Vol 16 No 6, June 2007
1009-1963/2007/16(06)/1510-06
Chinese Physics
© 2007 Chin. Phys. Soc.
and IOP Publishing Ltd

Energy diffusion controlled reaction rate in dissipative Hamiltonian systems*

Deng Mao-Lin(邓茂林) and Zhu Wei-Qiu(朱位秋)†

Department of Mechanics, State Key Laboratory of Fluid Power Transmission and Control, Zhejiang University, Hangzhou 310027*, China*

(Received 26 December 2006; revised manuscript received 25 January 2007)

In this paper the energy diffusion controlled reaction rate in dissipative Hamiltonian systems is investigated by using the stochastic averaging method for quasi Hamiltonian systems. The boundary value problem of mean first-passage time (MFPT) of averaged system is formulated and the energy diffusion controlled reaction rate is obtained as the inverse of MFPT. The energy diffusion controlled reaction rate in the classical Kramers bistable potential and in a two-dimensional bistable potential with a heat bath are obtained by using the proposed approach respectively. The obtained results are then compared with those from Monte Carlo simulation of original systems and from the classical Kramers theory. It is shown that the reaction rate obtained by using the proposed approach agrees well with that from Monte Carlo simulation and is more accurate than the classical Kramers rate.

Keywords: quasi Hamiltonian system, Kramers reaction rate theory, mean first-passage time, stochastic averaging

PACC: 0250, 0540, 0547

1. Introduction

Reaction rate theory is a branch of nonlinear science of importance to much of physics, chemistry and biology. The development of 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 theories are based on the pioneer research works of Eyring[1] and Kramers[2] etc., which are of basic importance for the understanding of the feature of reaction.[3] Classical Kramers reaction theory describes reactions as transitions over a potential barrier due to stochastic forces. Kramers derived the rate expressions for various ranges of damping forces, including strong damping (spatial diffusion regime) and weak damping (energy diffusion regimes). Although Kramers introduced his theory for describing chemical reaction, it has wide applicability to activated processes and has been modified or corrected in various ways by many researchers.[4−6] It has been shown that Kramers' rate and the inverse of mean first-passage time (MFPT) are universally equivalent.[7] Thus, the reaction rate can be determined through evaluating the MFPT. However, the class of processes for which the MFPT may be calculated is rather limited.

In the last decade, the stochastic averaging method for quasi Hamiltonian systems has been developed in mechanical/structural engineering field.[8−11] The term 'quasi-Hamiltonian system' means a weakly stochastically excited and dissipated Hamiltonian system. In the present paper, the stochastic averaging method for quasi-Hamiltonian systems formerly used in mechanical/structural engineering field is applied to the study of the energy diffusion controlled reaction rate in dissipative Hamiltonian systems. The procedure of dealing with a one-dimensional system under the classical Kramers bistable potential with a heat bath is illuminated in detail. The proposed approach is also applied to the reaction rate problem under a two-dimensional bistable potential with a heat bath. The obtained results are compared with those from Monte Carlo simulation of original systems and the classical Kramers theory.

2. Reaction rate in one-dimensional potential

A general model in the reaction rate theory is a bistable oscillator coupled to a heat bath. The me-

*Project supported by the National Natural Science Foundation of China (Key Grant No 10332030), the Specialized Research Fund for the Doctoral Program of Higher Education of China (Grant No 20060335125) and the National Science Foundation for Post-doctoral Scientists of China (Grant No 20060390338).
†Corresponding author. E-mail: wqzhu@yahoo.com

chanical realization of the oscillator is a reacting particle of mass m moving in a potential $U(x)$ with two local minima. The bath exerts a linear damping force and a Gaussian white random force. The motion of the reaction system is then described by the following Langevin equation:

$$m\frac{\mathrm{d}^2x}{\mathrm{d}t^2}+\gamma\frac{\mathrm{d}x}{\mathrm{d}t}+\frac{\mathrm{d}U(x)}{\mathrm{d}x}=\sqrt{2D}\xi(t), \qquad (1)$$

