Reactive flux theory for finite potential barriers

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Motivated by developing a simple, accurate, and widely applicable approach to incorporate the finite barrier correction in analytical calculation of the escape rate, the reactive flux theory for finite barriers is proposed. For higher temperatures, instead of at the top of the barrier in the original reactive flux theory, the starting point of the trajectories of Brownian particles is removed into a position inside the potential well where the probability distribution can be regarded as an equilibrium one, and the potential barrier is replaced with an equivalent parabolic potential barrier. The equivalent potential barrier frequency can be obtained by two schemes. The population is also calculated more realistically for finite barriers. The theoretical method is tested by a Brownian particle moving in a cubic metastable potential and subjected to Gaussian white noise. The numerical simulation results confirm the approach satisfactorily until lower reduced barrier heights.

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I. INTRODUCTION

Kramers's seminal paper about a diffusional model of chemical reactions [1] has found various generalizations, for example, to higher dimensional problems [2] and cases with memory friction [3]. In most of these investigations, the barrier height V_b measured in units of thermal energy k_BT is assumed to be sufficiently large so a rate description is meaningful at all and any nonlinear force can safely be neglected on the thermal length scale at the barrier [4]. Mel'nikov and Meshkov (MM) [5] first proposed Kramers turnover theory for Ohmic friction, Pollak, Grabert, and Hanggi (PGH) [6] then used the normal mode representation of the dissipative Hamiltonian in the vicinity of the barrier to derive a continuum limit expression which was valid for the whole range of damping strengths and is applicable to an arbitrary memory friction. These turnover theories were established on the basis that the barrier height is much greater than the thermal energy ($V_b \gg k_BT$).

However, the potential barrier height is not very large in numerical calculations or in many physical applications. The numerical study of the Kramers problem at low damping [7] showed that finite barrier effects are important and a very slow convergence to the infinite barrier limit of the system was observed. It has been found that the large differences between analytical calculations and exact numerical results in the underdamped regime for the hopping rate in a periodic potential are essentially due to finite barrier effects [8]. There are two kinds of major methods for finite barrier correction. One is based on the Fokker-Planck equation, another is based on the Hamiltonian-equivalent formulation of the generalized Langevin equation (GLE). These approaches are the perturbation theories. Within the framework of MM theory, a consistent expansion method in terms of the small parameters of the problem was proposed [9]. The analytical result in the regime of a weak friction provides a quantitative estimation of finite barrier corrections in the small parameter T/V_b (about $\leqslant 0.2$). Near the turnover region, a simple interpolating expression was used to give satisfactory results. Within the framework of Fokker-Planck processes in the spatial diffusion regime, finite barrier corrections of the escape rate were determined for a particle crossing a barrier out of a metastable well by means of the flux over population expression, the Rayleigh quotient, and the mean first passage time to the stochastic separatrix [10]. An improvement of the Kramers function by means of a perturbation theory allows one to calculate corrections to the rate. The result is a series representation in powers of the nonlinear part of the force near the barrier. The rate processes that a reactive coordinate in a symmetric double well coupled to a harmonic mode were investigated in the limit of large damping. Combining the Rayleigh quotient and perturbation theory, finite barrier corrections were systematically studied [11]. The smallest eigenvalue of the Smoluchowski operator was yielded approximately by perturbation corrections to the conventional Kramers-Langer trial function. For moderate anisotropy parameters of damping, the rate expression is in excellent agreement with the numerically exact results. The Kramers Fokker-Planck model for activated rate processes was solved for all friction values in Ref. [12], including finite barrier corrections. A constrained Gaussian integration transformation was introduced and the phase space was extended, which allows the definition of the unstable mode energy. A systematic small-friction-low-temperature expansion was then performed in the extended phase space. The unified treatment for all friction values is due to the possibility of transition state theory in extended phase space. The Hamiltonian equivalent for the GLE and the normal modes were introduced within the context of the reactive flux method in Ref. [13]. By utilizing the synthesis of the variational transition state theory approach and the perturbation theory introduced by PGH, the leading term expression in inverse reduced barrier height expansion for the rate was given, which is valid for arbitrary time-dependent friction in the spatial diffusion regime. The finite barrier corrections

