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Nonlinearly coupled generalized Fokker-Planck equation for rotational relaxation

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We have investigated the stochastic dynamics of a one dimensional rotor with C_3 symmetry and zero barrier to rotation about the symmetry axis. Angular momentum correlation functions derived from various stochastic dynamics models were compared to the corresponding correlation functions obtained from a molecular dynamics simulation [G. Widmalm, R. W. Pastor, and T. E. Bull, J. Chem. Phys. **94**, 4097 (1991)]. None of the existing classical models agrees with the simulation; and we have shown in general that no linearly coupled generalized Langevin equation with Gaussian random noise can reproduce the simulation results. A quantum stochastic dynamics model [T. E. Bull, Chem. Phys. **143**, 381 (1990)] extrapolated to the classical limit does, however, agree with the computer simulations. But this model is limited to very small molecules because the matrices involved become prohibitively large for even moderately sized molecules. In order to address some of these limitations, we have constructed a nonlinearly coupled rotor-bath model for the rotor. The form of the nonlinear coupling between the rotor and bath is determined by the symmetry of the rotor. A classical nonlinearly coupled generalized Langevin equation and its corresponding nonlinearly coupled Fokker-Planck equation were derived from this microscopic rotor-bath model using the projection operator formalism. In the limit of white noise, these equations reduce to the standard equations derived with linear coupling. With colored noise, however, the linearly and nonlinearly coupled equations are distinct. Angular momentum correlation functions calculated with this nonlinearly coupled Fokker-Planck equation are in excellent agreement with the simulations both in terms of the short time Gaussian decay and long time exponential tail and in terms of the magnitudes of the correlation functions. Collision operators derived from this model should therefore provide a more accurate connection between experimentally measured quantities and the underlying microscopic dynamics.

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I. INTRODUCTION

There is a continuum of stochastic dynamics models which are characterized by the ratio of the mass of the solvent hard sphere to the mass of the solute hard sphere. At one extreme, the Fokker-Planck-Langevin (FPL) model [1,2] is essentially the dynamics of a bowling ball in a sea of ping pong balls. The probability distribution of momenta of the bowling ball after a collision, averaged over the ensemble of ping pong balls, is a very narrow Gaussian distribution about its momentum before the collision. In the middle, the Bhatnagar-Gross-Krook (BGK) model [3,4] is essentially the dynamics of a billiard ball in a sea of billiard balls of the same mass and diameter. When two balls collide they exchange their momenta and energies. Thus the distribution of momenta after a collision is unrelated to the momentum before a collision and each collision completely randomizes the momentum. At the other extreme, the Lorentz model [5] is essentially the dynamics of a ping pong ball in a sea of bowling balls. In the one dimensional version, the distribution of momenta of the ping pong ball following a collision is a narrow Gaussian distribution about the negative of its momentum before the collision.

These three models and all intermediate models were unified into a continuum of models for translational motion by Wigner and Wilkins [6,7]. Widom [8] extended their collision kernel to rough circle models of rotational relaxation. Based on Widom's kernel and quantum mechanical density matrix relaxation theories developed by Redfield [9] and Hubbard [10], Bull [11] developed quantum mechanical models which are analogous to the classical FPL and one dimensional BGK models in the Markovian limit. (The BGK model is the same as the extended diffusion theory [12] in this system [13].) The quantum mechanical models will be referred to as analogs of the classical FPL and BGK models in both the Markovian and non-Markovian regimes, although the analogy is correct only in the Markovian limit.

The fundamental difference between the models is the way collisions change the angular momentum [13]. The correlation functions of polynomials of the momentum in systems with no stationary potential provide a direct measure of the effects of these collisions. Specifically, in the absence of collisions the angular momentum correlation functions are constants, since the angular momentum is constant. Conversely, the decay of the functions is attributable solely to the collisions and the decay behavior can be used to characterize the effects of collisions.

Since the Hermite polynomials of the angular momentum are eigenvectors of the collision operator associated with Widom's kernel [14], these polynomials form a convenient basis for calculating the correlation functions. In particular, the normalized correlation function of the nth rank Hermite polynomial $H_n(x)$ is defined as

$$C_n(t)=\frac{\langle H_n(x(t))H_n(x(0))\rangle}{\langle H_n(x(0))H_n(x(0))\rangle}\ , \tag{1.1}$$

where $x=J/\sqrt{2Ik_BT}$ is a dimensionless variable, J and I are the angular momentum and moment of inertia of the rotor, T is the temperature, and k_B is Boltzmann's constant.

In order to investigate the various stochastic models of rotational motion, Widmalm, Pastor, and Bull [15] performed molecular dynamics simulations of a methyl group attached to a stationary bead. The methyl group was treated as a rigid body and its symmetry axis was fixed. It had zero barrier to internal rotation and was immersed in water. Zhang [16] has recently confirmed these results in new molecular dynamics simulations using a different parameter set for the atomic model of the methyl group and water molecules.

Figure 1 shows the normalized correlation functions of the first and second rank Hermite polynomials of the methyl group's angular momentum calculated from Widmalm's simulation [15]. Two important features are evident in these correlation functions. First, both correlation functions show a rapid Gaussian-like decay at short times. Second, the normalized correlation function of the second rank Hermite polynomial is larger than that of the first rank polynomial for most times.

Also shown in Fig. 1 are the predictions of the non-Markovian quantum stochastic dynamics analog of the FPL model at 310 K and extrapolated to the classical limit [11]. The excellent agreement between this model and the simulation indicates that the quantum theory contains some fundamentally correct attributes, while the extrapolation to the classical limit shows that these attributes are not primarily quantum mechanical in nature. Furthermore, the much poorer agreement between the quantum analog of the BGK model (not shown) and the simulation results indicates that the FPL model is preferred for this system.

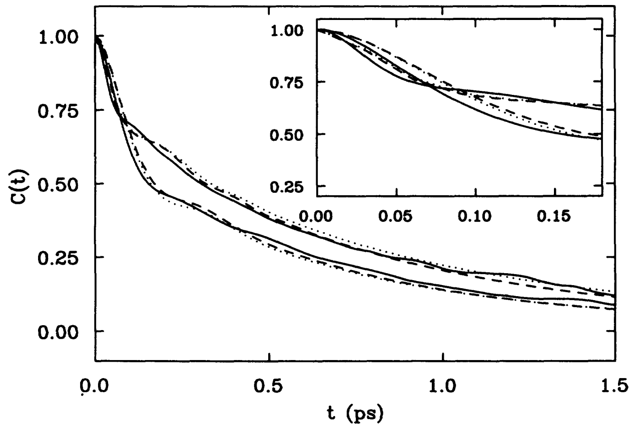

FIG. 1. The normalized correlation functions of the first (lower curves at times $t>0.1$ ps) and second (upper curves at $t>0.1$ ps) rank Hermite polynomials of the angular momentum of a methyl group in water. The solid lines are the results of a molecular dynamics simulation [15], the dotted lines are the predictions of the stochastic quantum dynamics model at a temperature $T=310$ K, and the dashed lines are the predictions of the dynamics model extrapolated to the classical limit. The angular momentum correlation time (area under the correlation function of the first rank Hermite polynomial) is $\tau_J=0.48$ ps and the time constant for the exponential memory function (the noise correlation time) is $\tau=0.079$ ps. The inset shows the short time behavior of the correlation functions.

Calculations with the quantum analog of the FPL model, however, are limited to relatively small molecules and groups since the size of the matrices involved becomes prohibitively large for even moderately sized molecules. It is therefore important to develop classical stochastic models that reproduce the simulation results. These models should provide a more accurate description of the microscopic dynamics than is provided by existing classical models and they can serve as a basis for developing collision operators that can be applied to larger groups and molecules.

An analogous idea has been developed by Lynden-Bell *et al.* [17] to improve the description of motion around the symmetry axis of acetonitrile. Specifically, they investigated a linear Langevin equation with a threefold potential and a non-Gaussian Kubo oscillator model in order to better reproduce certain features of time correlation functions calculated from simulations.

In the present work, however, we generalize the FPL model to include non-Markovian effects such as nonlocal dissipation and colored noise. It is well known that the stochastic dynamics equation associated with the FPL model is a linear Langevin equation, and a *linearly* coupled generalized Langevin equation therefore is a straightforward generalization, i.e.,

$$I\ddot{\phi}(t)=-\int_{-\infty}^{t}\gamma(t-s)\dot{\phi}(s)ds+\eta(t)\ , \tag{1.2}$$

where $\gamma(t)$ is the dissipation kernel, $\eta(t)$ is the colored noise, and the internal potential is zero. Note that the dissipation is a linear force [linearly proportional to the angular velocity $\dot{\phi}(t)$] and the noise is additive.

It is shown in Appendix A that if the noise source in (1.2) is *Gaussian* random (white or colored), then the angular momentum $J(t)=I\dot{\phi}(t)$, which satisfies the *linearly* coupled generalized Langevin equation with zero stationary potential (1.2) is also *Gaussian* random. By definition, correlation functions of Gaussian random variables are *pairwise decomposable.* And, as shown in Appendix B, if the correlation functions of a variable $x(t)$ are pairwise decomposable, then

$$C_n(t)=[C_1(t)]^n\ . \tag{1.3}$$

Consequently, if we assume Gaussian random noise and the validity of Eq. (1.2), then the normalized correlation function of the second rank Hermite polynomial of the angular momentum must be less than that of the first rank Hermite polynomial (for $t>0$) since the latter is less than 1. However, the simulation displays the opposite relationship for most of the time shown. Therefore, in order to reproduce the simulation results with a Langevin equation, it is necessary to revise the assumptions of linear coupling and/or Gaussian random noise.

In an attempt to improve the stochastic dynamics model for a one dimensional threefold symmetric rotor, we reexamined the microscopic model of the methyl group and its interaction with solvent molecules. We found that nonlinear coupling between the rotor and its environment appears naturally in the transformation from Cartesian to polar coordinates. More important, the form of the nonlinear coupling is determined by the symmetry properties of the rotor.

We show that the leading coupling terms for a methyl group are $a_c \cos 3\phi$ and $a_s \sin 3\phi$, where a_c and a_s are functions of the dynamical variables of the solvent molecules. These correspond to the coupling terms x^3, x^2y, xy^2, and y^3 in the Cartesian coordinate system. They are highly nonlinear and are the same form as the coupling used in the quantum mechanical model [11].

Using this nonlinear coupling, we propose a *rotor-bath* model for a methyl group immersed in a solvent. The solvent is modeled by an ideal thermal bath which consists of two sets of harmonic oscillators with different frequencies. The coupling between the rotor and bath is linear in the bath coordinates, but nonlinear in the rotor coordinate. At a microscopic level, this system-bath model is standard in nonequilibrium statistical mechanics and has been used frequently both in classical and quantum mechanics [18–22].

By using the powerful *projection operator method* developed by Zwanzig and others [18,19,23,24], the irrelevant bath variables can be eliminated systematically, resulting in a nonlinearly coupled generalized Langevin equation. This equation has the usual features of the linearly coupled generalized Langevin equation: a dissipative force and a noise source. However, the dissipative force now is nonlinear and the noise is multiplicative.

A Fokker-Planck-type master equation for the phase space probability distribution of the rotor is also derived from the rotor-bath model. An important feature of the master equation is that both the diffusion and dissipation "coefficients" are no longer constants, but depend on the angular momentum J. It is shown that this unique feature drives the dynamics of the rotor in a fundamentally different way.

In the limit of white noise, these nonlinearly coupled equations reduce to the Langevin and Fokker-Planck equations derived with linear coupling. With colored noise, however, the linearly and nonlinearly coupled equations are distinct.

In the next section the rotor-bath model is developed and the form of the nonlinear coupling is determined from a consideration of the rotor's symmetry. In Sec. III a nonlinearly coupled generalized Langevin equation is derived. The derivation of the corresponding Fokker-Planck-type master equation is given in Sec. IV. Correlation functions calculated from solving the nonlinear master equation are presented in Sec. V and are compared with correlation functions derived from the simulations. The discussion and conclusion are presented in Sec. VI. Some details of the derivations are contained in a series of appendixes.

