle f_0\,|\,(iL)^m\,|\,f_0\rangle}{\langle f_0\,|\,f_0\rangle}=\frac{M\omega_a^2}{k_BT}\frac{1}{3N}\sum_{\vec{q}j}\frac{\hbar}{2M\omega_{\vec{q}j}}[\langle a_{\vec{q}j}\,|\,(iL)^m\,|\,a_{\vec{q}j}\rangle+\langle a^{\dagger}_{\vec{q}j}\,|\,(iL)^m\,|\,a^{\dagger}_{\vec{q}j}\rangle]$$
$$=\omega_a^2\left\langle\frac{1}{2\omega^2_{\vec{q}j}}[(-i\omega_{\vec{q}j}-\Gamma_{\vec{q}j})^m+(i\omega_{\vec{q}j}-\Gamma_{\vec{q}j})^m]\right\rangle . \tag{21}$$

The explicit expressions of the lowest few moments s_m are (omitting for simplicity the indices $\vec{q}j$ on $\omega_{\vec{q}j}$ and $\Gamma_{\vec{q}j}$, whenever this does not generate confusion)

$$s_0=1 ,$$
$$s_1=\omega_a^2\left\langle-\frac{\Gamma}{\omega^2}\right\rangle ,$$
$$s_2=\omega_a^2\left\langle\frac{-\omega^2+\Gamma^2}{\omega^2}\right\rangle ,$$
$$s_3=\omega_a^2\left\langle\frac{3\omega^2\Gamma-\Gamma^3}{\omega^2}\right\rangle ,$$
$$s_4=\omega_a^2\left\langle\frac{\omega^4-6\omega^2\Gamma^2+\Gamma^4}{\omega^2}\right\rangle , \tag{22}$$
$$s_5=\omega_a^2\left\langle\frac{-5\omega^4\Gamma+10\omega^2\Gamma^3-\Gamma^5}{\omega^2}\right\rangle ,$$
$$s_6=\omega_a^2\left\langle\frac{-\omega^6+15\omega^4\Gamma^2-15\omega^2\Gamma^4+\Gamma^6}{\omega^2}\right\rangle ,$$

$$s_7=\omega_a^2\left\langle\frac{7\omega^6\Gamma-35\omega^4\Gamma^3+21\omega^2\Gamma^5-\Gamma^7}{\omega^2}\right\rangle,$$

$$s_8=\omega_a^2\left\langle\frac{\omega^8-28\omega^6\Gamma^2+70\omega^4\Gamma^4-28\omega^2\Gamma^6+\Gamma^8}{\omega^2}\right\rangle,$$

and so on.

The average over the Brillouin zone in Eq. (22) could be performed using finite sets of special points along the concepts proposed by Baldereschi[20] and implemented by several authors.[21] From the knowledge of the phonon frequencies and phonon lifetimes, we can calculate with Eqs. (21) or (22) and the Dupuis algorithm the parameters of the Mori chain. This solves the problem of modeling any real thermal bath of a solid.

The modeling of a real thermal bath with an equivalent one involving only a few variables is of value for an improved comprehension of a number of problems such as gas-solid collisions,[5] the electron-phonon system of the Kubo school.[18] The full potentialities of the modeling method do not appear to have been thoroughly exploited in the literature. This paper, however, is confined to the modeling problem and for this purpose it is convenient to provide the exact expression of the autocorrelation function of the atomic displacement, against which one can check the few-body simulation. In fact the system of coupled oscillators is one of the very few examples of a many-body system, in which a number of properties can be calculated exactly. From Eqs. (14), (16), and (20) we have for the correlation function

$$\Phi_0(t)=\frac{\langle f_0\,|\,f_0(t)\rangle}{\langle f_0\,|\,f_0\rangle}=\omega_a^2\left\langle\frac{1}{\omega_{\vec{q}j}^2}\cos\omega_{\vec{q}j}te^{-\Gamma_{\vec{q}j}t}\right\rangle,\tag{23a}$$

while its Laplace transform is

$$\hat{\Phi}_0(z)=\omega_a^2\left\langle\frac{z+\Gamma_{\vec{q}j}}{\omega_{\vec{q}j}^2[(z+\Gamma_{\vec{q}j})^2+\omega_{\vec{q}j}^2]}\right\rangle.\tag{23b}$$

The application of the results of this section to the cases of the Einstein and Debye models is illuminating, and is considered below.

