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# Energy diffusion controlled reaction rate of reacting particle driven by broad-band noise

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**Abstract.** The energy diffusion controlled reaction rate of a reacting particle with linear weak damping and broad-band noise excitation is studied by using the stochastic averaging method. First, the stochastic averaging method for strongly nonlinear oscillators under broad-band noise excitation using generalized harmonic functions is briefly introduced. Then, the reaction rate of the classical Kramers' reacting model with linear weak damping and broad-band noise excitation is investigated by using the stochastic averaging method. The averaged Itô stochastic differential equation describing the energy diffusion and the Pontryagin equation governing the mean first-passage time (MFPT) are established. The energy diffusion controlled reaction rate is obtained as the inverse of the MFPT by solving the Pontryagin equation. The results of two special cases of broad-band noises, i.e. the harmonic noise and the exponentially corrected noise, are discussed in details. It is demonstrated that the general expression of reaction rate derived by the authors can be reduced to the classical ones via linear approximation and high potential barrier approximation. The good agreement with the results of the Monte Carlo simulation verifies that the reaction rate can be well predicted using the stochastic averaging method.

**PACS.** 02.50.-r Probability theory, stochastic processes, and statistics – 05.40.-a Fluctuation phenomena, random processes, noise, and Brownian motion – 05.45.-a Nonlinear dynamics and chaos

## 1 Introduction

The development of the reaction rate theory began in the 19th century with the observation of Arrhenius that the log of reaction rate is proportional to the reciprocal temperature. Modern reaction rate theory is based on the pioneering research works performed by Eyring, Kramers and etc., which are of basic importance for the understanding of the features of reactions [1–3]. Kramers' classical reaction theory describes reaction as transiting potential barrier of a particle under action of random force. One crucial point in the Kramers' theory on the transition rate is the white noise assumption about the character of the random force acting on the particle. In practice, especially under the effect of nonlinear collision, however, the white noise assumption may be not satisfied. As the real random force may have various power spectral densities (PSD), it is significant to investigate the transition rates in the case of colored noises including the harmonic noise and exponentially correlated noise [4–11].

The reaction rate of bistable potential driven by colored noises has been obtained by dealing with the Smoluchowski equation [3–7] short of the inertial term. Although the formula so obtained is simpler, it is valid only for overdamped cases. The explicit expression of escape rate in a Morse potential well with memory kernel friction and exponentially correlated noise was derived by Carmeli and Nitzan [12]. According to the view that the escape dynamics is determined by the motion along the unstable normal mode, Pollak et al. studied the turnover problem of reacting particles moving in a piecewise continuous parabolic potential and exponentially decaying memory [13]. In the case of exponentially correlated noise, by using analogue computers, Marchesoni et al. have reported that the $\tau$-dependent of transition rate $k(\tau)$ is different in the overdamped case ($\sim\exp(-k_\infty\tau)$) and underdamped limit ($\sim\exp(-k_0\tau^2)$) [5]. Other than the case of overdamped friction and exponentially correlated noise, there is no exhaustive theory to obtain the reaction rate in the case of underdamped friction and general broad-band colored noises.

In this paper, we apply the stochastic averaging method to study the reaction rate of a reacting particle driven by broad-band noises and with linear weak damping. In Section 2, the stochastic averaging method [14,15] is introduced as well as the concept of generalized harmonic functions, and the averaged Itô equation governing the energy diffusion process and the corresponding Pontryagin equation governing the MFPT are established. The analytical expression for the transition rate as the inverse of the MFPT [16] is obtained by solving the Pontryagin equation in Section 3. As PSD is included in

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the final formula for the transition rate, the analytical result is valid for all cases of broad-band noises. As two examples, the results for two special broad-band noises, i.e., the harmonic noise and exponentially correlated noise, are discussed in Section 4. It is shown that the general expression of reaction rate obtained in this paper can be reduced to the Kramers' rate for Gaussian white noise and Marchesoni's approximate formula for exponentially correlated noise through linear approximation and high potential barrier approximation [5]. The corresponding Monte Carlo simulation is conducted to verify the theoretical results and to determine the applicability range of the stochastic averaging method.

