

## Quantum and classical Fokker-Planck equations for a Gaussian-Markovian noise bath

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(Received 9 April 1990; revised manuscript received 30 November 1990)

The quantum Fokker-Planck equation for a Gaussian-Markovian bath is deduced by applying a method proposed by Tanimura and Kubo [J. Phys. Soc. Jpn. **58**, 101 (1989)]. The results are expressed in the form of simultaneous differential equations in terms of density operators and can treat strong system-bath interactions where the correlated effects of the noise play an important role. The classical Fokker-Planck equation for a Gaussian-Markovian noise is obtained by performing the Wigner transformation, and its equilibrium state is shown to be the Maxwell-Boltzmann distribution. The method is convenient for numerical studies. Calculations for quantum-system harmonic oscillators and the double-well potential problems are demonstrated for cases of Gaussian-white noise and Gaussian-Markovian noise.

### I. INTRODUCTION

The topic of Brownian motion has received considerable attention. One of the traditional approaches used for this problem is based on the Fokker-Planck (FP) equation describing a time evolution of the distribution functions for the Brownian motion of particles.<sup>1,2</sup> For a distribution function  $W(p, q; t)$  with the momentum  $p$  and the position  $q$  of the particles, the Fokker-Planck equation (Kramers equation) has the form

$$\frac{\partial}{\partial t} W(p, q; t) = \left[ -\frac{p}{M} \frac{\partial}{\partial q} + \frac{\partial U(q)}{\partial q} \frac{\partial}{\partial p} + \frac{\eta}{M} \frac{\partial}{\partial p} \left[ p + \frac{M}{\beta} \frac{\partial}{\partial p} \right] \right] W(p, q; t). \quad (1.1)$$

Here  $U(q)$  is the potential,  $\eta$  is the friction constant,  $M$  is the mass of the particle, and  $\beta = 1/k_B T$  is the inverse temperature of the environment (the heat bath). This equation can be obtained from the Langevin equation

$$\begin{aligned} \frac{dp}{dt} &= -\frac{\partial U(q)}{\partial q} - \frac{\eta}{M} p + R(t), \\ \frac{dq}{dt} &= \frac{p}{M}, \end{aligned} \quad (1.2)$$

where the random force  $R(t)$  is assumed to be of a Gaussian-white noise type, such that

$$\langle R(t) \rangle = 0, \quad \langle R(t') R(t) \rangle = \frac{2\eta}{\beta} \delta(t' - t). \quad (1.3)$$

The quantum-mechanical generalization of the FP equation can be obtained from a system composed of a single degree of freedom (the particle system  $A$ ) coupled to the collection of harmonic oscillators (the bath system  $B$ ). The total Hamiltonian is given by

$$H = \frac{\hat{P}^2}{2M} + U_b(\hat{Q}) - \hat{Q} \sum_j c_j \hat{x}_j + \sum_j \left[ \frac{\hat{p}_j^2}{2m_j} + \frac{m_j \omega_j^2 \hat{x}_j^2}{2} \right]. \quad (1.4)$$

The above Hamiltonian describes a particle (mass  $M$ , coordinate  $\hat{Q}$ , and momentum  $\hat{P}$ ) moving in a potential  $U_b(\hat{Q})$  ( $b$  represents the bare potential) and interacting linearly with the harmonic oscillators (coordinate  $\hat{x}_j$  and momentum  $\hat{p}_j$ ). All information about the bath which is required by a reduced description of the particle is contained in the spectral density

$$J(\omega) = \hbar \omega \sum_j \left[ \frac{c_j^2}{4m_j \omega_j^2} \right] [\delta(\omega - \omega_j) + \delta(\omega + \omega_j)], \quad (1.5)$$

and the initial temperature of the bath. For the white (Ohmic) noise spectrum  $J(\omega) = \hbar \eta \omega / 2\pi$  with a high-temperature bath, Caldeira and Leggett<sup>3</sup> deduced an equation of motion (i.e., the quantum FP equation) for the density matrix elements of the particle  $\rho(Q, Q'; t)$  with the form

$$\begin{aligned} \frac{\partial}{\partial t} \rho(Q, Q'; t) &= -\frac{i}{\hbar} \mathcal{L}_A(Q, Q') \rho(Q, Q'; t) \\ &\quad - \frac{\eta}{2M} (Q - Q') \left[ \frac{\partial}{\partial Q} - \frac{\partial}{\partial Q'} \right] \rho(Q, Q'; t) \\ &\quad - \frac{\eta}{\beta \hbar^2} (Q - Q')(Q - Q') \rho(Q, Q'; t). \end{aligned} \quad (1.6)$$

Here,

$$\mathcal{L}_A(Q, Q') \equiv -\frac{\hbar^2}{2M} \left[ \frac{\partial^2}{\partial Q^2} - \frac{\partial^2}{\partial Q'^2} \right] + U(Q) - U(Q'), \quad (1.7)$$

and we have used the renormalized potential

$$\begin{aligned}
U(Q) &= U_b(Q) - \int_{-\infty}^{\infty} d\omega \left[ \frac{J(\omega)}{\hbar\omega} \right] Q^2 \\
&= U_b(Q) - \eta\delta(0)Q^2. \tag{1.8}
\end{aligned}$$

Note that, using Eq. (1.8), we can rewrite the Hamiltonian Eq. (1.4) as

$$\begin{aligned}
H &= \frac{\hat{P}^2}{2M} + U(\hat{Q}) \\
&+ \sum_j \left[ \frac{\hat{p}_j^2}{2m_j} + \frac{m_j\omega_j^2}{2} \left[ \hat{x}_j - \frac{c_j\hat{Q}}{m_j\omega_j^2} \right]^2 \right], \tag{1.9}
\end{aligned}$$

$$\begin{aligned}
\frac{\partial}{\partial t} \hat{\rho}(t) &= -\frac{i}{\hbar} \left[ \frac{\hat{P}^2}{2M} + U_b(\hat{Q}) \right] \hat{\rho}(t) \\
&- \frac{1}{\hbar^2} \hat{Q} \times(0) \int_0^\infty d\tau \int_{-\infty}^\infty d\omega e^{-i\omega\tau} J(\omega) \left[ \hat{Q} \circ(-\tau) + \coth \left[ \frac{\beta\hbar\omega}{2} \right] \hat{Q} \times(-\tau) \right] \hat{\rho}(t), \tag{1.10}
\end{aligned}$$

where  $\hat{\rho}(t)$  is the density operator of the particle system,  $\hat{Q}(t)$  is the Heisenberg operator of the position, and the hyperoperators  $\times$  and  $\circ$  are defined by

$$\begin{aligned}
\hat{Q} \times \hat{\rho} &= \hat{Q}\hat{\rho} - \hat{\rho}\hat{Q}, \\
\hat{Q} \circ \hat{\rho} &= \hat{Q}\hat{\rho} + \hat{\rho}\hat{Q}, \tag{1.11}
\end{aligned}$$

respectively. We may rewrite a part of the second term in Eq. (1.10) in the form

$$\begin{aligned}
&-\frac{1}{\hbar^2} \hat{Q} \times \int_0^\infty d\tau \int_{-\infty}^\infty d\omega \frac{d}{d\tau} \left[ \frac{e^{-i\omega\tau}}{-i\omega} \right] J(\omega) \hat{Q}(-\tau) \hat{\rho}(t) \\
&= -\frac{1}{\hbar^2} \hat{Q} \times \left[ \int_{-\infty}^\infty d\omega e^{-i\omega\tau} \left[ \frac{iJ(\omega)}{\omega} \right] \hat{Q}(-\tau) \right]_0^\infty + \int_0^\infty d\tau \int_{-\infty}^\infty d\omega e^{i\omega\tau} \left[ \frac{iJ(\omega)}{\omega} \right] \dot{\hat{Q}}(-\tau) \hat{\rho}(t). \tag{1.12}
\end{aligned}$$

Thus the assumption of white noise,  $J(\omega) = \hbar\eta\omega/2\pi$ , and a high-temperature bath,  $\coth(\beta\hbar\omega/2) \approx 2/(\beta\hbar\omega)$ , permits us to rewrite Eq. (1.10) in the form

$$\frac{\partial}{\partial t} \hat{\rho}(t) = -\frac{i}{\hbar} \mathcal{L}_A \hat{\rho}(t) - \frac{\eta}{2M\hbar} \hat{Q} \times \left[ i\hat{P} + \frac{2M}{\beta\hbar} \hat{Q} \times \right] \hat{\rho}(t). \tag{1.13}$$

Here,

$$\mathcal{L}_A \hat{\rho} = \left[ \frac{\hat{P}^2}{2M} + U(\hat{Q}) \right] \hat{\rho}, \tag{1.14}$$

and  $U(Q)$  is given by Eq. (1.8). This is the quantum FP equation in the operator representation and agrees with Eq. (1.6) in the coordinate representation.

