Binary collision model for quantum Brownian motion

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A binary collision model for phenomena of quantum dissipation is developed. Unlike the harmonic oscillator model, widely used for over thirty years, this model assumes nonlinear coupling between system and environment, and is applicable to both bosonic and fermionic baths. The system interacts with an ideal bath through binary collisions only. Solutions for the classical and quantum-mechanical problems in the case of free Brownian motion are presented, and the quantum-classical correspondence for nonequilibrium processes is established. It is shown that in the Brownian motion limit the two models lead to identical dynamical behavior, provided the coupling coefficients in the harmonic oscillator Hamiltonian are temperature dependent. For cases of bath particles of finite mass and number the two models lead to different results. Linear response theory for the model is developed, and the results are compared with those for the harmonic oscillator model. At the end, possible applications of the model are suggested.

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I. INTRODUCTION

The theory of open quantum systems and quantum dissipation phenomena is, and has been for several decades, a major area of research in physics and chemistry. Most often researchers are interested in an open system with a small number of degrees of freedom in contact with a ''bath'' of a complex nature, whose number of degrees of freedom tends to infinity. The open system is interacting with its environment, and its properties and evolution are strongly affected by the interaction. The problem is to find a relatively simple and tractable way to account for the influence of the environment on the open system and to derive an equation for the reduced dynamics of the system.

The simplest dissipative process, Brownian motion (BM), has received much attention from both chemists and physicists, especially from researchers working on reaction rate theory. Physicists' interest in this process comes in connection with macroscopic dissipative tunneling, while chemists are mostly interested in studies of condensed phase reaction dynamics. The classical theory of BM is well understood. The process can be described by the Langevin equation

$$M\ddot{X}+\eta\dot{X}+V'(X)=F(t), \tag{1}$$

which describes, say, a colloidal particle of mass M immersed in a viscous fluid. η is the damping constant, V the potential acting on the particle, and $F(t)$ the fluctuating force, a Gaussian random process with

$$\langle F(t)\rangle=0, \tag{2}$$

$$\langle F(t)F(t')\rangle=2\eta kT\delta(t-t'). \tag{3}$$

Equivalently, one can use the Fokker-Plank equation, which in the case of $V=0$ reads

$$\frac{\partial\rho}{\partial t}+\frac{\partial(\rho\dot{X})}{\partial X}+\frac{\partial(\rho\dot{P})}{\partial P}=\eta kT\frac{\partial^2\rho}{\partial P^2} \tag{4}$$

with

$$\dot{X}=\frac{P}{M},\quad \dot{P}=-\frac{\eta P}{M}, \tag{5}$$

and describes the relaxation to equilibrium of the phase space density ρ of the Brownian particle.

The two equations above are valid in the classical regime. If we observe the reaction rate of some process at low temperature, however, quantum tunneling affects the rate, and the classical description is inadequate [1]. The question is, how to describe BM in quantum mechanics?

Over the last thirty years there have been many attempts to solve this problem, most of them unsatisfactory for one reason or another. Kostin's approach violated the superposition principle [2]. Various authors obtained a kind of ''quantum Langevin equation'' [3,4] valid for the special case of a harmonic oscillator. Others used a time-dependent mass [5,6] but this approach is not consistent with the uncertainty principle [7]. A canonical quantization procedure for complex variables was proposed by Dekker [8], who artificially introduced noise sources in the equations, which is questionable too. The master equation of Oppenheim and Romero-Rochin [9] has many nice features, but leads to negative probabilities [10] and therefore is not completely satisfactory.

The most successful approach to the problem of quantum BM so far is based on the so called harmonic oscillator (HO) or Caldeira-Leggett model, which treats the Brownian particle as a point mass interacting with an infinite collection of harmonic oscillators of various frequencies [11–15]. This method has several precursors in the literature [3,16]. The Hamiltonian of the composite system is

$$\hat{H}=\hat{H}_S+\hat{H}_R+\hat{H}_I, \tag{6}$$

where

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$$\hat{H}_S=\frac{\hat{P}^2}{2M}+\hat{V}(\hat{X}) \tag{7}$$

is the Hamiltonian of the isolated system,

$$\hat{H}_R=\sum_{i=1}^{N}\frac{1}{2}\left(\frac{\hat{p}_i^2}{m_i}+m_i\omega_i^2\hat{q}_i^2\right) \tag{8}$$

describes the reservoir of N harmonic oscillators, and

$$\hat{H}_I=-\sum_{i=1}^{N}\hat{F}_i(\hat{X})\hat{q}_i+\triangle\hat{V}(\hat{X}) \tag{9}$$

is the interaction term. The term $\triangle\hat{V}$ is added to compensate for frequency-renormalization effects induced by the first term in the expression for $\hat{H}_I$. Usually, for simplicity, a bilinear system-reservoir coupling is imposed, that is, in Eq. (9)

$$\hat{F}_i(\hat{X})=c_i\hat{X}. \tag{10}$$

The HO model for quantum BM can be used to model quantum dissipation phenomena through ''quantum Langevin equations'' for the momentum operator of the Brownian particle, or by employing the functional integral approach for deriving the reduced density operator of the system. An exhaustive review of work done with this model is given by Weiss [15], and for quantum reaction rate theory in [1].

In this paper we develop a binary collision model for quantum BM and the phenomena of quantum dissipation, a model that does not assume linear system-reservoir coupling, is applicable to both bosonic and fermionic baths, and originates in a somewhat more physical picture of BM: a heavy particle moves through an ideal gas of light particles, experiencing instantaneous uncorrelated binary collisions with them. In Sec. II we present the model. In Sec. III we show that the model leads to the well known process of BM in classical mechanics, while two solutions for the quantum problem are presented in Sec. IV. Section V develops linear response theory for the model and establishes the correspondence between this model and the HO model. In Sec. VI we discuss possible applications of the model and conclude. Some formal derivations are given in Appendixes A and B.

II. BINARY COLLISION MODEL

A Brownian particle of mass *M*, immersed in an ideal gas of bath particles, interacts with the bath through binary collisions. These are not quite standard binary collisions; the Hamiltonian we use for the model, which is one dimensional, is this:

$$\hat{H}=\frac{\hat{P}^2}{2M}+\sum_{i=1}^{N}\frac{\hbar\omega_i}{2}\left(e^{i2p_i\hat{X}/\hbar}a_{-i}^{\dagger}a_i+e^{-i2p_i\hat{X}/\hbar}a_i^{\dagger}a_{-i}\right)+\sum_{i=1}^{N}\epsilon_i(a_i^{\dagger}a_i+a_{-i}^{\dagger}a_{-i}). \tag{11}$$

Here $\hat{P}$ and $\hat{X}$ are the momentum and coordinate operators of the Brownian particle, p_i—a scalar, not an operator—is the momentum of the ith bath particle, $a_i^{\dagger}$ (a_i) creates (destroys) a bath particle of momentum $+p_i$, $a_{-i}^{\dagger}$ (a_{-i}) creates (destroys) a bath particle of momentum $-p_i$, the $\{\omega_i\}$ are collision frequencies, and ϵ_i is the energy of a bath particle with momentum $\pm p_i$,

$$\epsilon_i=\frac{p_i^2}{2m}. \tag{12}$$

Plank's constant $\hbar$ is henceforth taken to be unity. The same model would describe BM in a potential $\hat{V}(\hat{X})$ by simply adding this term to the Hamiltonian (11).