in PGH theory [14] come from the temperature dependence of energy loss for [15] finite temperature of the bath and the energy dependence of the energy loss. The finite barrier corrections significantly improves the accuracy of the theoretical estimates for low to moderate frictions, especially in the underdamped regime. The failure of finite barrier corrections to PGH theory for lower barrier heights and higher frictions is because PGH theory is based on a perturbation expansion valid for small inverse barrier heights and weak frictions. The decrease of the energy loss with increasing friction in PGH theory is unphysical; an *ad hoc* improved version of PGH theory was proposed by ignoring this unphysical decrease and using the maximal value of the energy loss for the moderate to high friction regime. The corrected PGH theory with finite barrier corrections brings it into reasonable agreement with numerically exact results. For the cubic potential and exponential memory friction [16], comparison of PGH theory with finite barrier corrections with numerically exact simulation results shows that the finite barrier corrections to depopulation factor significantly decrease the error of PGH theory for short memory. In the strong friction long memory time limit, finite barrier corrections to the depopulation factor in PGH theory fail, which is probably due to the fundamental assumption that consecutive traversals of the well are independent of each other is no longer valid. The failure of finite barrier corrections for the spatial diffusion factor was also found. A modification version of PGH theory was proposed in Ref. [17] by choosing a small parameter in perturbation expansion. The modified turnover theory is superior to the standard PGH theory in the moderate to strong damping regimes, as demonstrated by a cubic potential with Ohmic friction. Considering that the energy interval of the escaping particle is bounded from below, a finite barrier correction was introduced. The finite barrier corrected PGH theory is quite accurate over the whole friction range up to reduced barrier height 4. For lower reduced barrier height 2, incorporating the finite barrier correction leads to a much worse estimate in the underdamped regime. The supposedly small expansion parameter is not small in this case, so the leading order finite barrier correction provided in this paper is insufficient.

Two approaches mentioned above suffer from some limitations. The Fokker-Planck equation approach relies on the existence of a Fokker-Planck equation, which is not always the case for a generalized Langevin equation with an arbitrary potential. Moreover, the approach is based on a perturbation expansion; the leading order correction usually performed in literature is insufficient for lower barrier heights. The equivalent Hamiltonian approach in perturbation theory for weak damping; extrapolation to the spatial diffusion regime is questionable, as mentioned above. In addition, it is difficult to obtain a simple analytical expression from the finite barrier correction to the PGH theory. Therefore, simple, accurate, and widely applicable analytical approaches deserve investigation.

In the traditional reactive flux formulation, an initial equilibrium distribution is assumed for the trajectories of particles starting at the top of the barrier. It is not necessary to wait for low-energy particles (the vast majority of all the particles) at the bottom of one well to climb up to the top of the barrier, leading to an enormous numerical savings [18–20]. The method of reactive flux is not only a useful starting point of numerical methods but also a useful starting point for deriving analytical results. In the context of the reactive flux method, the Kramers formula was rederived [18] and the Grote and Hynes' rate expression for spatial diffusion regime was recovered in the presence of non-Markovian friction [21]. The equilibrium state assumption at the top of the barrier is reasonable for higher potential barriers because the current is small. It is no longer a good approximation for lower potential barriers where the current is not small enough. In the present paper, the motion of the particle is described by a Langevin equation with a metastable potential. We remove the starting point of the trajectories into the potential well where the probability distribution can be viewed as an equilibrium one; the analytical expression of escape rate is derived in the context of reactive flux method, which incorporates the finite barrier corrections in a simple manner. The proposed approach is probably applicable to various noises with Gaussian distribution.

II. REACTIVE FLUX THEORY FOR FINITE BARRIERS

We consider that a Brownian particle of unit mass moves in a metastable potential, the dynamics of the particle is described by the Langevin equation,

$$\ddot{x} + \gamma \dot{x}(t) + V'(x) = \xi(t), \tag{1}$$

where $\xi(t)$ is a zero mean Gaussian white noise that satisfies the fluctuation-dissipation theorem,

$$\langle \xi(t)\xi(t')\rangle = 2k_B T\gamma\delta(t-t'), \tag{2}$$

k_B is the Boltzmann constant, T is the temperature of the heat bath, $V(x)$ is a cubic metastable potential,

$$V(x) = -ax^2 + bx^3 + \frac{4a^3}{27b^2}, \tag{3}$$

and $a = 2/3, b = -4/27$ are taken in the present paper, such that the potential barrier height is $V_b = 2$ and the barrier top is located at $x_b = 0$. The situation is just the one considered by Kramers. Kramers replaced the potential in the vicinity of the barrier with a parabolic potential in the spatial diffusion regime, in which the barrier frequency is given by $\omega_b^2 = -V''(x = x_b)$. A current-carrying probability density was worked out through solving the corresponding Fokker-Planck equation; the famous Kramers formula is then derived using the current divide population approach,

$$k = \frac{\omega_0}{2\pi\omega_b}\left[\sqrt{\omega_b^2 + \gamma^2/4} - \gamma/2\right]\exp(-V_b/k_BT), \tag{4}$$

where ω_0 is the potential well frequency given by $\omega_0^2 = V''(x = x_w)$ and x_w is the position of the bottom of the potential well.