where the mass m of reacting particle is generally taken to be one unit. $\xi(t)$ is a normalized Gaussian white noise with mean value $\langle\xi(t)\rangle = 0$ and correlation function $\langle\xi(t)\xi(t+\tau)\rangle = \delta(\tau)$. The strength D of the random force is related to damping constant γ and temperature T of the heat bath by the Einstein relation $D = \gamma k_{\mathrm{B}}T$, where k_{B} is the Boltzmann constant. The potential

$$U(x) = ax^2 - \sqrt{ab}x^3 + bx^4/4, \quad a, b > 0, \qquad (2)$$

is shown in Fig.1. The energy difference or potential barrier between the saddle point and the minima is $\Delta U = a^2/4b$.

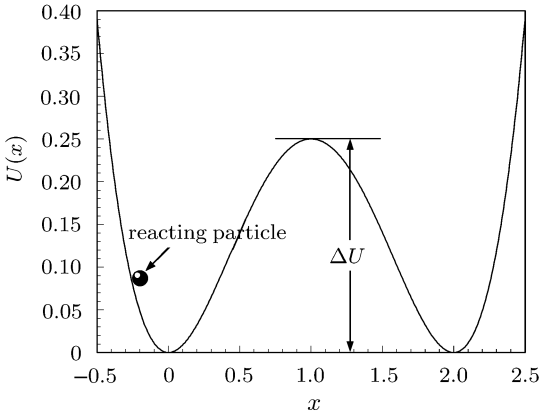


Fig.1. A reacting particle moving in the classical Kramers bistable potential governed by Eq.(2) with $a = 1$ and $b = 1$.

The random force $\xi(t)$ is caused by the heat bath and drives the particle out of the stable state. There are realizations of the random force that drive the particle from one stable state over the saddle point to the other stable state. The bistable oscillator is just one of the simplest examples of this widespread and important effect. It has many different applications in physics, chemistry, biology and technical sciences. For example, a molecule may exist in two different configurations A and B. In a solvent, transitions between the two configurations denoted by $A \Leftrightarrow B$ may occur. In the energy landscape of the molecule, the two configurations A and B correspond to two minima which are separated by potential barrier. The interaction with solvent molecules provides the necessary energy to overcome this hindrance.[12] Assuming that the solvent acts with many weak collisions on a fast time scale, we find that the reaction can be described by a Langevin equation such as Eq.(1) where $U(x)$ is a conveniently defined potential of mean force. Characteristic for the reaction system is the transition over the barrier that acts as a bottleneck for the dynamics. The transition rate was derived according to two different damping regimes.[3] According to classical Kramers theory, in the moderate and large damping γ regime, the transition rate is approximately given by

$$k_{\mathrm{I}} = \Big[\Big(\frac{\gamma^2}{4}+\omega_{\mathrm{b}}^2\Big)^{1/2}-\frac{\gamma}{2}\Big]\frac{\omega_0}{2\pi\omega_{\mathrm{b}}}\exp\Big(\frac{-\Delta U}{k_{\mathrm{B}}T}\Big). \qquad (3)$$

Here ω_0 is the angular frequency associated with potential minimum where the transition starts and ω_{b} is the angular frequency associated with potential maximum where the transition happens. It is easy to show by using Eq.(2) that $\omega_0 = \sqrt{2a}$ and $\omega_{\mathrm{b}} = \sqrt{a}$. The MFPT in large damping case can also be obtained by neglecting the inertial term $m\mathrm{d}^2x/\mathrm{d}t^2$ in bistable system (1).[13−15] On the other hand, in the weak damping regime, the transition rate is controlled by energy diffusion and approximately given by

$$k_{_W} = \frac{\gamma\Delta U}{k_{\mathrm{B}}T}\exp\Big(\frac{-\Delta U}{k_{\mathrm{B}}T}\Big). \qquad (4)$$

Combining the two kinds of transition rates Eqs.(3) and (4), one arrives at an estimation for general transition rate

$$k_{_T} = (k_{_W}^{-1} + k_{\mathrm{I}}^{-1})^{-1}, \qquad (5)$$

which is applicable in the weak, moderate and large damping regimes. For the system parameters used in Ref.[16], the numerical results from Eqs. (4) and (5) and Monte Carlo simulation of original system (1) are shown in Fig.2 by using dash lines and symbols • ♦ respectively. It is seen that Eqs.(4) and (5) are quite good approximations of the reaction rate. In the following a more accurate reaction rate in weak damping regime will be obtained by using the stochastic averaging method for quasi Hamiltonian systems [8] and by evaluating the MFPT of the averaged systems.