The relationship between the quantal density operator and the classical phase distribution is shown via the Wigner transformation, which is presented in the form<sup>6</sup>

$$W(p, q; t) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{ipq'/\hbar} \langle q - q'/2 | \hat{\rho}(t) | q + q'/2 \rangle dq'. \tag{1.15}$$

The rule is that all operators consisting of  $\hat{P}$  and  $\hat{Q}$  have to be replaced according to<sup>7</sup>

which is the Hamiltonian for the potential  $U(Q)$  with a counter term.<sup>4</sup> We may use the above Hamiltonian as the definition for the system of Eq. (1.6) instead of Eq. (1.4). Also notice that the second term in Eq. (1.8) has an infinite constant for this white noise case, which becomes finite for a colored noise as we will show in Sec. II.

The same result can be obtained from the quantum master equation approach which is usually derived by the projection operator method assuming a weak system-bath interaction. For the Hamiltonian (1.4), this can be written as<sup>2,5</sup>

$$A(\hat{P}, \hat{Q}) \hat{\rho}(t) \rightarrow A \left[ p + \frac{\hbar}{2i} \frac{\partial}{\partial q}, q - \frac{\hbar}{2i} \frac{\partial}{\partial p} \right] W(p, q; t), \tag{1.16}$$

$$\hat{\rho}(t) A(\hat{P}, \hat{Q}) \rightarrow A \left[ p - \frac{\hbar}{2i} \frac{\partial}{\partial q}, q + \frac{\hbar}{2i} \frac{\partial}{\partial p} \right] W(p, q; t),$$

where  $A(\hat{P}, \hat{Q})$  is any operator of  $\hat{P}$  and  $\hat{Q}$ . This puts Eq. (1.13) in the form

$$\begin{aligned}
\frac{\partial}{\partial t} W(p, q; t) &= \left\{ -\frac{p}{M} \frac{\partial}{\partial q} + \frac{1}{i\hbar} \left[ U \left[ q - \frac{\hbar}{2i} \frac{\partial}{\partial p} \right] \right. \right. \\
&\quad \left. \left. - U \left[ q + \frac{\hbar}{2i} \frac{\partial}{\partial p} \right] \right] \right. \\
&\quad \left. + \frac{\eta}{M} \frac{\partial}{\partial p} \left[ p + \frac{M}{\beta} \frac{\partial}{\partial p} \right] \right\} W(p, q; t). \tag{1.17}
\end{aligned}$$

Note that the FP equation was also derived by Dekker from the quantum master equation, although Dekker's equation has extra terms which are absent from Eq. (1.17) since he has assumed a different system-bath interaction.<sup>8,9</sup> Also notice that the semiclassical Langevin equation similar to Eq. (1.2) has been obtained from the

quantum-mechanical approach with the use of the path-integral method<sup>10</sup> and is consistent with the FP equation (1.17). Equation (1.17) agrees with the FP equation (1.1) in the classical limit  $\hbar \rightarrow 0$ . Then the potential,  $U(Q)$  [not  $U_b(Q)$ ], can be regarded as the corresponding potential for the classical Fokker-Planck equation (1.1). In fact, if we put  $U(Q)=0$ , the Hamiltonian in Eq. (1.9) guarantees the translation invariance, which is the property required for free Brownian particles.

The above discussions are restricted to the white noise case. An extension of the classical FP equation to the colored noise case has been well studied recently using stochastic differential equations.<sup>11</sup> However, an extension of the quantum FP equation to the colored noise bath is not well addressed. In this paper we use the method developed in Ref. 5 to derive the quantum FP equation for a system interacting with a Gaussian-Markovian bath. The results are expressed in the form of simultaneous differential equations and can treat not only

a colored noise but also strong system-bath interaction. The classical FP equation for a Gaussian-Markovian noise can be obtained by performing the Wigner transformation and its equilibrium state is shown to be the Maxwell-Boltzmann distribution. Numerical calculations for the system of the harmonic oscillator and the double-well potential are performed for the case of the Gaussian-white noise and the Gaussian-Markovian noise interactions.

## II. THE QUANTUM AND THE CLASSICAL FOKKER-PLANCK EQUATION FOR A GAUSSIAN-MARKOVIAN BATH

Consider the matrix elements of the reduced density operator of the particle (system  $A$ ) in the path-integral language. For the Hamiltonian Eq. (1.9), this is written in the form<sup>12</sup>

$$\rho(Q, Q'; t) = \int dQ_i \int dQ'_i \int_{Q(t_i)=Q_i}^{Q(t)=Q} D[Q(\tau)] \int_{Q'(t_i)=Q'_i}^{Q'(t)=Q'} D[Q'(\tau)] \langle Q_i | \hat{\rho}(t_i) | Q'_i \rangle \exp \left[ \frac{i}{\hbar} S_A(Q; t, t_i) \right] \times F(Q, Q'; t, t_i) \exp \left[ -\frac{i}{\hbar} S_A(Q'; t, t_i) \right], \quad (2.1)$$

where  $D[Q(\tau)]$  represents the functional integral of  $Q(\tau)$ , and  $S_A(Q; t, t_i)$  is the action of the particle given by

$$S_A(Q; t, t_i) = \int_{t_i}^t d\tau \left[ \frac{1}{2} M \dot{Q}^2 - U(Q) \right]. \quad (2.2)$$

The influence functional  $F(Q, Q'; t, t_i)$  is expressed as<sup>3,13</sup>

$$F(Q, Q'; t, t_i) = \exp \left[ \left[ -\frac{i}{\hbar} \right]^2 \int_{t_i}^t d\tau' \left[ i\bar{L}_1(\tau' - t_i) [Q(\tau') - Q'(\tau')] [Q(t_i) + Q'(t_i)] + i \int_{t_i}^{\tau'} d\tau \bar{L}_1(\tau' - \tau) [Q(\tau') - Q'(\tau')] [\dot{Q}(\tau) + \dot{Q}'(\tau)] + \int_{t_i}^{\tau'} d\tau L_2(\tau' - \tau) [Q(\tau') - Q'(\tau')] [Q(\tau) - Q'(\tau)] \right] \right], \quad (2.3)$$

where

$$i\bar{L}_1(t) = i \int_{-\infty}^{\infty} d\omega \frac{J(\omega)}{\omega} \cos(\omega t), \quad (2.4)$$

$$L_2(t) = \int_{-\infty}^{\infty} d\omega J(\omega) \coth \left[ \frac{\beta \hbar \omega}{2} \right] \cos(\omega t), \quad (2.5)$$

and  $J(\omega)$  is given by Eq. (1.5). To derive the above expression we have used the factorized initial condition

$$\hat{\rho}_{A+B}(t_i) = \hat{\rho}(t_i) \hat{\rho}_B^c, \quad (2.6)$$

where  $\hat{\rho}(t)$  is the initial density operator of  $A$  (the particle), and  $\hat{\rho}_B^c$  is the equilibrium density operator of  $B$  (the bath) at inverse temperature  $\beta = 1/k_B T$ . Note that here we use the factorized initial condition, but we will discuss the correlated case in the next section.

The density operator of the particle can be constructed from its matrix elements in Eq. (2.1) as

$$\hat{\rho}(t) = \int dQ \int dQ' |Q\rangle \rho(Q, Q'; t) \langle Q'|. \quad (2.7)$$

The following procedure runs closely parallel to that developed in Ref. 5, except here we use Eq. (2.3) for the influence functional. Assuming the spectral function in the Drude form, which corresponds to the Ohmic dissipation with the Lorentzian cutoff,

$$J(\omega) = \frac{\hbar \eta}{2\pi} \frac{\omega \gamma^2}{\gamma^2 + \omega^2}, \quad (2.8)$$

we can write

$$i\bar{L}_1(t) = i \frac{\hbar \eta \gamma}{2} e^{-\gamma t}, \quad (2.9)$$

$$L_2(t) = \frac{\hbar \eta \gamma^2}{2} \left[ \cot \left[ \frac{\beta \hbar \gamma}{2} \right] e^{-\gamma t} - \sum_{k=1}^{\infty} \frac{4k\pi}{(\beta \hbar \gamma)^2 - (2k\pi)^2} e^{-2k\pi t / \beta \hbar} \right]. \quad (2.10)$$

For a high-temperature bath,  $\beta \hbar \gamma \leq 1$ , which corresponds

to  $T \geq 10$  K, for the noise correlation time  $t_c = 1/\gamma \approx 1$  ps, the terms in the sum of Eq. (2.10) can be neglected. (The low-temperature corrections due to the terms in the

sum can be made by using the method discussed in Appendix A.) The hierarchical elements, which had been used in Ref. 5, are now given by

$$\begin{aligned} \rho_n(Q, Q'; t) = & \int dQ_i \int dQ'_i \int_{Q(t_i)=Q_i}^{Q(t)=Q} \mathcal{D}[Q(\tau)] \int_{Q'(t_i)=Q'_i}^{Q'(t)=Q'} \mathcal{D}[Q'(\tau)] \langle Q_i | \hat{\rho}(t_i) | Q'_i \rangle \\ & \times \left[ -i \frac{\eta\gamma}{2} e^{-\gamma t} \left\{ i e^{-\gamma t_i} [Q(t_i) + Q'(t_i)] \right. \right. \\ & \quad \left. \left. + \int_{t_i}^t d\tau e^{\gamma\tau} \left[ i [\dot{Q}(\tau) + \dot{Q}'(\tau)] + \gamma \cot \left[ \frac{\beta\hbar\gamma}{2} \right] [Q(\tau) - Q'(\tau)] \right] \right\} \right]^n \\ & \times \exp \left[ \frac{i}{\hbar} S_A(Q; t, t_i) \right] F(Q, Q'; t, t_i) \exp \left[ -\frac{i}{\hbar} S_A(Q'; t, t_i) \right]. \end{aligned} \quad (2.11)$$