IV. MODELING OF PHONON BATHS IN SOME PARTICULAR CASES

A. Harmonic phonon bath in the Einstein approximation

In the Einstein approximation all the phonon frequencies are replaced by an average value ω_0; furthermore, in the harmonic approximation the damping parameters vanish.

Eq. (22) for the moments gives

$$s_0=1,\ s_1=0,\ s_2=-\omega_0^2,$$

$$s_3=0,\ s_4=\omega_0^4,\ s_5=0,$$

$$s_6=-\omega_0^6,\ s_7=0,\ s_8=\omega_0^8,$$

etc. The Dupuis determinants are

$$D_0=1,\ D_1=-\omega_0^2,\ D_2=D_3=\cdots=0.$$

From Eqs. (9) we see that $\lambda_i=0$ and the only nonvanishing parameter is $\Delta_1^2=\omega_0^2$. The continuous fraction of Eq. (7) is exactly truncated in the form

$$\hat{\Phi}_0(z)=\frac{1}{z+\dfrac{\omega_0^2}{z}}=\frac{z}{z^2+\omega_0^2}.\tag{24}$$

The simplicity of the present model allows us to recover the above result also starting from Eq. (23b).

B. Anharmonic phonon bath in the Einstein approximation.

As a second illustrative example, we consider the case in which all phonon frequencies $\omega_{\vec{q}j}$ are replaced by an average value ω_0 and all damping parameters $\Gamma_{\vec{q}j}$ are replaced by an average value Γ_0.

Equation (22) for the moments gives

$$s_0=1,\ s_1=-\Gamma_0,\ s_2=-\omega_0^2+\Gamma_0^2,$$

$$s_3=3\omega_0^2\Gamma_0-\Gamma_0^3,\ s_4=\omega_0^4-6\omega_0^2\Gamma_0^2+\Gamma_0^4,$$

$$s_5=-5\omega_0^4\Gamma_0+10\omega_0^2\Gamma_0^3-\Gamma_0^5,$$

$$s_6=-\omega_0^6+15\omega_0^4\Gamma_0^2-15\omega_0^2\Gamma_0^4+\Gamma_0^6,$$

$$s_7=7\omega_0^6\Gamma_0-35\omega_0^4\Gamma_0^3+21\omega_0^2\Gamma_0^5-\Gamma_0^7,$$

$$s_8=\omega_0^8-28\omega_0^6\Gamma_0^2+70\omega_0^4\Gamma_0^4-28\omega_0^2\Gamma^6+\Gamma_0^8,$$

etc. The Dupuis determinants are

$$D_0=1,\ D_1=-\omega_0^2,\ D_2=D_3=\cdots=0.$$

From Eqs. (9) we see that

$$\lambda_0=\lambda_1=-\Gamma_0,\ \Delta_1^2=\omega_0^2$$

while $\Delta_2^2=0$. We have thus the truncated continuous fraction

$$\hat{\Phi}_0(z)=\frac{1}{z+\Gamma_0+\dfrac{\omega_0^2}{z+\Gamma_0}}=\frac{z+\Gamma_0}{(z+\Gamma_0)^2+\omega_0^2}.\tag{25}$$

The simplicity of the present model allows to recover again the above result also starting from Eq. (23b).

C. Harmonic phonon bath

We consider now the case of a generical phonon bath, with the only assumption that the damping parameters are negligible. The moments, given by Eq. (22), are

$$s_0=1,\ s_1=0,\ s_2=-\omega_a^2\ ,$$
$$s_3=0,\ s_4=\omega_a^2\langle\omega^2\rangle,\ s_5=0\ ,$$
$$s_6=-\omega_a^2\langle\omega^4\rangle,\ s_7=0,\ s_8=\omega_a^2\langle\omega^6\rangle\ ,$$

etc. The Dupuis determinants up to D_4 are

$$\begin{aligned}
D_0&=1\ ,\\
D_1&=-\omega_a^2\ ,\\
D_2&=-\omega_a^4(\langle\omega^2\rangle-\omega_a^2)\ ,\\
D_3&=-\omega_a^6(\langle\omega^2\rangle-\omega_a^2)(\langle\omega^2\rangle^2-\langle\omega^4\rangle)\ ,\\
D_4&=-\omega_a^8(\langle\omega^2\rangle^2-\langle\omega^4\rangle)\\
&\quad\times[(\langle\omega^2\rangle-\omega_a^2)(\langle\omega^6\rangle-2\langle\omega^2\rangle\langle\omega^4\rangle+\langle\omega^2\rangle^3)\\
&\quad-(\langle\omega^2\rangle^2-\langle\omega^4\rangle)^2]\ .
\end{aligned}\tag{26}$$