The Hamiltonian (11) describes instantaneous binary collisions—when a bath particle of momentum $+p_i$ disappears, one of momentum $-p_i$ appears—and these collisions conserve momentum—the Brownian particle gains the momentum $2p_i$ lost by the bath—but in these collisions the bath neither gains nor loses energy. In each collision the momentum of a bath particle is simply reversed, as if the particle had bounced off a *stationary* Brownian particle. This is therefore a Hamiltonian that *approximates* the dynamics of a heavy particle in an ideal gas of light particles; the smaller the mass ratio m/M, the better the approximation. Nevertheless, Eq. (11) is a perfectly proper Hamiltonian in its own right. Energy is conserved, but when the Brownian particle loses energy, the energy lost is stored in the *interaction*.

The approach is similar to that of the Bhatnagar-Gross-Krook (BGK) model for gas kinetics [17], which gives a kinetic equation simpler than the Boltzmann equation: here also we have a model that simplifies the dynamics of a heavy particle in a gas of light particles but still captures the essence of that dynamics, the frequent exchange of small amounts of momentum between heavy particle and gas.

Since the bath energy never changes, we drop the last term in Hamiltonian (11).

The bath particles may be bosons, fermions, or a mixture of both types. For bosons, a_i and $a_i^{\dagger}$ satisfy

$$[a_i,a_j]=0,\quad [a_i^{\dagger},a_j^{\dagger}]=0,\quad [a_i,a_j^{\dagger}]=\delta_{ij}. \tag{13}$$

For fermions, the corresponding operators (we will call them b_i's) satisfy

$$\{b_j,b_k\}=0,\quad \{b_j^{\dagger},b_k^{\dagger}\}=0,\quad \{b_j,b_k^{\dagger}\}=\delta_{jk}. \tag{14}$$

In both cases the number operator for particles of, say, momentum $+p_j$ is

$$N_j=a_j^{\dagger}a_j. \tag{15}$$

We will cast the Hamiltonian in a different form, which will allow us to treat the classical and quantum equations for the time derivative $\dot{\hat{P}}$ analogously and to use the same formalism for both bosonic and fermionic baths. We use a trick invented by Schwinger [18] (who used it for bosonic operators only). Let

$$\hat{L}_{x,i}=\frac{1}{2}\,(a^\dagger_{-i}a_i+a^\dagger_i a_{-i}),$$

$$\hat{L}_{y,i}=\frac{i}{2}(a^\dagger_{-i}a_i-a^\dagger_i a_{-i}), \tag{16}$$

$$\hat{L}_{z,i}=\frac{1}{2}(a^\dagger_i a_i-a^\dagger_{-i}a_{-i}).$$

It is easy to prove that $\hat{L}_{x,i}$, $\hat{L}_{y,i}$, and $\hat{L}_{z,i}$ are the components of an angular momentum $\hat{\vec{L}}_i$, regardless of whether the creation and annihilation operators describe bosons or fermions [19]. The $\hat{L}_{z,i}$ component of the angular momentum takes values up to $(N_i+N_{-i})/2$, so the total angular momentum quantum number L_i is proportional to the total number of bath particles with momentum $\pm p_i$. In the fermionic case we have

$$b^\dagger_i b_i+b^\dagger_{-i}b_{-i}=N_i+N_{-i}=\text{const}\in\{0,1,2\}. \tag{17}$$

The case $N_i+N_{-i}=0$ is trivial, as is the case $N_i+N_{-i}=2$, for then binary collisions cannot scatter a bath particle from $+p_i$ to $-p_i$ or vice versa, the final states being already occupied. For a fermionic bath, then, we may assume $L_i=1/2$.

Using Eqs. (16) we can write the Hamiltonian (11) in the form

$$\hat{H}=\frac{\hat{P}^2}{2M}+\sum_{i=1}^{N}\omega_i\hat{\vec{B}}_i\cdot\hat{\vec{L}}_i, \tag{18}$$

where the vector $\hat{\vec{B}}_i$ is defined as

$$\hat{\vec{B}}_i\equiv\{\cos(2p_i\hat{X}),\sin(2p_i\hat{X}),0\}. \tag{19}$$

The Hamiltonian (18) models a Brownian particle interacting with angular momenta which precess around an axis determined by the instantaneous position of the particle. We next show that this model Hamiltonian, in the appropriate limit, in fact generates classical BM.

III. CLASSICAL BROWNIAN MOTION

Our goal is to derive an equation for $\dot{P}$, the rate of momentum change of the classical Brownian particle. We start from the five equations of motion of the variables involved in the classical Hamiltonian (18) ($\{,\}$ is the Poisson bracket):

$$\dot{L}_{x,i}=\{L_{x,i},H\}=\omega_i\sin(2p_iX)L_{z,i}, \tag{20}$$

$$\dot{L}_{y,i}=\{L_{y,i},H\}=-\omega_i\cos(2p_iX)L_{z,i}, \tag{21}$$

$$\dot{L}_{z,i}=\{L_{z,i},H\}=\omega_i[\cos(2p_iX)L_{y,i}-\sin(2p_iX)L_{x,i}], \tag{22}$$

$$\dot{X}=\{X,H\}=\frac{P}{M}, \tag{23}$$

$$\dot{P}=\{P,H\}=-\frac{\partial H}{\partial X}=-\sum_{i=1}^{N}2\omega_i p_i \times[-\sin(2p_iX)L_{x,i}+\cos(2p_iX)L_{y,i}]. \tag{24}$$

Equation (24) is simply

$$\dot{P}=-\sum_{i=1}^{N}2p_i\dot{L}_{z,i}. \tag{25}$$

From the definition of $L_{z,i}$ [Eq. (16)] it is evident that Eq. (25) is nothing but an expression of conservation of momentum. We differentiate Eq. (22) again and obtain

$$\ddot{L}_{z,i}+\omega_i^2L_{z,i}=-2\omega_ip_i\dot{X}\,\vec{B}_i\cdot\vec{L}_i\equiv f_i(t). \tag{26}$$

We formally solve the inhomogeneous Eq. (26) and calculate $\dot{L}_{z,i}(t)$, getting

$$\dot{L}_{z,i}(t)=\dot{L}_{z,i,h}(t)+\int_0^t\cos[\omega_i(t-t')]f_i(t')dt', \tag{27}$$

with

$$\dot{L}_{z,i,h}(t)=-\omega_iL_{z,i}(0)\sin(\omega_it)+\omega_ib\cos(\omega_it), \tag{28}$$

where

$$b=\cos[2p_iX(0)]L_{y,i}(0)-\sin[2p_iX(0)]L_{x,i}(0). \tag{29}$$

Substituting Eq. (27) in Eq. (25), we obtain

$$\dot{P}(t)=\int_0^t\left(\sum_{i=1}^{N}4p_i^2\omega_i\vec{B}_i\cdot\vec{L}_i(t')\cos[\omega_i(t-t')]\right)\times\frac{P}{M}(t')dt'-\sum_{i=1}^{N}2p_i\dot{L}_{z,i,h}(t). \tag{30}$$