Then,  $\rho_0(Q, Q'; t)$  is equal to  $\rho(Q, Q'; t)$ . The time derivatives of  $\rho_n(Q, Q'; t)$  follow as

$$\begin{aligned} \frac{\partial}{\partial t} \rho_0(Q, Q'; t) = & -\frac{i}{\hbar} \mathcal{L}_{-1}(Q, Q') \rho_0(Q, Q'; t) - \frac{i}{\hbar} (Q - Q') \rho_1(Q, Q'; t), \\ \frac{\partial}{\partial t} \rho_1(Q, Q'; t) = & -\left[ \frac{i}{\hbar} \mathcal{L}_{-1}(Q, Q') + \gamma \right] \rho_1(Q, Q'; t) - \frac{i}{\hbar} (Q - Q') \rho_2(Q, Q'; t) - \frac{i}{\hbar} \Theta_F(Q, Q') \rho_0(Q, Q'; t), \\ & \vdots \\ \frac{\partial}{\partial t} \rho_n(Q, Q'; t) = & -\left[ \frac{i}{\hbar} \mathcal{L}_{-1}(Q, Q') + n\gamma \right] \rho_n(Q, Q'; t) - \frac{i}{\hbar} (Q - Q') \rho_{n+1}(Q, Q'; t) - \frac{ni}{\hbar} \Theta_F(Q, Q') \rho_{n-1}(Q, Q'; t), \\ & \vdots \end{aligned} \quad (2.12)$$

where  $\Theta_F(Q, Q')$  represents

$$\begin{aligned} \Theta_F(Q, Q') = & \frac{\hbar\eta\gamma}{2M} \left[ \frac{\partial}{\partial Q} - \frac{\partial}{\partial Q'} \right] \\ & + M\gamma \cot \left[ \frac{\beta\hbar\gamma}{2} \right] (Q - Q'). \end{aligned} \quad (2.13)$$

The Liouvillian  $\mathcal{L}_{-1}(Q, Q')$  is defined by Eq. (1.7), however, the renormalized potential is now given by

$$U(Q) = U_b(Q) - \frac{\eta\gamma}{2} Q^2. \quad (2.14)$$

Equation (2.12) is an extension of the quantum FP equation to the case of the Gaussian-Markovian interaction and is a main result of this study. The factors  $(Q - Q')$  and  $\Theta_F(Q, Q')$  have appeared corresponding to the phonon creation and annihilation processes. Thus the elements  $\rho_n(Q, Q'; t)$  represent the  $n$ -phonon dressed state at time  $t$ .

From the definition of  $\rho_n(Q, Q'; t)$ , the initial condition for Eq. (2.12) can be written as

$$\rho_0(Q, Q'; t_i) = \rho(Q, Q'; t_i), \quad \rho_n(Q, Q'; t_i) = 0 \quad (n \geq 1). \quad (2.15)$$

This corresponds to the factorized initial condition Eq. (2.6); however, our equation can take account of correlat-

ed (unfactorized) initial conditions by choosing nonzero elements of  $\rho_n(Q, Q'; t_i)$ . (See Ref. 14.)

We can evaluate the simultaneous equations (2.12), since the hierarchical elements  $\rho_k(Q, Q'; t)$  ( $k > N$ ) do not play a dominant role for large  $N$ . To see this point, consider the following equation:

$$\begin{aligned} \frac{\partial}{\partial t} \rho_N(Q, Q'; t) = & -\left[ \frac{i}{\hbar} \mathcal{L}_{-1}(Q, Q') + N\gamma \right] \rho_N(Q, Q'; t) \\ & - \frac{i}{\hbar} (Q - Q') \rho_{N+1}(Q, Q'; t) \\ & - \frac{Ni}{\hbar} \Theta_F(Q, Q'; t) \rho_{N-1}(Q, Q'; t), \end{aligned} \quad (2.16)$$

and

$$\begin{aligned} \frac{\partial}{\partial t} \rho_k(Q, Q'; t) = & -\left[ \frac{i}{\hbar} \mathcal{L}_{-1}(Q, Q') + k\gamma \right] \rho_k(Q, Q'; t) \\ & - \frac{i}{\hbar} (Q - Q') \rho_{k+1}(Q, Q'; t) \\ & - \frac{ki}{\hbar} \Theta_F(Q, Q'; t) \rho_{k-1}(Q, Q'; t) \end{aligned} \quad (k > N). \quad (2.17)$$

Equation (2.17) can be formally solved as

$$\rho_k(Q, Q'; t) = -\frac{i}{\hbar} \int_{t_i}^t d\tau \exp \left[ -\frac{i}{\hbar} \mathcal{L}_A(Q, Q') - k\gamma \right] (t - \tau) [(Q - Q')\rho_{k+1}(Q, Q'; \tau) + k\Theta_F(Q, Q')\rho_{k-1}(Q, Q'; \tau)] \quad (k > N) . \quad (2.18)$$

If  $k\gamma$  is large enough compared with the characteristic frequency of the system  $\omega_A$ , the time kernel can be replaced by the  $\delta$  function and Eq. (2.18) becomes

$$\rho_k(Q, Q'; t) = -\frac{i}{\hbar} \frac{1}{k\gamma} (Q - Q')\rho_{k+1}(Q, Q'; t) - \frac{i}{\hbar\gamma} \Theta_F(Q, Q')\rho_{k-1}(Q, Q'; t) \quad (k > N) . \quad (2.19)$$

The above hierarchical equation can be solved for  $\rho_{N+1}(Q, Q'; t)$  as

$$\rho_{N+1}(Q, Q'; t) = \frac{-i}{\hbar\gamma + (Q - Q') \frac{1}{(N+1)\hbar\gamma + (Q - Q') \frac{(N+1)}{(N+2)\hbar\gamma + \dots} \Theta_F(Q, Q')}} \Theta_F(Q, Q') \rho_N(Q, Q'; t) . \quad (2.20)$$

Since the continued fractional part becomes constant for large  $N\gamma$ , we have

$$\rho_{N+1}(Q, Q'; t) \approx -\frac{i}{\hbar\gamma} \Theta_F(Q, Q') \rho_N(Q, Q'; t) . \quad (2.21)$$

Inserting the above into Eq. (2.16), we have the anchor equation for Eq. (2.12) in the form

$$\begin{aligned} \frac{\partial}{\partial t} \rho_N(Q, Q'; t) = & - \left[ \frac{i}{\hbar} \mathcal{L}_A(Q, Q') + N\gamma \right] \rho_N(Q, Q'; t) \\ & - \frac{1}{\hbar^2\gamma} (Q - Q') \Theta_F(Q, Q') \rho_N(Q, Q'; t) \\ & - \frac{Ni}{\hbar} \Theta_F(Q, Q'; t) \rho_{N-1}(Q, Q'; t) . \end{aligned} \quad (2.22)$$

Thus, in view of the above discussions, the set of equations (2.12) can be written in the closed form and evaluated. If the damping constant is large,  $\gamma \gg \omega_A$ , which corresponds to the white noise limit (the Ohmic noise without cutoff), we may set  $N=0$  in Eq. (2.22) and we may recover the quantum Fokker-Planck equation (1.6) for the high-temperature limit  $\cot(\beta\hbar\gamma/2) \approx 2/(\beta\hbar\gamma)$ .

In operator form, the hierarchical equations (2.12) and the anchor equation (2.22) can be expressed as

$$\begin{aligned} \hat{\rho}_0(t) = & \frac{i}{\hbar} \mathcal{L}_A \hat{\rho}_0(t) - \frac{i}{\hbar} Q \times \hat{\rho}_1(t) , \\ \hat{\rho}_n(t) = & - \left[ \frac{i}{\hbar} \mathcal{L}_A + n\gamma \right] \hat{\rho}_n(t) \\ & - \frac{i}{\hbar} Q \times \hat{\rho}_{n+1}(t) - \frac{ni}{\hbar} \Theta_F \hat{\rho}_{n-1}(t) \quad (n \geq 1) , \end{aligned} \quad (2.23)$$

and

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}_N(t) = & - \left[ \frac{i}{\hbar} \mathcal{L}_A + N\gamma \right] \hat{\rho}_N(t) \\ & - \frac{1}{\gamma\hbar^2} Q \times \Theta_F \hat{\rho}_N(t) - \frac{Ni}{\hbar} \Theta_F \hat{\rho}_{N-1}(t) . \end{aligned} \quad (2.24)$$

Here,  $i\mathcal{L}_A$  is given by Eq. (1.14) and

$$\Theta_F = \frac{\hbar\eta\gamma}{2M} \left[ i\hat{P} \circ + M\gamma \cot \left[ \frac{\beta\hbar\gamma}{2} \right] \hat{Q} \times \right] . \quad (2.25)$$

The set of equations (2.23)–(2.25) are physically the same as the equations discussed in Ref. 5. However, to see the relation between the classical and quantum equation, the above expressions are more useful.