## 2 Stochastic averaging method based reaction rate prediction

For a strongly nonlinear system with single degree of freedom and subject to broad-band noises excitation, the governing equation can be written as

$$\ddot{X} + \varepsilon\gamma(X,\dot{X})\dot{X} + g(X) = \varepsilon^{1/2}\sum_{k=1}^{m} f_k(X,\dot{X})\xi_k(t) \quad (1)$$

where $g(X)$ is the strongly nonlinear conservative force, $\varepsilon$ denotes a small parameter, $\varepsilon\gamma(X,\dot{X})$ is the coefficient of quasi-linear weak damping, $\varepsilon^{1/2}f_k(X,\dot{X})$ are the amplitudes of random weak excitations, and $\xi_k(t)$ are the stationary broad-band random processes with correlation function $R_{kl}(\tau) = E[\xi_k(t)\xi_l(t+\tau)]$ or PSD $S_{kl}(\omega)$.

The conservative Hamiltonian system associated with system (1) is governed by

$$\ddot{x} + g(x) = 0. \quad (2)$$

The potential $U(x)$ is defined as

$$U(x) = \int_0^x g(u)du. \quad (3)$$

The functions $g(x)$ and $U(x)$ are assumed to satisfy the following four conditions:

(i) $g(0) = 0$;
(ii) There exists a point $x_0 > 0$ such that $g(x_0) \neq 0$ and $U(x_0) > 0$;
(iii) A point $x_1 < 0$ can be found such that $g(x_1) \neq 0$ and $U(x_1) = U(x_0)$;
(iv) For all $x_1 < x < x_0$, $U(x) < U(x_0)$.

Under these conditions, the Hamiltonian system (2) has periodic solution [14]

$$\begin{aligned} x(t) &= a\cos\phi(t) + b, \\ \dot{x}(t) &= -av(a,\phi)\sin\phi(t), \\ \phi(t) &= \psi(t) + \theta(t) \end{aligned} \quad (4)$$

where $a$ is the amplitude and $b$ is the symmetric center coordinate of displacement; $v(a,\phi)$ is the instantaneous angular frequency; $\theta(t)$ is the phase angle difference. $\cos\phi(t)$ and $\sin\phi(t)$ are called generalized harmonic functions. From equations (3) and (4), one can derive the following relations:

$$U(a+b) = U(-a+b) \quad (5)$$

$$v(a,\phi) = \frac{d\psi(t)}{dt} = \sqrt{\frac{2\left(U(a+b) - U(a\cos\phi + b)\right)}{a^2\sin^2\phi}} \quad (6)$$

$a$, $b$ and $v(a,\phi)$ can be obtained by solving equations (5) and (6). It is noted that the instantaneous angular frequency $v(a,\phi)$ is a function of $a$ and phase angle $\phi$. Subsequently, a new variable $h$ is introduced to denote $db/da$. The explicit expression for $h$ is

$$h = \frac{db}{da} = \frac{g(-a+b) + g(a+b)}{g(-a+b) - g(a+b)}. \quad (7)$$

The angular frequency $v\,(a,\phi)$ can be expanded into Fourier series with respect to $\phi$

$$v(a,\phi) = \frac{1}{2}v_0(a) + \sum_{n=1}^{\infty} v_n(a)\cos n\phi \quad (8)$$

where $v_0(a)/2$ is the mean angular frequency

$$\bar{\omega}_0(a) = \frac{1}{2}v_0(a) = \frac{1}{2\pi}\int_0^{2\pi} v(a,\phi)d\phi. \quad (9)$$

Based on this, the following approximate relation will be used in the stochastic averaging operation:

$$\phi(t) = \bar{\omega}_0(a)t + \theta(t). \quad (10)$$

For small $\varepsilon$, the response of quasi Hamiltonian system (1) is random periodic and of the form

$$\begin{aligned} X(t) &= A\cos\Phi(t) + B, \\ \dot{X}(t) &= -Av(A,\Phi)\sin\Phi(t), \\ \Phi(t) &= \Psi(t) + \Theta(t). \end{aligned} \quad (11)$$

By regarding equation (11) as a transformation from $X$, $\dot{X}$ to $A$, $\Phi$, the following equations about amplitude $A$ and phase angle $\Phi$ can be obtained from equation (1) [14]:

$$\begin{aligned} \frac{dA}{dt} &= \varepsilon m_1(A,\Phi) + \varepsilon^{1/2}\sigma_{1k}(A,\Phi)\xi_k(t), \\ \frac{d\Phi}{dt} &= \varepsilon m_2(A,\Phi) + \varepsilon^{1/2}\sigma_{2k}(A,\Phi)\xi_k(t), \\ k &= 1,2,\cdots,m. \end{aligned} \quad (12)$$

where

$$\begin{aligned} m_1 &= -A^2G\gamma(A\cos\Phi + B, -Av\sin\Phi)v^2\sin^2\Phi, \\ m_2 &= -AG\gamma(A\cos\Phi + B, -Av\sin\Phi)v^2(\cos\Phi + H)\sin\Phi, \\ \sigma_{1k} &= -AGf_k(A\cos\Phi + B, -Av\sin\Phi)v\sin\Phi, \\ \sigma_{2k} &= -Gf_k(A\cos\Phi + B, -Av\sin\Phi)v(\cos\Phi + H). \end{aligned} \quad (13)$$

in which $v = v(A,\Phi)$ and $G = 1/\left[g(A+B)(1+H)\right]$.

