Dynamical Reaction Coordinate in Thermally Fluctuating Environment in the Framework of Multidimensional Generalized Langevin Equations

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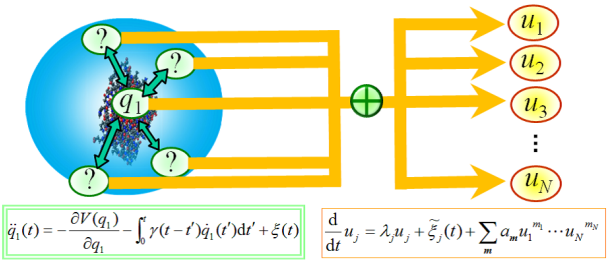
Nonlinear generalized Langevin equation with memory due to thermal environment is equivalent to a memoryless equation with increased dimensionality



A framework recently developed for the extraction of a dynamic reaction coordinate to mediate reactions buried in multidimensional Langevin equation is extended to the generalized Langevin equations without a priori assumption on the forms of the potential (in general, nonlinearly coupled systems) and the friction kernel. The equation of motion with memory effect can be transformed into an equation without memory at the cost of an increase in the dimensionality of the system, and hence the theoretical framework developed for the (nonlinear) Langevin formulation can be generalized to the non-Markovian process with colored noise. It is found that the increased dimension can be physically interpreted as effective modes of the fluctuating environment. As an illustrative example, we apply this theory to a multidimensional generalized Langevin equation for motion on the Müller-Brown potential surface with an exponential friction kernel. Numerical simulations find a boundary between the highly reactive region and the less reactive region in the space of initial conditions. The location of the boundary is found to depend significantly on both the memory kernel and the nonlinear couplings. The theory extracts a reaction coordinate whose sign determines the fate of the reaction taking into account the thermally fluctuating environments, the memory effect, and the nonlinearities. It is found that the location of the boundary of reactivity is satisfactorily reproduced as the zero of the statistical average of the new reaction coordinate, which is an analytical functional of both the original position coordinates and velocities of the system, and of the properties of the environment.

I. INTRODUCTION

Many chemical reactions and arrangements of the conformation of biomolecules occur in condensed phase under the influence of stochastic random forces and the friction exerted by the surrounding solvent molecules. Since the pioneering work by Kramers,[1] the Langevin equation has been often utilized to represent the dynamical processes in condensed phase. The chemical reaction was originally modeled as a stochastic motion surmounting a barrier on a one-dimensional potential surface along a chosen coordinate considered to describe the progress of the reaction. In his pioneering work Kramers found that the rate constant is proportional to the inverse of the friction constant γ in the case of high viscosity whilst it is proportional to γ in the case of low viscosity, resulting in a turn over in the dependence of the rate constant on γ. Later, Grote and Hynes[2] reformulated the theory of Kramers under the existence of memory by using a generalized Langevin equation. In a generalized Langevin equation, the acceleration of the position coordinate is determined by the gradient of the potential of mean force, the friction, and the external force arising from the environment. The friction depends linearly on the history of the velocity of the system, resulting in memory effects. If the friction kernel decays much more rapidly than the typical timescale of the reaction, the equation can be approximated by a Langevin equation without memory.

It was shown[3] by using the projection operator method that any high-dimensional Hamiltonian system can formally be cast into a generalized Langevin equation with a small number of variables. All the detailed dynamics of the "solvent" modes that are projected out are reflected in a time propagation of the external force and the friction kernel. The time evolution of the external force is also given by a form of generalized

Langevin equation[4], which then contains an external force of the next order. This procedure can be repeated until sufficient degrees of freedom have been taken and one can make some approximation to the remaining "random force." Zwanzig[5] showed that, if the solvent can be expressed as a collection of harmonic oscillators and the coupling with the system is bilinear, the random force can be regarded as a Gaussian random variable.

Supposing the shape of the potential at the barrier top is an inverse parabola along the chosen reaction coordinate, theory by Kramers[1] and by Grote and Hynes[2] can provide analytical formula for the rate constant dependent on the friction. Recently, Grote-Hynes theory has been successfully applied to complex systems with many degrees of freedom, such as enzymatic reactions.[6] In particular, it was shown that Kramers theory severely underestimates the transmission coefficient, implying the necessity of including the memory term in the generalized Langevin equation. The interplay of the multiple vibrational modes in the environment with the naïvely chosen reaction coordinate was also pointed out, although the analyses were performed only at the normal mode level. When the system contains multiple degrees of freedom, the effect of the nonlinear couplings within the system on the reaction dynamics should also be taken into account. It is a nontrivial issue whether we can construct the concept of "reaction coordinate," as a single one-dimensional coordinate (decoupled from other coordinates) that can describe the progress of the reaction and, in principle, predict the destination of the reaction, that is, reactants or products.

Bartsch *et al.*[7–10] scrutinized the geometrical structure of reaction in the framework of a multidimensional Langevin equation within the harmonic approximation, that is, each mode coupled bilinearly with each other. They introduced a shifted coordinate system that can take into account time-dependent fluctuating force. They showed that one can extract the reaction coordinate decoupled from the other nonreactive coordinates and hence extract the non-recrossing dividing surface (=transition state) in that shifted system. They also extended the treatment to the case of a generalized Langevin equation.[8] However, the existence of their reaction coordinate crucially depends on the harmonic approximation for the potential, and therefore could be validated only at very low temperature.

Recently, in order to extract the reaction coordinate and the no-return transition state for nonlinearly coupled multimode systems in a fluctuating environment, we have presented a theory[11–14] based on the concept of normal form[15] with the time-dependent formulation[16] within the framework of the multidimensional Langevin formulation. It was shown that, under certain conditions, a nonlinear coordinate transformation can be performed to provide a new reaction coordinate independent of all the other coordinates similarly to the case of Hamiltonian systems in the region of saddles.[17–36] The sign of this reaction coordinate solely can determine whether the reaction system proceeds to from the products or is reflected back to the reactants. The nonlinear formulation, however, was so far restricted to multidimensional Langevin equations without memory effects.

In this paper we generalize the theory[11–14] to generalized Langevin equations without postulating the forms of the potential or the friction kernel. We exploit the equivalence between the generalized Langevin equation with memory kernel and a memoryless equation of motion containing larger number of dimensions, which can be physically interpreted as a set of effective modes of the environment that affect the reaction dynamics. As an example, we analyze the reaction dynamics represented by a generalized Langevin equation on Müller-Brown potential[37] with an exponential friction kernel with several different damping timescales. It is found that the reaction coordinate and the reaction boundary determining the reactivity can be extracted from nonlinearly coupled multimode systems with thermal fluctuation even when there is memory.