By treating the system (1) as a stochastically excited and dissipated Hamiltonian system, we can obtain the following equivalent Itô stochastic differential equation from Eq.(1)

$$\mathrm{d}x = v\mathrm{d}t,$$

$$\mathrm{d}v = (-\mathrm{d}U(x)/\mathrm{d}x - \gamma v)\mathrm{d}t + \sqrt{2\gamma k_{\mathrm{B}} T}\mathrm{d}B(t), \quad (6)$$

where x is the so-called generalized displacement and $v = \mathrm{d}x/\mathrm{d}t$ is generalized momentum, $B(t)$ is unit Wiener process. The Hamiltonian or the total energy of Eq.(1) is

$$H = v^2/2 + U(x). \quad (7)$$

The Itô stochastic differential equation for $H(t)$ can be derived from Eq.(6) by using the Itô differential rule[17] as follows:

$$\mathrm{d}H = (-\gamma v^2 + \gamma k_{\mathrm{B}} T)\mathrm{d}t + v\sqrt{2\gamma k_{\mathrm{B}} T}\mathrm{d}B(t). \quad (8)$$

Among the three variables x, v and H in Eq.(8), only two variables are independent since v can be replaced by H by using the following transformation:

$$v = \sqrt{2H - 2U(x)}. \quad (9)$$

Assume that the damping is light and the excitation is weak. It is seen from Eq.(8) that the Hamiltonian H is a slowly varying process while the generalized displacement x and generalized momentum v are rapidly varying processes. According to a theorem due to Khasminskii,[18] the $H(t)$ process converges in probability to a one-dimensional diffusion process in a time interval $0 \le t \le T$, where $T \sim 0(\varepsilon^{-1})$. In other words, the H process may be replaced in the first approximation by a diffusion process.

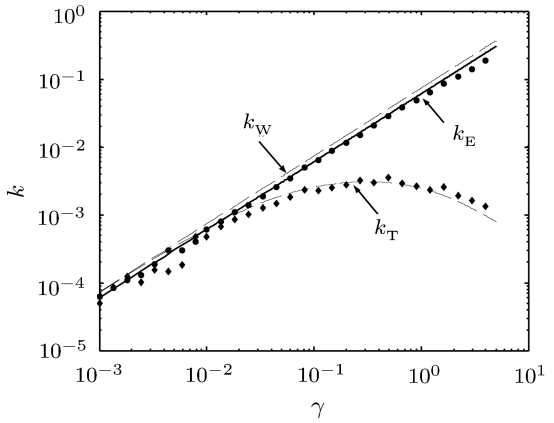


Fig.2. The reaction rate of system (1) with $a = 1$, $b = 1$ and $\Delta U/k_{\mathrm{B}}T = 4$. Solid line (—) denotes the theoretical results from Eq.(21), dash line (- - -) denotes the results from Eqs.(4), (5), the diamond (♦) and the dot (•) denote the associated simulation results.

The Itô equation for the limiting diffusion process of $H(t)$ can be obtained by applying time averaging to Eq.(8). Making use of the first equation in Eq.(6), i.e., $\mathrm{d}x = v\mathrm{d}t$, we can replace the time averaging by a space averaging with respect to x under the condition that H is kept constant. As a result, the averaged Itô equation for the Hamiltonian $H(t)$ is

$$\mathrm{d}H = m(H)\mathrm{d}t + \sigma^2(H)\mathrm{d}B(t). \quad (10)$$

By using space averaging, we derive the drift coefficient $m(H)$ and diffusion coefficient $\sigma^2(H)$ as follows:

$$\begin{aligned} m(H) &= \frac{1}{T(H)}\int_{\Omega}(-\gamma v^2 + \gamma k_{\mathrm{B}} T)\mathrm{d}x, \\ \sigma^2(H) &= \frac{1}{T(H)}\int_{\Omega}(2\gamma k_{\mathrm{B}} T v^2)\mathrm{d}x, \\ T(H) &= \int_{\Omega}(1/v)\mathrm{d}x, \\ \Omega &= \{x|U(x) \le H\}. \end{aligned} \quad (11)$$