This equation is exact; no approximations have been made. It looks like a generalized Langevin Equation (GLE):

$$\dot{P}=\int_0^t\gamma(t-t')\frac{P}{M}dt'+F(t), \tag{31}$$

with

$$\gamma(t-t')=\sum_{i=1}^{N}4p_i^2\omega_i\vec{B}_i\cdot\vec{L}_i(t')\cos[\omega_i(t-t')], \tag{32}$$

$$F(t)=-\sum_{i=1}^{N}2p_i\dot{L}_{z,i,h}(t). \tag{33}$$

But it is not: $\gamma(t-t')$ is a dynamical variable, as it contains the $\vec{B}_i\cdot\vec{L}_i(t')$'s. In a proper GLE $\gamma(t-t')$ should depend only on the difference $t-t'$ and should not be a dynamical variable, while the ''random force'' $F(t)$ should average to zero and satisfy the fluctuation-dissipation theorem of the second kind,

$$\langle F(t)\rangle=0, \tag{34}$$

$$\langle F(t)F(0)\rangle = -kT\gamma(t). \tag{35}$$

We now find conditions under which Eq. (30) becomes a proper GLE. First, we require that the $\vec{B}_i\cdot\vec{L}_i(t')$'s be essentially constant in time,

$$\vec{B}_i\cdot\vec{L}_i \approx \text{const}, \tag{36}$$

or

$$\frac{(d/dt)(\vec{B}_i\cdot\vec{L}_i)\triangle t}{\vec{B}_i\cdot\vec{L}_i} \ll 1. \tag{37}$$

A simple calculation shows that the above requirement is equivalent to the condition [19]

$$p_i \to 0. \tag{38}$$

This condition can be satisfied if the bath particles have vanishingly small mass, $m\to 0$. Then there must be many of them:

$$N\to\infty. \tag{39}$$

In that case $\gamma(t-t')$ is a sum of many terms [Eq. (32)], each involving a dot product $\vec{B}_i\cdot\vec{L}_i$, the values of which are distributed according to thermal equilibrium for the bath. The law of large numbers then implies that

$$\gamma(t-t') \approx \langle\gamma(t-t')\rangle. \tag{40}$$

With this approximation the kernel of Eq. (30) is no longer a dynamical variable, it is simply a function of $t-t'$.

Next we show that, under the same conditions, $F(t)$ is a proper random force. We may choose the origin $X(0)$ arbitrarily, so set

$$X(0)=0. \tag{41}$$

Equations (29) and (28) then read

$$b = L_{y,i}(0), \tag{42}$$

$$\dot{L}_{z,i,h}(t) = -\omega_i L_{z,i}(0)\sin(\omega_i t) + \omega_i L_{y,i}(0)\cos(\omega_i t). \tag{43}$$

Hence,

$$\langle F(t)\rangle = \sum_{i=1}^{N} 2p_i\omega_i[\langle L_{z,i}(0)\rangle\sin(\omega_i t) - \langle L_{y,i}(0)\rangle\cos(\omega_i t)]. \tag{44}$$

We assume a thermal initial distribution of bath angular momenta with respect to the initial Brownian particle position, $\rho(0)=(1/Z)\exp[-\beta H_b(0)]$, where Z is the partition function and

$$H_b(0) = \sum_{j=1}^{N} \omega_j L_{x,j}(0). \tag{45}$$

Then [19]

$$\langle L_{z,i}(0)\rangle = \langle L_{y,i}(0)\rangle = \langle L_{z,i}(0)L_{y,j}(0)\rangle = 0, \quad \forall i,j, \tag{46}$$

$$\langle L_{y,i}(0)L_{y,j}(0)\rangle = \langle L_{y,i}^2(0)\rangle\delta_{i,j}, \tag{47}$$

with

$$\langle L_{y,i}^2(0)\rangle = \frac{L_i}{\beta\omega_i}\left(\coth(\beta\omega_i L_i) - \frac{1}{\beta\omega_i L_i}\right), \tag{48}$$

which proves Eq. (34) and leads us to

$$\langle F(t)F(0)\rangle = \frac{1}{\beta}\sum_{i=1}^{N} 4p_i^2\omega_i L_i \times\left(\coth(\beta\omega_i L_i) - \frac{1}{\beta\omega_i L_i}\right)\cos(\omega_i t). \tag{49}$$

On the other hand, from Eq. (32) we have

$$\langle\gamma(t)\rangle = \sum_{i=1}^{N} 4p_i^2\omega_i\langle\vec{B}_i\cdot\vec{L}_i\rangle\cos(\omega_i t), \tag{50}$$

and it is easy to show [19] that in the limit $p_i\to 0$

$$\langle\vec{B}_i\cdot\vec{L}_i\rangle(t) \approx \langle\vec{B}_i\cdot\vec{L}_i\rangle(0) \approx L_i\left(\frac{1}{\beta\omega_i L_i} - \coth(\beta\omega_i L_i)\right), \tag{51}$$

so that

$$\langle\gamma(t)\rangle = \sum_{i=1}^{N} 4p_i^2\omega_i L_i\left(\frac{1}{\beta\omega_i L_i} - \coth(\beta\omega_i L_i)\right)\cos(\omega_i t). \tag{52}$$

Comparing Eqs. (49) and (52) we verify that

$$\langle F(t)F(0)\rangle = -kT\langle\gamma(t)\rangle. \tag{53}$$

The BM limit, then, is $p_i\to 0$, $N\to\infty$ [Eqs. (38) and (39)]; in this limit—and with the bath initially in thermal equilibrium with respect to the Brownian particle—the particle executes BM according to a proper GLE.

Equation (30) reduces to an ordinary Langevin equation, describing Markovian BM, if the frequencies $\{\omega_i\}$ are distributed as

$$\rho(\omega) = \begin{cases} \dfrac{-|\text{const}|}{p^2\omega\langle\vec{B}\cdot\vec{L}\rangle} & \text{if } \omega\leqslant\omega_f \\ 0 & \text{otherwise,} \end{cases} \tag{54}$$

where ω_f is a high-frequency cutoff; then

$$\langle\gamma(t-t')\rangle \approx \int_0^{\omega_f} 4p^2(\omega)\omega\langle\vec{B}\cdot\vec{L}\rangle(\omega)\cos[\omega(t-t')] \times\rho(\omega)d\omega \xrightarrow{\omega_f\to\infty} -|\text{const}'|\delta(t-t'), \tag{55}$$

and

$$\dot{P}=-\frac{|\mathrm{const}''|}{M}P+F(t). \tag{56}$$

IV. QUANTUM BROWNIAN MOTION

We will use the functional integral approach to derive the equilibrium reduced density operator of the dissipative system, and we will derive a quantum Langevin equation for the momentum operator of the system.

A. Path integral solution for the equilibrium reduced density matrix

We can write the Hamiltonian (18) as

$$\hat{H}=\hat{T}+\hat{V}, \tag{57}$$

where

$$\hat{T}=\frac{\hat{P}^2}{2M}, \tag{58}$$

$$\hat{V}=\sum_{i=1}^{N}\omega_i[\cos(2p_i\hat{X})\hat{L}_{x,i}+\sin(2p_i\hat{X})\hat{L}_{y,i}]. \tag{59}$$