Based on the Stratonovich-Khasminskii limit theorem [17,18], the amplitude process $A(t)$ in equation (12) converges weakly to a diffusion process as $\varepsilon \to 0$ in a time interval $T \propto 0(\varepsilon^{-1})$. This limiting diffusion process is governed by the following averaged Itô equation:

$$dA = m(A)dt + \sigma(A)dW(t) \tag{14}$$

where $W(t)$ is unit Wiener process. The drift coefficient and diffusion coefficient in equation (14) are

$$\begin{aligned} m(A) &= \left\langle m_1 + \int_{-\infty}^{0} \Big( (\partial\sigma_{1k}/\partial A)\left|_t\sigma_{1l}\right|_{t+\tau} \right. \\ &\quad \left. + (\partial\sigma_{1k}/\partial\Phi)\left|_t\sigma_{2l}\right|_{t+\tau} \Big) R_{kl}(\tau)d\tau \right\rangle_t, \\ \sigma^2(A) &= \left\langle \int_{-\infty}^{\infty} \left(\sigma_{1k}\left|_t\sigma_{1l}\right|_{t+\tau}\right) R_{kl}(\tau)d\tau \right\rangle_t, \\ k,l &= 1,2,\cdots,m. \end{aligned} \tag{15}$$

where $\langle\cdot\rangle_t$ denotes the time averaging operation, i.e.,

$$\langle\cdot\rangle_t = \lim_{T\to\infty}\frac{1}{T}\int_0^T (\cdot)\,dt. \tag{16}$$

In order to avoid the difficult time averaging, it is replaced by space averaging with respect to the phase angle $\Phi$. To obtain the explicit expressions for $m(A)$ and $\sigma^2(A)$, first expand those terms such as $\partial\sigma_{1k}/\partial A$, $\sigma_{1l}$ and etc. into Fourier series with respect to $\Phi$, integrate with respect to $\tau$ and then average with respect to $\Phi$ using the approximate relations in equation (10).

Note that there is a deterministic relation between the amplitude $A$ and the total energy $E$, i.e.,

$$E = U(A+B) = U(-A+B). \tag{17}$$

Eliminating $B$ in equation (17) yields deterministic function $E = E(A)$. The Itô equation governing energy $E$ can be obtained from the Itô equation (14) by using the Itô differential rule as following:

$$dE = \bar{m}(E)dt + \bar{\sigma}^2(E)dW(t) \tag{18}$$

where the drift coefficient and diffusion coefficient are

$$\begin{aligned} \bar{m}(E) &= \left\{\left(\frac{dE}{dA}\right)m(A) + \frac{1}{2}\left(\frac{d^2E}{dA^2}\right)\sigma^2(A)\right\}\Big|_{A=U^{-1}(E)-B}, \\ \bar{\sigma}^2(E) &= \left\{\left(\frac{dE}{dA}\right)^2\sigma^2(A)\right\}\Big|_{A=U^{-1}(E)-B}. \end{aligned} \tag{19}$$

Since we are interested in the behavior of transition over a potential barrier, the Pontryagin equation governing MFPT is derived from equation (18) as:

$$\bar{m}(E_0)\frac{\partial\tau}{\partial E_0} + \frac{1}{2}\bar{\sigma}^2(E_0)\frac{\partial^2\tau}{\partial E_0^2} = -1 \tag{20}$$

where $\tau$ is the MFPT which is a function of initial energy $E_0$. Here, the first-passage time of energy process $E(t)$ is defined as the time when energy reaches critical value $E_{\rm C}$ for the first time given the initial energy $E_0$ ($E_{min} \leqslant E_0 < E_{\rm C}$). The boundary conditions associated with equation (20) are

$$\tau(E_0 = E_{min}) = \text{finite}, \quad \tau(E_0 = E_{\rm C}) = 0. \tag{21}$$

Under the boundary conditions in equation (21), the following solution to equation (20) can be obtained:

$$\tau(E_0) = 2\int_{E_0}^{E_C} du \int_0^u \frac{1}{\bar{\sigma}^2(v)}\exp\left[-2\int_v^u \frac{\bar{m}(w)}{\bar{\sigma}^2(w)}dw\right]dv. \tag{22}$$

Based on the equivalence of reaction rate and the inverse of MFPT [16], the energy diffusion controlled transition rate with initial energy $E_0$ is

$$k_E = 1/\mu\tau(E_0). \tag{23}$$

It should be noted that $\mu = 1$ is valid only in the case of single metastable potential and in the case of bistable potential with disregarding the backward transition. When both of the forward and backward transition are considered, $\mu$ for bistable potential is equal to 2 in symmetric case and is determined by the ratio of phase volumes of the two states in asymmetric case [3].