II. RANDOM POTENTIALS FOR A METHYL GROUP AND ROTOR-BATH MODEL

Consider a methyl group attached to a large molecule. The methyl group is treated as a rigid body and is immersed in a solvent. Assuming the large molecule is fixed, the methyl group can only rotate about its symmetry axis and it is a one dimensional symmetric rotor. If the symmetry axis of the rotor is along the z axis, the three hydrogens of the methyl group are in the x-y plane and their coordinates are

$$x_1 = l_0 \cos\phi \,, \quad y_1 = l_0 \sin\phi \,, \tag{2.1a}$$

$$x_2 = l_0 \cos\left[\phi + \frac{2\pi}{3}\right] , \quad y_2 = l_0 \sin\left[\phi + \frac{2\pi}{3}\right] , \tag{2.1b}$$

$$x_3 = l_0 \cos\left[\phi + \frac{4\pi}{3}\right] , \quad y_3 = l_0 \sin\left[\phi + \frac{4\pi}{3}\right] , \tag{2.1c}$$

where ϕ is the rotational angle and l_0 is the distance between a hydrogen and the z axis. If $v(x,y)$ is the random interaction between a hydrogen in the methyl group and all the solvent molecules, then the potential of the whole methyl group is

$$V(\phi) = v(x_1,y_1) + v(x_2,y_2) + v(x_3,y_3) \,. \tag{2.2}$$

Expanding $v(x,y)$ about the origin ($x = y = 0$) (which is also the center of the methyl group) and keeping terms only up to third order in x and y, we obtain

$$V(\phi) = V_0 + a_c \cos(3\phi) + a_s \sin(3\phi) \,, \tag{2.3}$$

where

$$V_0 = 3v(0,0) + \frac{3}{4} l_0^2 \frac{\partial^2 v}{\partial x^2}(0,0) + \frac{3}{4} l_0^2 \frac{\partial^2 v}{\partial y^2}(0,0) \tag{2.4a}$$

does not exert a torque and

$$a_c = \frac{1}{8} l_0^3 \frac{\partial^3 v}{\partial x^3}(0,0) - \frac{3}{8} l_0^3 \frac{\partial^3 v}{\partial x \partial y^2}(0,0) \,, \tag{2.4b}$$

$$a_s = \frac{3}{8} l_0^3 \frac{\partial^3 v}{\partial x^2 \partial y}(0,0) - \frac{1}{8} l_0^3 \frac{\partial^3 v}{\partial y^3}(0,0) \tag{2.4c}$$

are two *independent* random variables. The random potential (2.3) can also be rewritten as

$$V(\phi) = V_0 + a' \cos 3(\phi - \phi_0) \,, \tag{2.5}$$

where

$$a' = \sqrt{a_c^2 + a_s^2} \tag{2.6a}$$

is the random amplitude and

$$\phi_0=\arctan\frac{a_s}{a_c} \tag{2.6b}$$

is the random phase. It is clear that the potential $V(\phi)$ has threefold rotational symmetry, i.e., it is invariant under the transformation $\phi\rightarrow\phi+2\pi/3$.

To mimic the above random interaction between the rotor and bath, we introduce a *rotor-bath model.* The Hamiltonian for both rotor and bath is

$$\begin{aligned}H(\phi,J,q_c,k_c,q_s,k_s)\\ &=H(\phi,J)+H_b(q_c,k_c,q_s,k_s)+H_{\text{int}}(\phi,q_c,q_s)\ ,\end{aligned} \tag{2.7}$$

where

$$H_a(\phi,J)=\frac{J^2}{2I}+U(\phi) \tag{2.8}$$

is the Hamiltonian of the rotor,

$$\begin{aligned}H_b(q_c,k_c,q_s,k_c)=&\sum_n\left\{\frac{k_{cn}^2}{2m_{cn}}+\frac{1}{2}m_{cn}\omega_{cn}^2q_{cn}^2\right\}\\&+\sum_n\left\{\frac{k_{sn}^2}{2m_{sn}}+\frac{1}{2}m_{sn}\omega_{sn}^2q_{sn}^2\right\}\end{aligned} \tag{2.9}$$

is the Hamiltonian of the thermal bath, and

$$H_{\text{int}}(\phi,q_c,q_s)=\sum_n\{C_{cn}q_{cn}A_c(\phi)\}+\sum_n\{C_{sn}q_{sn}A_s(\phi)\} \tag{2.10}$$

is the interaction between the rotor and bath. In the above equations, J is the angular momentum of the rotor, $I=3ml_0^2$ is the moment of inertia of the rotor, and $U(\phi)$ is the internal potential (barrier) of the rotor. The thermal bath is modeled by two sets of harmonic oscillators with masses m_{cn} and m_{sn} and natural frequencies ω_{cn} and ω_{sn}. The coordinates and canonical momenta of the bath oscillators are q_{cn}, q_{sn}, k_{cn}, and k_{sn}. The bath is coupled to the rotor by two nonlinear functions

$$A_c(\phi)=\tfrac{1}{3}\cos(3\phi)\ , \tag{2.10a}$$

$$A_s(\phi)=\tfrac{1}{3}\sin(3\phi)\ . \tag{2.10b}$$

The coupling constants are C_{cn} and C_{sn}.

III. NONLINEARLY COUPLED GENERALIZED LANGEVIN EQUATION

The equations of motion for the rotor-bath model derived from the total Hamiltonian (2.7) are

$$\begin{aligned}I\ddot{\phi}=&-\frac{\partial U(\phi)}{\partial\phi}-\frac{\partial A_c(\phi)}{\partial\phi}\sum_n\{C_{cn}q_{cn}\}\\&-\frac{\partial A_s(\phi)}{\partial\phi}\sum_n\{C_{cn}q_{cn}\}\ ,\end{aligned} \tag{3.1}$$

$$m_{cn}\ddot{q}_{cn}+m_{cn}\omega_{cn}^2q_{cn}=-C_{cn}A_c(\phi)\ , \tag{3.2a}$$

$$m_{sn}\ddot{q}_{sn}+m_{sn}\omega_{sn}^2q_{sn}=-C_{sn}A_s(\phi)\ . \tag{3.2b}$$

The formal solutions to (3.2a) and (3.2b) are

$$\begin{aligned}q_{cn}(t)=&q_{cn}(0)\cos(\omega_{cn}t)+\frac{k_{cn}(0)}{m_{cn}\omega_{cn}}\sin(\omega_{cn}t)\\&-\frac{C_{cn}}{m_{cn}}\int_0^t ds\frac{\sin[\omega_{cn}(t-s)]}{\omega_{cn}}A_c(\phi(s))\ ,\end{aligned} \tag{3.3a}$$

and

$$\begin{aligned}q_{sn}(t)=&q_{sn}(0)\cos(\omega_{sn}t)+\frac{k_{sn}(0)}{m_{sn}\omega_{sn}}\sin(\omega_{sn}t)\\&-\frac{C_{sn}}{m_{sn}}\int_0^t ds\frac{\sin[\omega_{sn}(t-s)]}{\omega_{sn}}A_s(\phi(s))\ ,\end{aligned} \tag{3.3b}$$

where $q_{cn}(0)$, $q_{sn}(0)$, $k_{cn}(0)$, and $k_{sn}(0)$ are the initial coordinates and momenta of the bath oscillators. Substituting (3.3a) and (3.3b) into (3.1) gives

$$\begin{aligned}I\ddot{\phi}=&-\frac{\partial U(\phi)}{\partial\phi}-2\frac{\partial A_c(\phi)}{\partial\phi}\int_0^t ds\frac{d\gamma_c(t-s)}{d(t-s)}A_c(\phi(s))\\&+\frac{\partial A_c(\phi)}{\partial\phi}\eta_c(t)-2\frac{\partial A_s(\phi)}{\partial\phi}\int_0^t\frac{d\gamma_s(t-s)}{d(t-s)}A_s(\phi(s))\\&+\frac{\partial A_s(\phi)}{\partial\phi}\eta_s(t)\ ,\end{aligned} \tag{3.4}$$

where

$$\gamma_c(s)=\sum_n\frac{C_{cn}^2}{2m_{cn}\omega_{cn}^2}\cos(\omega_{cn}s)\ , \tag{3.5a}$$

$$\gamma_s(s)=\sum_n\frac{C_{sn}^2}{2m_{sn}\omega_{sn}^2}\cos(\omega_{sn}s)\ , \tag{3.5b}$$

and

$$\eta_c(t)=-\sum_n C_{cn}\left\{q_{cn}(0)\cos(\omega_{cn}t)+\frac{k_{cn}(0)}{m_{cn}\omega_{cn}}\sin(\omega_{cn}t)\right\}\ , \tag{3.6a}$$

$$\eta_s(t)=-\sum_n C_{sn}\left\{q_{sn}(0)\cos(\omega_{sn}t)+\frac{k_{sn}(0)}{m_{sn}\omega_{sn}}\sin(\omega_{sn}t)\right\}\ . \tag{3.6b}$$

The functions defined in (3.5a) and (3.5b) are called damping kernels and the functions (3.6a) and (3.6b) are noise sources. Assuming that at time $t=0$ the bath is at thermal equilibrium with temperature T, then the averages for the bath oscillators are

$$\langle q_{cn}(0)\rangle=0\ ,\qquad \langle q_{cn}(0)^2\rangle=\frac{k_BT}{m_{cn}\omega_{cn}^2}\ ; \tag{3.7a}$$

$$\langle k_{cn}(0)\rangle=0\ ,\qquad \langle k_{cn}(0)^2\rangle=m_{cn}k_BT\ ; \tag{3.7b}$$

$$\langle q_{sn}(0)\rangle=0\ ,\qquad \langle q_{sn}(0)^2\rangle=\frac{k_BT}{m_{sn}\omega_{sn}^2}\ ; \tag{3.7c}$$

$$\langle k_{sn}(0)\rangle=0\ ,\qquad \langle k_{sn}(0)^2\rangle=m_{sn}k_BT\ ; \tag{3.7d}$$

and the averages of all other two point functions are

$$\langle q_{cn}(0)k_{cn}(0)\rangle=\langle q_{sn}(0)k_{sn}(0)\rangle=\langle q_{cn}(0)q_{sn}(0)\rangle=\langle k_c(0)k_{sn}(0)\rangle=\langle q_{cn}(0)k_{sn}(0)\rangle=\langle q_{sn}(0)k_{cn}(0)\rangle=0\ , \tag{3.7e}$$

where the average is taken over the Maxwell-Boltzmann distribution

$$\rho_b=\frac{1}{Z}\exp\left[-\frac{H_b}{k_BT}\right]\ , \tag{3.8}$$

with Z being a normalization constant. With the above relations it can be shown that

$$\begin{aligned}&\langle\eta_c(t)\rangle=0\ ,\\&\langle\eta_c(t_1)\eta_c(t_2)\rangle=2k_BT\gamma_c(t_1-t_2)\ ;\end{aligned} \tag{3.9a}$$

$$\begin{aligned}&\langle\eta_s(t)\rangle=0\ ,\\&\langle\eta_s(t_1)\eta_s(t_2)\rangle=2k_BT\gamma_s(t_1-t_2)\ ;\end{aligned} \tag{3.9b}$$

and

$$\langle\eta_c(t_1)\eta_s(t_2)\rangle=0\ . \tag{3.9c}$$

It is clear that, under these assumptions, $\eta_c(t)$ and $\eta_s(t)$ are two *independent* Gaussian noise sources.