II. THEORY

A. Generalized normal mode transformation

In this paper we use a generalized Langevin equation to describe chemical reactions under the effect of colored noise.

$$\ddot{q}_j = -\frac{\partial U}{\partial q_j} - \int_0^t d\tau \sum_{i=1}^{d} \gamma_{ij}(\tau)\dot{q}_i(t-\tau) + \xi_j(t), \qquad (1)$$

where $q_1, q_2, \ldots, q_d$ are position coordinates of the system (d is the number of degrees of freedom of the system), $U(q)$ the potential of mean force, $\gamma_{ij}(\tau)$ the friction kernel and $\xi_j(t)$ the random force exerted by the solvent. The friction kernel and the random force are related to each other through the fluctuation-dissipation theorem,

$$\langle \xi_i(t)\xi_j(t')\rangle = 2k_{\mathrm{B}}T\gamma_{ij}(|t-t'|), \qquad (2)$$

where $\langle\cdot\rangle$ denotes the ensemble average at equilibrium, k_{B} is Boltzmann constant and T temperature. The potential force is decomposed into the harmonic and the anharmonic terms:

$$-\frac{\partial U}{\partial q_j} = -\sum_{i=1}^{d} a_{ij}q_i + \sum_{k=1}^{\infty}\varepsilon^k \sum_{|m|=k+1} \alpha_{j,m} {q_1}^{m_1}\cdots{q_d}^{m_d}, \qquad (3)$$

where a_{ij} and $\alpha_{j,m}$ are the expansion coefficients of the linear and the higher order terms, respectively. The origin of the coordinate system is set to be at a stationary point on the potential $U(q)$. We introduce a formal parameter ε to employ the so-called normal form perturbation theory as in our recent work on multidimensional Langevin formulation.[11] The k-th order perturbation consists of the polynomial of degree $(k+1)$ in q. The crux to handle the nonlinearity is to regard the nonlinear term as a function of time through the time dependence of q_j's:

$$f_j(t) \stackrel{\mathrm{def}}{=} \sum_{k=1}^{\infty}\varepsilon^k \sum_{|m|=k+1} \alpha_{j,m} {q_1}^{m_1}(t)\cdots{q_d}^{m_d}(t). \qquad (4)$$

We also define

$$g_j(t) \stackrel{\mathrm{def}}{=} \xi_j(t) + f_j(t). \qquad (5)$$

Then Eq. (1) can be expressed as

$$\ddot{q}_j = -\sum_{i=1}^{d} a_{ij} q_i - \int_0^t d\tau \sum_{i=1}^{d} \gamma_{ij}(\tau)\dot{q}_i(t-\tau) + g_j(t). \tag{6}$$

Note that Eq. (6) is a generalized Langevin equation being nonlinear in q_j's, since the term $g_j(t)$ includes the nonlinear force, and the time dependence in g_j arises from ξ_j and f_j where the time dependence originates from q_j's.

We now follow the treatment of Bartsch *et al.*[8] with a modification which is necessary to include the nonlinearities. Let us consider a formal solution of Eq. (6) by using Laplace transform

$$\hat{q}_j(\lambda) = \int_0^{+\infty} \exp(-\lambda t) q_j(t) dt, \tag{7}$$

and its inverse

$$q_j(t) = \frac{1}{2\pi \mathrm{i}} \int_{c-\mathrm{i}\infty}^{c+\mathrm{i}\infty} \exp(\lambda t)\hat{q}_j(\lambda) d\lambda, \tag{8}$$

where the real constant c is taken on the right side of all the singularities of $\hat{q}_j(\lambda)$ on the complex plane. Eq. (6) is, then, transformed into the following form,

$$\begin{aligned} &\lambda^2 \hat{q}_j(\lambda) - \lambda q_j(0) - \dot{q}_j(0) \\ &= -\sum_{i=1}^{d} a_{ij}\hat{q}_i(\lambda) - \sum_{i=1}^{d} \hat{\gamma}_{ij}(\lambda)\{\lambda \hat{q}_i(\lambda) - q_i(0)\} + \hat{g}_j(\lambda). \end{aligned} \tag{9}$$

In matrix form,

$$\begin{aligned} &\lambda^2 \hat{q}(\lambda) - \lambda q(0) - \dot{q}(0) \\ &= -A\hat{q}(\lambda) - \hat{\Gamma}(\lambda)\{\lambda \hat{q}(\lambda) - q(0)\} + \hat{g}(\lambda), \end{aligned} \tag{10}$$

where $A = (a_{ij})$, $\Gamma = (\gamma_{ij})$, $q = (q_j)$, $g = (g_j)$, and the hat means Laplace transform as usual. By rearranging the terms, we have

$$\begin{aligned} &\left\{\lambda^2 + \lambda\hat{\Gamma}(\lambda) + A\right\}\hat{q}(\lambda) \\ &= \left\{\lambda + \hat{\Gamma}(\lambda)\right\} q(0) + \dot{q}(0) + \hat{g}(\lambda). \end{aligned} \tag{11}$$

We define

$$B(\lambda) \stackrel{\text{def}}{=} \lambda^2 + \lambda\hat{\Gamma}(\lambda) + A, \tag{12}$$

and the formal solution for $\hat{q}(\lambda)$ is then given by

$$\begin{aligned} \hat{q}(\lambda) &= B(\lambda)^{-1}\left[\left\{\lambda + \hat{\Gamma}(\lambda)\right\} q(0) + \dot{q}(0) + \hat{g}(\lambda)\right] \\ &= \lambda^{-1} q(0) + B(\lambda)^{-1}\left[-\lambda^{-1} A q(0) + \dot{q}(0) + \hat{g}(\lambda)\right]. \end{aligned} \tag{13}$$

By applying the inverse Laplace transformation, the formal solution (13) is brought back to the time domain:

$$\begin{aligned} q(t) = &\frac{1}{2\pi \mathrm{i}} \int_{c-\mathrm{i}\infty}^{c+\mathrm{i}\infty} d\lambda \exp(\lambda t) \\ &\Bigg[\lambda^{-1} q(0) + B(\lambda)^{-1}\dot{q}(0) - \lambda^{-1} B(\lambda)^{-1} A q(0) \\ &+ B(\lambda)^{-1} \int_0^{+\infty} dt' g(t') \exp(-\lambda t')\Bigg]. \end{aligned} \tag{14}$$

The integration over λ is evaluated by a complex path integral using residues. The poles of the matrix $B(\lambda)^{-1} = \left\{\lambda^2 + \lambda\hat{\Gamma}(\lambda) + A\right\}^{-1}$ coincide with the solutions of the nonlinear eigenvalue equation

$$\left[{\lambda_n}^2 + \lambda_n \hat{\Gamma}(\lambda_n) + A\right] v_n = 0. \tag{15}$$

To obtain the residues, we first diagonalize the matrix

$$B(\lambda) = \sum_i \beta_i(\lambda) w_i(\lambda) w_i(\lambda)^{\mathrm{T}}. \tag{16}$$