Using Eq.(9) to replace v by H and completing the integrations in Eq.(11), we can obtain the following compact expressions for $m(H)$ and $\sigma^2(H)$:

$$\begin{aligned} m(H) &= \gamma k_{\mathrm{B}} T - \gamma S(H), \\ \sigma^2(H) &= 2\gamma k_{\mathrm{B}} T S(H), \\ S(H) &= \frac{1}{3b}(a + \sqrt{a^2 - 4bH}\,) \\ &\quad \times \Big(a\frac{E(e)}{K(e)} - \sqrt{a^2 - 4bH}\Big), \\ e &= \frac{a - \sqrt{a^2 - 4bH}}{a + \sqrt{a^2 - 4bH}}, \end{aligned} \quad (12)$$

where the $K(\cdot)$ and $E(\cdot)$ in Eq.(12) are the complete elliptic integral of the first and second kind respectively. In fact, the coefficients in Eq.(12) can be written in a form of more clear physical sense

$$\begin{aligned} m(H) &= \gamma k_{\mathrm{B}} T - \frac{\gamma}{2\pi} I(H)\omega(H), \\ \sigma^2(H) &= \frac{1}{\pi}\gamma k_{\mathrm{B}} T I(H)\omega(H), \end{aligned} \quad (13)$$

where

$$I(H) = \oint \sqrt{2H - 2U(x)}\mathrm{d}x \quad (14)$$

is the action variable at energy level H, and

$$\omega(H) = 2\pi\partial H/\partial I \quad (15)$$

is the frequency of the undamped system at energy level H. The Fokker–Planck equation associated with Itô equation (10) is

$$\begin{aligned} \frac{\partial p(H,t)}{\partial t} = &-\frac{\partial}{\partial H}[m(H)p(H,t)] \\ &+ \frac{1}{2}\frac{\partial^2}{\partial H^2}[\sigma^2(H)p(H,t)]. \end{aligned} \quad (16)$$

The first-passage time of Hamiltonian process $H(t)$ is defined as the time when Hamiltonian reaches

critical value H_c for the first time the initial Hamiltonian is given to be $H_0 < H_c$. The Pontryagin equation governing the MFPT $\tau(H_0)$ is[19]

$$m(H_0)\frac{\mathrm{d}\tau}{\mathrm{d}H_0}+\frac{1}{2}\sigma^2(H_0)\frac{\mathrm{d}^2\tau}{\mathrm{d}H_0^2}=-1, \qquad (17)$$

where $H_{\min} \le H_0 \le H_c$. In the present case, the initial Hamiltonian is $H_{\min} = 0$ and the critical value of Hamiltonian is $H_c = \Delta U$. It can be shown from Eq.(12) that $S(H_{\min}) = 0$ at boundary $H_{\min}$. That is, $H_{\min}$ is a singular boundary of the first class. The following quantitative boundary condition for Eq.(17) at $H_{\min}$ can be obtained from Eq.(17) with $\sigma^2(H_{\min}) = 0$,

$$(\mathrm{d}\tau/\mathrm{d}H_0)|_{H_0=H_{\min}} = -1/\gamma k_{\mathrm{B}}T. \qquad (18)$$

The other boundary conditions at H_c is

$$\tau(H_0 = H_c) = 0. \qquad (19)$$

Under the boundary conditions (18) and (19), we can obtain the following exact solution of Eq.(17):

$$\tau(H_0)=2\int_{H_0}^{H_c}\mathrm{d}u\int_0^u\frac{1}{\sigma^2(v)} \times\exp\Big[-2\int_v^u\frac{m(w)}{\sigma^2(w)}\mathrm{d}w\Big]\mathrm{d}v. \qquad (20)$$