Integrating (3.4) by parts leads to

$$\begin{aligned}I\ddot{\phi}=&-\frac{\partial U_r(\phi)}{\partial\phi}-2\frac{\partial A_c(\phi)}{\partial\phi}\int_0^t ds\,\gamma_c(t-s)\frac{\partial A_c(\phi)}{\partial\phi}\dot{\phi}(s)\\&+\frac{\partial A_c(\phi)}{\partial\phi}\eta_c(t)\\&-2\frac{\partial A_s(\phi)}{\partial\phi}\int_0^t ds\,\gamma_s(t-s)\frac{\partial A_s(\phi)}{\partial\phi}\dot{\phi}(s)\\&+\frac{\partial A_s(\phi)}{\partial\phi}\eta_s(t)\ ,\end{aligned} \tag{3.10}$$

where

$$U_r(\phi)=U(\phi)-\gamma_c(0)[A_c(\phi)]^2-\gamma_s(0)[A_s(\phi)]^2 \tag{3.11}$$

is the renormalized internal potential of the rotor. Since

$$\frac{\partial A_c(\phi)}{\partial\phi}=-\sin(3\phi) \tag{3.12a}$$

and

$$\frac{\partial A_s(\phi)}{\partial\phi}=\cos(3\phi)\ , \tag{3.12b}$$

then

$$\begin{aligned}I\ddot{\phi}=&-\frac{\partial U_r(\phi)}{\partial\phi}-2\sin(3\phi)\int_0^t ds\,\gamma_c(t-s)\sin(3\phi)\dot{\phi}(s)\\&-\sin(3\phi)\eta_c(t)\\&-2\cos(3\phi)\int_0^t ds\,\gamma_s(t-s)\cos(3\phi)\dot{\phi}(s)\\&+\cos(3\phi)\eta_s(t)\ .\end{aligned} \tag{3.13}$$

This is a nonlinearly coupled generalized Langevin equation. The noise sources $\eta_c(t)$ and $\eta_s(t)$, which are multiplicative, are coupled to the rotor through the nonlinear coupling functions $\sin(3\phi)$ and $\cos(3\phi)$. The damping forces are also nonlinearly coupled and they contain two memory functions $\gamma_c(t)$ and $\gamma_s(t)$.

If we define the noise spectral densities as

$$I_c(\omega)=\sum_n\pi\frac{C_{cn}^2}{2m_{cn}\omega_{cn}}\delta(\omega-\omega_{cn}) \tag{3.14a}$$

and

$$I_s(\omega)=\sum_n\pi\frac{C_{sn}^2}{2m_{sn}\omega_{sn}}\delta(\omega-\omega_{sn})\ , \tag{3.14b}$$

then the dissipation kernels (3.5a) and (3.5b) can be rewritten as

$$\gamma_c(s)=\int_0^{+\infty}\frac{d\omega}{\pi}\frac{I_c(\omega)}{\omega}\cos(\omega s) \tag{3.15a}$$

and

$$\gamma_s(s)=\int_0^{+\infty}\frac{d\omega}{\pi}\frac{I_s(\omega)}{\omega}\cos(\omega s)\ . \tag{3.15b}$$

From the above definitions, it can be seen that these spectral densities depend only on the properties of the bath oscillator and the coupling between the bath and the rotor. For an isotropic fluid, we naturally have

$$I_c(\omega)\equiv I_s(\omega)\ , \tag{3.16}$$

so

$$\gamma_c(s)\equiv\gamma_s(s)=\gamma(s)\ . \tag{3.17}$$

A simple example of a spectral density is Ohmic dissipation

$$I_c(\omega)=\gamma_0\omega e^{-\omega^2/\Lambda^2}\ , \tag{3.18}$$

where Λ is the frequency cutoff. The damping kernel is

$$\gamma(s)=\gamma_0\frac{\Lambda}{2\pi^{1/2}}e^{-(1/4)\Lambda^2s^2}\simeq\gamma_0\delta(s)\ , \tag{3.19}$$

where we have assumed that the cutoff frequency Λ is very large. The Ohmic dissipation is a local damping force and it corresponds to a white noise source through the well known fluctuation-dissipation relations (3.9a) or (3.9b). For this special case, the Langevin equation (3.13) becomes

$$\begin{aligned}I\ddot{\phi}=&-\frac{\partial U_r(\phi)}{\partial\phi}-\gamma_0\dot{\phi}(s)\\&-\sin(3\phi)\eta_c(t)+\cos(3\phi)\eta_s(t)\ .\end{aligned} \tag{3.20}$$

In Appendix C, it is shown that the master equation for the probability distribution of the rotor which corresponds to (3.20) is the regular Fokker-Planck equation (C11). This means that the master equations for linearly and nonlinearly coupled systems are the same in the limit of white noise and local damping. With a colored noise spectrum, on the other hand, the damping force contains memory kernels and the resultant master equation is more complicated, as shown in the next section.

IV. NONLINEARLY COUPLED GENERALIZED FOKKER-PLANCK EQUATION FOR A FREE ROTOR

The probability distribution $W(\phi,J,q_c,k_c,q_s,k_s,t)$ for the rotor-bath model (2.7) satisfies the classical Liouville equation

$$\frac{\partial}{\partial t}W=\{H,W\}_{pb}\ , \tag{4.1}$$

where

$$\{f,g\}_{pb}=\{f,g\}_{pb}^{\phi}+\{f,g\}_{pb}^{c}+\{f,g\}_{pb}^{s} \tag{4.2}$$

and

$$\{f,g\}_{pb}^{\phi}=\frac{\partial f}{\partial \phi}\frac{\partial g}{\partial J}-\frac{\partial f}{\partial J}\frac{\partial g}{\partial \phi}\ , \tag{4.3a}$$

$$\{f,g\}_{pb}^{c}=\sum_n\left[\frac{\partial f}{\partial q_{cn}}\frac{\partial g}{\partial k_{cn}}-\frac{\partial f}{\partial k_{cn}}\frac{\partial g}{\partial q_{cn}}\right]\ , \tag{4.3b}$$

$$\{f,g\}_{pb}^{s}=\sum_n\left[\frac{\partial f}{\partial q_{sn}}\frac{\partial g}{\partial k_{sn}}-\frac{\partial f}{\partial k_{sn}}\frac{\partial g}{\partial q_{sn}}\right] \tag{4.3c}$$

denote the Poisson brackets of the arbitrary functions f and g. If the Liouville operator is defined as

$$\begin{aligned} i\hat{L}&=i\hat{L}_a+i\hat{L}_b+i\hat{L}_{\text{int}}\\ &\equiv\{H_a,\ \}_{pb}+\{H_b,\ \}_{pb}+\{H_{\text{int}},\ \}_{pb}\ , \end{aligned} \tag{4.4}$$

then (4.1) becomes

$$\frac{\partial}{\partial t}W=[i\hat{L}_a+i\hat{L}_b+i\hat{L}_{\text{int}}]W\ . \tag{4.5}$$

Define the *projection operator* $\hat{P}$ as [19]

$$\hat{P}f=\rho_b\int d\vec{b}\,f \tag{4.6}$$

and its complement as

$$\hat{P}'=1-\hat{P}\ , \tag{4.7}$$

where

$$\int d\vec{b}=\prod_n\int_{-\infty}^{+\infty}dq_{cn}\int_{-\infty}^{+\infty}dk_{cn}\int_{-\infty}^{+\infty}dq_{sn}\int_{-\infty}^{+\infty}dk_{sn} \tag{4.8}$$

is the integration over the phase space of the bath and ρ_b is the Maxwell-Boltzmann distribution for the thermal bath (3.8). Applying the projection operation $\hat{P}$ to the probability distribution of the rotor bath $W(\phi,J,q_c,k_c,q_s,k_s,t)$ results in

$$\hat{P}W=\rho_b\sigma\ , \tag{4.9}$$

where

$$\sigma(\phi,J,t)=\int d\vec{b}\,W(\phi,J,q_c,k_c,q_s,k_s,t) \tag{4.10}$$

is the reduced probability distribution for the rotor. It has been shown [23] that the master equation for $\sigma(\phi,J,t)$ is

$$\frac{\partial}{\partial t}\sigma(\phi,J,t)=\hat{S}\sigma(\phi,J,t)+\hat{R}\sigma(\phi,J,t)\ , \tag{4.11}$$

where $\hat{S}$ is the streaming operator

$$\begin{aligned} \hat{S}\sigma(\phi,J,t)&=i\hat{L}_a\sigma(\phi,J,t)\\ &=\left[\frac{\partial U(\phi)}{\partial\phi}\frac{\partial}{\partial J}-\frac{J}{I}\frac{\partial}{\partial\phi}\right]\sigma(\phi,J,t) \end{aligned} \tag{4.12}$$

and $\hat{R}$ is the collision operator

$$\begin{aligned} \hat{R}\sigma(\phi,J,t)=\int_{-\infty}^{t}ds\int d\vec{b}\,i\hat{L}_{\text{int}}e^{(t-s)\hat{P}'i\hat{L}\hat{P}'}\\ \times i\hat{L}_{\text{int}}\rho_b\sigma(\phi,J,s)\ . \end{aligned} \tag{4.13}$$

Here we have assumed that at initial time $t\rightarrow-\infty$, the rotor and the bath are not correlated, so that

$$W(t\rightarrow-\infty)=\rho_b\sigma(t\rightarrow-\infty) \tag{4.14}$$

and therefore

$$\hat{P}'W(t\rightarrow-\infty)=0\ . \tag{4.15}$$

Assuming that the coupling between the rotor and bath is weak, i.e., C_{cn} and C_{sn} are very small, then

$$H_{\text{int}}\ll H_a \tag{4.16}$$

and we can make the approximation

$$e^{(t-s)\hat{P}'i\hat{L}\hat{P}'}\simeq e^{(t-s)\hat{P}'(i\hat{L}_a+i\hat{L}_b)\hat{P}'} \tag{4.17}$$

in Eq. (4.13) or

$$\begin{aligned} \hat{R}\sigma(\phi,J,t)=\int_{-\infty}^{t}ds\int d\vec{b}\,i\hat{L}_{\text{int}}e^{(t-s)(i\hat{L}_a+i\hat{L}_b)}\\ \times i\hat{L}_{\text{int}}\rho_b\sigma(\phi,J,s)\ . \end{aligned} \tag{4.18}$$

With this approximation, Eq. (4.11) becomes (see Appendix D)

$$\begin{aligned} \frac{\partial}{\partial t}\sigma(\phi,J,t)=&\left[\frac{\partial U_r(\phi)}{\partial\phi}\frac{\partial}{\partial J}-\frac{J}{I}\frac{\partial}{\partial\phi}\right]\sigma(\phi,J,t)+2\int_{-\infty}^{t}ds\,\gamma_c(t-s)\frac{\partial A_c}{\partial\phi}\frac{\partial}{\partial J}e^{(t-s)i\hat{L}_a}\frac{\partial A_c}{\partial\phi}\frac{J}{I}\sigma(\phi,J,s)\\ &+2\int_{-\infty}^{t}ds\,\gamma_s(t-s)\frac{\partial A_s}{\partial\phi}\frac{\partial}{\partial J}e^{(t-s)i\hat{L}_a}\frac{\partial A_s}{\partial\phi}\frac{J}{I}\sigma(\phi,J,s)\\ &+2k_BT\int_{-\infty}^{t}ds\,\gamma_c(t-s)\frac{\partial A_c}{\partial\phi}\frac{\partial}{\partial J}e^{(t-s)i\hat{L}_a}\frac{\partial A_c}{\partial\phi}\frac{\partial}{\partial J}\sigma(\phi,J,s)\\ &+2k_BT\int_{-\infty}^{t}ds\,\gamma_s(t-s)\frac{\partial A_s}{\partial\phi}\frac{\partial}{\partial J}e^{(t-s)i\hat{L}_a}\frac{\partial A_s}{\partial\phi}\frac{\partial}{\partial J}\sigma(\phi,J,s)\ , \end{aligned} \tag{4.19}$$

where the dissipation kernels $\gamma_c(s)$ and $\gamma_s(s)$ are given by (3.5a) and (3.5b) and the renormalized internal potential of the rotor $U_r(\phi)$ is defined in (3.11).