The inverse matrix of B is then given by

$$B(\lambda)^{-1} = \sum_i \frac{1}{\beta_i(\lambda)} w_i(\lambda) w_i(\lambda)^{\mathrm{T}}. \tag{17}$$

At the eigenvalues $\lambda = \lambda_n$ in Eq. (15), one of $\beta_i(\lambda)$ becomes zero and the corresponding vector $w_i(\lambda)$ coincides with the eigenvector v_n. If the poles are simple, we can assume $\beta_1(\lambda_n) = 0$ without loss of generality. We then make a Taylor expansion around the pole $\lambda = \lambda_n$:

$$\beta_1(\lambda) = \beta_1'(\lambda_n)(\lambda - \lambda_n) + O\left((\lambda - \lambda_n)^2\right), \tag{18}$$

and obtain the residue

$$\begin{aligned} \operatorname*{Res}_{\lambda=\lambda_n} B(\lambda)^{-1} &= \kappa_n v_n v_n^{\mathrm{T}}, \\ \kappa_n &\stackrel{\text{def}}{=} \beta_1'(\lambda_n)^{-1}. \end{aligned} \tag{19}$$

By using these residues, Eq. (14) is written as

$$\begin{aligned} q(t) = \sum_n v_n \Bigg[&\exp(\lambda_n t)\kappa_n v_n^{\mathrm{T}}\left\{\dot{q}(0) - \lambda_n^{-1} A q(0)\right\} \\ &+ \kappa_n \int_0^t dt' \exp(\lambda_n (t-t')) v_n^{\mathrm{T}} g(t')\Bigg]. \end{aligned} \tag{20}$$

We now define normal mode coordinates u_n by the inside of [ ] in this equation:

$$\begin{aligned} u_n \stackrel{\text{def}}{=} &\exp(\lambda_n t)\kappa_n v_n^{\mathrm{T}}\left\{\dot{q}(0) - \lambda_n^{-1} A q(0)\right\} \\ &+ \kappa_n \int_0^t dt' \exp(\lambda_n (t-t')) v_n^{\mathrm{T}} g(t'). \end{aligned} \tag{21}$$

Then q and u are related by

$$q = \sum_n v_n u_n. \tag{22}$$

The inverse of Eq. (22) at $t = 0$ (*i.e.*, the initial condition of u) is given by Eq. (21)

$$u_n(0) = \kappa_n v_n^{\mathrm{T}}\left\{\dot{q}(0) - \lambda_n^{-1} A q(0)\right\}. \tag{23}$$

>From Eq. (21), it can be shown that u obeys the following equation of motion:

$$\dot{u}_n = \lambda_n u_n + \kappa_n v_n^{\mathrm{T}} g(t). \tag{24}$$

Here $g(t)=\xi(t)+f(q(t))$ [Eq. (5)] and f is a polynomial of q_j's [Eq. (4)]. Since q_j's are now linear combinations of u_n's [Eq. (22)], we can express f as polynomials of u_n's. Then we have

$$\dot{u}_n=\lambda_n u_n+\tilde{\xi}_n(t)+\sum_{k=1}^{\infty}\varepsilon^k\sum_{|m|=k+1}\beta_{j,m}{u_1}^{m_1}\cdots{u_N}^{m_N}, \quad (25)$$

where N is the total number of the normal modes, $\tilde{\xi}_n(t)\stackrel{\text{def}}{=}\kappa_n v_n^{\mathrm{T}}\xi(t)$ is the random force projected onto the nth normal mode, and $\beta_{j,m}$'s are the expansion coefficients obtained by substituting Eq. (22) into Eq. (4). The equation of motion (25) has the same form as the equation for u in the case of a multidimensional Langevin formulation[11,12], which allows us to follow the same normal form procedure[38–40] as presented in Refs. 11 and 12.

The only difference from the previous formulation[11,12] is the increase of dimension needed to describe the system, that is, N can be larger than $2d$ for some friction kernels (In Sec. II B, we demonstrate a case in which the friction kernel is expressed as a linear combination of exponential decays). The number and the values of the eigenvalues depend on the specific form of the friction kernel and that of the potential of mean force. We assume here that, as in the isolated system,[17–36] there is one eigenmode with a positive real eigenvalue (i.e., an unstable mode corresponding to the motion sliding down the barrier). We number this unstable mode as 1 ($\lambda_1>0$).

The number of eigenmodes can be more than $2d$. Note that the friction kernel Γ arises from dynamical interactions between the system and the surrounding solvents. Such extra eigenmodes can be regarded as normal modes of the extended system consisting of solute and solvent molecules. Moreover, the friction kernel does not necessarily contain all the motions of the solvent molecules but includes those which affect the motion of the solute. In Sec. II C, it is shown that the number of the eigenmodes is finite if the friction kernel has a simple form like cosines or exponential decays with integer powers of time, which have been found in molecular dynamics simulations.[41,42] Therefore the above procedure is a way of extracting the effective finite degrees of freedom from the vast (practically infinite) dimensions of solvents.

The equation of motion [Eq. (25)] for the normal mode coordinates u can be solved in terms of the time-dependent normal form perturbation theory,[11,38–40] which is a time-dependent classical analog of the Van Vleck perturbation theory studied in molecular spectroscopy. The details of the procedure are shown in previous works.[11] Briefly, we introduce a nonlinear coordinate transformation $u\mapsto y$. The unstable mode y_1 can be expressed as a polynomial expansion of u:

$$\begin{aligned}y_1=&u_1-S[\lambda_1,\tilde{\xi}_1](t)\\&+\sum_{k=1}^{\infty}\varepsilon^k\sum_{|m|\le k+1}W_m^{(k)}[\lambda,\xi](t){u_1}^{m_1}{u_2}^{m_2}\cdots{u_N}^{m_N},\end{aligned} \quad (26)$$

where the time-dependent coefficients $S[\lambda_1,\tilde{\xi}_1](t)$ and $W_m^{(k)}[\lambda,\xi](t)$ are linear and nonlinear functionals of the random force, respectively. The equation of motion for y_1 is independent of the other modes $y_2,y_3,\ldots,y_N$:

$$\dot{y}_1\approx\{\lambda_1+c_1(t)\}y_1, \quad (27)$$

with the coefficient $c_1(t)$ only depending on t and not on $y_2,\ldots,y_N$. Under a moderate condition for $c_1(t)$, that is,

$$\lim_{t\to+\infty}\left|\frac{1}{t}\int^t c_1(t')dt'\right|<\lambda_1 \quad (28)$$