Based on the equivalence of Kramers' reaction rate and the inverse of MFPT,[7] the energy diffusion controlled reaction rate k_{E} can be obtained as inverse of τ with initial energy $H_0 = 0$, that is

$$k_{\mathrm{E}} = 1/\tau(0). \qquad (21)$$

Some numerical results for the reaction rate obtained from Eq.(21) is shown in Fig.2 by using solid line. Comparing these results with simulation results (denoted by ♦, •), we see that the proposed approach yields more accurate result than the Kramers' result in the case of light damping.

It is noted that the rate expression in Eq.(21) is more general than that in Eq.(4). In fact, Eq.(21) can be reduced to Eq.(4) under some restrictive conditions. First, if the transition rate of the reacting particle is approximately estimated by using the linear model, then the action $I(H)$ and frequency $\omega(H)$ in Eq.(13) will be reduced to $I(H) = 2\pi H/\omega_0$ and $\omega(H) = \omega_0$ respectively. The integrals in Eq.(20) can then be completed exactly. The MFPT $\tau(0)$ and the associated estimation for transition rate k_{L} in linear case can be obtained as follows:

$$\tau(0)=\frac{1}{\gamma}\int_0^{\Delta U/k_{\mathrm{B}}T}\frac{\mathrm{e}^t-1}{t}\mathrm{d}t, \quad k_{\mathrm{L}} = 1/\tau(0). \qquad (22)$$

Under the same restrictive condition as that used in derivation of Eq.(4), i.e., $\Delta U/k_{\mathrm{B}}T \gg 1$, the following limit exists:

$$\lim_{x\to\infty}\Big[\Big(\int_0^x\frac{\mathrm{e}^t-1}{t}\mathrm{d}t\Big)\Big/\Big(\frac{1}{x}\mathrm{e}^x\Big)\Big]=1. \qquad (23)$$

By using this limit and the restrictive condition $\Delta U/k_{\mathrm{B}}T \gg 1$, Eq.(22) is further reduced to the following expressions:

$$\tau(0)=\frac{k_{\mathrm{B}}T}{\gamma\Delta U}\exp\Big(\frac{\Delta U}{k_{\mathrm{B}}T}\Big),$$
$$k_{\mathrm{W}}=\frac{\gamma\Delta U}{k_{\mathrm{B}}T}\exp\Big(\frac{-\Delta U}{k_{\mathrm{B}}T}\Big), \qquad (24)$$

where k_{W} in Eq.(24) is completely identical to the Kramers' expression in Eq.(4). The errors of Eqs.(22) and (24) or (4) relative to Eq.(21) for the parameters used in Fig.2 are illustrated in Fig.3. It is seen that the relative error between k_{W} and k_{E} is decreased as $\Delta U/k_{\mathrm{B}}T$ increases.

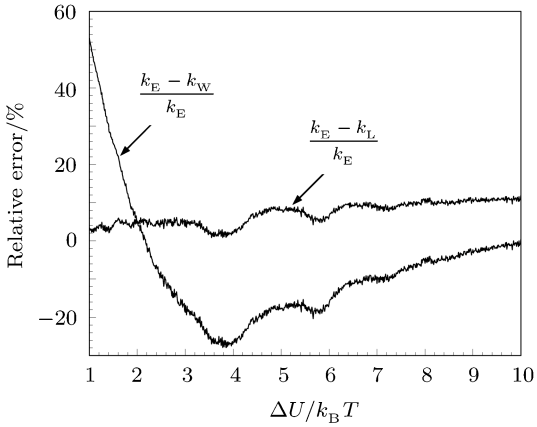


Fig.3. The relative error of Kramers estimation k_{W} in Eq.(4) and the linear estimation k_{L} in Eq.(22) for system (1) with $a = 1$, $b = 1$ and $\gamma = 0.01$.

