Dynamic pathways to mediate reactions buried in thermal fluctuations. II. Numerical illustrations using a model system

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The framework recently developed for the extraction of a dynamic reaction coordinate to mediate reactions buried in thermal fluctuation is examined with a model system. Numerical simulations are carried out for an underdamped Langevin equation with the Müller–Brown potential surface, which contains three wells and two saddles, and are compared to the prediction by the theory. Reaction probabilities for specific initial conditions of the system as well as their average over the Boltzmann distribution are investigated in the position space and in a space spanned by the position coordinates and the velocities of the system. The nonlinear couplings between the reactive and the nonreactive modes are shown to have significant effects on the reactivity in the model system. The magnitude and the direction of the nonlinear effect are different for the two saddles, which is found to be correctly reproduced by our theory. The whole position-velocity space of the model system is found to be divided into the two distinct regions: One is of mainly reactive (with reaction probability more than half) initial conditions and the other, the mainly nonreactive (with reaction probability less than half) ones. Our theory can actually assign their boundaries as the zero of the statistical average of the new reaction coordinate as an analytical functional of both the original position coordinates and velocities of the system (solute), as well as of the random force and the friction constants from the environment (solvent). The result validates the statement in the previous paper that the sign of the reaction coordinate thus extracted determines the fate of the reaction. Physical interpretation of the reactivity under thermal fluctuation that is naturally derived, thanks to the analyticity of the theoretical framework, is also exemplified for the model system. © 2009 American Institute of Physics. [doi:10.1063/1.3268622]

I. INTRODUCTION

Chemical reactions in condensed phase are subject to the effect of their environment with thermal fluctuations. The environment plays a pivotal role both to make the system to surmount and cross through the “barrier” of the reaction (i.e., energy activation), and also to deactivate the excited system to settle down in either the product or the reactant by failure of the reaction (i.e., energy dissipation). In the pioneering works by Kramers¹ and by Grote and Hynes,² they represented condensed phase reactions under thermal fluctuation in terms of Langevin and generalized Langevin equations. The reactions are represented as a motion along a single coordinate, the so-called reaction coordinate, feeling the potential of mean force and the random force with the friction constant or friction kernel (incorporating the memory effect on that coordinate) arisen from the surrounding environment. The system-bath Hamiltonian approach can formally bridge the descriptions of any Hamiltonian system and the generalized Langevin formulation projected onto a chosen coordinate.³–⁵ However, the question of what reaction coordinate the system actually follows in a thermally fluctuating environment still remains. Here, we use the term “reaction coordinate” as a single one-dimensional coordinate that can describe the progress of the reaction without referring to the other coordinates so that it can, in principle, predict the destination of the reaction, that is, reactants or products.

van der Zwan and Hynes³ and later Pollak⁶ showed in the harmonic bath Hamiltonian systems that the reaction rate of the Grote–Hynes formulation with an arbitrarily chosen reaction coordinate is exactly equivalent to that of the transition state theory if one chooses a reaction coordinate as an unstable normal coordinate of the total system (=system +bath). This reaction coordinate was decoupled from the rest, free from the recrossing problem, and can a priori identify the destination of the reaction at any instant solely by the value of that reaction coordinate. This indicates that the appropriate coordinate to mediate the reaction may have to involve all the coordinates of the system and the thermal bath because they are mutually coupled, in general.⁷

In the previous paper,⁵ we have presented a formulation for analyzing nonlinear dynamics of chemical reactions in the region of saddle in condensed phase. We adopted the description of the reaction system by multidimensional underdamped Langevin equation without any assumption for the form of the potential of mean force. The theory explicitly takes into account nonlinearities of the (reacting) system and their couplings with the surrounding environment via friction

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constants and fluctuating, stochastic random force. It was shown that under certain conditions, a coordinate transformation can be performed to give a new coordinate to mediate reaction that is decoupled from all the other coordinates, as a nonlinear function of the original coordinates and velocities of the system and the random force with the friction constants. The sign of the new reaction coordinate in the region of saddle can predict the fate of the reaction, that is, whether the trajectory will proceed to the product by overcoming the barrier or be carried back to the reactant.

In this article, in order to demonstrate the potential of the theory, we analyze nonlinear reaction dynamics of underdamped Langevin equation of a model system. We scrutinize how the theory can provide us with means to address the question of what determines the destination of the reaction in a thermally fluctuating environment.