## 3 Reaction rate of a particle excited by broad-band noise

In this section, the transition rate of a reacting particle with one-dimensional general potential and broad-band colored noise excitation is studied by using the stochastic averaging method introduced in the previous section. The equation of the system is of the form

$$\ddot{X} + \varepsilon\gamma\dot{X} + g(X) = \varepsilon^{1/2}\xi(t) \tag{24}$$

where $g(X) = \omega_0^2 X + \beta X^2 + \alpha X^3$ and the potential

$$U(X) = \omega_0^2 X^2/2 + \beta X^3/3 + \alpha X^4/4 \tag{25}$$

satisfy the four conditions (i)–(iv) listed in the last section. $\xi(t)$ is a broad-band colored noise with PSD $S(\omega)$. The small parameter $\varepsilon$ in equation (24) is combined with the damping coefficient $\gamma$ and noise $\xi(t)$ so that the damping force and the random excitation are weak. Several patterns of potentials such as single metastable, symmetric and asymmetric bistable potentials can be obtained from equation (25) through varying the parameters $\omega_0$, $\beta$ and $\alpha$.

Following the procedure described in Section 2, we obtain the following expression for MFPT:

$$\tau(0) = 2\int_0^{\Delta U} du \int_0^u \frac{1}{\bar{\sigma}^2(v)}\exp\left[-2\int_v^u \frac{\bar{m}(w)}{\bar{\sigma}^2(w)}dw\right]dv \tag{26}$$

where initial energy $E_0 = 0$ and potential barrier $E_{\rm C} = \Delta U$. The two coefficients $\bar{m}(E)$ and $\bar{\sigma}^2(E)$ in equation (26)

are evaluated as follows using equation (19):

$$m(A) = \frac{-\gamma G A^2}{16}\left(8\omega_0^2 + 16B\beta + 5A^2\alpha + 24B^2\alpha\right) + \frac{\pi G A}{8} \times \sum_{i=0}^{\infty}\left\{(v_i - v_{i+2})\left[\frac{d\big(GA(v_i - v_{i+2})\big)}{dA} + (i+1)(v_i + 2Hv_{i+1} + v_{i+2})G\right] S\Big((i+1)\bar{\omega}_0\Big)\right\},$$

$$\sigma^2(A) = \frac{\pi G^2 A^2}{4}\sum_{i=0}^{\infty}\left[(v_i - v_{i+2})^2 S\Big((i+1)\bar{\omega}_0\Big)\right] \quad (27)$$

where $G$, $B$, $H$, $v_i$ and $\bar{\omega}_0$ can be obtained directly or indirectly by replacing $a$, $b$ and $h$ in equations (7–9), (13) with $A$, $B$ and $H$, respectively.

The reaction rate is thus achieved using equation (23) where $\mu$ depends on the pattern of the potential and whether or not the backward transition is considered.

## 4 Reaction rate in two special broad-band noise cases

### 4.1 Harmonic noise

A harmonic noise can be produced from a harmonic oscillator driven by a Gaussian white noise. The PSD of the harmonic noise is of the form

$$S(\omega) = \frac{D}{\pi\left(\omega^2\Gamma^2 + (\omega^2 - \Omega^2)^2\right)} \quad (28)$$

where $\Gamma$ and $\Omega$ are the damping coefficient and natural frequency of the harmonic oscillator, respectively; $2D$ is the intensity of the input Gaussian white noise. The Einstein relation $D = \gamma k_{\mathrm{B}} T$ is applicable here, where $k_{\mathrm{B}}$ is the Boltzmann constant, $T$ is the temperature of the thermal environment and $\gamma$ is the damping coefficient. The PSD in equation (28) for three $\Gamma$ values are shown in Figure 1 using solid line. It is seen that many kinds of PSD including those for broad-band, flat narrow-band and narrow-band noises can be produced by adjusting $D$, $\Gamma$ and $\Omega$.