The reduced density matrix is

$$\rho_{X,X'}=\langle X'|\mathrm{tr}_{bath}(e^{-\beta\hat{H}})|X\rangle=\sum_{\{m_i\}}\langle X',\{m_i\}|e^{-\beta\hat{H}}|X,\{m_i\}\rangle, \tag{60}$$

where

$$|\{m_i\}\rangle=|m_1,\ldots,m_k,\ldots\rangle=|m_1\rangle\cdots|m_k\rangle\cdots, \tag{61}$$

and the $|m_k\rangle$'s are chosen to be the eigenvectors of $\hat{L}_{x,k}$. After a long calculation, in which the limits $p\rightarrow 0$ and $N\rightarrow\infty$ are taken, we reach the result [19]

$$\rho_{X,X'}=\langle X'|\mathrm{tr}_{bath}(e^{-\beta\hat{H}})|X\rangle=\prod_k f_1(k)\lim_{N\rightarrow\infty}\left(\frac{NM}{2\pi\beta}\right)^{N/2}\times\int\mathcal{D}X_t\exp\left(-\int_0^\beta d\tau\frac{M}{2}\dot{X}^2(\tau)+\int_0^\beta\int_0^\beta d\tau\, d\tau'\, K(|\tau-\tau'|)[X(\tau)-X(\tau')]^2\right), \tag{62}$$

where

$$K(|\tau-\tau'|)=\sum_i\frac{p_i^2\omega_i^2}{2\sinh(\omega_i\beta/2)}\frac{f_2(i)}{f_1(i)}\times\cosh\left[\omega_i\left(\frac{\beta}{2}-|\tau-\tau'|\right)\right], \tag{63}$$

with

$$f_1(i)=\sum_{m_i}e^{-\beta\omega_i m_i}, \tag{64}$$

$$f_2(i)=\sum_{m_i}m_i e^{-\beta\omega_i m_i}. \tag{65}$$

Note that the ratio f_2/f_1 is negative.

For the HO model [that is, the Hamiltonian (6) with Eqs. (7), (8), (9), and (10)] the reduced density matrix elements $\rho_{X,X'}$ obtained through the functional integral approach are of the same form as those in Eq. (62), but with a slightly different kernel [15]:

$$K_{\mathrm{HO}}(|\tau-\tau'|)=-\sum_i\frac{c_i^2}{8m_i\omega_i\sinh(\omega_i\beta/2)}\times\cosh\left[\omega_i\left(\frac{\beta}{2}-|\tau-\tau'|\right)\right]. \tag{66}$$

Thus, we can make the correspondence

$$c_i^2\leftrightarrow-4m_ip_i^2\omega_i^3\frac{f_2(i)}{f_1(i)}. \tag{67}$$

It is clear that with a suitable choice of parameters [with the c_i's being functions of temperature, due to the temperature dependence of $f_2(i)/f_1(i)$], in the BM limit the binary collision model leads to the same results for $\rho_{X,X'}$ as the HO model. This is not surprising, since in the BM limit only the linear terms in the expansion of the original nonlinear interaction Hamiltonian (18) contribute to the reduced density matrix. In order to obtain different dynamics it is necessary to find such an equation, derived from this binary collision model, which is true in general, not only in the BM limit. Applying the path integral approach outside this limit is prohibitively difficult; we need a different approach.

B. The quantum Langevin equation

We will derive an equation of motion for the first derivative of the momentum operator of the Brownian particle. The derivation will be analogous to that in Sec. III, except that we will work with operators instead of dynamical variables. Starting with the Hamiltonian (18), the five equations for the observables are

$$\dot{\hat{L}}_{x,i}=\omega_i\sin(2p_i\hat{X})\hat{L}_{z,i}, \tag{68}$$

$$\dot{\hat{L}}_{y,i}=-\omega_i\cos(2p_i\hat{X})\hat{L}_{z,i}, \tag{69}$$

$$\dot{\hat{L}}_{z,i}=\omega_i[\cos(2p_i\hat{X})\hat{L}_{y,i}-\sin(2p_i\hat{X})\hat{L}_{x,i}], \tag{70}$$

$$\dot{\hat{X}}=\frac{\hat{P}}{M}, \tag{71}$$

$$\dot{\hat{P}}=-\sum_{i=1}^{N}2p_i\hat{L}_{z,i}. \tag{72}$$

As in the classical case, Eq. (72) is an expression of conservation of momentum. Taking the second derivative of $\hat{L}_{z,i}$, after some algebra, we obtain [19]

$$\ddot{\hat{L}}_{z,i}+\omega_i^2\hat{L}_{z,i}=-\frac{\omega_i p_i}{M}\{\hat{\vec{B}}_i\cdot\hat{\vec{L}}_i,\hat{P}\}\equiv\hat{f}_i(t). \tag{73}$$

Then after solving for $\hat{L}_{z,i}$, calculating $\dot{\hat{L}}_{z,i}$, and substituting in Eq. (72), we arrive at [19]

$$\dot{\hat{P}}(t)=\int_0^t\sum_i \frac{2\omega_i p_i^2}{M}\{\hat{\vec{B}}_i\cdot\hat{\vec{L}}_i,\hat{P}\}\cos[\omega_i(t-t')]dt' -\sum_i 2p_i\dot{\hat{L}}_{z,i,h}(t), \tag{74}$$

where

$$\dot{\hat{L}}_{z,i,h}=-\omega_i\hat{L}_{z,i}(0)\sin(\omega_i t)+\omega_i\{\cos[2p_i\hat{X}(0)]\hat{L}_{y,i}(0) -\sin[2p_i\hat{X}(0)]\hat{L}_{x,i}(0)\}\cos(\omega_i t). \tag{75}$$

Equation (74) is exact. It is of the form

$$\dot{\hat{P}}(t)=\int_0^t\frac{1}{2}\left\{\hat{\gamma}(t-t'),\frac{\hat{P}}{M}\right\}dt'+\hat{F}(t), \tag{76}$$

which is not quite the form of a GLE. The kernel $\hat{\gamma}(t-t')$ is the operator

$$\hat{\gamma}(t-t')=\sum_i 4\omega_i p_i^2\hat{\vec{B}}_i\cdot\hat{\vec{L}}_i(t')\cos[\omega_i(t-t')], \tag{77}$$

and

$$\hat{F}(t)=-\sum_i 2p_i\dot{\hat{L}}_{z,i,h}(t). \tag{78}$$

As in the classical case, we can show that in the limit $p_i\to 0$, $\hat{\vec{B}}_i\cdot\hat{\vec{L}}_i$ is essentially independent of time, and Eq. (74) takes the form [19]

$$\dot{\hat{P}}(t)=\int_0^t\sum_i \frac{4\omega_i p_i^2}{M}\hat{\vec{B}}_i\cdot\hat{\vec{L}}_i\cos[\omega_i(t-t')]\hat{P}dt' -\sum_i 2p_i\dot{\hat{L}}_{z,i,h}(t), \tag{79}$$

or

$$\dot{\hat{P}}(t)=\int_0^t\hat{\gamma}(t-t')\frac{\hat{P}}{M}(t')dt'+\hat{F}(t). \tag{80}$$

In this equation $\hat{\gamma}(t-t')$ is still an operator. To have a BM process (in the sense of a GLE) we need to approximate $\hat{\gamma}(t-t')$ with a number. That can be done by averaging the above equation with respect to the following time-dependent Hamiltonian from linear response theory:

$$\hat{H}(t)=\hat{H}_0-f(t)\hat{X}, \tag{81}$$

where $\hat{H}_0$ is Hamiltonian (18) and $f(t)$ perturbs the system off equilibrium:

$$f(t)=\begin{cases}0 & \text{if } t<0\\ f(t)\neq 0 & \text{otherwise.}\end{cases} \tag{82}$$

Averaging based on $\hat{H}(t)$ to first order in f leads to the equation [19]

$$\langle\dot{\hat{P}}(t)\rangle=\int_0^t\left\langle\sum_i \frac{4\omega_i p_i^2}{M}\hat{\vec{B}}_i\cdot\hat{\vec{L}}_i\cos[\omega_i(t-t')]\hat{P}(t')\right\rangle dt' +f(t), \tag{83}$$

which we will write as

$$\langle\dot{\hat{P}}(t)\rangle=\int_0^t\left\langle\hat{\gamma}(t-t')\frac{\hat{P}}{M}(t')\right\rangle dt'+f(t). \tag{84}$$