The parameters of the Mori chain can be obtained using Eqs. (9) and (26). We note that all λ_i are zero because all odd moments s_{2n+1} are zero. For the coupling parameters we have

$$\begin{aligned}
\Delta_1^2&=\omega_a^2\ ,\\
\Delta_2^2&=\langle\omega^2\rangle-\omega_a^2\ ,\\
\Delta_3^2&=[\langle\omega^4\rangle-\langle\omega^2\rangle^2]/\Delta_2^2\ ,\\
\Delta_4^2&=\frac{\langle\omega^6\rangle-2\langle\omega^2\rangle\langle\omega^4\rangle+\langle\omega^2\rangle^3}{\Delta_2^2\Delta_3^2}-\Delta_3^2\ .
\end{aligned}\tag{27}$$

An alternative way to recover the results (27) has been presented in paper,[6] to which we refer for a detailed application to the Debye model and for a discussion of the relationship between the (Hermitian) Mori theory for modeling harmonic phonon baths and the original treatments[5] reported in the literature.

We could keep on with specific cases, consider reasonable interpolation schemes for phonon frequencies and lifetimes, and apply the powerful tools of the previous sections; however, we think that the examples so far reported have already made transparent the Mori modeling procedure also from an operational point of view.

V. CONCLUDING REMARKS

We wish to stress the significance of the results obtained with a few considerations on the specific case of spectroscopic applications. Suppose that the problem to be studied is the coupled electron-phonon system of the kind of Ref. 18. In such a case the interaction mode plays the typical role of a multiplicative stochastic variable.[22] Kubo showed how to build up the Fokker-Planck-type equation for the whole system in terms of the Fokker-Planck-type equation concerning only the multiplicative variable. It becomes, therefore, quite useful to succeed in building up the Fokker-Planck equation for any variable of interest. This aim can be accomplished as follows.

First of all, we relate the dynamical operator iL to the basis set of orthonormalized states,

$$|m_i\rangle=|f_i\rangle/\langle\tilde{f}_i|f_i\rangle^{1/2}\ .\tag{28}$$

Using the Eqs. (6) and (8), we obtain

$$iL=\begin{bmatrix}\lambda_0 & i\Delta_1 & 0 & 0\\ i\Delta_1 & \lambda_1 & i\Delta_2 & 0\\ 0 & i\Delta_2 & \lambda_2 & \vdots\\ 0 & 0 & \cdots & \ddots\end{bmatrix}\ .\tag{29}$$

It is convenient to transform the matrix of Eq. (29) into real form, with appropriate multiplication of rows and columns by phase factors. The operator of Eq. (29) is equivalent to the following one:

$$iL=\begin{bmatrix}\lambda_0 & \Delta_1 & 0 & \\ -\Delta_1 & \lambda_1 & \Delta_2 & \vdots\\ 0 & -\Delta_2 & \lambda_2 & \\ \cdots & \cdots & \cdots & \end{bmatrix}\ .\tag{30}$$

The equation of motion

$$\frac{d}{dt}f_0=iLf_0\ ,\tag{31}$$

when L is a generalized-Liouvillian, does not satisfy, in general, the requirement that for $t\to\infty$ a correct thermodynamical equilibrium must be attained because of the dissipative contributions.

This important requirement can be satisfied by replacing Eq. (31) with the following multidimensional Langevin equation:

$$\frac{d\vec{A}}{dt}=\underline{\Gamma}\cdot\vec{A}+\vec{F}(t)\ , \tag{32}$$

where $\underline{\Gamma}$ is given by the matrix of Eq. (30), and $\vec{A}$ is the vector of variables $(f_0,f_1,\ldots)$ regarded as being driven by the Liouvillian L.[13–15] The multidimensional stochastic force $\vec{F}$ has been introduced in order to account for the dampings present in the parameters λ_i''s. This stochastic force is defined through its matricial second moment as follows:

$$\langle F_iF_j(t)\rangle=2Q_{ij}\delta(t)\ . \tag{33}$$

The attainment of a correct thermodynamical equilibrium is insured by the following fluctuation-dissipation relation[23]:

$$\underline{\Gamma}\underline{E}^{-1}+\underline{E}^{-1}\underline{\Gamma}^{+}=-2\underline{Q}\ ,$$

where

$$(\underline{E}^{-1})_{ij}=\langle A_iA_j\rangle\ .$$

By following Ref. 23, it is then straightforward to arrive at the following Fokker-Planck equation:

$$\frac{\partial}{\partial t}P(\vec{A},t)=DP(\vec{A},t)\equiv\left[-\Delta_1\left[\frac{\partial}{\partial A_0}A_1-\frac{\partial}{\partial A_1}A_0\right]-\Delta_2\left[\frac{\partial}{\partial A_1}A_2-\frac{\partial}{\partial A_2}A_1\right]+\cdots\right.$$
$$\left.-\lambda_0\left[\frac{\partial}{\partial A_0}A_0-\frac{Q_{00}}{\lambda_0}\frac{\partial^2}{\partial A_0^2}\right]-\lambda_1\left[\frac{\partial}{\partial A_1}A_1-\frac{Q_{11}}{\lambda_1}\frac{\partial^2}{\partial A_1^2}\right]+\cdots\right]P(\vec{A},t)\ . \tag{34}$$

The operator D has to replace the rigorous one in any spectroscopical application of the results obtained in the present paper.

It is worthwhile to establish a link between the present paper and the wide literature on fluctuation and noise in physical systems[24–30]; in our opinion these papers[24–30] contain the germ of the ideas which will allow us to clarify some questions still unanswered within the context of our approach. First of all, we have in mind the cases where the high-temperature approximation cannot be made. In Ref. 25 it is shown how to build up "quantum mechanical" Fokker-Planck equations along the lines suggested by Wigner.[31] We believe that no theoretical difficulty should be met in joining the basic ideas of the present paper to the quantum-mechanical procedures described in such a literature. As a fruitful outcome of this theoretical reinforcement, it should be possible to build up the quantum-mechanical counterpart of Eq. (34).

A second important point concerns the quantum-mechanical extension of the regression of fluctuations, to which Lax gave decisive contributions.[25] In a later work Lax[30] established the complete equivalence between the Markoff property and the regression theorem. Therefore, after replacing the "real" thermal bath with his Markovian "simulation" we are in the right position to use this important theorem. This is the implicit reason why it has been possible to get a complete evaluation of the emission spectra of non-Markovian systems in the presence of strong driving fields.[32]

The algorithm developed in the present paper allows us to relate the variable of interest to a complete Markovian set of variables. This is indeed the main condition required for the regression theorem to be applied.[30]

Another related important point concerns the number of Mori states to be used for replacing the real non-Markovian thermal bath with an equivalent Markovian one at the desired degree of accuracy. Since our approach, when applied to Hermitian Liouvillians, recovers the results by Adelman and co-workers[5,33] we can refer to their important results for discussing the problem. Their work shows that a fairly limited number of additional variables allows one to get a faithful simulation of real thermal baths.

Our approach for building up "reduced" thermal baths is basically a development of the main ideas outlined having in mind the problem of radiationless decay in molecule.[34] With respect to the procedure of Adelman and co-workers,[5] our approach contains significant elements of originality. A major one consists in the fact that the theory of the present paper can also be applied in the case of non-Hermitian dynamical operators (effective Liouvillians or Fokker-Planck-type operators). This important feature of our approach, for example, allows our analysis to be extended to multiplicative stochastic processes,[35,36] the study of which is one of the major aims of current investigations on nonequilibrium statistical processes.

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[2]See, for instance, A. A. Maradudin, E. W. Montroll, G. H. Weiss, and I. P. Ipatova, in *Theory of Lattice Dynamics in the Harmonic Approximation,* Suppl. 3 of *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1971).

[3]For the self-consistent harmonic approximation and inclusion of anharmonic terms we refer, for instance, to P. F. Choquard, *The Anharmonic Crystals* (Benjamin, New York, 1967). See also S. H. Taole, H. R. Glyde, and R. Taylor, Phys. Rev. B 18, 2643 (1978); H. R. Glyde and M. G. Smoes, *ibid.* 22, 6391 (1980); R. C. Shukla, *ibid.* 22, 5997 (1980); 22, 5810 (1980), and references quoted therein.

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