II. THEORY

We present a brief summary of the theory we developed in the previous paper. Chemical reactions in condensed phase are described by a multidimensional Langevin equation,

\[ \ddot{q} = - \frac{\partial U}{\partial q} - \gamma q + \xi(t), \]

where \( q \) is the normal mode position coordinates of the system (solute), \( U \) is the potential (of the mean force), \( \gamma \) is the friction constant, and \( \xi(t) \) describes the random force from the solvent. Although the theory is applicable to systems of any dimensions, we illustrate the theory with a specific example of the Müller–Brown potential (See Sec. III) as \( U \), for which case we have two position coordinates \( q = (q_1, q_2) \). The trajectory calculation is performed with the random force sampled according to the fluctuation-dissipation theorem,

\[ \langle \xi(t)\xi(0)^T \rangle = 2k_BT\gamma \delta(t), \]

where \( \xi(0)^T \) is the transpose of the vector \( \xi(0) \), \( T \) is the temperature, and \( k_B \) is the Boltzmann constant. From the potential \( U \) can be expanded in a Taylor series,

\[ - \frac{\partial U}{\partial q_j} = -k_Bq_j + \sum_{m|j| = 2} \alpha_{jm}q_1^m \ldots q_n^m, \]

with the expansion coefficients \( k_j \) and \( \alpha_{jm} \) for the linear and the nonlinear parts, respectively. Here, \( |m| = \sum_j m_j \) and \( \sum_{|m| = 2} \) sums over combinations of \( m_j \) satisfying \( |m| \geq 2 \).

The theory introduces a nonlinear coordinate transformation that involves both the position \((q_1, q_2)\) and the velocity \((\dot{q}_1, \dot{q}_2)\) to introduce a special coordinate system \( y = (y_1, y_2, y_3, y_4) \). The purpose of the transformation is to make the equation of motion into the following form:

\[ \dot{y}_1 = \lambda_1 y_1 + c_1(y,t), \]
\[ \dot{y}_2 = \lambda_2 y_2 + c_2(y,t), \]
\[ \dot{y}_3 = \lambda_3 y_3 + c_3(y,t), \]
\[ \dot{y}_4 = \lambda_4 y_4 + c_4(y,t). \]

Here \( \lambda_1 > 0 \) is a positive real value, \( \lambda_2 < 0 \) is a negative real, and \( \lambda_3 \) and \( \lambda_4 \) are complex numbers with a negative real part, conjugate to each other. The coefficient \( c_1(t) \) depends only on time and not on the coordinates. The other terms \( c_j(y,t) \) \( (j = 2, 3, 4) \) can take any functional forms. The solution of Eq. (4) is given by

\[ y_1(t) = y_1(t_0) + \int_{t_0}^{t} (\lambda_1 + c_1(t')) dt', \]

where \( t_0 \) is a certain instant of time (the initial condition). If \( c_1(t) \) does not exceed \( \lambda_1 \) in magnitude [more precisely, see Eq. (34) of the previous paper], we have \( y_1(t) \rightarrow \pm \infty \) as \( t \rightarrow +\infty \). That is, the motion along \( y_1 \) is unstable, corresponding to the motion sliding down the barrier of reaction. The direction (the sign) of this motion along \( y_1 \) is determined by the initial sign of \( y_1(t_0) \) and does not change with time. One can thus predict the fate of the reaction (whether the reaction system proceeds to the products or goes back to the reactants) solely by the sign of \( y_1 \) at any instant when it is in the saddle region. This is thanks to the fact that the equation of motion along \( y_1 \) does not depend on the other coordinates \((y_2, y_3, y_4)\) in Eq. (4).

The detailed procedure for finding the transformation to make the equation into the form of Eq. (4) is given in the previous paper. The resulting transformation from the original coordinates \((q_1, q_2)\) to \( y_1 \) is generally expressed in the following form:

\[ y_1 = a_1(q_1 - S[\lambda_1, \xi_1](t)) + F_0[\xi_1](t) + \sum_{|m| = 2} w_q q_1^m \ldots q_n^m, \]

with \( \xi_1(t) \) expressing direct environment effect, \( S[\lambda_1, \xi_1](t) \) expresses environment effect, that is, the kick by the random force along the reactive normal mode direction. The terms with the coefficients \( w_q \) come from the linearity of the system (here, linearity means both nonlinear couplings among modes and nonlinearity also couple to each mode’s coordinate). The rest terms \( F_0[\xi_1](t) + F_m[\xi_1](t) \) are the combined effects of the environment and the nonlinearity in the sense that they arise only when there exist both the random force and the nonlinearity in the potential. For example, the terms of \( F_0[\xi_1](t) \) tell us how much the vibrational motion along the nonreactive mode changes the reactivity through nonlinear couplings between the nonreactive and the reactive modes when the nonreactive mode is excited by a kick from the environment.
Those of $F_m^{\xi}(t)$ tell us how much the amplitude of couplings among $(q, \dot{q})$ depends on the $\xi(t)$: The random force disturbs the position of the system on the potential, resulting in the change in the coupling strength.