In order to be able to approximate the above equation to the convenient form of a GLE, to which the fluctuation-dissipation theorem could be applied, the following must be true:

$$\left\langle\hat{\gamma}(t-t')\frac{\hat{P}}{M}(t')\right\rangle\approx\langle\hat{\gamma}(t-t')\rangle\left\langle\frac{\hat{P}}{M}(t')\right\rangle. \tag{85}$$

In Appendix A we prove that, in the BM limit, this is indeed the case. Thus, in the BM limit, Eq. (84) takes the form of a GLE:

$$\langle\dot{\hat{P}}(t)\rangle\approx\int_0^t\langle\hat{\gamma}(t-t')\rangle\left\langle\frac{\hat{P}}{M}(t')\right\rangle dt'+f(t). \tag{86}$$

Although Eq. (86) looks just like the corresponding classical GLE, the two equations differ because the classical and quantum averages of γ differ. That is not the case with the γ's in the classical and quantum GLE's obtained from the HO model; in that case the two are identical.

Is $\hat{F}(t)$ a proper ''random force'' operator? In Appendix B we outline the proof of the following results:

$$\langle\hat{F}(t)\rangle=0, \tag{87}$$

$$\langle\hat{\vec{B}}_i\cdot\hat{\vec{L}}_i\rangle=\frac{\sum_{m_i=-l_i}^{l_i} m_i e^{-\beta\omega_i m_i}}{\sum_{m_i=-l_i}^{l_i} e^{-\beta\omega_i m_i}}=\frac{f_2(i)}{f_1(i)}, \tag{88}$$

$$\tfrac{1}{2}[\langle\hat{F}(t)\hat{F}(0)\rangle+\langle\hat{F}(0)\hat{F}(t)\rangle] =-\sum_i 2p_i^2\omega_i^2\frac{f_2(i)}{f_1(i)}\coth\left(\frac{\beta\omega_i}{2}\right)\cos(\omega_i t). \tag{89}$$

Note that Eq. (88) shows that the quantity $f_2(i)/f_1(i)$ in the kernel (63) is in fact $\langle\hat{\vec{B}}_i\cdot\hat{\vec{L}}_i\rangle$. Hence,

$$\langle\hat{\gamma}(t-t')\rangle=\sum_i 4\omega_i p_i^2\frac{f_2(i)}{f_1(i)}\cos[\omega_i(t-t')]. \tag{90}$$

Taking the high temperature limit, $\beta\to 0$, or the limit $\hbar\to 0$ ($\hbar$ being implicit in all of our equations), and using

$$\lim_{x\to 0}\coth(x)=\frac{1}{x} \tag{91}$$

in Eq. (89), we obtain the quantum-mechanical analog of the classical fluctuation-dissipation theorem:

$$\lim_{\hbar\beta\to 0}\frac{1}{2}[\langle\hat{F}(t)\hat{F}(0)\rangle+\langle\hat{F}(0)\hat{F}(t)\rangle]=-kT\langle\hat{\gamma}(t)\rangle, \tag{92}$$

which is evident from a comparison with Eq. (53).

Thus, Eq. (74) is a quantum ''Langevin'' equation, corresponding to the classical equation (30). After averaging, as in the classical case, we could impose on it conditions under which it would converge to an ordinary Langevin equation describing a Markovian process [19], thus showing that our model can describe ''standard'' BM in both classical and quantum regimes.

V. LINEAR RESPONSE THEORY

We consider a perturbation from equilibrium driven by a small force $f(t)$ which vanishes for $t<0$,

$$t<0:\quad f(t)=0,$$

$$t\geqslant 0:\quad f(t)\neq 0. \tag{93}$$

Following Kubo [20], we start from the Hamiltonian

$$\hat{H}(t)=\hat{H}_0+\hat{H}'(t), \tag{94}$$

where

$$\hat{H}_0=\frac{\hat{P}^2}{2M}+\sum_i\ \omega_i\vec{\hat{B}}_i\cdot\vec{\hat{L}}_i \tag{95}$$

and

$$\hat{H}'(t)=-f(t)\hat{X}. \tag{96}$$

The density operator

$$\hat{\rho}(t)=\hat{\rho}_{eq}+\delta\hat{\rho}(t) \tag{97}$$

satisfies

$$\begin{aligned} i\frac{d}{dt}\hat{\rho}(t)&=[\hat{H}(t),\hat{\rho}(t)]\\ &=[\hat{H}_0+\hat{H}'(t),\hat{\rho}_{eq}+\delta\hat{\rho}(t)]\\ &\cong[-f(t)\hat{X},\hat{\rho}_{eq}]+[\hat{H}_0,\delta\hat{\rho}(t)] \end{aligned} \tag{98}$$

to first order in f, with solution

$$\delta\hat{\rho}(t)=i\int_0^t f(t')e^{-i\hat{H}_0(t-t')}[\hat{X},\hat{\rho}_{eq}]e^{i\hat{H}_0(t-t')}dt'. \tag{99}$$

Since $\langle\hat{P}\rangle_{eq}$ is zero, after some algebra we obtain [19]

$$\langle\hat{P}(t)\rangle=\frac{1}{Z}\mathrm{Tr}\{\delta\hat{\rho}(t)\hat{P}\}=i\int_0^t f(t')\langle[\hat{P}_H(t-t'),\hat{X}]\rangle_{eq}dt', \tag{100}$$

where $\hat{P}_H$ is the operator $\hat{P}$ in the Heisenberg picture.

Defining the response function $\chi(t-t')$ by

$$\langle\hat{X}(t)\rangle=\int_0^t f(t')\chi(t-t')dt' \tag{101}$$

and using

$$\langle\hat{P}(t)\rangle=M\frac{d}{dt}\langle\hat{X}(t)\rangle \tag{102}$$

together with Eq. (100), we obtain [19]

$$\langle\hat{X}(t)\rangle=\int_0^t if(t')\langle[\hat{X}_H(t-t'),\hat{X}]\rangle_{eq}dt', \tag{103}$$

and from the definition (101) we conclude that

$$\chi(t-t')=i\langle[\hat{X}_H(t-t'),\hat{X}]\rangle_{eq}. \tag{104}$$

Specializing to the case

$$f(t)=k\delta(t), \tag{105}$$

where k is a constant, we have

$$\langle\hat{X}(t)\rangle=k\chi(t), \tag{106}$$

and using our earlier results we find [19]

$$M\langle\ddot{\hat{X}}(t)\rangle=\int_0^t dt'\langle\hat{\gamma}(t-t')\rangle M\langle\dot{\hat{X}}(t')\rangle+f(t) \tag{107}$$

or

$$Mk\ddot{\chi}(t)=\int_0^t dt'\langle\hat{\gamma}(t-t')\rangle Mk\dot{\chi}(t')+k\delta(t), \tag{108}$$

which can be Fourier transformed to

$$-M\omega^2\tilde{\chi}(\omega)=-i\omega M\langle\tilde{\hat{\gamma}}(\omega)\rangle\tilde{\chi}(\omega)+1. \tag{109}$$