3. Reaction rate in multi-dimensional potential landscape

One more advantage of the proposed approach for estimating the reaction rate is that it is applicable to multi-dimensional quasi Hamiltonian systems. There are many situations which are described by the motion of a particle in a multi-dimensional potential landscape that can not be reduced to a single coordinate. For the reaction rate in multi-dimensional metastable field, Langer[20] studied the spatial diffusion controlled reaction rate in over damping case and obtained the following important result:

$$k_{\mathrm{L}}=\frac{\lambda}{2\pi}\sqrt{\frac{\det H_0}{|\det H_{\mathrm{b}}|}}\exp\Big(\frac{-\Delta U}{k_{\mathrm{B}}T}\Big), \qquad (25)$$

where λ is the positive Lyapunov exponent of the deterministic motion at the saddle point. H_0 and H_b are the Hessian matrix of the energy function at the metastable state and at the saddle point respectively.

To the authors' knowledge, there is no similar result in the light damping case. Now, the proposed approach is applied to investigate the energy diffusion controlled reaction rate in a two-dimensional bistable potential landscape. The system is governed by the following Langevin equations:

$$\begin{aligned}&\frac{\mathrm{d}^2x_1}{\mathrm{d}t^2}+\gamma\frac{\mathrm{d}x_1}{\mathrm{d}t}+\frac{\partial U(x_1,x_2)}{\partial x_1}=\sqrt{2\gamma k_{\mathrm{B}}T}\xi_1(t),\\&\frac{\mathrm{d}^2x_2}{\mathrm{d}t^2}+\gamma\frac{\mathrm{d}x_2}{\mathrm{d}t}+\frac{\partial U(x_1,x_2)}{\partial x_2}=\sqrt{2\gamma k_{\mathrm{B}}T}\xi_2(t),\end{aligned}\quad(26)$$

where $\xi_1(t)$ and $\xi_2(t)$ are independent Gaussian white noises of unit intensity. The two oscillators in system (26) are coupled by the bistable potential

$$\begin{aligned}&U(x_1,x_2)=-ax_1^2/2+bx_1^4/4+cx_2^2/2-\varepsilon x_1x_2,\\&a,b,c,\varepsilon>0,\end{aligned}\quad(27)$$

which is inseparable with respect to x_1 and x_2 as shown clearly in Fig.4, The potential difference ΔU between the saddle point and the minima in one well can be obtained easily. It is

$$\Delta U=(ac+\varepsilon^2)^2/4bc^2\,.\quad(28)$$

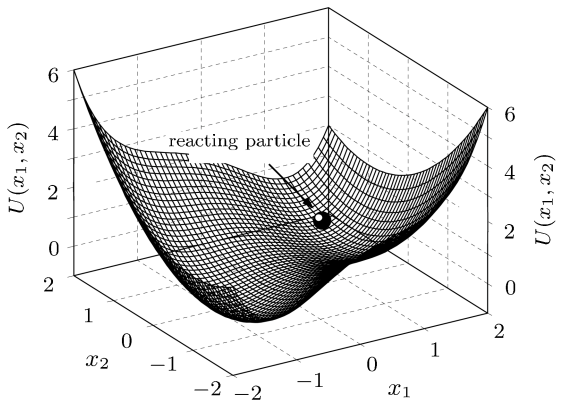


Fig.4. A reacting particle moving in two-dimensional bistable potential landscape governed by Eq.(27) with $a=1$, $b=1$, $c=1$ and $\varepsilon=0.5$.

System (26) can be converted into the following Itô stochastic differential equation:

$$\begin{aligned}&\mathrm{d}x_1=v_1\mathrm{d}t,\\&\mathrm{d}v_1=(-\partial U/\partial x_1-\gamma v_1)\mathrm{d}t+\sqrt{2\gamma k_{\mathrm{B}}T}\,\mathrm{d}B_1(t),\\&\mathrm{d}x_2=v_2\mathrm{d}t,\\&\mathrm{d}v_2=(-\partial U/\partial x_2-\gamma v_2)\mathrm{d}t+\sqrt{2\gamma k_{\mathrm{B}}T}\mathrm{d}B_2(t),\end{aligned}\quad(29)$$