The Kramers formula was also derived in the context of reactive flux formulation [18]. The main steps can be outlined in the following. The potential barrier is replaced by a parabolic potential barrier in the spatial regime. The trajectories of the particles start from the barrier top and an initial equilibrium distribution is assumed. Parallel to the original reactive flux formula, the stationary escape rate can be expressed as

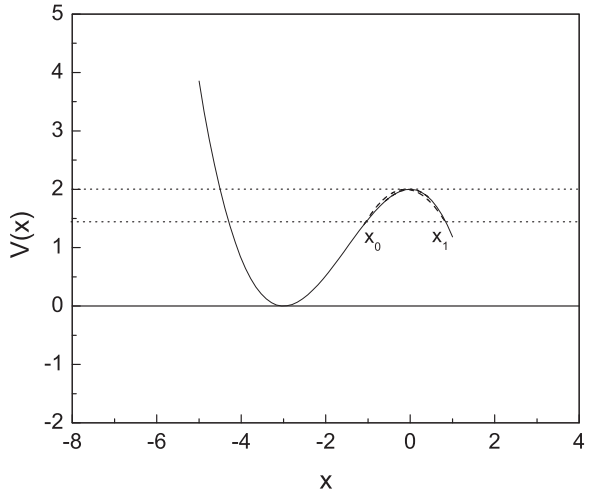

FIG. 1. The original potential (solid line) and the equivalent paraboloic potential (dashed line). x_0 is the starting point of the trajectories in reactive flux theory for finite barrier.

follows [22]:

$$k = \frac{\exp(-V_b/k_BT)}{Q}\int_{-\infty}^{\infty} dv_0 \exp\left(-v_0^2/2k_BT\right) \times v_0\chi(v_0, t\to\infty), \tag{5}$$

where Q is the partition function for particles in the potential well; $\chi(v_0, t)$ is called the characteristic function or reactivity index, it represents the passing probability of a particle with initial velocity v_0 over the barrier top at time t, given by

$$\chi(v_0, t) = \int_{x_b}^{\infty} dx \int_{-\infty}^{\infty} dv W(x, v, t; x_b, v_0). \tag{6}$$

Here $W(x, v, t; x_b, v_0)$ denotes the conditional probability density in phase space that corresponds to an ensemble of particles starting at (x_b, v_0) at $t = 0$. By solving the corresponding Fokker-Planck equation, W can be obtained analytically, which is a Gaussian distribution. Substitute it into Eq. (6) and combine Eqs. (5) and (6)—the Kramers formula is then derived. Although the initial equilibrium assumption at the top of the barrier is reasonable for large reduced potential barrier heights or low temperatures due to a small current, it is no longer a good approximation for finite barriers, because the current becomes larger as the temperature increases.

To extend the reactive flux theory to finite barriers, we remove the starting point of the trajectories to somewhere $x = x_0$ in the potential well where the probability distribution can be regarded as an equilibrium one, and replace the potential barrier from x_0 to x_1 with a equivalent parabolic barrier in the spatial diffusion regime (Fig. 1), so an analytical solution can be obtained. We expect both quasiequilibrium distribution and equivalent potential barriers are good approximations, therefore x_0 is so chosen that $V(x_0) = V_b - k_BT$, k_BT is just the average energy fluctuation of a quasiequilibrium distribution. The equivalent potential barrier is given by

$$V_e(x) = V_b - \tfrac{1}{2}\varpi_b^2 x^2, \tag{7}$$

ϖ_b is the equivalent potential barrier frequency, which will be determined later. The equivalent potential barrier reflects the whole shape of the potential in the barrier region, the continuity at $x = x_0, x_1$ is not required. The expression of the transition probability density in barrier region $x \in [x_0, x_1]$ is given by [22]

$$W(x, v, t; x_0, v_0) = N_1 \exp[-\alpha(x-\overline{x})^2 - \beta(v-\overline{v})^2 - \gamma(x-\overline{x})(v-\overline{v})], \tag{8}$$