Assuming the solvent is an isotropic fluid, then (3.17) holds and Eq. (4.19) can be further simplified to

$$\frac{\partial}{\partial t}\sigma(\phi,J,t)=\left[\frac{\partial U_r(\phi)}{\partial\phi}\frac{\partial}{\partial J}-\frac{J}{I}\frac{\partial}{\partial\phi}\right]\sigma(\phi,J,t)+2\int_{-\infty}^{t}ds\,\gamma(t-s)\frac{\partial}{\partial J}F(\phi,J,t-s)e^{(t-s)i\hat{L}_a}\frac{J}{I}\sigma(\phi,J,s)$$
$$+2k_BT\int_{-\infty}^{t}ds\,\gamma(t-s)\frac{\partial}{\partial J}F(\phi,J,t-s)e^{(t-s)i\hat{L}_a}\frac{\partial}{\partial J}\sigma(\phi,J,s)\ , \tag{4.20}$$

where the kernel $F(\phi,J,t)$ is

$$F(\phi,J,t)=\frac{\partial A_c(\phi)}{\partial\phi}e^{ti\hat{L}_a}\frac{\partial A_c(\phi)}{\partial\phi}+\frac{\partial A_s(\phi)}{\partial\phi}e^{ti\hat{L}_a}\frac{\partial A_s(\phi)}{\partial\phi}\ . \tag{4.21}$$

For a free rotor,

$$\frac{\partial U_r(\phi)}{\partial\phi}=0 \tag{4.22}$$

and, as shown in Appendix E,

$$F(\phi,J,s)=\cos\left[3\frac{J}{I}s\right]\ . \tag{4.23}$$

Consequently, Eq. (4.20) reduces to the integral-differential equation

$$\frac{\partial}{\partial t}\sigma(\phi,J,t)=-\frac{J}{I}\frac{\partial}{\partial\phi}\sigma(\phi,J,t)+2\int_{-\infty}^{t}ds\,\gamma(t-s)\frac{\partial}{\partial J}\cos\left[3\frac{J}{I}(t-s)\right]e^{(t-s)i\hat{L}_a}\frac{J}{I}\sigma(\phi,J,s)$$
$$+2k_BT\int_{-\infty}^{t}ds\,\gamma(t-s)\frac{\partial}{\partial J}\cos\left[3\frac{J}{I}(t-s)\right]e^{(t-s)i\hat{L}_a}\frac{\partial}{\partial J}\sigma(\phi,J,s)\ , \tag{4.24}$$

which is our main result. It is easy to see that the thermal equilibrium distribution of the rotor

$$\sigma_{\text{eq}}(\phi,J)\sim\exp\left[-\frac{H_a}{2k_BT}\right] \tag{4.25}$$

is an eigenfunction of (4.24) with zero eigenvalue, i.e., the master equation (4.24) satisfies the principle of detailed balance.

Further, it can be shown that

$$e^{(t-s)i\hat{L}_a}J\sigma(\phi,J,s)=[3^{(t-s)i\hat{L}_a}J][e^{(t-s)i\hat{L}_a}\sigma(\phi,J,s)]\ , \tag{4.26}$$

where the square brackets indicate that the operators operate only on functions within the square bracket. Also,

$$e^{(t-s)i\hat{L}_a}\frac{\partial}{\partial J}\sigma(\phi,J,s)$$
$$=\sum_{n=0}^{\infty}\frac{(t-s)^n}{n!}[i\hat{L}_a]^n\frac{\partial}{\partial J}\sigma(\phi,J,s)$$
$$=\sum_{n=0}^{\infty}\frac{(t-s)^n}{n!}\left[\frac{\partial}{\partial J}-\frac{n}{J}\right][i\hat{L}_a]^n\sigma(\phi,J,s)$$
$$=\frac{\partial}{\partial J}\sigma(\phi,J,t)+\frac{t-s}{J}\frac{\partial}{\partial t}\sigma(\phi,J,t)\ . \tag{4.27}$$

If the memory time is short, the integrands in Eq. (4.24) are negligible except at small values of $(t-s)$. Consequently, one can use the approximation

$$e^{(t-s)i\hat{L}_a}\sigma(\phi,J,s)\simeq e^{(t-s)(i\hat{L}_a+i\hat{R})}\sigma(\phi,J,s)$$
$$=\sigma(\phi,J,t) \tag{4.28}$$

in (4.26) and

$$\frac{\partial}{\partial t}\sigma(\phi,J,t)=(i\hat{L}_a+i\hat{R})\sigma(\phi,J,t)\simeq i\hat{L}_a\sigma(\phi,J,t) \tag{4.29}$$

in (4.27). This results in the short noise correlation time approximations

$$e^{(t-s)i\hat{L}_a}J\sigma(\phi,J,s)\simeq J\sigma(\phi,J,t) \tag{4.30}$$

and

$$e^{(t-s)i\hat{L}_a}\frac{\partial}{\partial J}\sigma(\phi,J,s)\simeq\frac{\partial}{\partial J}\sigma(\phi,J,t)+\frac{t-s}{J}i\hat{L}_a\sigma(\phi,J,t)\ . \tag{4.31}$$

Substituting (4.30) and (4.31) into (2.24) gives the master equation for a free Brownian rotor,

$$\frac{\partial}{\partial t}\sigma(\phi,J,t)=\left\{-\frac{J}{I}\frac{\partial}{\partial\phi}+\frac{\partial}{\partial J}D(\phi,J)\frac{J}{I}\right.$$
$$+k_BT\frac{\partial}{\partial J}D(\phi,J)\frac{\partial}{\partial J}$$
$$\left.+k_BT\frac{\partial}{\partial J}D'(\phi,J)\frac{\partial}{\partial\phi}\right\}\sigma(\phi,J,t)\ . \tag{4.32}$$

The first term on the right-hand side of (4.32) is the usual streaming term. The second and third terms are a diffusion term and a dissipation term, respectively. The last term is the abnormal diffusion term. In (4.32), the diffusion coefficient is

$$D(\phi,J)=\int_0^\infty ds\,\gamma(s)\cos\left[3\frac{J}{I}s\right] \tag{4.33}$$

and the abnormal diffusion coefficient is

$$D'(\phi,J)=\int_0^\infty ds\,s\,\gamma(s)\cos\left[3\frac{J}{I}s\right]\ . \tag{4.34}$$

Equation (4.32) is the master equation (4.24) in the limit of a short noise correlation time. It does not contain any explicit time integration. Nevertheless, it is still a master equation for a non-Markovian process; all of the non-Markovian characteristics are contained explicitly in the diffusion and dissipation coefficients (4.33) and (4.34). It is easy to verify that the master equation (4.32) in the limit of short noise correlation time also satisfies the principle of detailed balance.

In the white noise limit (3.19), we find that

$$D(J)=\gamma_0 \tag{4.35}$$

and

$$D'(J)=0 \tag{4.36}$$

and the master equation becomes

$$\frac{\partial}{\partial J}\sigma(\phi,J,t)=\left\{-\frac{J}{I}\frac{\partial}{\partial\phi}+\gamma_0\frac{\partial}{\partial J}\frac{J}{I}+\gamma_0 k_B T\frac{\partial^2}{\partial J^2}\right\}\sigma(\phi,J,t)\ , \tag{4.37}$$

which is the regular Fokker-Planck equation with zero internal potential [see Eq. (C11)]. This limiting case of the master equation can also be obtained by taking the white noise limit (3.19) directly in the master equation (4.24).

Specifically, if the damping kernel is an exponentially decaying function, namely,

$$\gamma(s)=\gamma_0\frac{1}{\tau}e^{-|s|/\tau}\ , \tag{4.38}$$

where τ is the memory time (which is also the noise correlation time), the corresponding spectral density is

$$I_c(\omega)=I_s(\omega)=\gamma_0\frac{1}{1+\tau^2\omega^2}\ . \tag{4.39}$$

In this case,

$$D(\phi,J)=\gamma_0\frac{1}{1+\left[3\frac{J}{I}\tau\right]^2} \tag{4.40}$$

and

$$D'(\phi,J)=\gamma_0\tau\frac{1-\left[3\frac{J}{I}\tau\right]^2}{\left[1+\left[3\frac{J}{I}\tau\right]^2\right]^2} \tag{4.41}$$

and the master equation becomes

$$\frac{\partial}{\partial t}\sigma(\phi,J,t)=\left\{-\frac{\partial}{\partial\phi}\frac{J}{I}+\gamma_0\frac{\partial}{\partial J}\frac{1}{1+\left[3\frac{J}{I}\tau\right]^2}\frac{J}{I}+\gamma_0 k_B T\frac{\partial}{\partial J}\frac{1}{1+\left[3\frac{J}{I}\tau\right]^2}\frac{\partial}{\partial J}+\gamma_0 k_B T\tau\frac{\partial^2}{\partial\phi\partial J}\frac{1-\left[3\frac{J}{I}\tau\right]^2}{\left[1+\left[3\frac{J}{I}\tau\right]^2\right]^2}\right\}\times\sigma(\phi,J,t)\ . \tag{4.42}$$

When the memory time goes to zero

$$\gamma(s)\rightarrow\gamma_0\delta(s) \tag{4.43}$$

and Eq. (4.42) reduces to (4.37).

V. APPLICATION: ANGULAR MOMENTUM CORRELATION FUNCTIONS

In this section, we use the master equation derived in the preceding section to compute angular momentum correlation functions of a free rotor. From the definition (1.1), the correlation function of the first rank Hermite polynomial of the angular momentum is

$$C_1(t)=\frac{\langle J(t)J(0)\rangle}{\langle J(0)J(0)\rangle}\ , \tag{5.1}$$

where

$$\langle J(t)J(0)\rangle=\int_0^{2\pi}d\phi_f\int_{-\infty}^{+\infty}dJ_f\int_0^{2\pi}d\phi_i\int_{-\infty}^{+\infty}dJ_i\,\sigma_{\text{eq}}(\phi_i,J_i)J_fJ_iG(\phi_f,J_f,t|\phi_i,J_i,0)\ . \tag{5.2}$$

In the above equation, $\sigma_{\text{eq}}(\phi,J)$ is the equilibrium probability distribution of the rotor (4.25) and $G(\phi,J,t|\phi_i,J_i,0)$ is the Green's function that satisfies the master equation (4.24) with the boundary condition

$$G(\phi,J,0|\phi_i,J_i,0)=\delta(\phi-\phi_i)\delta(J-J_i)\ . \tag{5.3}$$

From the identity

$$\delta(\phi-\phi_i)=\sum_n \frac{1}{2\pi}e^{in(\phi-\phi_i)} \tag{5.4}$$

and the expansion

$$G(\phi,J,t|\phi_i,J_i,0)=\sum_n \frac{1}{2\pi}e^{in(\phi-\phi_i)}G_n(J,t|J_i,0)\ , \tag{5.5}$$

it follows that

$$\langle J(t)J(0)\rangle=\int_{-\infty}^{+\infty}dJ_f\int_{-\infty}^{+\infty}dJ_i\sigma_{\text{eq}}(J_i)J_fJ_iG_0(J_f,t|J_i,0) \tag{5.6}$$

and the angular momentum correlation function only depends on the zeroth term of the full Green's function $G_0(J_f,t|J_i,0)$. This zeroth term Green's function satisfies the equation

$$\begin{aligned}\frac{\partial}{\partial t}G_0(J,t|J_0,0)&=2\int_0^{\infty}ds\,\gamma(s)\frac{\partial}{\partial J}\cos\left[3\frac{J}{I}s\right]\frac{J}{I}G_0(J,t|J_0,0)\\&\quad+2k_BT\int_0^{\infty}ds\,\gamma(s)\frac{\partial}{\partial J}\cos\left[3\frac{J}{I}s\right]\frac{\partial}{\partial J}G_0(J,t|J_0,0)\end{aligned} \tag{5.7}$$

with the boundary condition

$$G_0(J,0|J_i,0)=\delta(J-J_i)\ . \tag{5.8}$$

It is clear from Eq. (5.7) that since the internal potential of the rotor $U_r(\phi)$ is constant, $G_0(J,t|J_i,0)$ is decoupled from all other terms of the full Green's function, so there is no contribution from the angle variable ϕ. By introducing the dimensionless variable

$$u=\frac{J}{\sqrt{2Ik_BT}} \tag{5.9}$$

and taking the transformation

$$G_0(J,t|J_0,0)=\widetilde{G}_0(u,t|u_0,0)\frac{1}{\sqrt{2Ik_BT}}\times\exp\left[-\frac{J^2-J_0^2}{4Ik_BT}\right]\ , \tag{5.10}$$