(λ_1 arises from the zeroth order of the perturbation theory while the term c_1 is from the higher orders) the sign of y_1 solely determines the direction of the motion departing from the barrier, that is, whether the system undergoes the reaction to form the product or gets reflected back to the reactant. The value of y_1 as a function of the initial condition $(q(0),\dot{q}(0))$ is given by substituting Eq. (23) into Eq. (26). The result can also be expressed in the form of polynomials:

$$\begin{aligned}y_1=&a_1q_1+a_2\dot{q}_1-S[\lambda_1,\tilde{\xi}_1](t)+F_0[\xi](t)\\&+\sum\nolimits_{|m|\ge2}w_m{q_1}^{m_1}\cdots{q_d}^{m_d}{\dot{q}_1}^{m_{d+1}}\cdots{\dot{q}_d}^{m_{2d}}\\&+\sum_{|m|\ge1}F_m[\xi](t){q_1}^{m_1}\cdots{q_d}^{m_d}{\dot{q}_1}^{m_{d+1}}\cdots{\dot{q}_d}^{m_{2d}}.\end{aligned} \quad (29)$$

The first two terms correspond to the linear combination in Eq. (23). When we introduce position space normal mode coordinates, which diagonalize the Hessian matrix A, and the friction kernel does not have off-diagonal elements, we have only q_1 and $\dot{q}_1$ in the expression of u_1. In general cases, however, we should have a linear combination of all the q_j's and $\dot{q}_j$'s in the first parts of Eq. (29). The other terms in Eq. (29) originate from the effects of nonlinearity, with the coefficients $F_0[\xi](t)$ and $F_m[\xi](t)$, both nonlinear functionals of the random force. The terms with w_m (*i.e.*, without ξ) can be regarded as intrinsic nonlinear effects of the system, while others are combinations of the nonlinearity and the external random force. The transformation Eq. (29) depends on each specific instance of the random force $\xi(t)$. Since it is impossible to know the instance of the random force for all the time t in advance, we have suggested[11] to take the ensemble average of y_1 with respect to all the possible realizations of the random force:

$$\begin{aligned}\langle y_1\rangle=&a_1q_1+a_2\dot{q}_1+\bar{F_0}(k_{\mathrm{B}}T)\\&+\sum\nolimits_{|m|\ge2}w_m{q_1}^{m_1}\cdots{q_d}^{m_d}{\dot{q}_1}^{m_{d+1}}\cdots{\dot{q}_d}^{m_{2d}}\\&+\sum_{|m|\ge1}\bar{F_m}(k_{\mathrm{B}}T){q_1}^{m_1}\cdots{q_d}^{m_d}{\dot{q}_1}^{m_{d+1}}\cdots{\dot{q}_d}^{m_{2d}},\end{aligned} \quad (30)$$

where $\bar{F_0}(k_{\mathrm{B}}T)$ and $\bar{F_m}(k_{\mathrm{B}}T)$ are the ensemble averages of the corresponding coefficients in Eq. (29), and depend on the temperature through Eq. (2) instead of each instance of $\xi(t)$. Note that the transformations Eq. (29) and Eq. (30) are valid only for $t=0$ because Eq. (23) is only for $t=0$. For the purpose of judging the reactivity for a given initial condition $(q(0),\dot{q}(0))$, these equations are sufficient.

B. Proof of invertibility and noninvertibility of the normal mode transformation

In this subsection, we investigate an application of the present theory to a specific one-dimensional model coupled bilinearly to a harmonic bath. For this system, the relation between the total Hamiltonian (system + bath) and the generalized Langevin description has been established.[5] The goal of this subsection is to clarify the relation between the method presented in Sec. II A, which starts from the generalized Langevin equation, and the normal modes of the total Hamiltonian system.

It has been shown[5] that a generalized Langevin equation with Gaussian random force can be exactly derived if the "solvent" modes are harmonic oscillators and the interaction with the "solute" is bilinear. In this case, the total system is described in the region of a rank-one saddle by the following Hamiltonian:

$$H_{\rm total} = \frac{1}{2}{p_0}^2 - \frac{1}{2}b^2{q_0}^2 + U_{\rm NL}(q_0) + \sum_{j=1}^{N}\left[\frac{1}{2}{p_j}^2 + \frac{1}{2}\left(\omega_j q_j + \frac{c_j}{\omega_j}q_0\right)^2\right], \quad (31)$$

where q_0 and q_j for $j = 1, 2, \ldots, N$ are the position coordinates of the solute (= reactive mode) and the solvent (= nonreactive modes), respectively, p_0 and p_j their conjugate momenta. We have divided the potential along the reactive mode q_0 into the quadratic ($-\frac{1}{2}b^2{q_0}^2$, with b being a real number) and the nonlinear ($U_{\rm NL}(q_0)$) parts. The solvents are described as a set of harmonic oscillators with frequencies ω_j, interacting with the solute with the coupling constants c_j. Zwanzig[5] showed that this system is equivalent to a generalized Langevin equation

$$\ddot{q}_0 = b^2 q_0 - U'_{\rm NL}(q_0) - \int_0^t \gamma(\tau)\dot{q}_0(t-\tau)d\tau + \xi(t), \quad (32)$$

with the friction kernel given by

$$\gamma(\tau) = \sum_{j=1}^{N}\frac{{c_j}^2}{{\omega_j}^2}\cos(\omega_j\tau), \quad (33)$$

and the prime in $U'_{\rm NL}$ denotes the derivative with respect to q_0. The purpose of this subsection is to prove that the full phase space of the system, which is a $2(N+1)$-dimensional space parametrized by (q_0, q_1, …, q_N, p_0, p_1, …, p_N), can be completely recovered from the generalized Langevin equation, Eq. (32), if we know the exact form of the friction kernel of Eq. (33).

The harmonic part of the total Hamiltonian is expressed in matrix form

$$H_{\rm total} = \frac{1}{2}|p|^2 + \frac{1}{2}q^{\rm T}Kq + U_{\rm NL}(q_0), \quad (34)$$

where

$$q = \begin{pmatrix} q_0 \\ q_1 \\ \vdots \\ q_N \end{pmatrix}, p = \begin{pmatrix} p_0 \\ p_1 \\ \vdots \\ p_N \end{pmatrix},$$

$$K = \begin{pmatrix} -b^2 + c_0 & c_1 & c_2 & \cdots & c_N \\ c_1 & {\omega_1}^2 & 0 & \cdots & 0 \\ c_2 & 0 & {\omega_2}^2 & \ddots & \vdots \\ \vdots & \vdots & \ddots & \ddots & 0 \\ c_N & 0 & \cdots & 0 & {\omega_N}^2 \end{pmatrix},$$

$$c_0 = \sum_{j=1}^{N}\frac{{c_j}^2}{{\omega_j}^2}. \quad (35)$$

To find the relation between the method presented in Sec. II A and this total Hamiltonian description, we first consider the normal modes in the $2(N+1)$-dimensional Hamiltonian system. Let e_n be eigenvectors of the matrix K:

$$Ke_n = -{\lambda_n}^2 e_n, \qquad (n = 0, 1, \ldots, N), \quad (36)$$

where we have written the eigenvalues as $-{\lambda_n}^2$ for convenience in the following. λ_n is either pure imaginary (for nonreactive or elliptic modes) or pure real (for reactive or hyperbolic mode). The eigenvalues are the solution to the following equation[43]

$${\lambda_n}^2\left\{1 + \sum_{j=1}^{N}\frac{{c_j}^2}{{\omega_j}^2}\frac{1}{{\lambda_n}^2 + {\omega_j}^2}\right\} - b^2 = 0. \quad (37)$$