The classical Kramers bistable model is used in the following to illuminate the prediction of transition rate using the proposed method. A reacting particle moving in Kramers bistable potential is shown in Figure 2. The potential is defined as

$$U(X) = \varepsilon_1 X^2 - \sqrt{\varepsilon_1\varepsilon_2}X^3 + \frac{\varepsilon_2}{4}X^4, \quad \varepsilon_1, \varepsilon_2 > 0. \quad (29)$$

The potential barrier between the two stable equilibrium positions is $\Delta U = \varepsilon_1^2/4\varepsilon_2$. The parameters in equation (25) for this special case are

$$\omega_0 = \sqrt{2\varepsilon_1}, \quad \beta = -3\sqrt{\varepsilon_1\varepsilon_2}, \quad \alpha = \varepsilon_2. \quad (30)$$

Substituting equations (28) and (30) into equations (27), (19), (26) and (23) in sequence, the transition rate of a reacting particle in Kramers bistable potential can be evaluated.

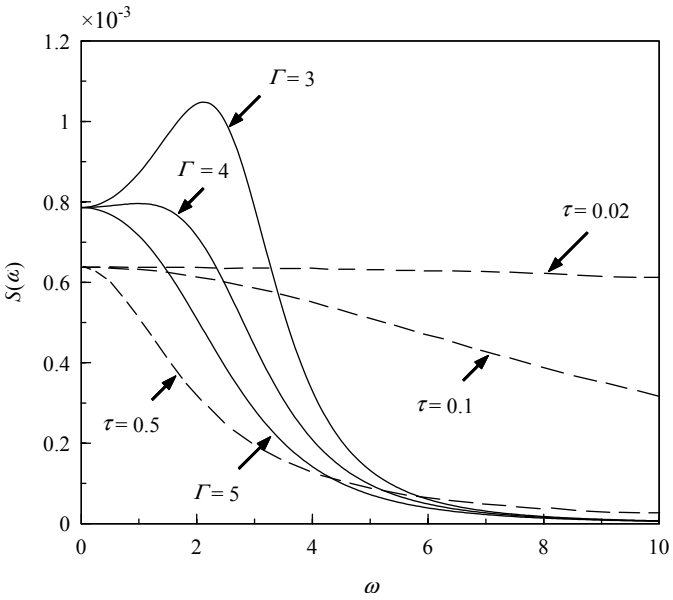


**Fig. 1.** The PSD of harmonic noise (28) with $D = 0.2$, $\Omega = 3$ denoted by solid line —— and the PSD of exponentially correlated noise (37) with $D = 0.002$ denoted by dashed line - - - - -.

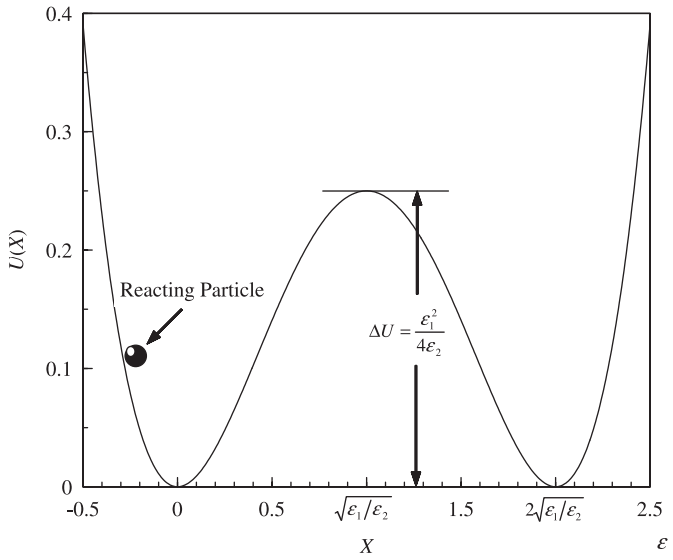


**Fig. 2.** A reacting particle moving in the classical Kramers bistable potential governed by equation (29) with $\varepsilon_1 = 1$, $\varepsilon_2 = 1$.