Eq. (5.7) becomes

$$\frac{\partial}{\partial t}\widetilde{G}_0(u,t|u_0,0)=-2\int_0^{\infty}ds\frac{1}{I}\gamma(s)\left[-\frac{1}{2}\frac{\partial}{\partial u}\cos(\lambda us)\frac{\partial}{\partial u}+\frac{1}{2}(u^2-1)\cos(\lambda us)-u\frac{\partial}{\partial u}\cos(\lambda us)\right]\widetilde{G}_0(u,t|u_0,0)\ , \tag{5.11}$$

where

$$\lambda=\left[18\frac{k_BT}{I}\right]^{1/2} \tag{5.12}$$

and the boundary condition (5.8) becomes

$$\widetilde{G}_0(u,0|u_i,0)=\delta(u-u_i)\ . \tag{5.13}$$

The angular momentum correlation function (5.6) then can be written as

$$\langle J(t)J(0)\rangle=(Ik_BT)\int_{-\infty}^{+\infty}du_f\int_{-\infty}^{+\infty}du_if_1(u_f)f_1(u_i)\widetilde{G}_0(u_f,t|u_i,0)\ , \tag{5.14}$$

where

$$f_n(u)=N_nH_n(u)e^{-(1/2)u^2} \tag{5.15}$$

is the well known normalized eigenfunction of the (quantum) harmonic oscillator, i.e.,

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial u^2}+\frac{1}{2}u^2\right]f_n(u)=(n+\tfrac{1}{2})f_n(u)\ , \tag{5.16}$$

$H_n(u)$ is the nth rank Hermite polynomial, and $N_n=(2\sqrt{\pi}2^nn!)^{-1/2}$ is a normalization constant. Expanding the Green's function $\widetilde{G}(u,t|u_i,0)$ as

$$\widetilde{G}(u,t|u_i,0)=\sum_{n,m}a_{nm}(t)f_n(u)f_m(u_i) \tag{5.17}$$

converts Eq. (5.11) into

$$\frac{d}{dt}a_{nm}(t)=-\sum_{n'}\frac{2}{I}\int_0^\infty ds\,\gamma(s)\int_{-\infty}^{+\infty}du\,f_n(u)\left[-\frac{1}{2}\frac{\partial}{\partial u}\cos(\lambda us)\frac{\partial}{\partial u}+\frac{1}{2}(u^2-1)\cos(\lambda us)-u\frac{\partial}{\partial u}\cos(\lambda us)\right]f_{n'}(u)a_{n'm}(s) \tag{5.18}$$

and the boundary condition (5.13) becomes

$$a_{nm}(0)=\delta_{nm}\ . \tag{5.19}$$

Substituting (5.17) into (5.14) yields

$$\langle J(t)J(0)\rangle=(Ik_BT)a_{11}(t) \tag{5.20}$$

and therefore the normalized correlation function of the first rank Hermite polynomial of the rotor is

$$C_1(t)=a_{11}(t)\ . \tag{5.21}$$

This result can be generalized to the normalized correlation functions of higher rank Hermite polynomials of the rotor, namely,

$$C_n(t)=\frac{\langle H_n(u(t))H_n(u(0))\rangle}{\langle H_n(u(0))H_n(u(0))\rangle}=a_{nn}(t)\ , \tag{5.22}$$

where $u(t)$ is defined in Eq. (5.9).

In the limit of a short noise correlation time, Eq. (5.11) can be simplified to

$$\frac{\partial}{\partial t}\tilde{G}_0(u,t|u_i,0)=\frac{\gamma_0}{I}\left[\frac{1}{2}\frac{\partial}{\partial u}\tilde{D}(u)\frac{\partial}{\partial u}-\frac{1}{2}[u^2-1]\tilde{D}(u)+\frac{1}{2}u\frac{\partial\tilde{D}(u)}{\partial u}\right]\tilde{G}_0(u,t|u_i,0)\ , \tag{5.23}$$

where

$$\tilde{D}(u)=\frac{1}{\gamma_0}\int_0^{+\infty}dt\,\gamma(t)\cos(\lambda ut)\ . \tag{5.24}$$

Note that in Eq. (5.23), the damping constant γ_0 has been written out explicitly, so the function $\tilde{D}(u)$ is dimensionless. Furthermore, Eq. (5.18) becomes

$$\frac{d}{dt}a_{nm}(t)=-\frac{\gamma_0}{I}\sum_{n'}h_{nn'}a_{n'm}(t)\ , \tag{5.25}$$

where the matrix elements are

$$h_{nn'}=\int_{-\infty}^{+\infty}du\,f_n(u)\left[-\frac{1}{2}\frac{\partial}{\partial u}\tilde{D}(u)\frac{\partial}{\partial u}+\frac{1}{2}[u^2-1]\tilde{D}(u)-\frac{1}{2}u\frac{\partial\tilde{D}(u)}{\partial u}\right]f_{n'}(u)\ . \tag{5.26}$$

A. White noise limit

In the white noise limit (4.35),

$$\tilde{D}(u)=1\ , \tag{5.27}$$

so that

$$h_{nn'}=n\delta_{nn'}\ . \tag{5.28}$$

As a result

$$a_{nm}(t)=e^{-n(\gamma_0/I)t}\delta_{nm} \tag{5.29}$$

and the angular momentum correlation function is

$$C_n(t)=e^{-n(\gamma_0/I)t}\ . \tag{5.30}$$

B. Colored noise with short memory time

For colored noise with an exponentially decaying correlation function (4.38), and a very *short* memory time τ,

$$\tilde{D}(u)=\frac{1}{1+\lambda^2\tau^2u^2}\simeq 1-\lambda^2\tau^2u^2\ , \tag{5.31}$$

where λ is given in (5.12). To this approximation, the matrix element (5.26) is

$$h_{nn'}=n\delta_{nn'}+\lambda^2\tau^2\Delta h_{nn'}\ , \tag{5.32}$$

where

$$\Delta h_{nn'}=-\int_{-\infty}^{+\infty}du\,f_n(u)\left[-\frac{1}{2}\frac{\partial}{\partial u}u^2\frac{\partial}{\partial u}+\frac{1}{2}u^2[u^2-3]\right]\times f_{n'}(u)\ . \tag{5.33}$$

It follows from the perturbation calculation that, to second order in τ,

$$C_n(t)=\exp\left[-(n+\lambda^2\tau^2\Delta h_{nn})\frac{\gamma_0}{I}t\right]\ , \tag{5.34}$$

where

$$\Delta h_{nn}=-n(n-\tfrac{1}{2})\ . \tag{5.35}$$

C. Colored noise with arbitrary memory time

For a more general colored noise source, the correlation functions can be calculated numerically. Taking the Laplace transformation

$$\tilde{a}_{nm}(p)=\int_0^\infty dt\,e^{-pt}a_{nm}(t) \tag{5.36}$$

on both sides of (5.18) gives

$$p\tilde{a}_{nm}(p)-a_{nm}(0)=-\sum_{n'}\frac{\gamma_0}{I}h_{nn'}(p)\tilde{a}_{n'm}(p)\ , \tag{5.37}$$

where

$$h_{nn'}(p)=\int_{-\infty}^{+\infty}du\, f_n(u)\left[-\frac{1}{2}\frac{\partial}{\partial u}\tilde{D}(u,p)\frac{\partial}{\partial u}+\frac{1}{2}[u^2-1]\tilde{D}(u,p)-\frac{1}{2}u\frac{\partial\tilde{D}(u,p)}{\partial u}\right]f_{n'}(u) \qquad (5.38)$$

and the kernel $\tilde{D}(u,p)$ is

$$\tilde{D}(u,p)=\frac{2}{\gamma_0}\int_0^{\infty}dt\, e^{-pt}\gamma(t)\cos(\lambda u t)\ . \qquad (5.39)$$

The matrix element $h_{nn'}(p)$ can be further written as

$$\begin{aligned}h_{nn'}(p)=&\tfrac{1}{2}\sqrt{(n+1)(n'+1)}\langle n+1|\tilde{D}(p)|n'+1\rangle\\&+\tfrac{1}{2}\sqrt{nn}\,\langle n-1|\tilde{D}(p)|n'-1\rangle\\&+\tfrac{1}{2}\langle n|\tilde{D}(p)|n'\rangle-(1+p\tau)\langle n|\tilde{D}^2(p)|n'\rangle\ ,\end{aligned} \qquad (5.40)$$

where

$$\langle n|\tilde{D}(p)|n'\rangle=\int_{-\infty}^{+\infty}du\, f_n(u)\tilde{D}(u,p)f_{n'}(u) \qquad (5.41a)$$

and

$$\langle n|\tilde{D}^2(p)|n'\rangle=\int_{-\infty}^{+\infty}du\, f_n(u)[\tilde{D}(u,p)]^2f_{n'}(u)\ . \qquad (5.41b)$$

For an exponentially decaying noise correlation function (4.38),

$$\tilde{D}(u,p)=\frac{1+p\tau}{(1+p\tau)^2+\lambda^2\tau^2u^2}\ . \qquad (5.42)$$

If τ is small, $p\tau$ can be omitted and Eq. (5.42) reduces to (5.23), the limit of a short noise correlation time.

Equation (5.37) can be further written in matrix form as

$$\left[p\mathbf{I}+\frac{\gamma_0}{I}\mathbf{h}(p)\right]\tilde{\mathbf{a}}(p)=\mathbf{a}(0)=\mathbf{I}\ , \qquad (5.43)$$

where $\mathbf{I}$ is the identity matrix. The solution to this matrix equation is

$$\tilde{\mathbf{a}}(p)=\left[p\mathbf{I}+\frac{\gamma_0}{I}\mathbf{h}(p)\right]^{-1}\ . \qquad (5.44)$$

The procedures for the numerical calculations are as follows: (1) the kernel $\tilde{D}(u,p)$ is computed from a given dissipation kernel $\gamma(t)$; (2) the matrix elements $\langle n|\tilde{D}(p)|n'\rangle$ and $\langle n|\tilde{D}^2(p)|n'\rangle$ are computed and, via Eq. (5.40), the matrix $\mathbf{h}$ is calculated; (3) the matrix inversion, Eq. (5.44), and inverse Laplace transform are taken to give $a_{11}(t)$ and $a_{22}(t)$, which are $C_1(t)$ and $C_2(t)$.

Figures 2–4 show a comparison of angular momentum correlation functions calculated from the molecular dynamics simulation [15] and the present theory. The noise correlation function is the exponentially decaying function (4.38). And for comparison, we chose $T=310$ K and $I=5.46\times10^{-40}$ g cm^2, which are comparable to the values used in the molecular dynamics simulation [15].

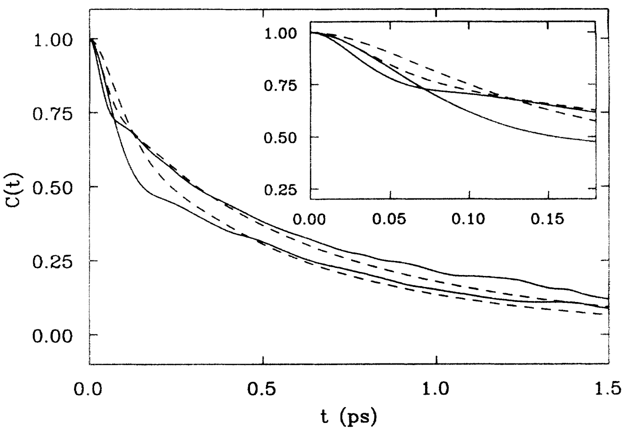

FIG. 2. The normalized correlation functions of the first (lower curves at times $t>0.12$ ps) and second (upper curves at $t>0.12$ ps) rank Hermite polynomials of the angular momentum of a methyl group in water. The solid lines are the results of a molecular dynamics simulation [15]. The dashed lines are the predictions of the nonlinearly coupled generalized Fokker-Planck equation (4.24) with an exponential dissipation kernel, i.e., the inverse Laplace transform of Eq. (5.44). The angular momentum correlation time is $\tau_J=0.48$ ps and memory time constant is $\tau=0.056$ ps. The inset shows the short time behavior of the correlation functions.