Hence,

$$\tilde{\chi}(\omega)=\frac{1}{M[-\omega^2+i\omega\langle\tilde{\hat{\gamma}}(\omega)\rangle]}, \tag{110}$$

which we write in the form

$$\tilde{\chi}(\omega)=\tilde{\chi}'(\omega)+i\tilde{\chi}''(\omega), \tag{111}$$

where

$$\tilde{\chi}'(\omega)=\frac{-1}{M[\omega^2+\langle\tilde{\hat{\gamma}}(\omega)\rangle^2]}, \tag{112}$$

$$\tilde{\chi}''(\omega)=\frac{-\langle\tilde{\hat{\gamma}}(\omega)\rangle}{M[\omega^3+\omega\langle\tilde{\hat{\gamma}}(\omega)\rangle^2]}. \tag{113}$$

Defining

$$C_+(t)=\langle\hat{X}(t)\hat{X}(0)\rangle_{eq}, \tag{114}$$

and using the relation [15]

$$\tilde{\chi}''(\omega)=\tfrac{1}{2}(1-e^{-\beta\omega})\tilde{C}_+(\omega), \tag{115}$$

we find

$$C_+(t)=-\frac{1}{\pi M}\int_{-\infty}^{\infty}d\omega\,\frac{\langle\tilde{\hat{\gamma}}(\omega)\rangle}{M[\omega^3+\omega\langle\tilde{\hat{\gamma}}(\omega)\rangle^2]}\,\frac{e^{-i\omega t}}{1-e^{-\beta\omega}}. \tag{116}$$

From $C_+(t)$ we can then calculate [15]

$$C_{PX}(t)=\langle\hat{P}(t)\hat{X}(0)\rangle_{eq}=M\frac{\partial}{\partial t}\langle\hat{X}(t)\hat{X}(0)\rangle_{eq}, \tag{117}$$

$$C_{XP}(t)=\langle\hat{X}(t)\hat{P}(0)\rangle_{eq}=-M\frac{\partial}{\partial t}\langle\hat{X}(t)\hat{X}(0)\rangle_{eq}, \tag{118}$$

$$C_{PP}(t)=\langle\hat{P}(t)\hat{P}(0)\rangle_{eq}=-M^2\frac{\partial^2}{\partial t^2}\langle\hat{X}(t)\hat{X}(0)\rangle_{eq}. \tag{119}$$

These are all the correlation functions needed to describe a stationary Gaussian process, which is the limiting case of our model in the BM limit, where it becomes equivalent to the linear system described by the HO model with linear damping [15,21].

It is interesting to compare the results of this model with those of the HO model of Caldeira and Leggett [12,15] described in Sec. I. Their Hamiltonian leads to a GLE of the form (31) in both classical and quantum cases, with

$$\gamma_{\mathrm{HO}}(t-t')=-\sum_{i=1}^{N}\frac{c_i^2}{m_i\omega_i^2}\cos[\omega_i(t-t')], \tag{120}$$

which compares with our $\hat{\gamma}$ in the BM limit, given by Eq. (90). In the same limit, the equilibrium properties of a system are described in both models by Eq. (62) for $\hat{\rho}_{X,X'}$, with the corresponding kernels (66) and (63). Thus, all differences between the two models are in the kernels K_{HO} and K at equilibrium and in the kernels γ_{HO} and γ that enter linear response theory. We have already shown that, if we make the coefficients c_i in K_{HO} temperature dependent, K_{HO} and K can be made equal. What about the kernels γ_{HO} and γ? Comparing Eqs. (120) and (90), we see that equality of the γ's is guaranteed by the same condition, Eq. (67), which guarantees equality of the K's. In the BM limit, then, the two models can be mapped onto one another: they are equivalent at equilibrium and within linear response theory.

VI. CONCLUSIONS

We have developed a binary collision model for quantum Brownian motion and we have compared it to the standard harmonic oscillator model. Unlike the HO model, our model allows nonlinear coupling between system and bath and could be useful in modeling processes involving strong system/bath interactions. Outside the BM limit, the binary collision model contains possible dynamics that could not be produced by the HO model, even in principle.

We have proved the equivalence of the two models in the BM limit. In this limit the equilibrium reduced density matrices derived from the two models can be mapped onto each other, provided the coupling coefficients in the HO model are temperature dependent. Thus, this model provides an alternative way to calculate the properties of quantum BM. There may be numerical advantages to using it, since each bath mode is associated with a spin—a few-level system—rather than with an oscillator.

An important feature of the model is its applicability to fermionic as well as bosonic baths. Such baths are quite common; an example is the electron gas in metals. Kondo [15,22] developed a model for metal impurities interacting with the electron gas; in certain limits the Kondo problem can be treated as a bosonic bath problem [15], in general not. In the binary collision model a fermionic bath represents a particular case of dissipative environment of spin-1/2 angular momenta. The fermionic nature of the bath is unimportant in the BM limit, but may have consequences outside that limit [23].

Finally, the binary collision model is simple and physical. Generalizations of it are easy to imagine and may be attractive choices for modeling other problems of quantum dissipation.

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APPENDIX A

In this Appendix we prove that in the BM limit Eq. (85) holds true. In order to calculate the appropriate average quantities we need the diagonal matrix elements of the thermal density operator $\hat{\rho}$ for the Hamiltonian (in the case of a linear perturbation):

$$\hat{H}(t)=\frac{\hat{P}^2}{2M}-f(t)\hat{X}+\sum_i\ \omega_i\vec{\hat{B}}_i(\hat{X})\cdot\vec{\hat{L}}_i\equiv\hat{T}-f\hat{X}+\hat{V}. \tag{A1}$$

Since on the right-hand side of Eq. (85) the leading order contribution to the average of $\hat{P}$ is in first order in f, we need to consider the average of $\hat{\gamma}$ to zeroth order in f only, so that the whole product remains linear in f. To avoid potential difficulties with the fact that for free BM the density operator corresponding to the Hamiltonian (A1) is not bounded, we will work with its diagonal elements in coordinate space, thus making the case of $X\to\infty$ irrelevant. Using the eigenvectors of $\hat{V}(\hat{X})$ as basis vectors, written as $|n(X)\rangle$, we need

$$\langle X,n(X)|e^{-\beta\hat{H}(t)}|X,n(X)\rangle = \lim_{N\to\infty}\langle X,n(X)|\underbrace{e^{-(\beta/N)\hat{T}}e^{(\beta/N)f\hat{X}}e^{-(\beta/N)\hat{V}}}_{N \text{ times}}\cdots e^{-(\beta/N)\hat{T}}e^{(\beta/N)f\hat{X}}e^{-(\beta/N)\hat{V}}|X,n(X)\rangle. \tag{A2}$$

Multiplying $N-1$ times by unity inside the matrix element we obtain

$$\langle X,n(X)|e^{-\beta\hat{H}(t)}|X,n(X)\rangle = \lim_{N\to\infty}\int dX_1\sum_{n_1}\cdots\int dX_{N-1} \times\sum_{n_{N-1}}\prod_{j=0}^{N-1}\langle X_{j+1},n_{j+1}(X_{j+1})| \times e^{-(\beta/N)\hat{T}}e^{(\beta/N)f\hat{X}}e^{-(\beta/N)\hat{V}}|X_j,n_j(X_j)\rangle, \tag{A3}$$

where

$$e^{-(\beta/N)\hat{V}}|X_j,n_j(X_j)\rangle=|X_j,n_j(X_j)\rangle e^{-(\beta/N)V(n_j)}. \tag{A4}$$