The semiclassical equation corresponding to Eq. (2.23) can be obtained by using the rule Eq. (1.16). Taking the classical limits  $\hbar \rightarrow 0$ , we have the following results:

$$\begin{aligned} \frac{\partial}{\partial t} W_0(p, q; t) = & -L_A(p, q)W_0(p, q; t) + \partial_p W_1(p, q; t) , \\ \frac{\partial}{\partial t} W_n(p, q; t) = & -[L_A(p, q) + n\gamma]W_n(p, q; t) \\ & + \partial_p W_{n+1}(p, q; t) \\ & + n\Theta_F(p)W_{n-1}(p, q; t) \quad (n \geq 1) . \end{aligned} \quad (2.26)$$

The anchor equation for the above is given by

$$\begin{aligned} \frac{\partial}{\partial t} W_N(p, q; t) = & -[L_A(p, q) + N\gamma]W_N(p, q; t) \\ & + \partial_p \Theta_F(p)W_N(p, q; t) \\ & + N\Theta_F(p)W_{N-1}(p, q; t) . \end{aligned} \quad (2.27)$$

Here, we put

$$\begin{aligned} -L_A(p, q) = & -\frac{p}{M} \frac{\partial}{\partial q} + \frac{\partial U(q)}{\partial q} \frac{\partial}{\partial p} , \\ \partial_p = & \frac{\partial}{\partial p} , \\ \Theta_F(p) = & \frac{\eta\gamma}{M} \left[ p + \frac{M}{\beta} \frac{\partial}{\partial p} \right] . \end{aligned} \quad (2.28)$$

The above result is the FP equation for a Gaussian-Markovian noise. For the white noise limit  $\gamma \rightarrow \infty$ , we may set  $N=0$  and this agrees with the FP equation (1.1). The above result can be obtained from the Langevin approach by assuming Gaussian-Markovian noise (Appendix B).

From Eq. (2.15) the initial condition for Eq. (2.26) is

written as  $W_0(p, q, t_i) = W(p, q; t_i)$  and  $W_n(p, q; t_i) = 0$  ( $n > 0$ ). For this condition, the Laplace transform of  $W_0(p, q; t)$  takes the form

$$Z[s] = \frac{1}{s + L_A(p, q) + \partial_p} \frac{1}{s + \gamma + L_A(p, q) + \partial_p} \frac{1}{s + 2\gamma + L_A(p, q) + \partial_p} \frac{1}{s + 3\gamma + L_A(p, q) + \partial_p} \cdots \Theta_F(p) \quad (2.30)$$

The equilibrium distribution  $W^e(p, q)$  can be evaluated as

$$W^e(p, q) = \lim_{t \rightarrow \infty} W_0(p, q; t) = \lim_{s \rightarrow 0} s W_0[p, q; s]. \quad (2.31)$$

The Maxwell-Boltzmann distribution

$$W^e(p, q) = C \exp \left[ -\beta \left( \frac{p^2}{2M} + U(q) \right) \right] \quad (2.32)$$

satisfies Eq. (2.31) with Eqs. (2.29) and (2.30), where  $C$  is the normalization constant.

### III. NUMERICAL CALCULATION FOR A HARMONIC OSCILLATOR SYSTEM

The equation of motion (2.12) can be numerically evaluated by using matrix expressions for the operators  $H_A$ ,  $Q$ ,  $\partial/\partial Q$ , and  $\rho_n(Q, Q'; t)$ , which can be obtained by introducing finite difference expressions. Here, we use a one-dimensional coordinate with  $L$  mesh points, so the operators  $H_A$ ,  $Q$ , and  $\partial/\partial Q$  are expressed by  $L \times L$  ma-

$$W_0[p, q; s] = Z[s] W_0(p, q; t_i), \quad (2.29)$$

where

trices. The hierarchical elements  $\rho_n(Q, Q'; t)$  can be expressed by an  $L \times L \times (N+1)$  matrix, where  $N$  is the cutoff number of the hierarchical elements. Equation (2.12) becomes then a simultaneous differential equation for the matrix elements. We solve this equation by using the fourth-order Runge-Kutta method. First we demonstrate our method for the harmonic potential. Here we choose the following potential for the main system A:

$$U(Q) = \begin{cases} \frac{M\omega_A^2}{2} Q^2 & (t \leq 0) \\ \frac{M\omega_A^2}{2} Q^2 + FQ & (t > 0) \end{cases} \quad (3.1)$$

in which  $\omega_A$  is the characteristic frequency of  $A$  and  $F$  is the constant corresponding to the force. The initial condition at time  $t = t_i$  ( $t_i \leq 0$ ) is chosen to be in the factorized form,

$$\rho_0(Q, Q'; t_i) = \left[ \frac{M\omega_A}{2\pi\hbar \sinh(\beta\hbar\omega_A)} \right]^{1/2} \exp \left[ \frac{-M\omega_A}{2\hbar \sinh(\beta\hbar\omega_A)} \left[ (Q^2 + Q'^2) \cosh(\beta\hbar\omega_A) - 2QQ' \right] \right], \quad (3.2)$$

$$\rho_n(Q, Q'; t_i) = 0 \quad (n \geq 1).$$

The operator  $\rho_0(Q, Q'; t_i)$  is the equilibrium state of  $A$  itself at the inverse temperature  $\beta$  at time  $t \leq 0$ . However, this is not the equilibrium state of the system  $A+B$ , since this neglects the correlated effects of the system-bath interaction, which can be set by  $\rho_n(Q, Q'; t_i) \neq 0$ . In our formulation, the system comes to this correlated equilibrium state, even though we started from the factorized initial condition, if we set  $|t_i|$  for a sufficiently longer time than the characteristic time of the system. We may regard this correlated equilibrium state (at  $t=0$ ) as the correlated initial condition for Eq. (2.12).

Figures 1 and 2 show the time evolution of the density elements of  $A$ ,  $\rho_0(Q, Q; t)$ , at time  $t \geq 0$  for a strong-coupling strength ( $\eta=5$ ) in the case of the Gaussian-white interaction ( $\gamma=\infty$  or  $N=0$ ) and the Gaussian-Markovian interaction ( $\gamma=1$ ), respectively. The other parameters are chosen to be

$$M = 1.0, \quad \omega_A = 2.0, \quad \beta = 0.4, \quad F = 6.0, \quad (3.3)$$

in which we set  $\hbar=1$ . In order to get the correlated initial conditions at time  $t=0$ , we set  $t_i = -60$  in the case of Fig. 2. The number of the mesh points  $L$  is chosen to be  $L=50$  and, for the Gaussian-Markovian cases, the number of cutoff  $N$  is  $N=50$ . The error caused by the cutoff on the dynamics of the system is checked by changing  $N$ .

In Figs. 1 and 2, the wave packet of  $A$  goes from the old equilibrium state centered at  $Q=0$  to the new equilibrium state centered at  $Q=\frac{3}{2}$  with the motion of the underdamped oscillator. In Fig. 2, the heights of peaks are also slightly oscillating. Compared with the white noise case, Fig. 1, the damping for the motion in Fig. 2 is weak. The reason is that the high-frequency oscillators of the bath do not contribute to the damping in the Markovian case because of the frequency cutoff  $\gamma$ . The cutoff frequency  $\gamma$  relates to the noise correlation time  $\tau_c$  as  $\tau_c = 1/\gamma$ , and the phenomena caused by the cutoff are sometimes referred to as the "memory effects" of the bath.

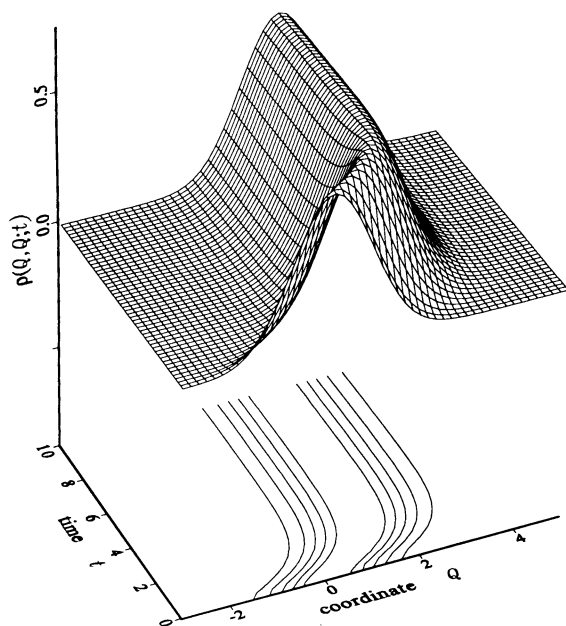


FIG. 1. Time evolution of the wave packet of the particle system  $A$  for a strong-coupling strength,  $\eta=5$  in the case of the Gaussian-white interaction ( $\gamma = \infty$ ).