There are two independent, adjustable parameters in the present theory, namely, the noise correlation time τ and the damping constant γ_0. However, for each value of τ, the value of γ_0 was determined by requiring that the simulation and the stochastic model produce the same value for the angular momentum correlation time τ_J, which is defined as the time integral of $C_1(t)$. Specifically, these parameters are related by $\tau_J=\tilde{a}_{11}(0)=\mathbf{h}^{-1}(0)_{11}I/\gamma_0$. The memory time τ was then varied to obtain the best fit to $C_1(t)$ and $C_2(t)$, simultaneously. As can be seen, the stochastic theory and the simulations are in excellent agreement with $\tau=0.079$ ps and the simulation value of $\tau_J=0.48$ ps. At shorter

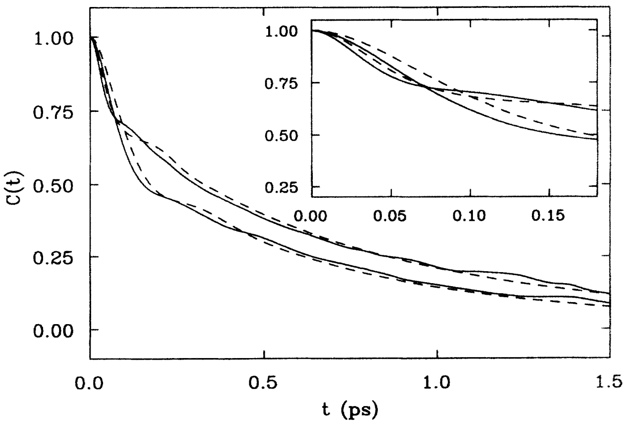

FIG. 3. The same as Fig. 2 except that the memory time constant is $\tau=0.079$ ps. Note that, in this figure, the adjustable parameters have the same values as in Fig. 1.

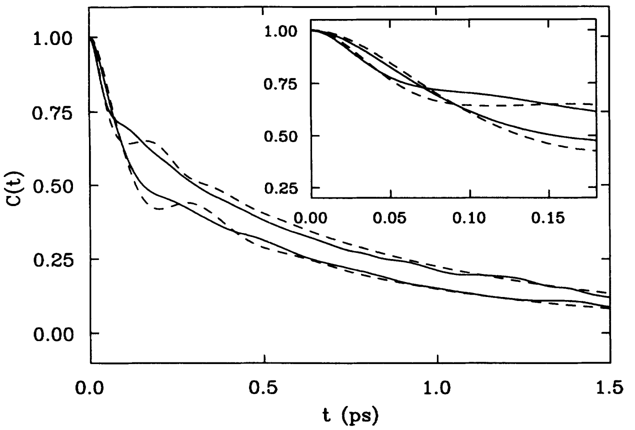

FIG. 4. The same as Fig. 2 except that the memory time constant is $\tau=0.102$ ps.

values of τ, the rotor is overdamped, while longer values of τ produce oscillations or the so called cage effect.

These results are virtually identical to those obtained from the stochastic quantum dynamics model, which indicates that the essential features of the latter have been captured in the classical model.

VI. CONCLUSION

We have developed a stochastic dynamics model for a rigid one dimensional rotor with threefold symmetry. The derivation uses a general form of random interaction between the rotor and the thermal bath. The intrinsic symmetry of the rotor dictates the form of this rotor-bath coupling, which turns out to be highly nonlinear.

From this model, the stochastic dynamics equation was derived using the standard projection operator method. The resultant equation has the usual damping term and noise source. The noise may be colored and the damping force may contain a memory function, depending on the characteristics of the thermal bath. While the noise and damping satisfy the well known fluctuation dissipation relation, they are coupled to the dynamical variables of the rotor through the nonlinear functions determined by the symmetry of the rotor.

A Fokker-Planck-type master equation was also derived from the same model using the same method. It is an integral-differential equation that satisfies detailed balance and therefore is consistent with the laws of thermodynamics. In the white noise limit, the master equation reduces to the regular Fokker-Planck equation, which suggests that the nonlinearity becomes important only for non-Markovian processes.

This stochastic dynamics model for rotational motion can also be viewed as the classical analog of a quantum stochastic dynamics model developed earlier [11]. The rotor-bath model and the form of nonlinear coupling between the rigid rotor and the bath are identical, although the microdynamics (quantum versus classical) are different.

The angular momentum correlation functions of a free rotor were calculated numerically. The results were found to be in excellent agreement with correlation functions calculated from a molecular dynamics simulation of a methyl group attached to a large molecule immersed in a water. The agreement with the simulation is due to two essential features of the present theory. First, the correct form of nonlinear coupling between the rotor and the bath was used. This produced a normalized correlation function of the second rank Hermite polynomial that, at long times, is larger than the correlation function of the first rank Hermite polynomial. Second, the master equation (4.24) was solved exactly using Laplace transforms. This produced the proper short time behavior of the correlation functions.

These results indicate that the nonlinearly coupled, non-Markovian stochastic dynamics equation or master equation and its three dimensional analogs should be used in place of the linearly coupled generalized Langevin equation when describing rotational relaxation. The resultant collision operator should provide a more accurate connection between experimentally measured quantities and the underlying microscopic dynamics.

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APPENDIX A

The *linearly* coupled generalized Langevin equation of a *free* Brownian particle is

$$M\dot{v}(t)+\int_{-\infty}^{t} ds\,\gamma(t-s)v(s)=\eta(t)\ , \tag{A1}$$

where $x(t)$ is the (generalized) coordinate and $v(t)=\dot{x}(t)$ is the (generalized) velocity. If the noise $\eta(t)$ is Gaussian random (colored or white) with zero mean, then

$$\langle \eta(t)\rangle=0 \tag{A2a}$$

and the two point correlation function is

$$\langle \eta(t_1)\eta(t_2)\rangle=\gamma(t_1-t_2)\ , \tag{A2b}$$

where the average $\langle\ \rangle$ is taken over the functional probability distribution

$$P[\eta]=N_0\exp\left[-\tfrac{1}{2}\int_{-\infty}^{+\infty}dt_1\int_{-\infty}^{+\infty}dt_2\,\eta(t_1)\gamma(t_1-t_2)^{-1}\times\eta(t_2)\right]\ , \tag{A3}$$

with N_0 being the normalization constant. The higher moments of a Gaussian random process are *pairwise decomposable*, i.e.,

$$\langle \eta(t_1)\eta(t_2)\eta(t_3)\rangle = 0 \ , \tag{A4a}$$

$$\begin{aligned}\langle \eta(t_1)\eta(t_2)\eta(t_3)\eta(t_4)\rangle &= \langle \eta(t_1)\eta(t_2)\rangle\langle \eta(t_3)\eta(t_4)\rangle \\ &\quad + \langle \eta(t_1)\eta(t_3)\rangle\langle \eta(t_2)\eta(t_4)\rangle \\ &\quad + \langle \eta(t_1)\eta(t_4)\rangle\langle \eta(t_2)\eta(t_3)\rangle \ ,\end{aligned} \tag{A4b}$$

and so on.

It can be shown that the Fourier transform of Eq. (A1) is

$$iM\omega\tilde{v}(\omega)+\Gamma(\omega)\tilde{v}(\omega)=\tilde{\eta}(\omega) \ , \tag{A5}$$

with

$$\tilde{v}(\omega)=\int_{-\infty}^{+\infty} dt\, e^{-i\omega t-\epsilon|t|}v(t) \ , \tag{A6a}$$

$$\tilde{\gamma}(\omega)=\int_{-\infty}^{+\infty} dt\, e^{-i\omega t-\epsilon|t|}\gamma(t) \ , \tag{A6b}$$

$$\tilde{\eta}(\omega)=\int_{-\infty}^{+\infty} dt\, e^{-i\omega t-\epsilon|t|}\eta(t) \ , \tag{A6c}$$

and

$$\Gamma(\omega)=\tilde{\gamma}(\omega)+2\int_{-\infty}^{+\infty}\frac{d\omega'}{2\pi}\frac{i(\omega'-\omega)}{(\omega'-\omega)^2+\epsilon^2}\tilde{\gamma}(\omega') \ , \tag{A7}$$

where ϵ is an infinitesimal positive number that is introduced to guarantee that the integrals in (A6a)–(A6c) converge. Further, from (A5),

$$\tilde{v}(\omega)=\frac{\tilde{\eta}(\omega)}{iM\omega+\Gamma(\omega)} \tag{A8}$$

is a linear mapping from $\tilde{\eta}(\omega)$ to $\tilde{v}(\omega)$ in the frequency domain. With this linear mapping, it can be shown that the two point correlation function of $v(t)$ is

$$\langle v(t_1)v(t_2)\rangle = G(t_1-t_2) \ , \tag{A9}$$

where

$$\begin{aligned}G(t)=\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}e^{i\omega t}&\frac{1}{iM\omega+\Gamma(\omega)} \\ &\times 2k_bT\tilde{\gamma}(\omega)\frac{1}{-iM\omega+\Gamma(-\omega)}\end{aligned} \tag{A10}$$

and

$$2k_bT\tilde{\gamma}(\omega)=\langle\tilde{\eta}(\omega)\tilde{\eta}(-\omega)\rangle \tag{A11}$$

is the two point correlation function of the noise in the frequency domain. Similar expressions can be derived for the n point correlation functions from the linear mapping (A8). Since the correlation functions of the noise are pairwise decomposable, the correlation functions of $v(t)$ and thus $x(t)$ are also pairwise decomposable, and these variables are therefore Gaussian random.

APPENDIX B

Let $x(t)$ be a Gaussian random variable with zero mean and a two point correlation function

$$\langle x(t_1)x(t_2)\rangle = G_0(t_1-t_2) \ , \tag{B1}$$

where the average $\langle\ \rangle$ is taken over the functional probability distribution similar to (A3). The higher moments of a Gaussian random process are *pairwise decomposable*, as in Eqs. (A4a) and (A4b). By rescaling the random variable

$$x(t)\rightarrow y(t)=\frac{1}{\sqrt{G_0(0)}}x(t) \ , \tag{B2}$$

then

$$G_0(t)\rightarrow G(t)=\frac{G_0(t)}{G_0(0)} \tag{B3}$$

so that

$$\langle y(t)y(t)\rangle = G(0)\equiv 1 \ . \tag{B4}$$

If $\mathcal{H}_n(y)$ is the nth Hermite polynomial derived from the weight function $\exp(-y^2/2)$, then

$$y\mathcal{H}_n(y)=\mathcal{H}_{n+1}(y)+n\mathcal{H}_{n-1}(y) \ . \tag{B5}$$

Multiplying both sides by $\mathcal{H}_{m+1}(y(t))$ and taking the average gives

$$\begin{aligned}\langle \mathcal{H}_{m+1}(y(t))y(0)\mathcal{H}_n(y(0))\rangle &= \langle \mathcal{H}_{m+1}(y(t))\mathcal{H}_{n+1}(y(0))\rangle \\ &\quad + n\langle \mathcal{H}_{m+1}(y(t))\mathcal{H}_{n-1}(y(0))\rangle \ .\end{aligned} \tag{B6}$$