where $v_1=\mathrm{d}x_1/\mathrm{d}t$ and $v_2=\mathrm{d}x_2/\mathrm{d}t$, $B_1(t)$ and $B_2(t)$ are independent unit Wiener processes. The total energy of system is $H=(v_1^2+v_2^2)/2+U(x_1,x_2)$ which is the only first integral of the Hamiltonian system associated with system (26). Using Itô differential rule, we can obtain the following Itô stochastic differential equation for $H(t)$ from Eq.(26)

$$\begin{aligned}\mathrm{d}H=&(-\gamma v_1^2-\gamma v_2^2+2\gamma k_{\mathrm{B}}T)\mathrm{d}t\\&+v_1\sqrt{2\gamma k_{\mathrm{B}}T}\mathrm{d}B_1(t)\\&+v_2\sqrt{2\gamma k_{\mathrm{B}}T}\mathrm{d}B_2(t).\end{aligned}\quad(30)$$

For the case of light damping, it is seen from Eq.(30) that the energy is a slowly varying process. Based on Khasminskii's theorem,[18] we can obtain the averaged Itô equation of the form of Eq.(10) by the time averaging of Eq.(30). In this case, we can use the first equation in Eq.(29) to replace the time averaging by space averaging with respect to x_1. Using the expression for H we can replace v_1 in Eq.(30) by H. To eliminate x_2 and v_2, further averaging with respect to x_2 and v_2 is conducted. The last averaging is based on the following ergodic hypothesis: the evolution of a completely non-integrable Hamiltonian system takes it, with equal probability, through all states which are accessible from the starting point subject to the constraint of energy conservation.[21] As a result, the averaged drift coefficient and diffusion coefficient are

$$\begin{aligned}&m(H)=2\gamma k_{\mathrm{B}}T-2\gamma H+2\gamma G(H),\\&\sigma^2(H)=4\gamma k_{\mathrm{B}}TH-4\gamma k_{\mathrm{B}}TG(H),\\&G(H)=\iint\limits_{\Omega}U(x_1,x_2)\mathrm{d}x_1\mathrm{d}x_2\Big/\iint\limits_{\Omega}\mathrm{d}x_1\mathrm{d}x_2,\\&\Omega=\{(x_1,x_2)|U(x_1,x_2)\le H\}.\end{aligned}\quad(31)$$

The integration region Ω in Eq.(31) is shown in Fig.5 and $G(H)$ is the mean potential in this region. The critical Hamiltonian is $H_{\mathrm{c}}=0$ and the initial Hamiltonian is $H_{\min}=-\Delta U$. The MFPT $\tau(H_0)$ for the original system (26) can be obtained approximately by substituting the coefficients in Eq.(31) into Pontryagin equation (17) and then solving it together with proper boundary conditions. The energy diffusion controlled reaction rate is then obtained by Eq.(21). The numerical result is shown in Fig.6. It is seen from Fig.6 that the theoretical result is in good agreement with that from Monte Carlo simulation of Eq.(26).

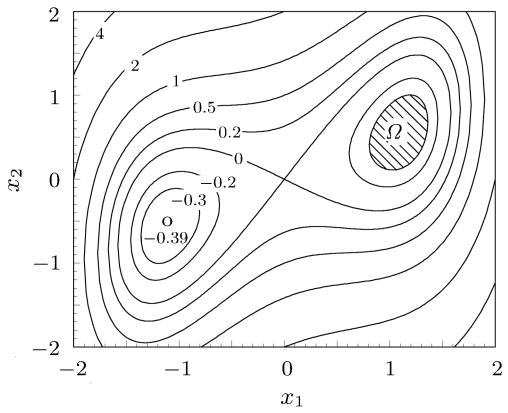


Fig.5. Contour of the potential (27). The numbers are the values of potential. The shadow part Ω is an integration region for Eq.(31). The parameters are the same as those in Fig.4.