The components of the eigenvectors are given by[43]

$$e_n = \begin{pmatrix} e_{0n} \\ e_{1n} \\ \vdots \\ e_{Nn} \end{pmatrix},$$

$$e_{0n} = \left\{1 + \sum_{j=1}^{N}\frac{{c_j}^2}{({\lambda_n}^2 + {\omega_j}^2)^2}\right\}^{-1/2},$$

$$e_{jn} = -\frac{c_j}{{\lambda_n}^2 + {\omega_j}^2}e_{0n} \qquad (j = 1, \ldots, N). \quad (38)$$

Since the matrix K is symmetric, the eigenvectors form an orthonormal set

$$e_n^{\rm T}e_m = \delta_{nm}, \quad (39)$$

where δ is Kronecker's delta. By using these eigenvectors, we define the phase space normal mode coordinates as

$$\tilde{u}_n = 2^{-1/2}\left(e_n^{\rm T}q + \lambda_n^{-1}e_n^{\rm T}p\right),$$

$$\tilde{u}_{N+1+n} = 2^{-1/2}\left(e_n^{\rm T}p - \lambda_n e_n^{\rm T}q\right) \qquad (n = 0, \ldots, N), \quad (40)$$

whose inverse transformation is

$$q = 2^{-1/2}\sum_{n=0}^{N} e_n\left(\tilde{u}_n - \lambda_n^{-1}\tilde{u}_{N+1+n}\right),$$
$$p = 2^{-1/2}\sum_{n=0}^{N} e_n\left(\tilde{u}_{N+1+n} + \lambda_n\tilde{u}_n\right). \tag{41}$$

Substituting Eq. (41) into the Hamiltonian equation of motion obeying Eq. (34) we obtain the equation of motion for $\tilde{u}$:

$$\frac{d}{dt}\tilde{u}_n = \lambda_n\tilde{u}_n - \frac{1}{2^{1/2}\lambda_n}e_{0n}U'_{\rm NL}(q_0),$$
$$\frac{d}{dt}\tilde{u}_{N+1+n} = -\lambda_n\tilde{u}_{N+1+n} - \frac{1}{2^{1/2}}e_{0n}U'_{\rm NL}(q_0). \tag{42}$$

Here the argument q_0 of $U'_{\rm NL}$ is replaced by

$$q_0 = 2^{-1/2}\sum_{n=0}^{N} e_{0n}\left(\tilde{u}_n - \lambda_n^{-1}\tilde{u}_{N+1+n}\right), \tag{43}$$

resulting in the coupled differential equation of $\tilde{u}$ only. The terms $U'_{\rm NL}(\tilde{\mathbf{u}})$ are $O(\tilde{u}^2)$. For a positive real value of λ_n, $\tilde{u}_n$ grows exponentially from the origin ($\tilde{u}_n = \tilde{u}_{N+1+n} = 0$) while $\tilde{u}_{N+1+n}$ asymptotically converges to it. In the harmonic approximation, these two modes correspond to the motions departing from and converging to the barrier top along the normal mode reaction coordinate. On the other hand, for pure-imaginary numbers of λ_n, $\tilde{u}_n$ and $\tilde{u}_{N+1+n}$ represent the motions of oscillation perpendicular to the reaction coordinate.

The question to be addressed here is whether these equations of motion in the full phase space can be reconstructed solely from the generalized Langevin equation (32) with respect to the single coordinate q_0. The method presented in Sec. II A can be applied to this system by substituting into Eq. (12) the Laplace transform of the friction kernel Eq. (33) given by

$$\hat{\gamma}(\lambda) = \sum_{j=1}^{N}\frac{{c_j}^2}{{\omega_j}^2}\frac{\lambda}{\lambda^2+{\omega_j}^2}. \tag{44}$$

Then we have

$$B(\lambda) = \lambda^2\left(1+\sum_{j=1}^{N}\frac{{c_j}^2}{{\omega_j}^2}\frac{1}{\lambda^2+{\omega_j}^2}\right) - b^2. \tag{45}$$

The eigenvalue equation $B(\lambda) = 0$ coincides with Eq. (37). Note that the eigenvalues appear in pairs of opposite sign because Eq. (45) is symmetric for the sign of λ. We number the eigenvalues such that $\lambda_{N+1+n} = -\lambda_n$ for $n = 0, 1, \ldots, N$ so as to be consistent with Eq. (42). Since the system is one-dimensional, the eigenvector is $v_n = (1)$. We also find by Eq. (19)

$$\kappa_n^{-1} = \left.\frac{dB(\lambda)}{d\lambda}\right|_{\lambda=\lambda_n} = 2\lambda_n e_{0n}^{-2}. \tag{46}$$

By defining the normal mode coordinates u_n according to Eqs. (22)-(24) in Sec. II A, we then have

$$q_0 = \sum_{n=0}^{2N+1} u_n,$$
$$\dot{u}_n = \lambda_n u_n + \frac{e_{0n}^2}{2\lambda_n}\left\{-U'_{\rm NL}(q_0) + \xi(t)\right\}. \tag{47}$$

In order to establish the equivalence of Eqs. (42) and (47), we first note that the random force in this case can be expressed as in Ref. 5:

$$\xi(t) = \sum_{j=1}^{N}\left(a_j\cos\omega_j t + b_j\sin\omega_j t\right). \tag{48}$$

Then one can see that substituting the following transformation from $\tilde{u}_n$ to u_n into Eqs. (42) and (43) gives Eq. (47):

$$\begin{aligned} u_n =& 2^{-1/2}e_{0n}\tilde{u}_n \\ &+ \sum_{j=1}^{N}\frac{\kappa_n}{\lambda_n^2+\omega_j^2}\Big\{a_j\left(-\lambda_n\cos\omega_j t + \omega_j\sin\omega_j t\right) \\ &+ b_j\left(-\lambda_n\sin\omega_j t - \omega_j\cos\omega_j t\right)\Big\}, \\ u_{N+1+n} =& -2^{-1/2}e_{0n}\tilde{u}_{N+1+n} \\ &- \sum_{j=1}^{N}\frac{\kappa_n}{\lambda_n^2+\omega_j^2}\Big\{a_j\left(\lambda_n\cos\omega_j t + \omega_j\sin\omega_j t\right) \\ &+ b_j\left(\lambda_n\sin\omega_j t - \omega_j\cos\omega_j t\right)\Big\}. \end{aligned} \tag{49}$$

In conclusion, we have proved that the whole $(2N+1)$-dimensional phase space is recovered from the generalized Langevin equation (32) if the friction kernel Eq. (33) is known exactly. In many cases, however, the friction kernel is approximated by exponential functions, exponentially damped trigonometric functions, or a sum of a small number of such terms. The approximation is often satisfactory. As we will see in Sec. II C, the number of normal modes obtained by the method in Sec. II A is relatively small for such simple forms of the friction kernel. The normal modes in this case can be regarded as representative modes that effectively describe the motion of the solvent with a certain small dimensionality. Thus, if the friction kernel is given only approximately, we cannot, and do not need to, recover the true phase space that involves many (practically infinite) solvent modes, but can extract a small number of modes that describe the solvent dynamics effectively whenever the friction kernel exerted by the solvent is approximated well.