It is noted that the general expression for transition rate in equations (26) and (23) can be reduced to the classical Kramers rate [2] by the following reasoning: (i) In the case of linear approximation, i.e., harmonic potential approximation, the nonlinear parameters $\beta$ and $\alpha$ vanish and thus $g(X) = \omega_0^2 X^2$. The following parameters can be obtained from equations (5–9)

$$\bar{\omega}_0(A) = \omega_0, \quad B = 0, \quad H = 0, \quad v_i(A) = 0, \quad (i = 1, 2, \cdots). \quad (31)$$

Substituting equation (31) into equations (27) and (19), one can obtain the reduced drift coefficients and diffusion coefficients

$$m(A) = -\frac{1}{2}\gamma A + \frac{\pi}{2\omega_0^2 A}S(\omega_0), \quad \sigma^2(A) = \frac{\pi}{\omega_0^2}S(\omega_0),$$
$$\bar{m}(E) = -\gamma E + \pi S(\omega_0), \quad \bar{\sigma}^2(E) = 2\pi E S(\omega_0). \qquad (32)$$

Substituting $\bar{m}(E)$ and $\bar{\sigma}^2(E)$ in equation (32) into equations (26) and (23), a simplified expression for the transition rate can be derived as:

$$k_E = \left(\frac{1}{\gamma}\int_0^Z \frac{e^t - 1}{t}dt\right)^{-1}, \quad Z = \frac{\gamma \Delta U}{\pi S(\omega_0)} \qquad (33)$$

(ii) If the potential barrier $\Delta U$ is sufficiently high, i.e., $\gamma\Delta U/\pi S(\omega_0) \gg 1$, considering the following limit

$$\lim_{Z\to\infty}\left[\int_0^Z \frac{e^t - 1}{t}dt \Big/ \frac{1}{Z}e^Z\right] = 1 \qquad (34)$$

we can obtain a simplified expression for the transition rate:

$$k_E = \frac{\gamma^2 \Delta U}{\pi S(\omega_0)}\exp\left(\frac{-\gamma\Delta U}{\pi S(\omega_0)}\right) \qquad (35)$$

(iii) Furthermore, in the case of white noise $S(\omega_0) = D/\pi$, noting the Einstein relation $D = \gamma k_{\mathrm{B}}T$, the transition rate can be simplified as:

$$k_E = \frac{\gamma \Delta U}{k_{\mathrm{B}}T}\exp\left(\frac{-\Delta U}{k_{\mathrm{B}}T}\right) \qquad (36)$$

which is the same as that given by Kramers for the case of weak damping and white noise [2].

Some numerical results obtained by using the proposed method and from Monte Carlo simulations are shown in Figure 3, where solid lines represent for analytical results, •, ♦, ■ for the simulation results of energy controlled transition rate, and ∘, ♢, □ for the simulation results of spatial transition rate. The spatial transition rate is the inverse of the MFPT for the first-passage of displacement $X(t) > \sqrt{\varepsilon_1/\varepsilon_2}$ (see Fig. 2). It is indicated that in the case of weak damping the two rates are close to each other and the analytical results agree well with both of simulation results. It is shown in Figure 4 that equation (23) is valid for various shapes of PSD $S(\omega)$. However, we can see that the reaction rate of a particle in bistable potential under narrow-band random excitation can not be well predicted by using the proposed method, especially when the PSD peak is located near the natural frequency of the system. In such cases, the external resonance should be considered and the averaged Itô equations will be two-dimensional.

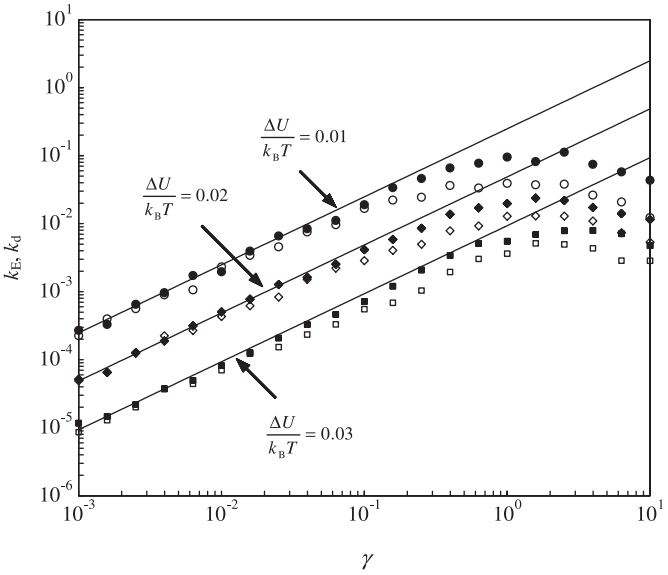


**Fig. 3.** The energy diffusion controlled transition rate $k_{\mathrm{E}}$ in equation (26) of system (24) subject to harmonic noise with PSD (28). $\Omega = 3$, $\Gamma = 10$, $D$ is determined by equation (28) and $D = \gamma k_B T$. —— denotes the analytical results; •, ♦, ■ denote the corresponding simulation results and ∘, ♢, □ denote the spatial transition rate which defined by the random process $X(t) > \sqrt{\varepsilon_1/\varepsilon_2}$ for the first time.