It is important to note that $V(n_j)$ does not depend on X_j, as it is the energy of interaction *relative* to the orientation of the vector $\vec{B}_i$. Thus,

$$\langle X_{j+1},n_{j+1}|e^{-(\beta/N)\hat{T}}e^{(\beta/N)f\hat{X}}e^{-(\beta/N)\hat{V}}|X_j,n_j\rangle = \sqrt{\frac{NM}{2\pi\beta}}e^{-(NM/2\beta)(X_{j+1}-X_j)^2}e^{(\beta/N)fX_j} \times e^{-(\beta/N)V(n_j)}\langle n_{j+1}|n_j\rangle, \tag{A5}$$

and

$$\langle X,n|e^{-\beta\hat{H}(t)}|X,n\rangle = \lim_{N\to\infty}\left(\frac{NM}{2\pi\beta}\right)^{N/2}\int dX_1\sum_{n_1}\cdots\int dX_{N-1} \times\sum_{n_{N-1}}\exp\left(-\sum_{j=0}^{N-1}\frac{NM}{2\beta}(X_{j+1}-X_j)^2+\sum_{k=0}^{N-1}\frac{\beta}{N}fX_k\right) \times\exp\left(-\sum_{l=0}^{N-1}\frac{\beta}{N}V(n_l)\right)\prod_{m=0}^{N-1}\langle n_{m+1}|n_m\rangle. \tag{A6}$$

Let us consider the elements $\langle n_{j+1}(X_{j+1})|n_j(X_j)\rangle$ and expand:

$$\langle n_{j+1}(X_{j+1})|n_j(X_j)\rangle\approx\langle n_{j+1}(X_{j+1})|n_j(X_{j+1})\rangle +\langle n_{j+1}(X_{j+1})|n_j'(X_{j+1})\rangle\delta X +\tfrac{1}{2}\langle n_{j+1}(X_{j+1})|n_j''(X_{j+1})\rangle\delta^2X. \tag{A7}$$

In $\vec{\tilde{B}}_i\cdot\vec{\tilde{L}}_i$, $\hat{X}$ always appears multiplied by p_i, so we have $n_j'(X)\propto p_i$, etc. The first term on the right-hand side of Eq. (A7) is δ_{n_{j+1},n_j}. Consider the second term: (1) If $n_{j+1}=n_j$, we may assume that $\langle n_{j+1}|n_j'\rangle=0$; that amounts to assigning a phase factor to each eigenvector. (2) If $n_{j+1}\neq n_j$, the term $\langle n_{j+1}|n_j'\rangle$ is proportional to $p_i\delta X$. The last term is of order $O(p_i^2\delta^2X)$. Thus,

$$\langle n_{j+1}(X_{j+1})|n_j(X_j)\rangle\approx\delta_{n_{j+1},n_j}+(1-\delta_{n_{j+1},n_j})O(p_i\delta X) +O(p_i^2\delta^2X),$$

and

$$\prod_{j=0}^{N-1}\langle n_{j+1}|n_j\rangle\approx[\delta_{n,n_{N-1}}+(1-\delta_{n,n_{N-1}})O(p_i\delta X) +O(p_i^2\delta^2X)]\cdots[\delta_{n_1,n}+(1-\delta_{n_1,n}) \times O(p_i\delta X)+O(p_i^2\delta^2X)]. \tag{A8}$$

Consider the path for which $n_j=n_{j+1}$, $\forall j\in[0,N-1]$. For this particular path we have

$$\prod_{j=0}^{N-1}\langle n_{j+1}|n_j\rangle\approx 1+Np_i^2\delta^2X+N(N+1)p_i^4(\delta^2X)^2+\cdots\approx 1, \tag{A9}$$

since $p_i\to 0$ and $\delta X\propto N^{-1/2}$. We see that terms of even power of $p_i\delta X$ make a negligible contribution to the path integral.

Now consider a path for which there is a mismatch between some n_{j+1} and n_j, say at $j=k$. Such a path will contribute to the path integral with

$$\cdots\int dX_{k+1}\int dX_k\cdots e^{-(MN/2\beta)(X_{k+2}-X_{k+1})^2} \times e^{-(MN/2\beta)(X_{k+1}-X_k)^2} \times e^{-(MN/2\beta)(X_k-X_{k-1})^2} \times e^{(\beta/N)f(X_{k+1}+X_k)}p_i\underbrace{(X_{k+1}-X_k)}_{\delta X_k}=0. \tag{A10}$$

To zeroth order in f this contribution is zero because reversing the path would lead to the interchange of X_{k+1} and X_k, which means the same contribution but with opposite sign. The same is true for any term containing an odd power of $p_i\delta X$.

Hence, to zeroth order in f, the only nonvanishing contribution to the path integral for a given X comes from the path for which all $|n_j\rangle$'s are the same, that is, $|n_j\rangle \equiv |n\rangle, \forall j$. For this path,

$$\prod_{j=0}^{N-1} \langle n_{j+1}(X_{j+1})|n_j(X_j)\rangle \approx \prod_{j=0}^{N-1} \delta_{n_{j+1},n_j}, \tag{A11}$$

and therefore

$$\langle X,n|e^{-\beta\hat{H}(t)}|X,n\rangle = \lim_{N\to\infty}\left(\frac{NM}{2\pi\beta}\right)^{N/2}\int_X^X \mathcal{D}X_t \times\exp\left[-\int_0^\beta d\tau\left(\frac{M}{2}\dot{X}^2(\tau) - fX(\tau)\right)\right]e^{-\beta V(n)}, \tag{A12}$$

where we have used

$$\sum_{j=0}^{N-1}\frac{MN}{2\beta}(X_{j+1}-X_j)^2 = \sum_{j=0}^{N-1}\epsilon\frac{M}{2}\left(\frac{X_{j+1}-X_j}{\epsilon}\right)^2 \approx \int_0^\beta d\tau\frac{M}{2}\dot{X}^2(\tau), \tag{A13}$$

etc.

We will write

$$\hat{\gamma} \equiv \sum_i \hat{A}_i, \tag{A14}$$

where the definition of $\hat{A}_i$ (with eigenvalues A_i) is obvious. Starting from the Schwarz inequality

$$\left|\left\langle\left(\sum_i \hat{A}_i - \overline{A}\right)\hat{P}(t')\right\rangle\right|^2 \leqslant \left\langle\left(\sum_i \hat{A}_i - \overline{A}\right)^2\right\rangle\langle\hat{P}^2(t')\rangle, \tag{A15}$$

where

$$\overline{A} \equiv \left\langle \sum_i \hat{A}_i\right\rangle, \tag{A16}$$

we have

$$\left\langle\left(\sum_i \hat{A}_i - \overline{A}\right)^2\right\rangle = \left\langle\sum_i \hat{A}_i\sum_j \hat{A}_j\right\rangle - \left\langle\sum_i \hat{A}_i\right\rangle^2, \tag{A17}$$

with

$$\left\langle\sum_i \hat{A}_i\sum_j \hat{A}_j\right\rangle = \frac{1}{Z}\int dX\sum_{n(X)}\left\langle X,n(X)\left|\sum_i \hat{A}_i\sum_j \hat{A}_j \times e^{-\beta\hat{H}}\right|X,n(X)\right\rangle = \frac{1}{Z}\sum_n\left(\sum_i A_i\right)_n\left(\sum_j A_j\right)_n e^{-\beta V(n)} \times\text{const}, \tag{A18}$$

where Z is the partition function, such that

$$\sum_n e^{-\beta V(n)}\times\text{const} = Z. \tag{A19}$$

In Eq. (A18) the sum over i (or j) includes a large number of the eigenvalues A_i, distributed according to thermal equilibrium for the bath. Therefore, we can apply the law of large numbers and write

$$\left(\sum_i A_i\right)_n \approx \left(\sum_i A_i\right), \tag{A20}$$

which means that the sums are approximately independent of the state n. Hence, from Eqs. (A18), (A19), and (A20), it follows that

$$\left\langle\sum_i \hat{A}_i\sum_j \hat{A}_j\right\rangle \approx \left(\sum_i A_i\right)^2. \tag{A21}$$