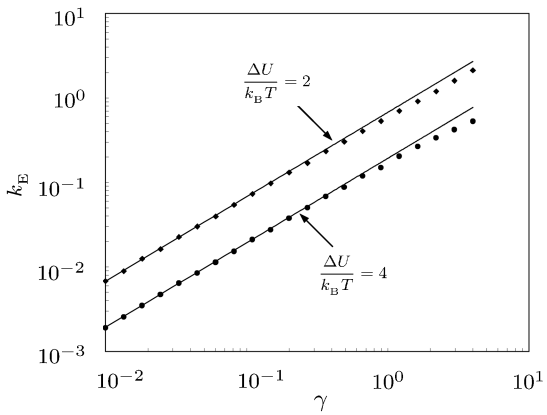


Fig.6. The energy diffusion controlled reaction rate of system (26). The theoretical result obtained from Eq.(21) is denoted by solid line (—) and the simulation result of original system (26) is denoted by symbols (♦) and (•). The parameters are the same as those in Fig.4.

4. Conclusions

In the present paper a new approach for evaluating the energy diffusion controlled reaction rate in dissipative Hamiltonian systems has been proposed based on the stochastic averaging method for quasi Hamiltonian systems and the equivalence of inverse MFPT and Kramers reaction rate. It has been shown that for the classical Kramers model the proposed approach is more general than the Kramers theory in the sense that it is applicable for larger parameter ranges and the result reduces to the Kramers' result in the limiting case of $\Delta U/k_{\mathrm{B}}T \gg 1$. One more significant advantage of the proposed approach is that it is applicable to predict the energy diffusion controlled rate in multidimensional potential landscape. It has been shown through comparison with the Monte Carlo simulation that the proposed approach yields accurate results. Thus, the proposed approach is very promising in prediction of energy diffusion controlled reaction rate.

References

[1] Eyring H 1935 *J. Chem. Phys.* **3** 107

[2] Kramers K A 1940 *Phys.* **4** 284

[3] Hänggi P, Talkner P and Borkovec M 1990 *Rev. Mod. Phys.* **62** 251

[4] Chandrasekhar S 1943 *Rev. Mod. Phys.* **15** 1

[5] van Kampen N G 1981 *Stochastic Processes in Physics and Chemistry* (Amsterdam: North-Holland)

[6] Risken H 1984 *The Fokker-Planck Equation, Methods of Solution and Applications* (Berlin: Springer)

[7] Reimann P, Schmid G J and Hänggi P 1999 *Physical Review* E **60** R1

[8] Zhu W Q and Yang Y Q 1997 *ASME J. Applied Mech.* **64** 157

[9] Zhu W Q, Huang Z L and Yang Y Q 1997 *ASME J. Applied Mech.* **64** 975

[10] Zhu W Q, Huang Z L and Suzuki Y 2002 *Int. J. Nonlinear Mech.* **37** 419

[11] Deng M L and Zhu W Q 2004 *Acta Phys. Sin.* **53** 2029 (in Chinese)

[12] Ebeling W, Schimansky-Geier L and Romanovsky Y M 2002 *Stochastic Dynamics of Reacting Biomolecules* (Singapore: World Scientific)

[13] Jin Y F, Xu W, Ma S J and Li W 2005 *Acta Phys. Sin.* **54** 3480 (in Chinese)

[14] Xu W, Jin Y F, Li W and Ma S J 2005 *Chin. Phys.* **14** 1077

[15] Ning L J, Xu W and Yang X L 2007 *Acta Phys. Sin.* **56** 25 (in Chinese)

[16] Cartling B 1987 *J. Chem. Phys.* **87** 2638

[17] Itô K 1951 *Mem. Amer. Math. Soc.* **4** 289

[18] Khasminskii R Z 1968 *Kibernetika* **4** 260 (in Russian)

[19] Pontryagin L S, Andronov A A and Vitt A A 1933 *J. Exp. Theor. Phys.* **3** 165

[20] Langer J S 1969 *Ann. Phys.* (N.Y.) **54** 258

[21] Binney J J, Dowrick N J, Fisher A J and Newman M E J 1992 *The Theory of Critical Phenomena, An Introduction to the Renormalization Group* (Oxford: Clarendon)