Equation (9) above can be calculated only when one knew the instance of the random force $\xi(t)$ for all the past and the future time in advance. In practice, however, what one may assume a priori is the statistical properties of $\xi(t)$ as an ensemble rather than a single instance. In the previous paper,\(^4\) using the statistical properties of random force such as the fluctuation-dissipation theorem, we also analytically formulated the ensemble average of the reaction coordinate $y_1$ over all realizations of $\xi(t)$,

$$\langle y_1 \rangle = a_1 q_1 + a_2 \dot{q}_1 + \bar{F}_m(k_B T) + \sum_{j=1}^{2n} \sum_i w_{j}^m q_j^{m1} \cdots q_j^{m(m+1)} \cdots q_j^{m2n}$$

$$+ \sum_{j=1}^{2n} \bar{F}_m(k_B T) q_j^{m1} \cdots q_j^{m(m+1)} \cdots q_j^{m2n}, \tag{10}$$

where the time-independent coefficients $\bar{F}_m(k_B T)$ and $\bar{F}_m(k_B T)$ are the averages of the corresponding terms in Eq. (9) and are functions of temperature through Eq. (2). The direct environment effect vanishes by taking the average of $\xi(t)$.

### III. MODEL SYSTEM

As a model system we use the Müller–Brown potential,\(^9\) which has often been used as a test system for searching algorithms of minima and saddle points. The potential $U$ is expressed in terms of two position coordinates $(Q_1, Q_2)$ by

$$U(Q_1, Q_2) = \sum_{i=1}^{4} A_i \exp[a_i(Q_1 - Q_{1,0})^2 + b_i(Q_1 - Q_{1,0})(Q_2 - Q_{2,0})] + c_i(Q_2 - Q_{2,0})^2], \tag{11}$$

with $A=(A_1, A_2, A_3, A_4)=(-200, -100, -170, 15)$, $a=(-1, -1, -6.5, 0.7)$, $b=(0, 0, 11, 0.6)$, and $c=(-10, 10, -6.5, 0.7)$, $Q_{1,0} = (1, 0, -0.5, -1)$, and $Q_{2,0} = (0, 0.5, 1.5, 1)$. The contour plot of the potential is shown in Fig. 1(a). This system possesses three minima and two saddle points. The locations, energies, and normal mode frequencies (without friction) of the stationary points are summarized in Table I. The normal mode frequencies at the two saddles (without friction) simply reflect the curvatures of the potential. The friction constant is set to be proportional to unit matrix $\gamma_{ij}=30 \delta_{ij}$. This value was regarded as the underdamped case because it is of the same order with the normal mode frequency of the system.

In the simulation we prepared initial conditions around the saddle points, and then propagated the trajectory until it “settles down” in either of the wells. The propagation was performed by the method proposed by Ermak and Buckholz\(^{10}\) with the random force sampled according to the fluctuation-dissipation theorem with time step $10^{-3}$. As a criterion for the destination of the reaction, the system was judged to have settled down in the well when the energy (defined as the kinetic energy plus the potential) becomes less than $U_{\min}+2k_B T$ after leaving the region of the saddle. Here $U_{\min}$ is the potential at the bottom of each well and $2k_B T$ the average thermal energy of two degrees of freedom.

<table>
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<th>Name</th>
<th>$Q_1$</th>
<th>$Q_2$</th>
<th>Energy</th>
<th>Normal mode frequencies</th>
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<tbody>
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<td>-147</td>
<td></td>
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<tr>
<td>Minimum 2</td>
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<td>0.028</td>
<td>-108</td>
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<td>Minimum 3</td>
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<td>0.467</td>
<td>-81</td>
<td></td>
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<tr>
<td>Saddle 1</td>
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<td>0.293</td>
<td>-72</td>
<td>27.1</td>
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<tr>
<td>Saddle 2</td>
<td>-0.822</td>
<td>0.624</td>
<td>-40</td>
<td>27.4</td>
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IV. RESULTS AND DISCUSSION

A. An illustrative example of reactive and nonreactive trajectories

Figure 2 shows two examples of trajectories with the contours of the potential. The green line shows a reactive trajectory that starts on one side of the barrier, which is here defined naively as \( q_1=0 \), passes over it and goes to the other side. The red line is a nonreactive trajectory that crosses the barrier but is reflected back into its original region.