#### IV. NUMERICAL CALCULATION FOR A DOUBLE-WELL SYSTEM

Next we demonstrate our calculation for a double-well potential modeling of the problem of the chemical reaction rates.<sup>15</sup> Here we use the following potential corresponding to a gauche-trans isomerization for  $n$ -butane:

$$U(Q) = \begin{cases} \frac{1}{2}M\omega_A^2(Q+q_A)^2 & (Q < -a) \\ U_0 - \frac{1}{2}M\omega_1^2Q^2 & (-a \leq Q \leq b) \\ U_B + \frac{1}{2}M\omega_B^2(Q-q_B)^2 & (b < Q) \end{cases} \quad (4.1)$$

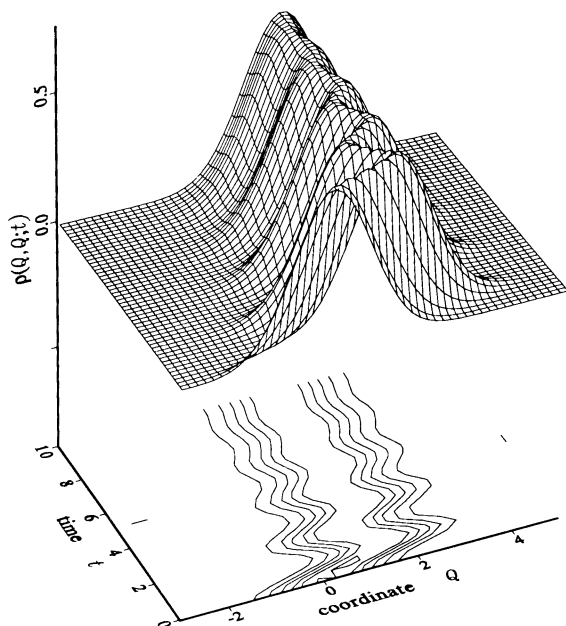


FIG. 2. Same as Fig. 1 except in the case of the Gaussian-Markovian interaction ( $\gamma=1$ ).

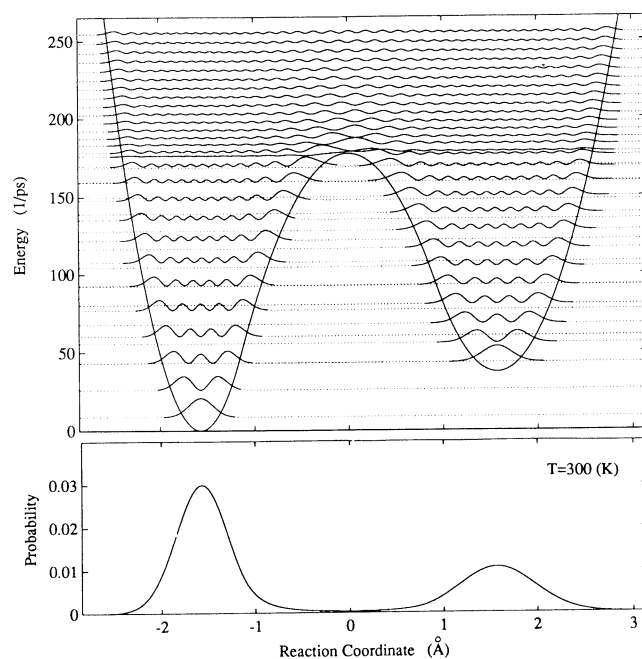


FIG. 3. Gauche-trans isomerization potential for  $n$ -butane and its equilibrium state at  $T=300$  K.

In the above, parameters are given by

$$\begin{aligned} M &= 1.85 \times 10^{-26} \text{ kg}, & \omega_1 &= 1.06 \times 10^{13} \text{ s}^{-1}, \\ U_0 &= 1.87 \times 10^{-20} \text{ J}, & U_B &= 0.44 \times 10^{-20} \text{ J}, \\ q_A &= q_B = 1.57 \text{ \AA} \end{aligned} \quad (4.2)$$

and  $\omega_A$ ,  $\omega_B$ ,  $a$ , and  $b$  are chosen to ensure that  $U(Q)$  and  $dU(Q)/dQ$  are continuous (see Fig. 3).<sup>16</sup> To study the transition between the wells we computationally carry out a linear response experiment. Although this is a cumbersome procedure it is necessary for making contact with the experimentally observable rate constant. The rate constant applies to a long-time steady-state situation and it requires dynamics from a correctly equilibrated state in which the bath is quantum-mechanically correlated with the double-well system. Our procedure is directly equivalent to the eigenperturbation experiment.<sup>17,18</sup> We introduce a perturbation for the right well written as

$$U'(Q) = U(Q) + \epsilon U_0 \Theta(Q), \quad (4.3)$$

where  $\Theta(Q)$  represents the step function. For numerical work, we put  $\epsilon=0.005$ . By turning on perturbation for a sufficient time and numerically integrating the hierarchy equations the system comes to a perturbed equilibrium state. By this perturbation, the population of the right well is shifted to the left well compared with the unperturbed equilibrium state. After the system comes to this perturbed equilibrium state, the perturbation is turned off (this defines time  $t=0$ ). Now the populations, equilibrated with the perturbation, are no longer in equilibrium and will have to reequilibrate to those of the unperturbed system. This change can be monitored by introducing the difference of the population in the right well from the unperturbed equilibrium state, which is defined by

$$\delta N(t) = \int_{-\infty}^{\infty} \rho(Q, Q; t) \Theta(Q) dQ - \int_{-\infty}^{\infty} \rho^e(Q, Q) \Theta(Q) dQ. \quad (4.4)$$

Here,  $\rho(Q, Q; t)$  is the density element of the double-well system calculated from Eq. (2.12) and we set  $\rho^e(Q, Q) = \rho(Q, Q; t \rightarrow \infty)$ . By the preequilibration process the initial condition  $\rho(Q, Q; 0)$  for Eq. (2.12) is the equilibrium state for the perturbed potential  $U'(Q)$ , and is a correlated initial condition.

The chemical reaction rate is a transition rate between the well and can be defined by

$$k(t) = \frac{(d/dt)\delta N(t)}{\delta N(t)} = -\frac{d}{dt} \ln[\delta N(t)]. \quad (4.5)$$

In the above, since  $\delta N(t)$  and  $d\delta N(t)/dt$  are expected to be proportional to the perturbation  $\epsilon$ , for small  $\epsilon$ ,  $k(t)$  does not depend on  $\epsilon$ . The quantity computed in this way is exactly the same as the Kubo transformed reactive flux correlation function.<sup>19,20</sup> It differs in detail, but is equivalent in final value to the reactive flux function used by Voth, Chandler, Miller, and co-workers.<sup>21</sup>

In the following, we show classical and quantum results of chemical reaction rates for various coupling strengths in the cases of the Gaussian-white and the Gaussian-Markovian bath at the temperature  $T=300$  K ( $\beta\hbar=0.025$  ps).

#### A. Classical reaction rates for Gaussian-white bath

First we discuss the chemical reaction rates calculated from the classical Fokker-Planck equation (1.1). The numerical calculations were performed by using the fourth-order Runge-Kutta method for finite difference expressions of the coordinate and the momentum space (here we use  $400 \times 150$  mesh). Figure 4 shows the reaction rates for different coupling strengths,  $\zeta = \eta/M$  ( $\text{ps}^{-1}$ ). We normalized these reaction flux functions by  $k_{\text{TST}} = 0.09 \text{ ps}^{-1}$  (the classical transition state theory value) which agrees with the initial value  $k(0)$ . The initial rates in the classical case are determined by the free

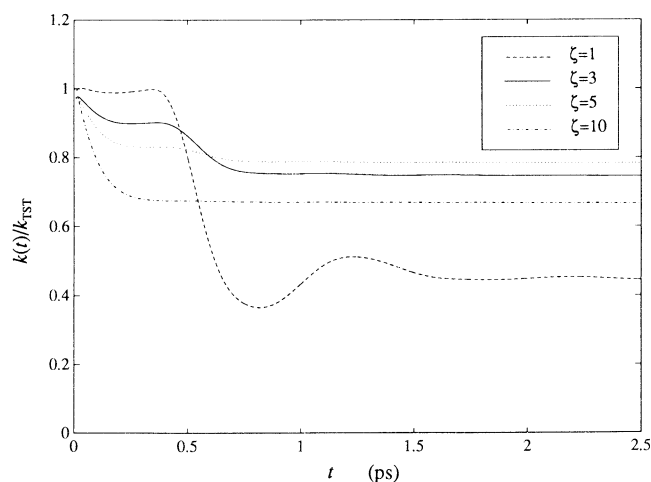


FIG. 4. Chemical reaction rates calculated from the classical Fokker-Planck equation for different coupling strength  $\zeta$  ( $\text{ps}^{-1}$ ).

motion of the equilibrium molecules near the barrier top. For classical systems the dissipation effect from the bath on these molecules does not change the probability of being at the transition state. Soon the molecules are scattered by the bath system through the interaction or bounce off the side of the potential well. These effects lead to recrossing and a reduction in  $k(t)$ , as discussed in many papers.<sup>18,22</sup> For weak interactions  $\zeta=1, 3$ , and  $5$ , the bath ultimately provides a source of activation for the molecules and the rate constants increase with the coupling strength.<sup>23</sup> This is the energy controlled regime. However, for the strong interaction,  $\zeta=10$ , molecules which have crossed the barrier may suffer collisions before reflecting from the potential well and reaction rates decrease with coupling strength; this is the diffusion limited regime.