where N_1 is a normalization constant, given by $N_1 = \frac{1}{2\pi}(4\alpha\beta - \gamma^2)^{1/2}$. $\alpha = 1/2\sigma_{11}^{-1}$, $\beta = 1/2\sigma_{22}^{-1}$, $\gamma = \sigma_{12}^{-1} = \sigma_{21}^{-1}$, σ^{-1} is the inverse matrix of variance matrix σ, the element of the latter is $\sigma_{ij} = \langle[x_i - \overline{x}_i][x_j - \overline{x}_j]\rangle$ $(x_1 = x, x_2 = v)$. The variances $\sigma_{ij}(t)$ can be analytically calculated due to the corresponding Langevin equation is a linear one. In expression (8), $\overline{x} = x_0G_{11} + v_0G_{12}$, $\overline{v} = x_0G_{21} + v_0G_{22}$, and G_{ij} is the Green's function of the corresponding homogeneous Langevin equation.

The characteristic function χ can be obtained by substituting expression (8) into Eq. (6) and performing the integration

$$\chi(v_0, t) = \frac{1}{2}\left[1 + \mathrm{erf}\left(\sqrt{\alpha - \frac{\gamma^2}{4\beta}}\,\overline{x}\right)\right]. \tag{9}$$

The long time limit is given by

$$\chi(x_0, v_0, t\to\infty) = \frac{1}{2}\left[1 + \mathrm{erf}\left(\sqrt{\frac{-\lambda_2}{2\gamma k_BT}}(\lambda_1 x_0 + v_0)\right)\right], \tag{10}$$

where λ_1, λ_2 are two roots of the following characteristic equation:

$$\lambda^2 - \gamma\lambda - \varpi_b^2 = 0, \tag{11}$$

given by

$$\lambda_1 = \frac{\gamma + \sqrt{4\varpi_b^2 + \gamma^2}}{2}, \qquad \lambda_2 = \frac{\gamma - \sqrt{4\varpi_b^2 + \gamma^2}}{2}. \tag{12}$$

The escape rate k is obtained,

$$\begin{aligned} k &= \int_{-\infty}^{\infty} dv_0 v_0 W(x_0, v_0)\chi(x_0, v_0, t\to\infty) \\ &= \frac{1}{n}\exp\left(-\frac{V_b - 1/2\varpi_b^2 x_0^2}{k_BT}\right)\int_{-\infty}^{\infty} dv_0 v_0 \\ &\quad\times \exp\left(-\frac{v_0^2}{2k_BT}\right)\chi(x_0, v_0, t\to\infty), \end{aligned} \tag{13}$$

where n is the population in potential well region $x \in (-\infty, x_b]$, but the time-decay factor has been canceled by the same factor in the numerator. Performing a partial integration, we arrive at

$$k = \frac{1}{n}\exp\left(-\frac{V_b - 1/2\varpi_b^2 x_0^2}{k_BT}\right)k_BT\,\frac{-\lambda_2}{2\pi\gamma k_BT}\int_{-\infty}^{\infty} dv_0 \times \exp\left[-\frac{v_0^2}{2k_BT} + \frac{\lambda_2}{2\gamma k_BT}(\lambda_1 x_0 + v_0)^2\right]. \tag{14}$$

Performing the Gaussian integration over v_0, we arrive at a similar formula as Kramers:

$$k = \frac{1}{n}\exp\left(-\frac{V_b}{k_BT}\right)\frac{k_BT}{\varpi_b}|\lambda_2| = \frac{k_BT}{n\varpi_b}\left[\sqrt{\varpi_b^2+\gamma^2/4}-\gamma/2\right]\exp\left(-\frac{V_b}{k_BT}\right). \quad (15)$$

The population n can be expressed as

$$n = \int_{-\infty}^{x_0} dx\int_{-\infty}^{\infty} dv_0\frac{1}{Q}\exp\left(-\frac{v_0^2}{2k_BT}\right)\exp\left(-\frac{V(x)}{k_BT}\right) + \int_{x_0}^{x_b} dx\int_{-\infty}^{\infty} dv_0 P_s(x, v_0), \quad (16)$$

where P_s is the remarkable Kramers stationary probability density [1,23]. Because the second term in above expression is small, the Kramers stationary probability density for high barriers is used for simplicity. In contrast to applying equilibrium probability density in the usual calculation of population, a more realistic expression is used here, and the difference is obvious for lower barrier heights (for example, when the reduced barrier height $V_b/kT = 2, 2.5$, the difference is about 5.2% and 2.3%.). When $T \to 0$, the equivalent barrier frequency ϖ_b tends to ω_b, and n can be integrated out using harmonic potential well approximation, such that the escape rate expression (15) naturally reduces to the Kramers formula. The finite barrier correction comes from two aspects: One is that the original barrier frequency ω_b defined by $\omega_b^2 = -V''(x = x_b)$ is replaced by an equivalent barrier frequency ϖ_b; another is that the population n in Kramers approach is corrected in terms of expression (16).