In Fig. 3(a), the same trajectories are plotted in position \( (q_1) \) and velocity \( (\dot{q}_1) \) along the reactive direction. The velocity fluctuates more significantly than the position due to the random force. The direction of \( q_1 \) in the configuration space is shown in Fig. 2. In Fig. 3(a), we also show the normal mode coordinates \( (u_1, u_2) \) in the position-velocity space that diagonalize the linear part [see Eqs. (7) and (8) in the previous paper]. The normal mode coordinate \( u_1 \) corresponds to the unstable motion sliding down the barrier.

Figure 3(b) shows plots of the two trajectories in the relative coordinates \( (x_1, x_2) \) introduced in Sec. IIB in the previous paper. The trajectories have become much smoother than the corresponding plots in Fig. 3(a). This implies that the shift of coordinates \( x \) incorporates the effect of the random force to some extent. However, the nonreactive trajectory starts at \( x_1>0 \), crosses the line \( x_1=0 \), and finally returns to the left side of the figure. Therefore this line still does not function as the boundary of reaction when significant nonlinearities exist in the potential \( U \).

Figure 3(c) plots the two trajectories in the normal form (NF) coordinates \( (y_1, y_2) \) (see Sec. IIC in the previous paper). The coordinates are calculated by partial NF up to the second order perturbation. It is clearly seen that \( y_1=0 \) separates correctly the reactive and the nonreactive trajectories. This means that the newly introduced reaction coordinate \( y_1 \) can tell the reactivity of the system correctly even in the presence of fluctuating environment and nonlinearity.

B. Reaction probabilities

Figure 4 shows the numerical results of reaction probabilities \( P_{\text{reaction}} \), for three different temperatures \( k_B T \).
We took each surface of constant \( q_1 \) as functions of \( q_1 = 0 \), 1, 3, as functions of \( q_1 \) (i.e., the reactive normal mode in the coordinate space). The reaction probability for a surface of \( q_1 = \alpha \) is given by

\[
P_{\text{reaction}}(q_1 = \alpha) = \frac{\int dq dq P(q,q) \exp(-E(q,q)/k_B T)}{\int dq dq \delta(q_1 - \alpha) \exp(-E(q,q)/k_B T)}.
\]  

(12)

We took each surface of constant \( q_1 \) on which all the other \((q,\dot{q})\) are sampled according to the Boltzmann distribution. Then the trajectory calculation was performed starting from these initial conditions with different instances of random forces \( \xi \) satisfying Eq. (2) with the same \( k_B T \). \( P(q,\dot{q}) \) and \( E(q,q) \) denote the reaction probability for a given initial condition \((q,\dot{q})\) and a sum of the kinetic and the potential energies, respectively,

\[
E(q,q) = (q_1^2 + q_2^2)/2 + U(q_1,q_2).
\]  

(13)

Here \( k_B T = 0 \) corresponds to the situation where there is no random force [Eq. (2)] and no initial excitation along the nonreactive mode. Therefore \( P_{\text{reaction}} \) is either 0 or 1. The positive side \((q_1 > 0)\) is reactive and the negative side \((q_1 < 0)\) is nonreactive. Therefore the halfway point \((P_{\text{reaction}} = 1/2)\) at \( q_1 = 0 \) can be regarded as the boundary between the reactive and nonreactive initial conditions at zero temperature. As the temperature increases, \( P_{\text{reaction}} \) takes intermediate values between 0 and 1. This results in broadening of the plot of \( P_{\text{reaction}} \) in Fig. 4 compared to the steplike behavior at \( k_B T = 0 \). The major origin of this broadening was found to be the fluctuation of the direct solvent effect \( \delta[\lambda,\xi(t)] \) in Eq. (9) for the ensemble of \( \xi(t) \). In nonzero temperature, the halfway point \( P_{\text{reaction}} = 1/2 \) can also be regarded as a boundary of reaction that divides the space (one dimension in this case) into a “mainly reactive” \((P_{\text{reaction}} > 1/2)\) region and a “mainly nonreactive” \((P_{\text{reaction}} < 1/2)\) one. The boundary is slightly shifted to the negative-\(q_1\) direction for saddle 1 [Fig. 4(a)] and significantly to the positive-\(q_1\) direction for saddle 2 [Fig. 4(b)]. It implies that the normal mode picture \( q_1 \) cannot provide us insights about the fate of the reaction (except at zero temperature). In order to identify the location of the reaction boundary that divides the space into mainly reactive and mainly nonreactive regions, one cannot assign without trajectory calculations (unless one has information of \( y_1 \) in Sec. II). Next we show the results of normal form calculations formulated in the previous paper which was applied to the Müller–Brown system. Normal form calculations have been performed up to the second order of perturbation. In Fig. 5, the surface \( q_1 = 0 \) is taken and the reaction probability on the surface is plotted against the averaged normal form reaction coordinate \( \gamma_1 \). The reaction probability for a surface of \( \gamma_1 \) = \( \beta \) is given by

\[
P_{\text{reaction}}(\gamma_1) = \beta; \gamma_1 = 0 = \frac{\int dq dq \delta(q_1 - \beta) P(q,q) \exp(-E(q,q)/k_B T)}{\int dq dq \delta(q_1 - \beta) \exp(-E(q,q)/k_B T)}.
\]  