C. Dimensionality of the extended system

In Sec. II A, it was found that the generalized Langevin equation with memory [Eq. (1)] is equivalent with the memoryless equation of motion [Eq. (25)], with an increase in dimensionality. In Sec. II B, we showed an example of this in-

creased dimensionality for the case of a friction kernel being a sum of cosine functions. In this subsection, we investigate how much the dimension increases in the case of multi-exponentially decaying kernels. In the case of uniform friction expressed by the sum of exponentials, the equation is reduced to polynomials, for which we definitely know the number of solutions for the nonlinear eigenvalue equation (15). Suppose the friction kernel has the following form:

$$\gamma_{ij}(\tau) = \delta_{ij} \sum_{\ell=1}^{L} g_\ell \exp\left(-\mu_\ell \tau\right), \tag{50}$$

that is, a multi-exponentially decaying function. Here, δ_{ij} is Kronecker's delta, L a certain integer, and g_ℓ and μ_ℓ some constants (complex in general). The constants μ_ℓ can take complex values, so that Eq. (50) includes exponentially decaying trigonometric functions as its special cases. As discussed in Sec. II A and Sec. II B, the expression by Eq. (50) may not be exact, but can be regarded as an approximate fit to the true friction kernel. It is expected that many functions that decay for large τ can be fitted satisfactorily if the number L is taken sufficiently large.

The Laplace transform of Eq. (50) is

$$\hat{\gamma}_{ij}(\lambda) = \delta_{ij} \sum_{\ell=1}^{L} g_\ell \frac{1}{\lambda + \mu_\ell}. \tag{51}$$

By introducing position space normal mode coordinates in advance, we can diagonalize the Hessian matrix A of the potential function:

$$A = \mathrm{diag}(-{\omega^\ddagger}^2, {\omega_2}^2, {\omega_3}^2, \ldots, {\omega_d}^2), \tag{52}$$

where $\omega^\ddagger$, and $\omega_2, \ldots, \omega_d$ are real numbers whose squares correspond to the curvature of the potential at the saddle points, and we have assigned the unstable direction as mode 1. In order for Eq. (15) to have a solution $v_n \neq 0$, we have

$$\begin{aligned} &\det\left({\lambda_n}^2 + \lambda_n \hat{\Gamma}(\lambda) + A\right) \\ &= \left({\lambda_n}^2 + \lambda_n \sum_{\ell=1}^{L} g_\ell \frac{1}{\lambda_n + \mu_\ell} - {\omega^\ddagger}^2\right) \\ &\quad \times \prod_{j=2}^{d} \left({\lambda_n}^2 + \lambda_n \sum_{\ell=1}^{L} g_\ell \frac{1}{\lambda_n + \mu_\ell} + {\omega_j}^2\right) \\ &= 0. \end{aligned} \tag{53}$$

By multiplying $\left(\prod_{\ell=1}^{L}(\lambda_n + \mu_\ell)\right)^d$ on both sides, We have a polynomial equation with degree $(L+2)d$, with $(L+2)d$ solutions in general. Without the effect of environment ($\Gamma = 0$), the system has $2d$ dimensions corresponding to the positions and the velocities. The addition of one exponential term in Eq. (50) increases the effective dimension of the system by d.

If the eigenvalue λ_n satisfies

$${\lambda_n}^2 + \lambda_n \sum_{\ell=1}^{L} g_\ell \frac{1}{\lambda_n + \mu_\ell} - {\omega^\ddagger}^2 = 0, \tag{54}$$

the corresponding eigenvector is given by $v_n = (1, 0, \ldots, 0)$, and if

$${\lambda_n}^2 + \lambda_n \sum_{\ell=1}^{L} g_\ell \frac{1}{\lambda_n + \mu_\ell} + {\omega_j}^2 = 0, \tag{55}$$

we have $v_n = (0, \ldots, 0, \overset{j}{\check{1}}, 0, \ldots, 0)$.

The above can easily be extended to the case of exponential decays multiplied by integer powers (k_ℓ) of time:

$$\gamma_{ij}(\tau) = \delta_{ij} \sum_{\ell=1}^{L} g_\ell \tau^{k_\ell} \exp\left(-\mu_\ell \tau\right), \tag{56}$$

whose Laplace transform is

$$\hat{\gamma}_{ij}(\lambda) = \delta_{ij} \sum_{\ell=1}^{L} g_\ell \frac{k_\ell!}{(\lambda + \mu_\ell)^{1+k_\ell}}, \tag{57}$$

The nonlinear eigenvalue equation gives a polynomial of degree $\left(2 + \sum_{\ell=1}^{L}(1+k_\ell)\right) d$, which is the dimension of the extended system.

III. A MODEL SYSTEM

As an illustrative example to demonstrate our theory we analyze a model system with Müller-Brown potential,[37] which has three minima and two saddle points. The detailed description of the potential surface can be found in Ref. 37 and also in Refs. 11–14. For the friction kernel, we use a single exponential function:

$$\gamma_{ij}(\tau) = \delta_{ij} \gamma_0 \exp(-\mu\tau), \tag{58}$$

with $\gamma_0 = 900$ and $\mu = 30$. Here, the value of $\mu = 30$ is set to be of the same order as the normal mode frequency of the system. The value $\gamma_0 = 900 = 30^2$ is also chosen to be of the same time scale as the system. [Note that the physical dimensionality of γ_0 is square of inverse time, as seen from Eqs. (1) and (58)].

In this paper we focus on the saddle with the higher energy, which was found to be subject to larger nonlinearity.[12] To compare the present theory with the results of numerical simulations, trajectory calculations are performed by the method of Ref. 44. For calculating reaction probabilities, trajectories are judged to have settled in the well region when the energy (kinetic plus potential) becomes less than $2k_BT$ above the minima. The factor 2 corresponds to the fact that this system has two degrees of freedom.