The equivalent potential barrier frequency can be determined by two schemes. One is to let the equivalent potential approach the original potential in the barrier region—the equivalent potential barrier frequency is provided by the minimization of the following average:

$$I = \int_{x_0}^{x_1} dx[V(x) - V_e(x)]^2 P_{\rm eq}(x), \quad (17)$$

where $P_{\rm eq}(x)$ is the Boltzmann distribution normalized in the barrier region, in which the potential $V_e(x)$ is used. The equivalent potential $V_e(x)$ is obtained specifically as follows: The straight line $V = V_b - k_BT$ crosses the original potential line at x_0 and x_1, the potential is approximated by a parabolic potential in region $[x_0, x_1]$ with the top at $(\frac{x_0+x_1}{2}, V_b)$ (see Fig. 1). The integration (17) can be worked out analytically using an error function with an imaginary variable, and location of the minimal value can be determined numerically. Another scheme is to let the steady state Fokker-Planck equation with equivalent potential approach the steady-state Fokker-Planck equation with original potential, the equivalent barrier frequency is provided by the minimization of the following average:

$$I = \int_{x_0}^{x_1} dx\int_{-\infty}^{\infty} dv\left[\left(\hat{L}_{\rm FP} - \hat{L}^e_{\rm FP}\right)P_{\rm eq}(x, v)\right]^2 P_{eq}(x, v), \quad (18)$$

where $\hat{L}_{\rm FP}, \hat{L}^e_{\rm FP}$ are Fokker-Planck operators corresponding to original potential and equivalent potential, respectively, $P_{\rm eq}(x, v)$ is the equilibrium distribution in phase space. Two schemes are in essential approaching the original potential with an equivalent parabolic potential in barrier region. For the parameters used in the present paper, numerical results show that two schemes produce almost the same equivalent barrier frequency. The first scheme relies on the existence of a Fokker-Planck equation and the second scheme is universal, which makes the proposed method widely applicable.

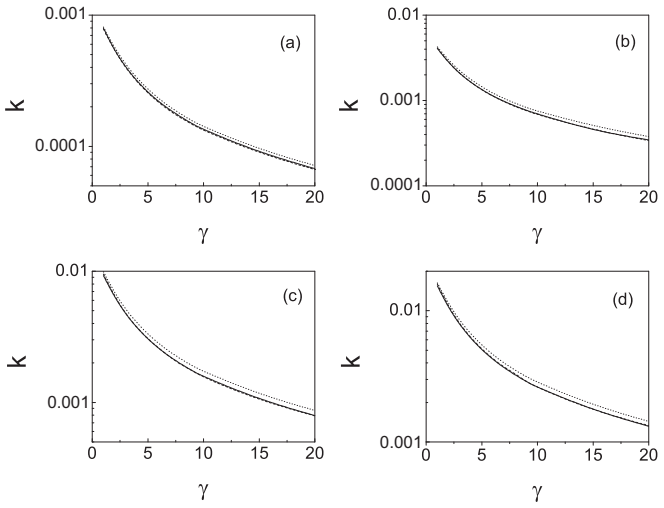

FIG. 2. The escape rate as a function of damping, where $V_b = 2$, (a) $T = 0.4$, $\varpi_b^2 = 1.286$, (b) $T = 0.6$, $\varpi_b^2 = 1.260$, (c) $T = 0.8$, $\varpi_b^2 = 1.231$, (d) $T = 1$, $\varpi_b^2 = 1.194$. The solid lines are theoretical results, the dashed lines are numerical simulation results, and the dotted lines are the original Kramers theoretical results.