(14)
Here $\langle y_1 \rangle$ is calculated as a function of $(q, \dot{q})$ by Eq. (10). In the sampling by the Boltzmann distribution in Eq. (14), the initial conditions for $(q, \dot{q})$ except $q_1$ are “restricted” (or highly populated) near zero in the region of the saddle point except at very high temperature $T$ because the energy of the system $E$ in the Boltzmann factor increases as the size of these variables increases. However, since $q_1$ is along the unstable direction of the potential, the Boltzmann factor increases the statistical weight for large $|q_1|$ so that expansions such as Eq. (3) cannot be validated. Since our interest in the present paper is the dynamics in the saddle region, we have posed the condition $q_1=0$ into Eq. (14) in order to perform the sampling in the saddle region. Note also that the condition $\langle y_1 \rangle=\beta$ makes no restriction on the $|q_1|$ to small values (e.g., $y_1=0$ forms the unstable manifold emanating from the saddle region; see also Fig. 3). In Fig. 5, we take the same simulation data for $q_1=0$ as used in the numerical simulation of Fig. 4. One can see that as the order of the perturbation increases, the halfway point $P_{\text{reaction}}=1/2$ comes closer to the origin $\langle y_1 \rangle=0$. This shows that the normal form theory correctly gives the location of the boundary of reaction between the mainly reactive region and the mainly nonreactive region even in the presence of thermal fluctuation.

Normal form theory presented in this paper is capable of providing physical insights into the observed behavior of reaction probabilities, as analytical expressions for the reaction coordinate are available. Explicit expressions for the averaged normal form reaction coordinate $\langle y_1 \rangle$ are obtained up to the second order,

$$\langle y_1^{(2)} \rangle = 11.887q_1 + 0.258q_1 + 0.007k_B T$$
$$+ \sum_{2 \leq |m| \leq 3} w_m q_1^m q_2^m q_1^{m_1} q_2^{m_2} (30 \text{ terms})$$
$$+ 0.008k_B T q_1 + 0.002k_B T q_1 - 0.033k_B T q_2$$
$$+ 0.005k_B T q_2$$

(15)

for saddle 1 and

$$\langle y_1^{(2)} \rangle = 12.041q_1 + 0.260q_1 - 0.020k_B T$$
$$+ \sum_{2 \leq |m| \leq 3} w_m q_1^m q_2^m q_1^{m_1} q_2^{m_2} (30 \text{ terms})$$
$$+ 0.087k_B T q_1 + 0.002k_B T q_1 + 0.015k_B T q_2$$
$$- 0.001k_B T q_2$$

(16)

for saddle 2, where the terms are aligned in the same order as Eq. (10). (The full expressions of $\langle y_1 \rangle$ including the numerical values of $w_m$ and also the normal form reaction coordinate $y_1$ before taking the ensemble average of random force are available online in supplementary material of this paper[5]). In the right hand side of each equation, the first two or $q_1$ and $q_1$ with constant coefficients come from the linear approximation [Eq. (8) in the previous paper]. The third term originating from $F_m[\xi](t)$ makes the shift of the coordinate origin observed in Fig. 4 (see below). The last four terms linear (at least up to second order) in $q$ and $q$ with temperature-dependent coefficients originate from the environment-mediated coupling effect [Eq. m[\xi](t)$ of the force from the environment on the landscape of potential $U$, resulting in the change in the coupling strength. To begin, let us briefly look into the “structure” of these expressions. As first indicated by Van der Zwan and Hynes,[5] the coordinate to mediate the reaction involves all the coordinates and velocities of the system and the thermal bath. The appearance of $q_2$ and $q_2$ is the effect of nonlinear couplings because they mean that the excitation along the nonreactive mode influences the reaction. There are only linear terms in $q$ and $q$ for the environment-mediated coupling effect $[\tilde{F}_m(k_B T)]$, while the polynomial with the coefficients $w_m$ is cubic. This is due to the truncation in Eqs. (15) and (16) at the second order perturbation $[O(\varepsilon^2)]$. Note that the order assign is such that the element $S[\lambda_j, \xi_j](t)$ is of $O(\varepsilon)$ [see Eqs. (11) and (12) in the previous paper]. We have temperature-dependent coefficients in the third term and the last four terms, corresponding to $\tilde{F}_0(k_B T)$ and $\tilde{F}_m(k_B T)$ in Eq. (10), respectively. They arise from convolutions or products of $S[v, \xi_j](t)$ such as $\langle S[v, S[v_1, \xi_j]]S[v_2, \xi_j] \rangle$ and
The numbers \( \nu_i \) are combinations of \( \lambda_j \) as in Eq. (26) of the previous paper.\(^5\) Before taking the ensemble average of \( \xi(t), F_0(k_B T)\xi(t) \) and \( F_m\xi(t) \) contain 355 and 612 terms, respectively.\(^6\) It was also found that the more the friction constant \( \gamma \) increases, the more the contributions of velocities \( q \) in \( y_1 \) and \( y_2 \) tends to decrease in magnitude (see the supplementary material available online of this paper\(^1\)). This provides us with the firm basis to address the questions of what size of frictions make the effect of moment of inertia negligible.