Using the integral form of $\mathcal{H}_n(y)$ [25]

$$\mathcal{H}_n(y)=\int_{-\infty}^{+\infty}\frac{d\sigma}{\sqrt{2\pi}}e^{-\sigma^2/2}(y+i\sigma)^n \ , \tag{B7}$$

the left-hand side of Eq. (B6) can be written as

$$\langle \mathcal{H}_{m+1}(y(t))y(0)\mathcal{H}_n(y(0))\rangle = \int_{-\infty}^{+\infty}\frac{d\sigma_1}{\sqrt{2\pi}}e^{-\sigma_1^2/2}\int_{-\infty}^{+\infty}\frac{d\sigma_2}{\sqrt{2\pi}}e^{-\sigma_2^2/2}\langle [y(t)+i\sigma_1]^{m+1}y(0)[y(0)+i\sigma_2]^n\rangle \ . \tag{B8}$$

Since correlation functions of the Gaussian random variable $y(t)$ are pairwise decomposable, then

$$\begin{aligned}\langle [y(t)+i\sigma_1]^{m+1}y(0)[y(0)+i\sigma_2]^n\rangle &= (m+1)\langle [y(t)+i\sigma_1]y(0)\rangle\langle [y(t)+i\sigma_1]^m[y(0)+i\sigma_2]^n\rangle \\ &\quad + n\langle y(0)[y(0)+i\sigma_2]\rangle\langle [y(t)+i\sigma_1]^{m+1}[y(0)+i\sigma_2]^{n-1}\rangle \ .\end{aligned} \tag{B9}$$

Since

$$\langle [y(t)+i\sigma_1]y(0)\rangle = \langle y(t)y(0)\rangle = G(t) \tag{B10}$$

and

$$\langle y(0)[y(0)+i\sigma_2]\rangle = \langle y(0)y(0)\rangle = 1 \ , \tag{B11}$$

Eq. (B9) becomes

$$\begin{aligned}\langle [y(t)+i\sigma_1]^{m+1}y(0)[y(0)+i\sigma_2]^n\rangle &= (m+1)\langle y(t)y(0)\rangle \\ &\quad \times\langle [y(t)+i\sigma_1]^m[y(0)+i\sigma_2]^n\rangle \\ &\quad + n\langle [y(t)+i\sigma_1]^{m+1}[y(0)+i\sigma_2]^{n-1}\rangle\end{aligned} \tag{B12}$$

or

$$\begin{aligned}\langle \mathcal{H}_{m+1}(y(t))y(0)\mathcal{H}_n(y(0))\rangle &= (m+1)\langle y(t)y(0)\rangle\langle \mathcal{H}_m(y(t))\mathcal{H}_n(y(0))\rangle \\ &\quad + n\langle \mathcal{H}_{m+1}(y(t))\mathcal{H}_{n-1}(y(0))\rangle \ .\end{aligned} \tag{B13}$$

Subtracting Eq. (B6) from (B13) yields

$$\begin{aligned}\langle \mathcal{H}_{m+1}(y(t))\mathcal{H}_{n+1}(y(0))\rangle &= (m+1)\langle y(t)y(0)\rangle\langle \mathcal{H}_m(y(t))\mathcal{H}_n(y(0))\rangle \ .\end{aligned} \tag{B14}$$

Repeated application of the relation (B14) gives the result

$$\langle \mathcal{H}_m(y(t))\mathcal{H}_n(y(0))\rangle = m!\delta_{mn}\langle y(t)y(0)\rangle^n \tag{B15}$$

or

$$\frac{\langle \mathcal{H}_n(y(t))\mathcal{H}_n(y(0))\rangle}{\langle \mathcal{H}_n(y(0))\mathcal{H}_n(y(0))\rangle} = \left[\frac{\langle y(t)y(0)\rangle}{\langle y(0)y(0)\rangle}\right]^n . \tag{B16}$$

Since the regular Hermite polynomials $H_n(y)$ are related to $\mathcal{H}_n(y)$ through

$$\mathcal{H}_n(y) = 2^{-n/2}H_n\left[\frac{y}{\sqrt{2}}\right] , \tag{B17}$$

the relation between the normalized correlation functions of the nth and first rank Hermite polynomials of a Gaussian random variable is

$$C_n(t) = [C_1(t)]^n \ . \tag{B18}$$

APPENDIX C

The nonlinear Langevin equation in the white noise and local damping limits (3.20) can be rewritten [26] as

$$\dot{x}_\alpha(t) = g_\alpha(x) + \sum_i h_{\alpha i}(x)\eta_i(t) \ , \tag{C1}$$

where $x_1=\phi$, $x_2=J$,

$$g_1 = \frac{J}{I} \ , \tag{C2a}$$

$$g_2 = -\frac{\partial U_r(\phi)}{\partial \phi} - \gamma_0\frac{J}{I} \ , \tag{C2b}$$

and

$$h_{11} = h_{12} = 0 \ , \tag{C3a}$$

$$h_{21} = -\cos(3\phi) \ , \tag{C3b}$$

$$h_{22} = \sin(3\phi) \ . \tag{C3c}$$

$\eta_1(t)$ and $\eta_2(t)$ are two Gaussian white noise sources with

$$\begin{aligned}&\langle \eta_i(t)\rangle = 0 \ , \\ &\langle \eta_i(t_1)\eta_j(t_2)\rangle = N_{ij}\delta(t_1-t_2) \ ,\end{aligned} \tag{C4}$$

where

$$N_{ij} = 2k_bT\delta_{ij} \ . \tag{C5}$$

The classical phase space probability distribution $\sigma(\phi,J,t)=\sigma(x,t)$ satisfies the Fokker-Planck equation [19]

$$\frac{\partial}{\partial t}\sigma(x,t) = \left\{-\sum_\alpha \frac{\partial}{\partial x_\alpha}k_\alpha + \frac{1}{2}\sum_{\alpha,\beta}\frac{\partial^2}{\partial x_\alpha \partial x_\beta}b_{\alpha\beta}\right\}\sigma(x,t) \ , \tag{C6}$$

where

$$k_\alpha = g_\alpha + \frac{1}{2}\sum_{\beta,i}\frac{\partial h_{\alpha i}}{\partial x_\beta}h_{\beta j}N_{ij} \tag{C7}$$

and

$$b_{\alpha\beta} = h_{\alpha i}h_{\beta j}N_{ij} \ . \tag{C8}$$

It can be shown that

$$k_1 = g_1 \ , \tag{C9a}$$

$$k_2 = g_2 \ , \tag{C9b}$$

and

$$b_{11} = b_{12} = b_{21} = 0 \ , \tag{C10a}$$

$$b_{22} = 2\gamma_0 k_b T \ . \tag{C10b}$$

With these relations, the Fokker-Planck equation for the rotor in the limit of white noise and no memory becomes

$$\begin{aligned}\frac{\partial}{\partial t}\sigma(\phi,J,t) = \Bigg\{&-\frac{J}{I}\frac{\partial}{\partial \phi} - \frac{\partial U_r(\phi)}{\partial \phi}\frac{\partial}{\partial \phi} + \gamma_0\frac{\partial}{\partial J}\frac{J}{I} \\ &+ \gamma_0 k_b T\frac{\partial^2}{\partial J^2}\Bigg\}\sigma(\phi,J,t) \ .\end{aligned} \tag{C11}$$

APPENDIX D

In this appendix, we present more explicit expressions for the collision operator (4.18). Since the Poisson bracket is a linear differential operator, it can be expanded as in (4.2) to obtain

$$\begin{aligned}\{H_{\rm int},\rho_b\sigma(s)\}_{pb}&=\{A_c(\phi)B_c(q_c)+A_s(\phi)B_s(q_s),\rho_b\sigma(s)\}_{pb}\\&=A_c(\phi)\sigma(s)\{B_c(q_c),\rho_b\}^c_{pb}+B_c(q_c)\rho_b\{A_c(\phi),\sigma(s)\}^\phi_{pb}\\&\quad+A_s(\phi)\sigma(s)\{B_s(q_s),\rho_b\}^s_{pb}+B_s(q_s)\rho_b\{A_s(\phi),\sigma(s)\}^\phi_{pb}\ ,\end{aligned}\tag{D1}$$

where $\{\ ,\ \}^c_{pb}$, $\{\ ,\ \}^s_{pb}$, and $\{\ ,\ \}^\phi_{pb}$ are the Poisson brackets for the variables (q_{cn},k_{cn}),(q_{sn},k_{sn}), and (ϕ,J) alone, defined in (4.3a)–(4.3c). We also denote

$$B_c(q_c)=\sum_n C_{cn}q_{cn}\ ,\tag{D2a}$$

$$B_s(q_s)=\sum_n C_{sn}q_{sn}\ .\tag{D2b}$$

The collision operator (4.18) can be expanded to

$$\begin{aligned}\hat R\sigma(\phi,J,t)=\int_{-\infty}^{t}ds[&\alpha_{c1}(t-s)\{A_c(\phi),e^{(t-s)i\hat L_a}\{A_c(\phi),\sigma(\phi,J,s)\}^\phi_{pb}\}^\phi_{pb}\\&+\alpha_{c2}(t-s)A_c(\phi)e^{(t-s)i\hat L_a}\{A_c(\phi),\sigma(\phi,J,s)\}^\phi_{pb}\\&+\alpha_{c3}(t-s)\{A_c(\phi),e^{(t-s)i\hat L_a}A_c(\phi)\sigma(\phi,J,s)\}^\phi_{pb}\\&+\alpha_{c4}(t-s)A_c(\phi)e^{(t-s)i\hat L_a}A_c(\phi)\sigma(\phi,J,s)\\&+\alpha_{s1}(t-s)\{A_s(\phi),e^{(t-s)i\hat L_a}\{A_s(\phi),\sigma(\phi,J,s)\}^\phi_{pb}\}^\phi_{pb}\\&+\alpha_{s2}(t-s)A_s(\phi)e^{(t-s)i\hat L_a}\{A_s(\phi),\sigma(\phi,J,s)\}^\phi_{pb}\\&+\alpha_{s3}(t-s)\{A_s(\phi),e^{(t-s)i\hat L_a}A_s(\phi)\sigma(\phi,J,s)\}^\phi_{pb}\\&+\alpha_{s4}(t-s)A_s(\phi)e^{(t-s)i\hat L_a}A_s(\phi)\sigma(\phi,J,s)]\ ,\end{aligned}\tag{D3}$$

where

$$\alpha_{c1}(s)=\int d\vec b\,B_c(q_c)e^{si\hat L_b}B_c(q_c)\rho_b\ ,\tag{D4a}$$

$$\alpha_{c2}(s)=\int d\vec b\{B_c(q_c),e^{si\hat L_b}B_c(q_c)\rho_b\}^c_{pb}\ ,\tag{D4b}$$

$$\alpha_{c3}(s)=\int d\vec b\,B_c(q_c)e^{si\hat L_a}\{B_c(q_c),\rho_b\}^c_{pb}\ ,\tag{D4c}$$

$$\alpha_{c4}(s)=\int d\vec b\{B_c(q_c),e^{si\hat L_b}\{B_c(q_c),\rho_b\}^c_{pb}\}^c_{pb}\ ,\tag{D4d}$$

and $\alpha_{s1}(s)$, $\alpha_{s2}(s)$, $\alpha_{s3}(s)$, and $\alpha_{s4}(s)$ are given by analogous formulas. It is straightforward to show that

$$\alpha_{c2}(s)=\alpha_{c4}(s)=0\ ,\tag{D5a}$$

$$\alpha_{c1}(s)=2k_bT\gamma_c(s)\ ,\tag{D5b}$$

$$\alpha_{c3}(s)=2\frac{d}{ds}\gamma_c(s)\ ,\tag{D5c}$$

and

$$\alpha_{s2}(s)=\alpha_{s4}(s)=0\ ,\tag{D6a}$$

$$\alpha_{s1}(s)=2k_bT\gamma_s(s)\ ,\tag{D6b}$$

$$\alpha_{s3}(s)=2\frac{d}{ds}\gamma_s(s)\ ,\tag{D6c}$$

where $\gamma_c(s)$ and $\gamma_s(s)$ are two damping kernels defined in (3.5a) and (3.5b). Substituting (D5) and (D6) into (D3) yields

$$\begin{aligned}\hat R\sigma(\phi,J,t)=2\int_{-\infty}^{t}ds\Bigg\{&k_bT\gamma_c(t-s)\{A_c(\phi),e^{(t-s)i\hat L_a}\{A_c(\phi),\sigma(\phi,J,s)\}^\phi_{pb}\}^\phi_{pb}\\&+\frac{d\gamma_c(t-s)}{d(t-s)}\{A_c(\phi),e^{(t-s)i\hat L_a}A_c(\phi)\sigma(\phi,J,s)\}^\phi_{pb}\\&+k_bT\gamma_s(t-s)\{A_s(\phi),e^{(t-s)i\hat L_a}\{A_s(\phi),\sigma(\phi,J,s)\}^\phi_{pb}\}^\phi_{pb}\\&+\frac{d\gamma_s(t-s)}{d(t-s)}\{A_s(\phi),e^{(t-s)i\hat L_a}A_s(\phi)\sigma(\phi,J,s)\}^\phi_{pb}\Bigg\}\ .\end{aligned}\tag{D7}$$