IV. RESULTS AND DISCUSSION

Figure 1 shows the reaction probability P_{reaction} as a function of the initial value of q_1 with the initial values of the other coordinates $(q_2, \dot{q}_1, \dot{q}_2)$ fixed to zero. In the case $k_BT = 0$, the random force is zero because of Eq. (2). Therefore the

trajectory is uniquely determined for each single initial condition. The value of the reaction probability is then either 0 or 1. The boundary between the reactive ($P_{\rm reaction} = 1$) and the nonreactive ($P_{\rm reaction} = 0$) initial conditions coincides with $q_1 = 0$, showing negligible nonlinear effect due to $(q_2, \dot{q}_2)|_{t=0} = (0,0)$. As the temperature increases [Fig. 1(b)], the reaction probability is no longer 0 or 1, due to the stochastic nature of the random force. We can still find the distinction between the regions with mainly reactive ($P_{\rm reaction} > 1/2$) and mainly nonreactive ($P_{\rm reaction} < 1/2$) initial conditions. The boundary of the two regions migrates toward the positive q_1. As the temperature further increases [Fig. 1(c)], the boundary moves further. This migration of the reaction boundary with the temperature was found in the case of a Langevin equation with white noise,[12] in which the physical interpretation was also given: The nonreactive mode $(q_2, \dot{q}_2)$ is thermally excited by the kick from the environment. The vibrational excitation then affects the reactivity through nonlinear couplings with the reactive mode. The nonlinear coupling between the reactive and the nonreactive modes originates from the curved shape of the ridge of the potential. Here we have found that a similar phenomenon occurs in the case of the generalized Langevin equation.

The thermal average of the reaction coordinate y_1 taken over realizations of random force [Eq. (30)] can be regarded as a function of $(q_1, q_2, \dot{q}_1, \dot{q}_2)|_{t=0}$. Since we set $(q_2, \dot{q}_1, \dot{q}_2)|_{t=0} = (0,0,0)$, we can calculate $\langle y_1 \rangle$ as a function of q_1 only. The vertical lines in Fig. 1 shows the value of q_1 at which $\langle y_1 \rangle$ becomes zero. On one side of the line we have $\langle y_1 \rangle > 0$, and on the other side $\langle y_1 \rangle < 0$. The arrows in the figure indicate which region is which. It is seen that the positive (negative) sign of $\langle y_1 \rangle$ corresponds to high (low) reaction probability. In other words, the results of the normal form calculation reproduces the numerical results for the reactivity, including the migration of the reaction boundary.

We next check the dependence on the friction kernel by changing the parameter μ. Figure 2 shows similar plots with different values of μ. The temperature is $k_{\rm B}T = 3$, corresponding to Fig. 1(c). Comparing Fig. 2(a), Fig. 1(c), and Fig. 2(b) (in the order of increasing μ), we can see that the migration from the origin $q_1 = 0$ to the actual reaction boundary (defined by $\langle y_1 \rangle = 0$) projected onto the positive $q_1$axis is less pronounced as μ increases. This can be understood from the fact that the excitation of the non-reactive mode by the external force becomes enhanced due to Eq. (2) as the value of μ decreases. The figure shows that the extent of the migration of the reaction boundary is correctly reproduced by the present theory for all the values of μ shown here.

Figure 3 shows the reaction probability as a function of $(q_2, \dot{q}_2)|_{t=0}$. with $(q_1, \dot{q}_1)|_{t=0} = (0, 0.4)$. Different values of $(q_2, \dot{q}_2)|_{t=0}$ lead to different reaction probabilities due to nonlinear couplings between the nonreactive and the reactive modes. The set of points for which $\langle y_1 \rangle = 0$ is indicated by the purple curve. Here also we can see that the set $\langle y_1 \rangle = 0$ obtained by the present theory gives the correct reaction boundary subject to nonlinearity and thermally fluctuating force in the generalized Langevin equation.

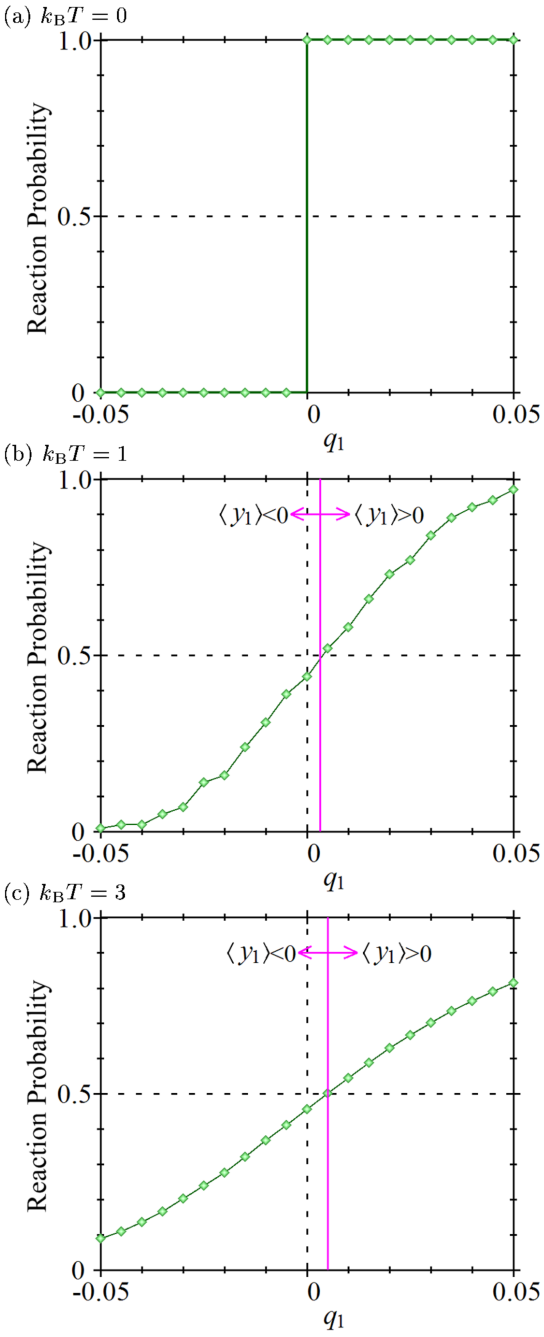


FIG. 1: Reaction probabilities as functions of $q_1|_{t=0}$ with the initial values of other coordinates fixed to zero. The temperature is (a)$k_{\rm B}T = 0$, (b)$k_{\rm B}T = 1$, and (c)$k_{\rm B}T = 3$. Diamonds show the results of numerical simulations. Vertical lines indicate the value of q_1 for which the averaged reaction coordinate $\langle y_1 \rangle$ becomes zero. Arrows show the regions where $\langle y_1 \rangle > 0$ and $\langle y_1 \rangle < 0$.