#### B. Quantum reaction rates for Gaussian-white bath

Figure 5 shows the reactive flux functions calculated using the linear response procedure from the quantum Fokker-Planck equation (1.6). The mesh size  $L$  is chosen to be  $L=200$  for the coordinate region from  $Q = -3.5$  to  $3$  Å. Tunneling is only a small perturbation in this temperature regime. The main difference between classical and quantum results is in the initial period. In the quantum results (Fig. 5) the initial rates vanish, whereas as they have an initial finite value in the classical results, Fig. 4. The quantum results started from zero quickly rise and agree with the classical results about at  $t=0.025$  ps, which is equal to the thermal time  $\beta\hbar$ . This phenomenon, first noted by Costley and Pechukas,<sup>24</sup> comes from the quantum smearing of the transition state. Figures 6 and 7 show the time evolution of the density operators for  $\zeta=1$  and  $5$ , respectively. Since the difference of density elements caused by the perturbation is so small, we set  $\Delta\rho(Q, Q; t) = \rho(Q, Q; t) - \rho(Q, Q; T)$ , where we set  $T=3$  ps, instead of  $\rho(Q, Q; t)$  for the  $z$  axis. In both figures, the change of the density elements at the top of the barrier can be observed at the initial stages.

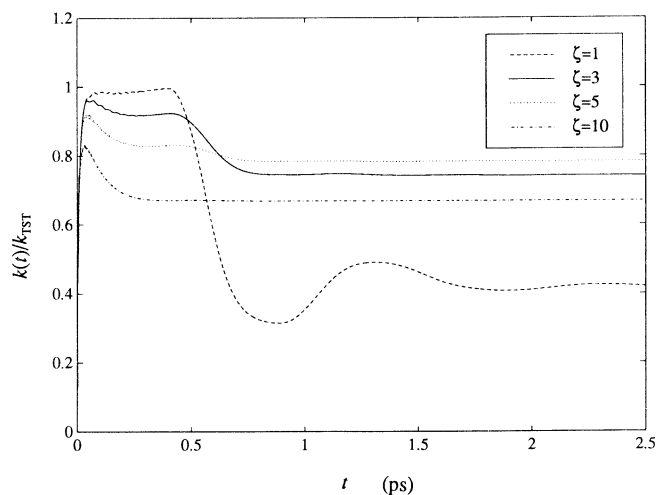


FIG. 5. Chemical reaction rates calculated from the quantum Fokker-Planck equation.



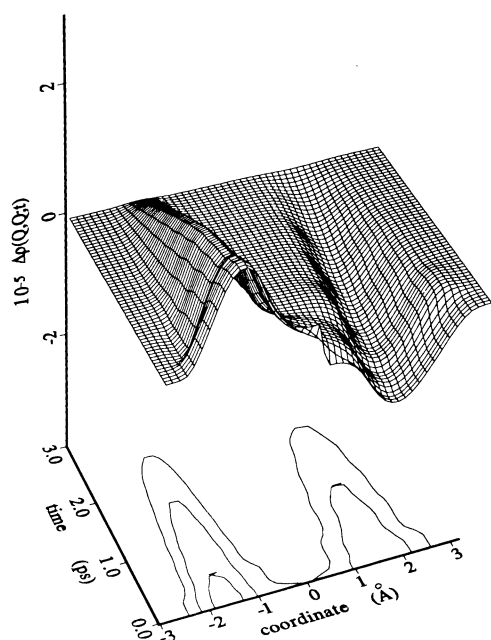


FIG. 6. Time evolution of  $\Delta\rho(Q,Q;t)$  in the case of the Gaussian-white bath for weak coupling  $\zeta=1$ .

### C. Quantum reaction rates for Gaussian-Markovian bath

Finally, we show the results from the quantum Fokker-Planck equation for the Gaussian-Markovian bath. To perform the calculation, we use the same mesh as the quantum Gaussian-white case. We set  $\gamma=10\text{ ps}^{-1}$  and hierarchical elements are taken into account from  $N=5$  to 15. In Fig. 8 the effective damping from the bath is weak compared with the Gaussian-white cases. As in the classical analysis the reason is that the high-frequency oscillators of the bath no longer contribute to the damp-

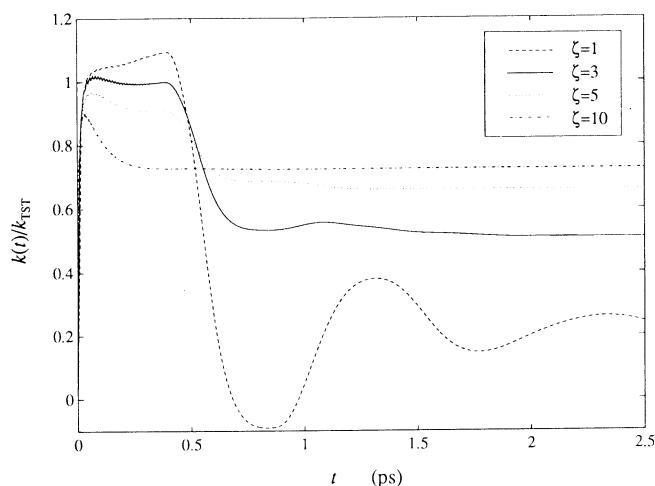


FIG. 8. Chemical reaction rates calculated from the quantum Fokker-Planck equation for the Gaussian-Markovian bath.

ing in the Markovian case because of the frequency cutoff  $\gamma$ . Figures 9 and 10 illustrate the time evolution of  $\Delta\rho(Q,Q;t)$  for  $\zeta=1$  and 5. These figures show the oscillating motions typical of the underdamped case.

Our results here are restricted to the near classical regime  $T=300\text{ K}$ . Using Eq. (2.12), we can perform the calculation down to  $T=100\text{ K}$ . If we take into account the second correction of temperature discussed in Appendix A, results can be taken into the tunneling dominated regime at  $T\geq 20\text{ K}$ . At these low temperatures numerical difficulties arise in the linear response procedure because of the large gradients of population. Application of our formalism to the study of the tunneling processes will be presented in a planned paper where a thin barrier potential is studied.

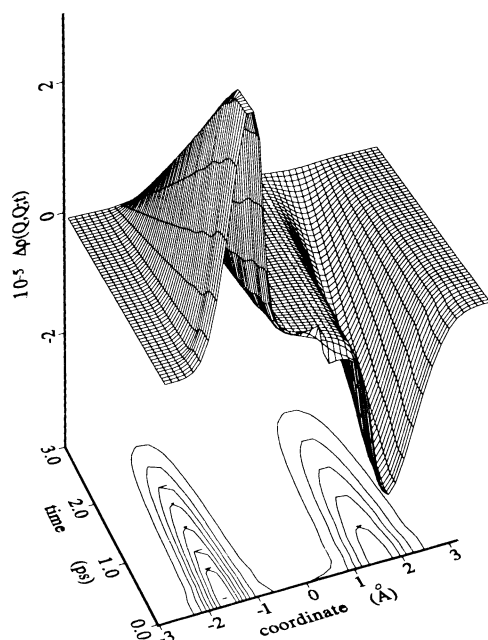


FIG. 7. Same as Fig. 6, except  $\zeta=5$ .

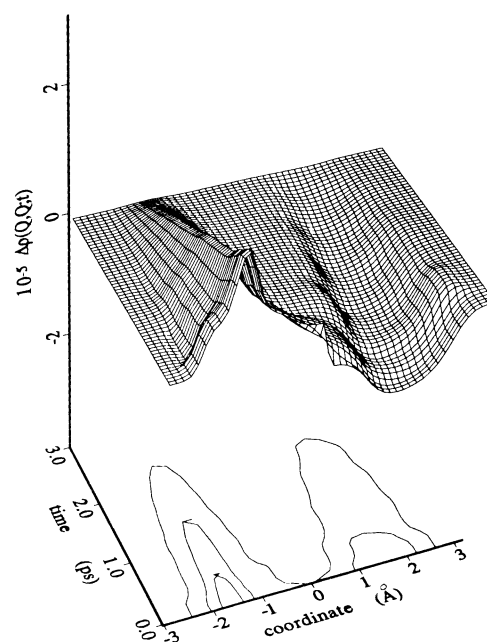
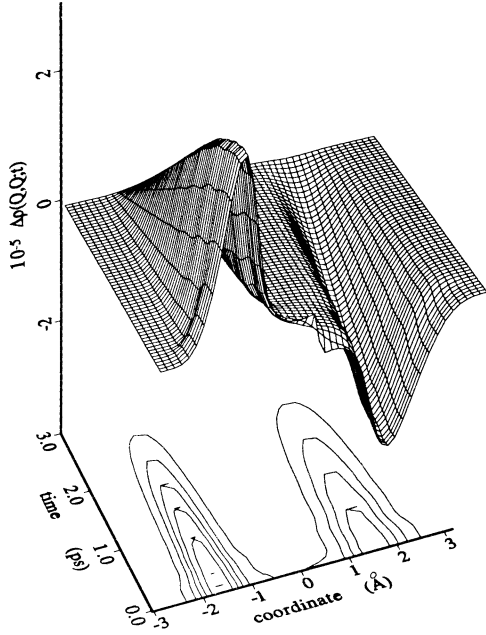


FIG. 9. Time evolution of  $\Delta\rho(Q,Q;t)$  in the case of the Gaussian-Markovian bath for weak interaction  $\zeta=1$ .