Let us turn to the following question: “What is the primary driving force to make the reaction boundary \( P_{\text{reaction}} = 1/2 \) migrate?” In Fig. 4 it was found that the direction of the migration of the boundary is to \( q_1 < 0 \) for saddle 1 and \( q_1 > 0 \) for saddle 2. The amount of the shift is larger for saddle 2 than that for saddle 1, and it increases when temperature \( T \) increases. In fact, simple observation of the third term in Eqs. (15) and (16) already tells some feature of the shift, because it increases with temperature, has opposite sign for the two saddles and its absolute value is larger for saddle 2 than saddle 1. The interpretation for the shift for the case of \( \langle q_2, q_1, q_2 \rangle_{t=0} = (0, 0, 0) \) is given as follows: From Eqs. (15) and (16),

\[
\langle y(2)_1 \rangle = 0.007k_B T + (11.887 + 0.008k_B T)q_1 + O(q_1^2)
\]

for saddle 1 and

\[
\langle y(2)_2 \rangle = -0.020k_B T + (12.041 + 0.087k_B T)q_1 + O(q_1^2)
\]

for saddle 2. This implies that in the vicinity of \( q_1 = 0 \), \( \langle y_1 \rangle = \vec{F}_\nu + (a_1 + \vec{F}_\nu)\dot{q}_1 \) (\( \vec{F}_\nu \) is the coefficient of \( q_1 \) in environment-mediated coupled terms). Then, \( \dot{q}_1 \) at the reaction boundary of \( P_{\text{reaction}} = 1/2 \), where \( \langle y_1 \rangle = 0 \) is given by \( q_1 = -\vec{F}_\nu/a_1 \) since \( a_1 \) arises from the linear approximation which is much larger than the \( \vec{F}_\nu \). Namely, the primary driving force to shift the reaction boundary outward from \( q_1 = 0 \) mainly originates from \( \vec{F}_\nu \). The sign of \( \vec{F}_\nu \) depends on the nonlinear couplings between the reactive \( q_1 \) and nonreactive mode \( q_2 \) in the region of the saddle.

By comparing the term \( \vec{F}_0[k_B T] \) with the corresponding terms \( F_0\xi(t) \) before taking the average,\(^1\) we can see that this term comes from terms of the following types:

\[
\langle S[v_1, \xi_1]\rangle\langle S[v_2, \xi_1]\rangle, \quad \langle S[v_1, \xi_1]\rangle\langle S[v_2, \xi_1]\rangle,
\]

\[
\langle S[v_1, \xi_2]\rangle\langle S[v_2, \xi_2]\rangle, \quad \langle S[v_1, \xi_2]\rangle\langle S[v_2, \xi_2]\rangle,
\]

(17)

with \( v_1, v_2 \) being some constants. Note that terms like \( \langle S[v_1, \xi_1]\rangle\langle S[v_2, \xi_1]\rangle \) do not contribute to \( \vec{F}_0[k_B T] \) because in this paper, we use uniform friction \( \gamma = 0 \). The contribution can be evaluated quantitatively for each term. For saddle 2, we have found that 77% of contribution is from \( \xi_2 \), whereas 76% is from \( \xi_1 \) for saddle 1. Since \( \xi_2 \) is the random force along the direction of the nonreactive mode, the interpretation for saddle 2 is as follows: The nonreactive mode vibration is first excited by the kick from the solvent. The ridge of the potential surface around saddle 2 [Fig. 1(c)] has a curved shape toward the positive direction of \( q_1 \). Hence, as the nonreactive vibrational mode is excited, the effective position of the barrier along the reactive direction shifts toward the positive side.