V. SUMMARY AND OUTLOOK

The theoretical framework recently developed for the analysis of reaction dynamics of nonlinearly coupled systems in a thermally fluctuating environment expressed by white noise, was generalized to the case of colored noise by using the (nonlinear) generalized Langevin equation. The equation of mo-

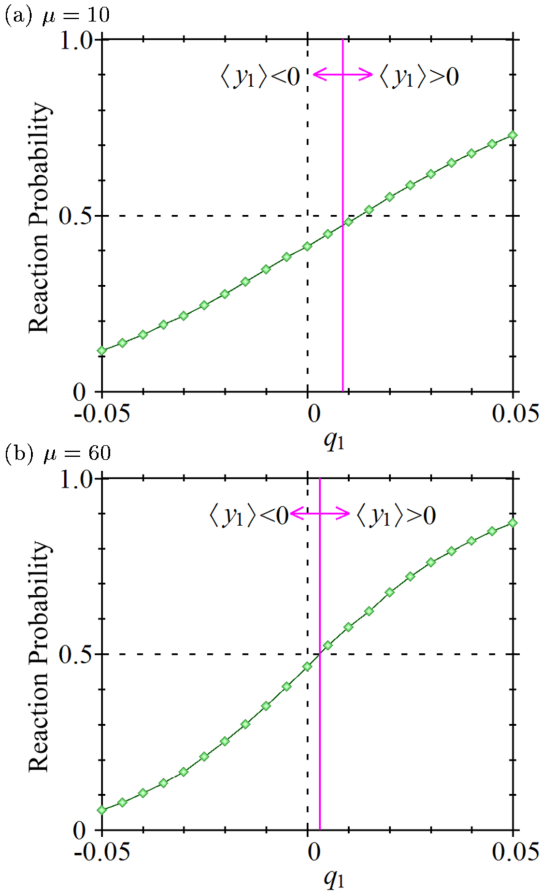


FIG. 2: Reaction probabilities as functions of $q_1|_{t=0}$ with the initial values of other coordinates fixed to zero. The parameters are set as $k_B T = 3$ and (a) $\mu = 10$, (b) $\mu = 60$, with the other parameters set equal to the values in Fig. 1. Diamonds show the results of numerical simulations. Vertical lines indicate the value of q_1 for which the averaged reaction coordinate $\langle y_1 \rangle$ becomes zero. Arrows show the regions where $\langle y_1 \rangle > 0$ and $\langle y_1 \rangle < 0$.

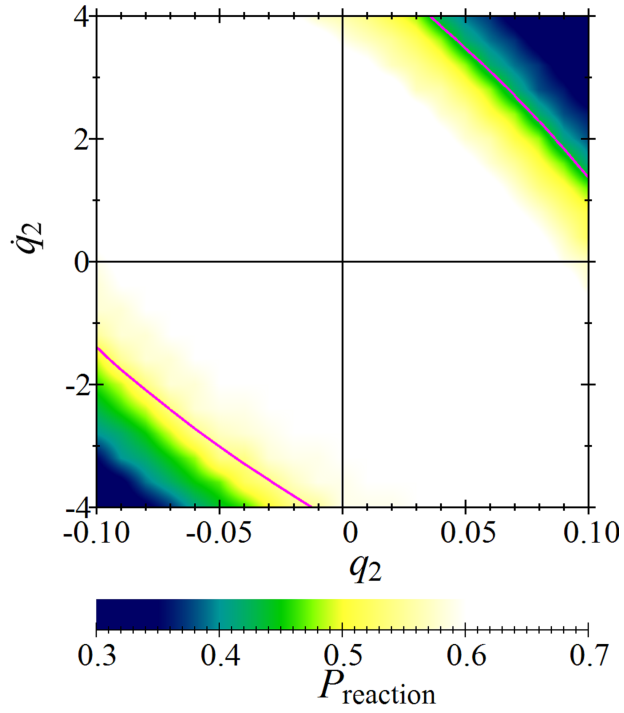


FIG. 3: Reaction probability as a function of $(q_2, \dot{q}_2)|_{t=0}$ with the initial values of the other coordinates fixed to $(q_1, \dot{q}_1)|_{t=0} = (0, 0.4)$ at $k_B T = 1$. Solid curves indicate the set of points for which the averaged reaction coordinate $\langle y_1 \rangle$ becomes zero.

tion with memory effect can be cast into the equation without memory, at the cost of an increase of the dimension of the system. This fact enables us to utilize the same framework for the Langevin equation to the non-Markovian process with colored noise. It was found that the increased dimension can be physically interpreted as effective modes of the fluctuating environment. To support this interpretation, we have investigated the relationship between the effective modes thus found and the underlying system-bath Hamiltonian in which the system is bilinearly coupled with a bath represented by a collection of harmonic oscillators. For a generalized Langevin equation derived from the system-bath Hamiltonian it was found that there exists a one-to-one correspondence between these two representations, if the exact form of the friction kernel is known at least for such class of Hamiltonian systems. To check the validity of the present theory we analyzed the reaction dynamics represented by a generalized Langevin equation on a Müller and Brown potential[37] with a single exponential friction kernel with several different damping timescales. The reaction probability as a function of the initial condition in the saddle region was calculated by trajectory simulations. The whole position-velocity space of the system was found to be divided into regions of mainly reactive and mainly nonreactive initial conditions. Due to the effect of nonlinearity and memory, the reaction boundary does not coincide with the surface $q_1 = 0$ and migrates toward a region remote from the surface of $q_1 = 0$. It was found that the present theory can analytically assign the migrating reaction boundary observed in the results of numerical simulation, which is given as zero of the new reaction coordinate y_1 as a functional of both the positions and velocities of the system as well as the colored noise and the friction kernel.

In reality it is almost impossible to identify the precise form of the friction kernel derived from the total Hamiltonian composed of the system and the environment of infinitely many dimensions. Even if it were possible, it would not shed light on the mechanism of reaction dynamics because the amount of information would be infinite. [in addition, the total Hamiltonian does not necessarily fall into the form of Eq. (31)]. Rather, it is more meaningful to extract an appropriate description by a lower-dimensional dynamical system that can effectively represent the effects of the complexity of nonlinear dynamics of the system in a thermally fluctuating media in terms of an approximant of the friction kernel with a simple functional form, such as a linear combination of exponentials or exponentially damped trigonometric functions [Eq. (50) or (56)]. For the practical application, it will be interesting to evaluate the friction kernel from realistic molecular dynamics

(MD) simulations,[6,41,42] and fit the numerical friction kernel to the form of Eq. (50) or (56). Such numerical evaluation of friction kernel with the corresponding random force can then be utilized as inputs to the present formulation. It is expected that the extra modes with low dimensions compared with the actual dimension of the environment, thus extracted with the approximate friction kernel, capture the subset of the environmental degrees of freedom exhibiting significant effects on the dynamics of the system.

VI. ACKNOWLEDGMENTS

We thank Profs. Turgay Uzer and Thomas Bartsch for letting us know their research in advance. This work has been supported by Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists (to SK) and by JSPS, JST/CREST, Priority Area 'Molecular Theory for Real Systems' (to TK). The computations were partially performed using the Research Center for Computational Science, Okazaki, Japan.

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