FIG. 10. Same as Fig. 9, except  $\zeta = 5$ .

## V. CONCLUSIONS

In this paper a quantum FP equation for a Gaussian-Markovian bath valid for arbitrary coupling is derived. This approach permits the treatment of the colored noise with the strong system-bath interaction. By choosing the initial conditions for the hierarchical elements, one can treat correlated (unfactorized) initial conditions.

The equation derived here is physically the same as the equation derived in Ref. 5. The Fokker-Planck picture,

however, offers clearer physical insight into the relation between the classical and quantum regimes. For example, by performing the Wigner transformation and taking the classical limit, one deduces the classical FP equation for Gaussian-Markovian noise.

Since our equation is expressed as the simultaneous differential equations instead of the integro-differential equations such as the generalized quantum Langevin equation, we can easily handle it numerically. This is the main point of this paper. As a demonstration of this approach the time evolution of harmonic systems and a double-well problem were studied. Applications of this approach to problems of direct practical interest are planned to be presented in forthcoming papers.

## ACKNOWLEDGMENTS

One of the authors (Y. T.) is grateful for useful discussions with K. Hess, A. J. Leggett, V. B. Pevzner, and J. Bude. Computations for this work have been performed on the Ardent Titan and the Apollo DN10000. Support by National Scientific Foundation Grant No. DMR 89-20538 is acknowledged.

## APPENDIX A: LOW-TEMPERATURE CORRECTIONS FOR EQUATIONS (1.6) AND (2.12)

Low-temperature corrections for Eq. (2.12) can be obtained along the same line as Ref. 14. Here we take into account the first term in the sum of Eq. (2.10), which will be a good approximation of  $iL_2(t)$  for  $\beta\hbar\gamma \leq 5$ , which corresponds to  $T \geq 2$  K for  $\gamma = 1$  ps $^{-1}$ . The influence functional corresponding to this is denoted by  $F'(Q, Q'; t, t_i)$ . We define the hierarchical element in the form

$$\begin{aligned} \rho_{nj}(Q, Q'; t) = & \int dQ_i \int dQ'_i \int_{Q(t_i)=Q_i}^{Q(t)=Q} D[Q(\tau)] \int_{Q'(t_i)=Q'_i}^{Q'(t)=Q'} D[Q'(\tau)] \langle Q_i | \hat{\rho}(t_i) | Q'_i \rangle \\ & \times \left[ -i \frac{\eta\gamma}{2} e^{-\gamma t} \left\{ i e^{-\gamma t_i} [Q(t_i) + Q'(t_i)] \right. \right. \\ & \quad \left. \left. + \int_{t_i}^t d\tau e^{\gamma\tau} \left[ i [\dot{Q}(\tau) + \dot{Q}'(\tau)] + \gamma \cot \left[ \frac{\beta\hbar\gamma}{2} \right] [Q(\tau) - Q'(\tau)] \right] \right\} \right]^n \\ & \times \left[ \int_{t_i}^t d\tau e^{-\gamma(t-\tau)} \Theta_1(Q, Q') \right]^j \exp \left[ \frac{i}{\hbar} S_A(Q; t, t_i) \right] F'(Q, Q'; t, t_i) \exp \left[ -\frac{i}{\hbar} S_A(Q'; t, t_i) \right], \end{aligned} \quad (\text{A1})$$

where we set  $\gamma_1 = 2\pi/\beta\hbar$  and

$$\Theta_1(Q, Q') = -\frac{2\pi\hbar\eta\gamma^2}{(\beta\hbar\gamma)^2 - (2\pi)^2} (Q - Q'). \quad (\text{A2})$$

The hierarchical equation for the density element is then

$$\begin{aligned} \frac{\partial}{\partial t} \rho_{nj}(Q, Q'; t) = & - \left[ \frac{i}{\hbar} \mathcal{L}_A(Q, Q') + n\gamma + j\gamma_1 \right] \rho_{nj}(Q, Q'; t) - \frac{i}{\hbar} (Q - Q') \rho_{n+1j}(Q, Q'; t) \\ & - \frac{i}{\hbar} (Q - Q') \rho_{nj+1}(Q, Q'; t) - \frac{in}{\hbar} \Theta_F(Q, Q') \rho_{n-1j}(Q, Q'; t) - \frac{ij}{\hbar} \Theta_1(Q, Q') \rho_{nj-1}(Q, Q'; t). \end{aligned} \quad (\text{A3})$$

for  $N\gamma \gg \omega_A$  or  $J\gamma_1 \gg \omega_A$ , where  $\omega_A$  is the characteristic frequency of the system, we have

$$\rho_{N+1,J}(\mathcal{Q}, \mathcal{Q}'; t) = -\frac{i(N+1)}{\hbar[(N+1)\gamma + J\gamma_1]} \Theta_F(\mathcal{Q}, \mathcal{Q}') \rho_{N,J}(\mathcal{Q}, \mathcal{Q}'; t) - \frac{iJ}{\hbar[(N+1)\gamma + J\gamma_1]} \Theta_1(\mathcal{Q}, \mathcal{Q}') \rho_{N+1,J-1}(\mathcal{Q}, \mathcal{Q}'; t), \quad (\text{A4})$$

or

$$\rho_{N,J+1}(\mathcal{Q}, \mathcal{Q}'; t) = -\frac{iN}{\hbar[N\gamma + (J+1)\gamma_1]} \Theta_F(\mathcal{Q}, \mathcal{Q}') \rho_{N-1,J+1}(\mathcal{Q}, \mathcal{Q}'; t) - \frac{i(J+1)}{\hbar[N\gamma + (J+1)\gamma_1]} \Theta_1(\mathcal{Q}, \mathcal{Q}') \rho_{N,J}(\mathcal{Q}, \mathcal{Q}'; t). \quad (\text{A5})$$

Then we have the anchor equation for Eq. (A3) in the form

$$\begin{aligned} \frac{\partial}{\partial t} \rho_{N,j}(\mathcal{Q}, \mathcal{Q}'; t) = & - \left[ \frac{i}{\hbar} \mathcal{L}_A(\mathcal{Q}, \mathcal{Q}') + N\gamma + j\gamma_1 \right] \rho_{N,j}(\mathcal{Q}, \mathcal{Q}'; t) \\ & - \frac{i}{\hbar} \sum_{m=0}^j \left[ \prod_{\alpha=0}^m \frac{-i(N+1)}{\hbar[(N+1)\gamma + (j-\alpha)\gamma_1]} \right] (\mathcal{Q} - \mathcal{Q}') [\Theta_1(\mathcal{Q}, \mathcal{Q}')]^m \Theta_F(\mathcal{Q}, \mathcal{Q}') \rho_{N,j-m}(\mathcal{Q}, \mathcal{Q}'; t) \\ & - \frac{i}{\hbar} (\mathcal{Q} - \mathcal{Q}') \rho_{N,j+1}(\mathcal{Q}, \mathcal{Q}'; t) - \frac{iN}{\hbar} \Theta_F(\mathcal{Q}, \mathcal{Q}') \rho_{N-1,j}(\mathcal{Q}, \mathcal{Q}'; t) \\ & - \frac{iJ}{\hbar} \Theta_1(\mathcal{Q}, \mathcal{Q}') \rho_{N,j-1}(\mathcal{Q}, \mathcal{Q}'; t) \quad (N\gamma \gg \omega_A), \end{aligned} \quad (\text{A6})$$

$$\begin{aligned} \frac{\partial}{\partial t} \rho_{n,J}(\mathcal{Q}, \mathcal{Q}'; t) = & - \left[ \frac{i}{\hbar} \mathcal{L}_A(\mathcal{Q}, \mathcal{Q}') + n\gamma + J\gamma_1 \right] \rho_{n,J}(\mathcal{Q}, \mathcal{Q}'; t) - \frac{i}{\hbar} (\mathcal{Q} - \mathcal{Q}') \rho_{n+1,J}(\mathcal{Q}, \mathcal{Q}'; t) \\ & - \frac{i}{\hbar} \sum_{k=0}^n \left[ \prod_{\alpha=0}^k \frac{-i(J+1)}{\hbar[(n-\alpha)\gamma + (J+1)\gamma_1]} \right] (\mathcal{Q} - \mathcal{Q}') [\Theta_F(\mathcal{Q}, \mathcal{Q}')]^k \Theta_1(\mathcal{Q}, \mathcal{Q}') \rho_{n-k,J}(\mathcal{Q}, \mathcal{Q}'; t) \\ & - \frac{iN}{\hbar} \Theta_F(\mathcal{Q}, \mathcal{Q}') \rho_{n-1,J}(\mathcal{Q}, \mathcal{Q}'; t) - \frac{iJ}{\hbar} \Theta_1(\mathcal{Q}, \mathcal{Q}') \rho_{n,J-1}(\mathcal{Q}, \mathcal{Q}'; t) \quad (J\gamma_1 \gg \omega_A), \end{aligned} \quad (\text{A7})$$