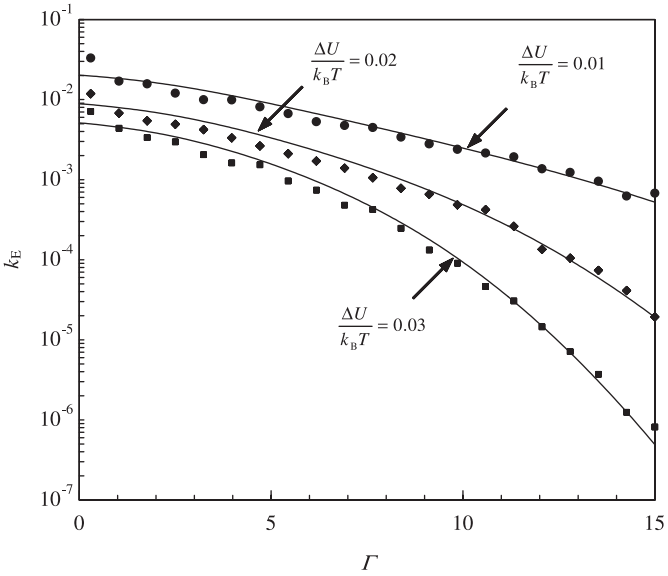


**Fig. 4.** The energy diffusion controlled transition rate $k_{\mathrm{E}}$ in equation (26) as the function of correlation time $\tau$. $\Omega = 3$, $\gamma = 0.01$. —— denotes the analytical results; •, ♦, ■ denote the corresponding simulation results.

### 4.2 Exponentially correlated noise

Another important colored noise model often used in theoretical analysis and analogical experiment is the exponentially correlated noise [3,5]. This colored noise can be produced from one-dimensional linear system driven by Gaussian white noise. The correlation function $R(t)$ and PSD $S(\omega)$ of the exponentially correlated noise are

$$R(t) = \frac{D}{\tau}\exp\left(-\frac{|t|}{\tau}\right), \quad S(\omega) = \frac{D}{\pi(\tau^2\omega^2 + 1)} \qquad (37)$$

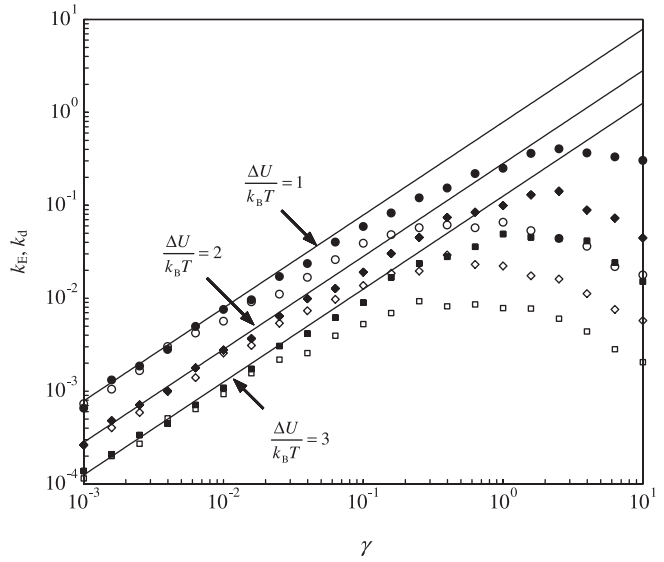


**Fig. 5.** The energy diffusion controlled transition rate $k_E$ in equation (26) of system (24) subject to exponentially correlated noise with PSD (37). $\tau = 0.2$. $D$ is determined by equation (37) and $D = \gamma k_B T$. —— denotes the analytical results; •, ♦, ■ denote the corresponding simulation results and ○, ♢, □ denote the spatial transition rate which defined by the random process $X(t) > \sqrt{\varepsilon_1/\varepsilon_2}$ for the first time.