Due to the order assignment in the theory [see Eqs. (11) and (12) in the previous paper], all the terms in Eq. (17) are assigned \( O(e) \). Therefore the shift of the origin for the case of \( \langle q_2, q_1, q_2 \rangle_{t=0} = (0, 0, 0) \) is accounted for by the first order perturbation. In fact, the increase in the order to the second order does not improve the situation very much [see Figs. 5(a) and 5(b)]. The initial condition of \( \langle q_2, q_1, q_2 \rangle_{t=0} = (0, 0, 0) \) is of course one example and the physical interpretation of which terms dominate a shift (whenever it exists) in \( q_1 \) depends on the initial condition.

One of the striking consequences of our theory is this: such “two-step” scenario of direct nonreactive mode excitation by the solvent followed by interaction of the nonreactive mode with the reactive mode can be called “combined effect” of the solvent and the nonlinearity inside the solute. By the direct excitation of the nonreactive mode, we mean the transition state trajectory [Eq. (11) in the previous paper] introduced by Bartch et al.\(^\text{12-14}\) In their theory, however, the coupling among the normal modes were ignored so that the motion along the normal mode reactive coordinate was independent of the nonreactive modes. Under the existence of coupling, however, the excitation of the nonreactive mode can affect the reaction through the nonlinear coupling between the reactive and the nonreactive modes. Our theory here is capable of handling such general nonlinear cases.

We have stated that the coefficient \( c_1(t) \) appearing in the equation of motion of \( y_1 \) [Eq. (4)] must not exceed \( \lambda_1 \) in magnitude in order that the sign of \( y_1 \) determines the fate of the reaction. Here we check the condition in the present numerical example by calculating the mean and variance of \( c_1(t) \). For saddle 1 and \( k_B T = 3 \), it gives

\[
\lambda_1 = 15.988, \quad \langle c_1(t) \rangle = -2.594,
\]

\[
\langle (c_1(t) - \langle c_1(t) \rangle)^2 \rangle^{1/2} = 4.778,
\]

(18)

and for saddle 2 with the same temperature,

\[
\lambda_1 = 16.239, \quad \langle c_1(t) \rangle = -0.449,
\]

\[
\langle (c_1(t) - \langle c_1(t) \rangle)^2 \rangle^{1/2} = 5.560.
\]

(19)

Thus it is confirmed that \( c_1(t) \) is smaller than \( \lambda_1 \) at least on average.

C. Dynamical dividing surfaces buried in a thermal fluctuation

Figure 6 shows the reaction probability at saddle 2 as a function of nonreactive normal mode coordinates \( \langle q_2, q_2 \rangle_{t=0} \) by the gradation of color. There the initial conditions for the reactive mode is fixed to \( q_1_{|t=0} = 0 \), and \( q_1_{|t=0} = 0.1, 0.3, \) and 0.5, for (a), (b), and (c), respectively. The dependence of the reaction probability on the nonreactive mode, seen as the nonuniformity in the plot, is a consequence of the nonlinear coupling between the reactive and the nonreactive modes. Although the probability is not 0 or 1 due to the stochastic nature of the random force, we can still find a distinction between mainly reactive region (that with lighter colors), and mainly nonreactive region (with darker colors).
FIG. 6. Reaction probability as a function of nonreactive mode coordinates \((q_1, q_2)\) at \(t=0\) obtained from numerical simulations with \(k_B T=1\) at saddle 2. The initial values for the reactive mode are fixed to \(q_1|_{t=0}=0\) and \(q_1|_{t=0}=0.1, 0.3,\) and 0.5, for (a), (b), and (c), respectively. Purple line is given by \((y_1)=0\) calculated by second order normal form. It is seen that the line locates the boundary between the mainly reactive and the mainly nonreactive regions.

The purple line in Fig. 6 is given by \((y_1)=0\) from the second order normal form calculation, which can be obtained as an analytical function of \(q\) and \(\dot{q}\) of the system without performing any trajectory calculation. For \(\dot{q}_1|_{t=0}=0.1\), the mainly reactive region is small centered around the origin. As \(\dot{q}_1\) increases, the region becomes larger and the probability at the center also increases. In all the cases, the line given by \((y_1)=0\) correctly separates the mainly reactive and the mainly nonreactive regions.