$$\begin{aligned} \frac{\partial}{\partial t} \rho_{N,J}(\mathcal{Q}, \mathcal{Q}'; t) = & - \left[ \frac{i}{\hbar} \mathcal{L}_A(\mathcal{Q}, \mathcal{Q}') + N\gamma + J\gamma_1 \right] \rho_{N,J}(\mathcal{Q}, \mathcal{Q}'; t) \\ & - \frac{i}{\hbar} \sum_{m=0}^J \left[ \prod_{\alpha=0}^m \frac{-i(N+1)}{\hbar[(N+1)\gamma + (J-\alpha)\gamma_1]} \right] (\mathcal{Q} - \mathcal{Q}') [\Theta_1(\mathcal{Q}, \mathcal{Q}')]^m \Theta_F(\mathcal{Q}, \mathcal{Q}') \rho_{N,J-m}(\mathcal{Q}, \mathcal{Q}'; t) \\ & - \frac{i}{\hbar} \sum_{k=0}^N \left[ \prod_{\alpha=0}^k \frac{-i(J+1)}{\hbar[(N-\alpha)\gamma + (J+1)\gamma_1]} \right] (\mathcal{Q} - \mathcal{Q}') [\Theta_F(\mathcal{Q}, \mathcal{Q}')]^k \Theta_1(\mathcal{Q}, \mathcal{Q}') \rho_{N-k,J}(\mathcal{Q}, \mathcal{Q}'; t) \\ & - \frac{iN}{\hbar} \Theta_F(\mathcal{Q}, \mathcal{Q}') \rho_{N-1,J}(\mathcal{Q}, \mathcal{Q}'; t) - \frac{iJ}{\hbar} \Theta_1(\mathcal{Q}, \mathcal{Q}') \rho_{N,J-1}(\mathcal{Q}, \mathcal{Q}'; t) \quad (N\gamma, J\gamma_1 \gg \omega_A). \end{aligned} \quad (\text{A8})$$

In the Gaussian-white noise limit,  $\gamma \gg \omega_A$ , we may set  $N=0$  in the above equations. Then we have

$$\begin{aligned} \frac{\partial}{\partial t} \rho_{0,j}(\mathcal{Q}, \mathcal{Q}'; t) = & - \left[ \frac{i}{\hbar} \mathcal{L}_A(\mathcal{Q}, \mathcal{Q}') - \frac{1}{\hbar^2 \gamma} (\mathcal{Q} - \mathcal{Q}') \Theta_F(\mathcal{Q}, \mathcal{Q}') + j\gamma_1 \right] \rho_{0,j}(\mathcal{Q}, \mathcal{Q}'; t) \\ & - \frac{i}{\hbar} (\mathcal{Q} - \mathcal{Q}') \rho_{0,j+1}(\mathcal{Q}, \mathcal{Q}'; t) - \frac{iJ}{\hbar} \Theta_1(\mathcal{Q}, \mathcal{Q}') \rho_{0,j-1}(\mathcal{Q}, \mathcal{Q}'; t), \end{aligned} \quad (\text{A9})$$

and

$$\begin{aligned} \frac{\partial}{\partial t} \rho_{0,J}(\mathcal{Q}, \mathcal{Q}'; t) = & - \left[ \frac{i}{\hbar} \mathcal{L}_A(\mathcal{Q}, \mathcal{Q}') - \frac{1}{\hbar^2 \gamma} (\mathcal{Q} - \mathcal{Q}') \Theta_F(\mathcal{Q}, \mathcal{Q}') + J\gamma_1 \right] \rho_{0,J}(\mathcal{Q}, \mathcal{Q}'; t) \\ & - \frac{1}{\hbar^2 \gamma_1} (\mathcal{Q} - \mathcal{Q}') \Theta_1(\mathcal{Q}, \mathcal{Q}') \rho_{0,J}(\mathcal{Q}, \mathcal{Q}'; t) - \frac{iJ}{\hbar} \Theta_1(\mathcal{Q}, \mathcal{Q}') \rho_{0,J-1}(\mathcal{Q}, \mathcal{Q}'; t), \end{aligned} \quad (\text{A10})$$

for  $J\gamma_1 \gg \omega_A$ . The above result is the low-temperature correction for the quantum Fokker-Planck equation (1.6).

#### APPENDIX B: DERIVATION OF EQ. (2.26) FROM THE LANGEVIN APPROACH

The classical Fokker-Planck equation for Gaussian-Markovian noise, Eq. (2.26), can be obtained from the

Langevin approach by assuming a Gaussian-Markovian noise. The motion for a particle modulated by a colored noise is expressed by the generalized Langevin equation.<sup>25</sup> For a quantum system corresponding to the Hamiltonian of Eq. (1.9), the generalized Langevin equation is written as<sup>26,27</sup>

$$\frac{d}{dt}p(t) = -\frac{\partial U(q)}{\partial q} - \frac{2}{\hbar} \int_{t_i}^t d\tau \bar{L}_1(t-\tau)p(\tau) + R(t), \quad (\text{B1})$$

$$\frac{dq}{dt} = \frac{p(t)}{M},$$

where the random noise  $R(t)$  has the following relations:

$$\langle R(t) \rangle = 0, \quad \langle R(t')R(t) \rangle = L_2(t'-t), \quad (\text{B2})$$

in which  $\bar{L}_1$  and  $L_2$  are defined by Eqs. (2.4) and (2.5), respectively. The stochastic Liouville equation for a distribution function  $f(p, q; t)$  corresponding to Eq. (B1) can be written as

$$\frac{\partial}{\partial t}f(p, q; t) = \Omega(p, q; t)f(p, q; t). \quad (\text{B3})$$

Here,

$$\Omega(p, q; t) = -\frac{\partial}{\partial q} \frac{p}{M} - \frac{\partial}{\partial p} \left[ -\frac{\partial U(q)}{\partial q} - \frac{2}{\hbar} \int_{t_i}^t d\tau \bar{L}_1(t-\tau)p(\tau) + R(t) \right], \quad (\text{B4})$$

with

$$U(q) = U_b(q) - \frac{\bar{L}_1(0)}{\hbar} q^2. \quad (\text{B5})$$

The distribution function for  $A$  is defined by  $W(p, q; t) = \langle f(p, q; t) \rangle$ , where  $\langle \rangle$  means an average of  $\Omega(p, q; t)$ , and we set the initial condition as

$$f(p, q; t_i) = W(p, q; t_i). \quad (\text{B6})$$

The stochastic process  $\Omega(p, q; t)$  is essentially Gaussian, and one obtains

$$\begin{aligned} W(p, q; t) &= \exp \left[ \int_{t_i}^t d\tau' \langle \Omega(p, q; \tau') \rangle + \int_{t_i}^t d\tau' \int_{t_i}^{\tau'} d\tau \langle \Omega(p, q; \tau') \Omega(p, q; \tau) \rangle \right] W(p, q; t_i) \\ &= \exp \left[ -\int_{t_i}^t d\tau' L_A(p, q) + \frac{\partial}{\partial p} \int_{t_i}^{\tau'} d\tau' \int_{t_i}^{\tau'} d\tau \left[ \frac{2p(\tau)}{\hbar} \bar{L}_1(\tau'-\tau) + \frac{\partial}{\partial p} L_2(\tau'-\tau) \right] \right] W(p, q; t_i), \end{aligned} \quad (\text{B7})$$

where  $L_A(p, q)$  is given by Eq. (2.28). For the spectral density Eq. (2.8) in the high-temperature limit,  $\bar{L}_1$  and  $L_2$  are in the form of exponentially decaying functions [see Eqs. (2.9) and (2.10)] which correspond to Doob's theorem for the Gaussian-Markovian processes. Thus by considering the time derivative of the following elements:

$$\begin{aligned} W_n(p, q; t) &= \left[ \int_{t_i}^t d\tau e^{-\gamma(t-\tau)} \frac{\eta\gamma}{M} \left[ p(\tau) + \frac{M}{\beta} \frac{\partial}{\partial p} \right] \right]^n \\ &\times \exp \left[ -\int_{t_i}^t d\tau' L_A(p, q) + \frac{\partial}{\partial p} \int_{t_i}^{\tau'} d\tau' \int_{t_i}^{\tau'} d\tau e^{-\gamma(\tau'-\tau)} \frac{\eta\gamma}{M} \left[ p(\tau) + \frac{M}{\beta} \frac{\partial}{\partial p} \right] \right] W(p, q; t_i), \end{aligned} \quad (\text{B8})$$

we may deduce the same hierarchical differential equation as Eq. (2.26).

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