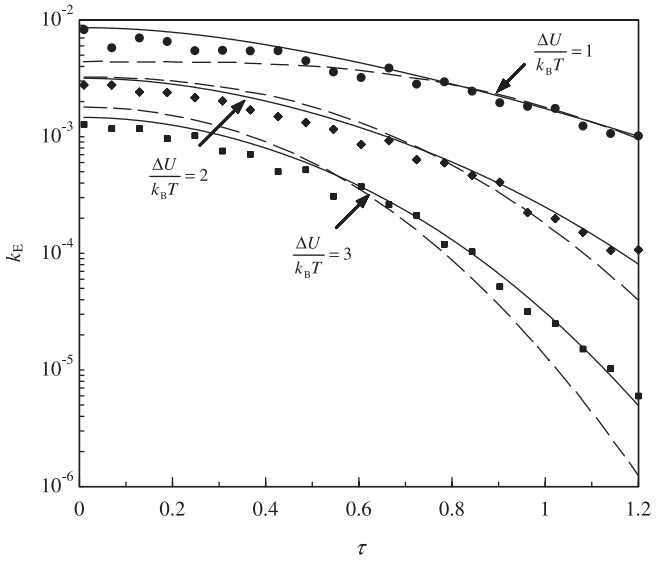


**Fig. 6.** The energy diffusion controlled transition rate $k_E$ in equation (26) as the function of correlation time $\tau$. $\gamma = 0.01$. —— denotes the analytical results (26); ------ denotes the Marchensoni's results (38); •, ♦, ■ denote the corresponding simulation results.

where $2D$ is the intensity of the input Gaussian white noise; $\tau$ is the correlation time. Some PSDs for exponentially correlated noises are shown in Figure 1 using dotted lines. It is shown that the bandwidth of the noise depends on $\tau$. As $\tau \to 0$, the exponentially correlated noise approaches white noise.

By using analogue computer to investigate the transition rate, Marchesoni et al. have reported that the $\tau$-dependent of transition rate $k(\tau)$ is in proportion to $\exp(-k_0\tau^2)$. In the absence of an exhaustive theory, Marchesoni et al. tested the plausibility of the simulation findings and derived the following approximate prediction for transition rate [5]:

$$k(\tau) = k(0)(1 + \omega_0^2\tau^2)\exp\left(\frac{-\Delta U}{k_B T}\omega_0^2\tau^2\right) \qquad (38)$$

where the transition rate $k(\tau)$ is regarded as a function of the correlation time $\tau$ and $k(0)$ is exactly the same as Kramers transition rate $k_E$ in equation (36). It is noted that in the limit $\tau \to 0$, equation (38) reduces to the experimental law $k(\tau) \sim \exp(-k_0\tau^2)$.

Noted that the general expression for transition rate equations (26) and (23) can also be reduced to equation (38) under the same conditions. As shown in the last section, after linear and high potential barrier approximations, the transition rate is given by equation (35). Substituting equation (37) into equation (35) yields

$$k_E = \frac{\gamma\Delta U}{k_B T}(1 + \omega_0^2\tau^2)\exp\left[\frac{-\Delta U}{k_B T}(1 + \omega_0^2\tau^2)\right] \qquad (39)$$

which is exactly the same as that in equation (38) noting that $k(0)$ in equation (38) is equal to $k_E$ in equation (36).

Some numerical results are shown in Figure 5, where solid lines represent for analytical results, •, ♦, ■ for the corresponding simulation results of energy diffusion controlled rate, and ○, ♢, □ for the simulation results of spatial transition rate. With the correlation time $\tau$ varying from 0 to 1.2, the noise with PSD (37) goes through from white noise to broad-band noise. Figure 6 shows the comparison of the analytical results obtained from equation (23), results from equation (38) and the simulation results as function of correlation time $\tau$. The satisfactory prediction for transition rate using (23) can be achieved even when broad-band noise has longer correlation time $\tau$.

## 5 Conclusions

In the present paper, the stochastic averaging method using generalized harmonic functions has been applied to the prediction of the energy diffusion controlled reaction rate of a reacting particle subject to broad-band colored noise excitation. In the case of weak damping and weak random excitation, the amplitudes of displacement and energy of the reacting particle are slowly varying processes that converge to one-dimensional diffusion processes. The averaged Itô stochastic differential equations governing the amplitudes and energy diffusion processes have been established. The MFPT of the energy diffusion process has been obtained by solving the corresponding Pontryagin equation. Then, the transition rate controlled by energy diffusion was determined as the inverse of the MFPT. As an example, the reaction rate of a particle in classical Kramers bistable potential and driven by a harmonic

noise or an exponentially correlated noise has been studied in detail. It has been shown that the expression for the transition rate is quite general and is applicable to various potentials and broad-band colored noises and that by taking linear approximation and high potential barrier approximation the general expression for reaction rate obtained in this paper can be reduced to the Kramers rate for white noise and Marchesoni's formula for exponentially correlated noise. Monte Carlo simulations have been performed to verify the analytical results. It is seen from the figures that in the linear weak damping case, the proposed theoretical method yields satisfactory results for the reaction rate. However, in the case of narrow-band noise, the proposed method fails to yield satisfactory results probably due to the external resonance.

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