III. COMPARISON WITH NUMERICAL SIMULATIONS

To examine the theoretical results obtained above, we simulate the Langevin equation using the second-order stochastic Runge-Kutta algorithm. We use the number of test particles $N = 2\times10^5$ and time step $dt = 5\times10^{-4}$ and $dt = 2\times10^{-4}$ (for larger damping) in the simulations. The results are stable for time steps less than such quantities. The simulation time is long enough to ensure the number of escaped particles is larger than 3×10^4. The particles are initially located at the bottom of the potential well $x = x_w$ with zero velocity. We use a dimensionless system of units in the simulations. The potential barrier height is taken as $V_b = 2$, the mass of the Brownian particle is $m = 1$. The temperature is measured in energy units ($k_B = 1$). Figure 2 exhibits the dependence of the Kramers rate on the frictions for different temperatures. Theoretical results are also plotted in the same figure with solid lines. The equivalent barrier frequency in analytical expression (15) is almost the same for two schemes (the relative error is less than 1%). By using the potential approach scheme, we have $\varpi_b^2 = 1.286(T = 0.4)$, $\varpi_b^2 = 1.260(T = 0.6)$, $\varpi_b^2 = 1.231(T = 0.8)$, and $\varpi_b^2 = 1.194(T = 1)$. Figure 2 indicates that the numerical simulation results confirm the proposed theoretical method until lower barrier heights (the minimal reduced barrier height in the figure is $V_b/k_BT = 2$). The analytical results agree with the simulation results satisfactorily as long as the escape dynamics is dominated by spatial diffusion across the barrier top, as specified by $\gamma > \omega_b$. The

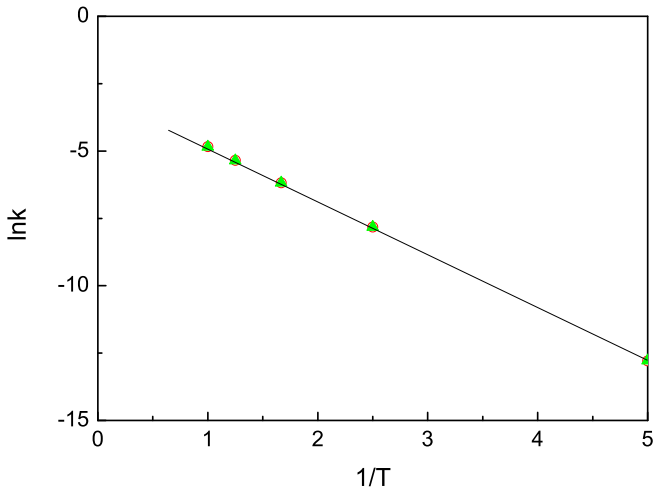

FIG. 3. The logarithm of escape rate as a function of inverse temperature. The circles are theoretical results, the triangles are numerical simulation results, where $V_b = 2$, $\gamma = 3$. The straight line is used to guide the eyes.

maximal relative error is about 2% for the applied parameters in the spatial diffusion regime. Comparison of our theoretical results with simulation results indicates that the accuracy of the theoretical results is not inferior to the PGH theory [17]. In particular, it is superior to the PGH theory up to the second perturbation theory [17] and the perturbation theory based on the Fokker-Planck equation [10] for lower barrier heights, where the expansion parameter is no longer small.

The dependence of escape rate on temperature is shown in Fig. 3. The theoretical results match well with the simulation results. Although the equivalent barrier frequency is temperature dependent, the Arrhenius law is still fulfilled for not too low barriers due to the population also being temperature dependent. The theoretical results can predict the deviation of Arrhenius law in lower barriers. The deviation is visible when the reduced barrier height reduces to 2, as shown in Fig. 3.

IV. SUMMARY

The purpose of the present paper is to develop a widely applicable analytical approach to incorporate finite barrier correction in the escape rate in a simple way. The reactive flux theory for finite barrier is proposed. We chose the starting point of the trajectories of Brownian particles inside the potential well, and replace the original potential barrier with an equivalent parabolic barrier. For the situation that a Brownian particle moves in a cubic metastable potential and is subjected to Gaussian white noise, the theoretical results match well with the simulation results in the spatial diffusion regime. The equivalent barrier assumption restricts the method to spatial diffusion regime because of the potential shape sensitivity for small damping. The equivalent potential barrier frequency is determined by two schemes: the Fokker-Planck equation approach and the potential approach. They yield almost the same frequency. The calculation of population is more realistic by considering the real probability distribution in the potential well. In contrast to the requirement that a Fokker-Planck equation is available in an arbitrary potential for some noise, only needed is the Fokker-Planck equation in a quadratic potential for this noise. The latter can be obtained for an arbitrary noise with Gaussian distribution [24] and its analytical solution is available [23]. If we think that the potential approach is applicable to an arbitrary Gaussian noise, the equivalent barrier frequency can be calculated in a simple manner and this makes the theoretical method applicable to a broad scope of noises.

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