Similarly,

$$\left\langle\sum_i \hat{A}_i\right\rangle \approx \left(\sum_i A_i\right). \tag{A22}$$

Therefore, Eq. (A17) becomes

$$\left\langle\left(\sum_i \hat{A}_i - \overline{A}\right)^2\right\rangle \approx 0; \tag{A23}$$

hence,

$$\left|\left\langle\left(\sum_i \hat{A}_i - \overline{A}\right)\hat{P}(t')\right\rangle\right|^2 \approx 0, \tag{A24}$$

or

$$\left\langle\sum_i \hat{A}_i\hat{P}(t')\right\rangle \approx \left\langle\sum_i \hat{A}_i\right\rangle\langle\hat{P}(t')\rangle, \tag{A25}$$

and the proof is complete.

APPENDIX B:

Here we outline the proof of several important results of Sec. IV. For details the reader is referred to [19]. First we calculate $\langle\hat{\vec{B}}_i\cdot\hat{\vec{L}}_i\rangle$, which is needed for the fluctuation-dissipation theorem of the second kind. We will work again in the basis set of eigenvectors of $\Sigma_i\hat{\vec{B}}_i\cdot\hat{\vec{L}}_i$:

$$\langle \hat{\vec{B}}_i\cdot\hat{\vec{L}}_i\rangle=\frac{\int dX\sum_{\vec{n}(X)}\langle X,n|\hat{\vec{B}}_i\cdot\hat{\vec{L}}_i e^{-\beta\hat{H}}|X,n\rangle}{\int dX\sum_{\vec{n}(X)}\langle X,n|e^{-\beta\hat{H}}|X,n\rangle}=\frac{\sum_{n_i}(\vec{B}_i\cdot\vec{L}_i)_{n_i}e^{-\beta\omega_i(\vec{B}_i\cdot\vec{L}_i)_{n_i}}}{\sum_{n_i}e^{-\beta\omega_i(\vec{B}_i\cdot\vec{L}_i)_{n_i}}},\tag{B1}$$

where

$$(\vec{B}_i\cdot\vec{L}_i)_{n_i}\equiv[\cos(2p_iX)L_{x,i}+\sin(2p_iX)L_{y,i}]_{n_i}\tag{B2}$$

should not depend on X, as explained earlier. Therefore, we can choose $X=0$. In that case,

$$(\vec{B}_i\cdot\vec{L}_i)_{n_i}\equiv(L_{x,i})_{n_i}\equiv m_i,\tag{B3}$$

where the m_i's are the possible values of $L_{x,i}$. Hence, in Eq. (B1) we can sum over the m_i's, arriving at

$$\langle \hat{\vec{B}}_i\cdot\hat{\vec{L}}_i\rangle=\frac{\sum_{m_i=-l_i}^{l_i}m_ie^{-\beta\omega_im_i}}{\sum_{m_i=-l_i}^{l_i}e^{-\beta\omega_im_i}}=\frac{f_2(i)}{f_1(i)}.\tag{B4}$$

To calculate the equilibrium average of the random force operator we need

$$\langle\hat{F}(t)\rangle=\sum_i 2p_i\omega_i\sin(\omega_it)\langle\hat{L}_{z,i}(0)\rangle-\sum_i 2p_i\omega_i\cos(\omega_it)\times\langle\cos[2p_i\hat{X}(0)]\hat{L}_{y,i}(0)\rangle+\sum_i 2p_i\omega_i\cos(\omega_it)\times\langle\sin[2p_i\hat{X}(0)]\hat{L}_{x,i}(0)\rangle.\tag{B5}$$

It is easy to prove that [19]

$$\langle\hat{L}_{z,i}(0)\rangle=\langle\cos[2p_i\hat{X}(0)]\hat{L}_{y,i}(0)\rangle=\langle\sin[2p_i\hat{X}(0)]\hat{L}_{x,i}(0)\rangle=0.\tag{B6}$$

Thus,

$$\langle\hat{F}(t)\rangle=0.\tag{B7}$$

We now consider Eq. (89), where

$$\begin{aligned}\langle\hat{F}(t)\hat{F}(0)\rangle=&-\sum_{i,j}4p_ip_j\omega_i\omega_j\sin(\omega_it)\langle\cos[2p_j\hat{X}(0)]\hat{L}_{z,i}(0)\hat{L}_{y,j}(0)\rangle+\sum_{i,j}4p_ip_j\omega_i\omega_j\sin(\omega_it)\\&\times\langle\sin[2p_j\hat{X}(0)]\hat{L}_{z,i}(0)\hat{L}_{x,j}(0)\rangle+\sum_{i,j}4p_ip_j\omega_i\omega_j\langle\cos[2p_i\hat{X}(0)]\cos[2p_j\hat{X}(0)]\hat{L}_{y,i}(0)\hat{L}_{y,j}(0)\rangle\\&\times\cos(\omega_it)-\sum_{i,j}4p_ip_j\omega_i\omega_j\langle\cos[2p_i\hat{X}(0)]\sin[2p_j\hat{X}(0)]\hat{L}_{y,i}(0)\hat{L}_{x,j}(0)\rangle\\&\times\cos(\omega_it)-\sum_{i,j}4p_ip_j\omega_i\omega_j\langle\sin[2p_i\hat{X}(0)]\cos[2p_j\hat{X}(0)]\hat{L}_{x,i}(0)\hat{L}_{y,j}(0)\rangle\\&\times\cos(\omega_it)+\sum_{i,j}4p_ip_j\omega_i\omega_j\langle\sin[2p_i\hat{X}(0)]\sin[2p_j\hat{X}(0)]\hat{L}_{x,i}(0)\hat{L}_{x,j}(0)\rangle\cos(\omega_it).\end{aligned}\tag{B8}$$

After calculating each of the six sums above separately [19], we arrive at

$$\langle\hat{F}(t)\hat{F}(0)\rangle=-\sum_i 2p_i^2\omega_i^2\frac{f_2(i)}{f_1(i)}\coth\left(\frac{\beta\omega_i}{2}\right)\cos(\omega_it)+i\sum_i 2p_i^2\omega_i^2\sin(\omega_it)\frac{f_2(i)}{f_1(i)}.\tag{B9}$$

In a similar fashion we calculate $\langle\hat{F}(0)\hat{F}(t)\rangle$ to be

$$\langle\hat{F}(0)\hat{F}(t)\rangle=-\sum_i 2p_i^2\omega_i^2\frac{f_2(i)}{f_1(i)}\coth\left(\frac{\beta\omega_i}{2}\right)\cos(\omega_it)-i\sum_i 2p_i^2\omega_i^2\sin(\omega_it)\frac{f_2(i)}{f_1(i)},\tag{B10}$$

and therefore

$$\tfrac{1}{2}[\langle\hat{F}(t)\hat{F}(0)\rangle+\langle\hat{F}(0)\hat{F}(t)\rangle]=-\sum_i 2p_i^2\omega_i^2\frac{f_2(i)}{f_1(i)}\coth\left(\frac{\beta\omega_i}{2}\right)\cos(\omega_it).\tag{B11}$$

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