In Fig. 7, we further add one dimension of the plot, i.e., \(\dot{q}_1\). The other coordinate, \(q_1\), takes the same value as Fig. 6. Three semitransparent surfaces show the section of the surface \((y_1)=0\) for \(k_B T=0, 1, 3\). The yellow horizontal plane is given by \(\dot{q}_1=0.3\) and therefore corresponds to the plot in Fig. 6(b). Basically, the system has more reaction probability for larger positive value of the velocity \(\dot{q}_1\) along the reactive mode. Thus the upper part of the figure is more reactive than the lower. However, the border between the mainly reactive and the mainly nonreactive regions shows dependence on \(q_2\), \(\dot{q}_2\), and the temperature.

By such plots, one can visually capture the physical interpretations given in the preceding paragraphs. Here the physical origins of the shapes of the surfaces are schematically superimposed in Fig. 7. All the three surfaces are curved in contrast to a plane of \(\dot{q}_1=\)const, implying that reactivities at each temperature depend on the nonreactive mode \((q_2, \dot{q}_2)\). This curved shape is interpreted as it primarily arises from the intrinsic nonlinear couplings of the system (i.e., the terms with \(w_m\)) because the dependence of reactivity exists even at \(k_B T=0\). The surface shifts upward in the direction of \(\dot{q}_1\) as the temperature increases. The shift along \(\dot{q}_1\) can be explained in a similar way with that along \(q_1\), given in Sec. IV B. Note that the shift exists even at \((q_2, \dot{q}_2)\)=0 and we fix \(q_1=0\) in Fig. 7. In this case, at least from small \(\dot{q}_1\), we have \((y_1)=F_0(k_B T) + a_2 \dot{q}_1\). The reaction boundary \((y_1)=0\) can then be given by \(\dot{q}_1=F_0(k_B T) / a_2\). Thus the primary reason for the shift of the boundary surface with the temperature is the temperature dependence of \(F_0(k_B T)\), whose physical origin is the effect of the random force from the environment combined with the nonlinearity of the system, as has been explained in Sec. IV B. If the nonreactive mode \((q_2, \dot{q}_2)\) has nonzero values, the position of the reaction boundary changes due to the terms with \(w_m\) and \(F_m(k_B T)\) in Eq. (10). Then, due to the temperature dependence of \(F_m(k_B T)\), the shape (i.e., gradients, curvature, etc.) of the surface also changes with temperature rather than a parallel translation. In other words, the extent of the nonlinear couplings among the modes \((q, \dot{q})\) depend on the temperature, and therefore the change in the shape of the boundary surface can be interpreted as the environment-mediated coupling.

V. SUMMARY AND OUTLOOK

We demonstrated the potential of the framework we developed recently for the analyses of condensed phase chemical reactions. We used the Müller–Brown potential, which has distinct two saddles with three minima, as an illustrative example. Along the same direction recently established in many degrees of freedom, Hamiltonian systems that extract a new reaction coordinate decoupled from the other (nonreactive) coordinates from the phase space (one can see several
reviews7,15–21 and books22,23), our theory extracts a reaction coordinate (called \( y_1 \) in this paper) at least in the region of rank-one saddle, decoupled from the other (nonreactive) coordinates, from the reaction system even when it is embedded in a thermally fluctuating environment. The numerical simulations showed that reactive and nonreactive trajectories are separated by the boundary \( y_1 = 0 \), in which the nonlinearity and the solvent effects are explicitly taken into account. Even though taking the statistics of the fluctuating random force disables the unique determination of the fate of the nonreactive and the reactive modes.

In the preceding paper, we discussed the possible resonance mechanism to break down the existence of \( y_1 \), which makes reaction totally unpredictable (i.e., the birth of “full stochasticity” in reactions). In the model system with chosen temperatures and friction constants in this paper, we have not met such situation up to the order we considered.

Given, for instance, any specific value or a distribution of initial conditions in the barrier region (e.g., Ref. 24), our framework enables us to analytically calculate the probability distributions of \( y_1 \) (hence the reaction probability). For example, the linear shift [type (ii) in our classification] is zero on average but contributes to the fluctuation, whereas the terms second order in the random force [type (iv)] has nonzero average. These physical insights can help us to understand what type of specific, initial distribution should be prepared in the region of saddle, so as to lead us to a desired product. We believe that our theory can provide us with physical insights to control chemical reactions in a fluctuating media, although several things remain to be considered such as quantum effects.20,28 It is also expected to shed light on the mechanism of why biological (nonlinear) systems can robustly perform their functions under unpredictable, stochastic thermal fluctuation.

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1 H. A. Kramers, Physica (Amsterdam) 7, 284 (1940).
11 See EPAPS supplementary material at http://dx.doi.org/10.1063/1.3268622 for the full expressions of the reaction coordinate \( y_1 \) in terms of \( q_2,q_4 \).