Integrating the second term in (D7) by parts gives

$$\begin{aligned}2\int_{-\infty}^{t} ds\frac{d\gamma_c(t-s)}{d(t-s)}&\{A_c(\phi),e^{(t-s)i\hat{\mathcal{L}}_a}A_c(\phi)\sigma(\phi,J,s)\}_{pb}^{\phi}\\ &=-2\gamma_c(0)\{A_c(\phi),A_c(\phi)\sigma(\phi,J,t)\}_{pb}^{\phi}+2\gamma_c(t+\infty)\{A_c(\phi),A_c(\phi)\sigma(\phi,J,-\infty)\}_{pb}^{\phi}\\ &\quad+2\int_{-\infty}^{t} ds\,\gamma_c(t-s)\left\{A_c(\phi),\frac{d}{ds}e^{(t-s)i\hat{\mathcal{L}}_a}A_c(\phi)\sigma(\phi,J,s)\right\}_{pb}^{\phi}\ .\end{aligned}\tag{D8}$$

Equation (D8) can be simplified by noting that

$$\gamma_c(t+\infty)=0\ ,\tag{D9}$$

since we assume the memory function decays to zero at infinite time and

$$\{A_c(\phi),A_c(\phi)\sigma(\phi,J,t)\}_{pb}^{\phi}=\{\tfrac{1}{2}[A_c(\phi)]^2,\sigma(\phi,J,t)\}_{pb}^{\phi}\ .\tag{D10}$$

Also

$$\begin{aligned}\frac{d}{ds}e^{(t-s)i\hat{\mathcal{L}}_a}A_c(\phi)\sigma(\phi,J,s)&=e^{(t-s)i\hat{\mathcal{L}}_a}\left[A_c(\phi)\frac{d}{ds}\sigma(\phi,J,s)-i\hat{\mathcal{L}}_a A_c(\phi)\sigma(\phi,J,s)\right]\\ &\simeq e^{(t-s)i\hat{\mathcal{L}}_a}[A_c(\phi)i\hat{\mathcal{L}}_a\sigma(\phi,J,s)-i\hat{\mathcal{L}}_a A_c(\phi)\sigma(\phi,J,s)]\\ &=e^{(t-s)i\hat{\mathcal{L}}_a}\frac{\partial H_a}{\partial J}\frac{\partial A_c(\phi)}{\partial\phi}\sigma(\phi,J,s)\ ,\end{aligned}\tag{D11}$$

where we have used the approximation

$$\frac{d}{ds}\sigma(\phi,J,s)\simeq i\hat{\mathcal{L}}_a\sigma(\phi,J,s)\ ,\tag{D12}$$

since the collision operator $\hat{R}$ is already second order in C_{cn} and C_{sn}. By substituting (D9)–(D11) into (D8), we obtain

$$\begin{aligned}2\int_{-\infty}^{t} ds\frac{d\gamma_c(t-s)}{d(t-s)}&\{A_c(\phi),e^{(t-s)i\hat{\mathcal{L}}_a}A_c(\phi)\sigma(\phi,J,s)\}_{pb}^{\phi}\\ &\simeq\{-\gamma_c(0)[A_c(\phi)]^2,\sigma(\phi,J,t)\}_{pb}^{\phi}+2\int_{-\infty}^{t} ds\,\gamma_c(t-s)\left\{A_c(\phi),e^{(t-s)i\hat{\mathcal{L}}_a}\frac{\partial H_a}{\partial J}\frac{\partial A_c(\phi)}{\partial\phi}\sigma(\phi,J,s)\right\}_{pb}^{\phi}\ .\end{aligned}\tag{D13}$$

There is an analogous equation for the fourth term in (D7). By using these equations, the collision kernel becomes

$$\begin{aligned}\hat{R}\sigma(\phi,J,t)=&\{-\gamma_c(0)[A_c(\phi)]^2,\sigma(\phi,J,t)\}_{pb}^{\phi}+\{-\gamma_s(0)[A_s(\phi)]^2,\sigma(\phi,J,t)\}_{pb}^{\phi}\\ &+2\int_{-\infty}^{t} ds\,\gamma_c(t-s)\left\{A_c(\phi),e^{(t-s)i\hat{\mathcal{L}}_a}\frac{\partial H_a}{\partial J}\frac{\partial A_c(\phi)}{\partial\phi}\sigma(\phi,J,s)\right\}_{pb}^{\phi}\\ &+2\int_{-\infty}^{t} ds\,\gamma_s(t-s)\left\{A_s(\phi),e^{(t-s)i\hat{\mathcal{L}}_a}\frac{\partial H_a}{\partial J}\frac{\partial A_s(\phi)}{\partial\phi}\sigma(\phi,J,s)\right\}_{pb}^{\phi}\\ &+2k_bT\int_{-\infty}^{t} ds\,\gamma_c(t-s)\{A_c(\phi),e^{(t-s)i\hat{\mathcal{L}}_a}\{A_c(\phi),\sigma(\phi,J,s)\}_{pb}^{\phi}\}_{pb}^{\phi}\\ &+2k_bT\int_{-\infty}^{t} ds\,\gamma_s(t-s)\{A_s(\phi),e^{(t-s)i\hat{\mathcal{L}}_a}\{A_s(\phi),\sigma(\phi,J,s)\}_{pb}^{\phi}\}_{pb}^{\phi}\ .\end{aligned}\tag{D14}$$

APPENDIX E

From the definition (4.21), we have

$$F(\phi,J,t)=\cos(3\phi)e^{ti\hat{\mathcal{L}}_a}\cos(3\phi)+\sin(3\phi)e^{ti\hat{\mathcal{L}}_a}\sin(3\phi)\ .\tag{E1a}$$

We also define

$$\tilde{F}(\phi,J,t)=\cos(3\phi)e^{ti\hat{\mathcal{L}}_a}\sin(3\phi)-\sin(3\phi)e^{ti\hat{\mathcal{L}}_a}\cos(3\phi)\ .\tag{E1b}$$

It is obvious that

$$F(\phi,J,0)=1\ ,\tag{E2a}$$

$$\tilde{F}(\phi,J,0)=0\ .\tag{E2b}$$

It can be shown that

$$\frac{\partial}{\partial t}F=\{H_a,F\}_{pb}^{\phi}+3\frac{\partial H_a}{\partial J}\tilde{F}\tag{E3a}$$

and

$$\frac{\partial}{\partial t}\tilde{F}=\{H_a,\tilde{F}\}_{pb}^{\phi}-3\frac{\partial H_a}{\partial J}F\ . \qquad \text{(E3b)}$$

Combining (E3a) and (E3b) gives

$$\frac{\partial}{\partial t}(F+i\tilde{F})=\{H_a,(F+i\tilde{F})\}_{pb}^{\phi}-3i\frac{\partial H_a}{\partial J}(F+i\tilde{F})\ . \qquad \text{(E4)}$$

If it is a free rotor [see Eq. (4.22)], then $F+i\tilde{F}$ does not depend on ϕ, so

$$\{H_a,(F+i\tilde{F})\}_{pb}^{\phi}=0 \qquad \text{(E5)}$$

and

$$\frac{\partial}{\partial t}(F+i\tilde{F})=-i3\frac{J}{I}(F+i\tilde{F})\ . \qquad \text{(E6)}$$

The solution to Eq. (E6) with the initial conditions (E2a) and (E2b) is

$$F+i\tilde{F}=e^{-i3(J/I)t} \qquad \text{(E7)}$$

or

$$F(\phi,J,t)=\cos\left[3\frac{J}{I}t\right]\ . \qquad \text{(E8)}$$

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[1] G. E. Uhlenbeck and L. S. Ornstein, Phys. Rev. **36**, 823 (1930).

[2] S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943).

[3] D. Bohm and E. P. Gross, Phys. Rev. **75**, 1864 (1949).

[4] P. L. Bhatnagar, E. P. Gross, and M. Krook, Phys. Rev. **94**, 511 (1954).

[5] H. A. Lorentz, Proc. Acad. Amsterdam **78**, 438 (1905).

[6] E. P. Wigner and J. E. Wilkins, AEC Report No. D2275, 1944 (unpublished).

[7] M. R. Hoare, Adv. Chem. Phys. **20**, 135 (1971).

[8] B. Widom, J. Chem. Phys. **32**, 913 (1960).

[9] A. G. Redfield, IBM J. Res. Dev. **1**, 19 (1957).

[10] P. S. Hubbard, Rev. Mod. Phys. **33**, 249 (1963).

[11] T. E. Bull, Chem. Phys. **143**, 381 (1990).

[12] R. G. Gordon, J. Chem. Phys. **44**, 1830 (1966).

[13] T. E. Bull, Chem. Phys. **121**, 1 (1988).

[14] J. L. Skinner and P. G. Wolynes, J. Chem. Phys. **72**, 4913 (1980).

[15] G. Widmalm, R. W. Pastor, and T. E. Bull, J. Chem. Phys. **94**, 4097 (1991).

[16] The simulation consisted of a methyl group and 558 water molecules in a cubic box of 25.5945 Å at 293 K with periodic boundary conditions. The carbon of the methyl group was fixed at the origin. All bond lengths and angles of the methyl group were flexible. The parameter set was adopted from PARM22 of CHARMM (Chemistry at Harvard Macromolecular Mechanics) [A. MacKerell, M. Schlenkick, J.Brickmann, and M. Karplus (unpublished)]. We carried out the simulation to 300 ps.

[17] R. M. Lynden-Bell, R. A. Madden, D. T. Stott, and R. J. Tough, Mol. Phys. **58**, 193 (1986).

[18] R. Zwanzig, J. Stat. Phys. **9**, 215 (1973).

[19] R. Zwanzig, in *Systems Far from Equilibrium*, edited by L. Garrido (Springer-Verlag, New York, 1980).

[20] R. Feynmann and F. L. Vernon, Ann. Phys. (N.Y.) **24**, 118 (1963).

[21] A. O. Caldeira and Leggett, Physica A **121**, 587 (1983).

[22] B. L. Hu, Juan Pablo Paz, and Yuhong Zhang, Phys. Rev. D **45**, 2843 (1992).

[23] R. Kubo, M. Toda, and N. Hashitsume, *Statistical Physics* (Springer-Verlag, Berlin, 1978).

[24] H. Grabert, *Projection Operator Techniques in Nonequilibrium Statistic Mechanics,* edited by, G. Höhler, Springer Tracts in Modern Physics Vol. 95 (Springer, Berlin, 1982).

[25] Adapted from I. S. Gradsteyn and I. M. Ryzhik, *Tables of Series, Products, and Integrals* (VEB Deutscher Verlag der Wissenshaften, Berlin, 1963), p. 378.

[26] R. L. Stratonovich, in *Selected Translations in Mathematical Statistics and Probability* (American Mathematical Society, Providence, RI, 1972), p. 273; also in *Nonlinear Dynamical Systems,* edited by F. Moss and P. V. E. McCintock (Cambridge University Press, Cambridge, England, 1989), Vol. 1.