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Angaben zur Veröffentlichung / Publication details:

Berezhkovskii, Alexander M., Peter Talkner, Jens Emmerich, and Vladimir Yu. Zitserman. 1996. "Thermally activated traversal of an energy barrier of arbitrary shape." *The Journal of Chemical Physics* 105 (24): 10890–95. <https://doi.org/10.1063/1.472895>.



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Cite as: J. Chem. Phys. **105**, 10890 (1996); <https://doi.org/10.1063/1.472895>

Submitted: 16 July 1996 • Accepted: 18 September 1996 • Published Online: 04 June 1998

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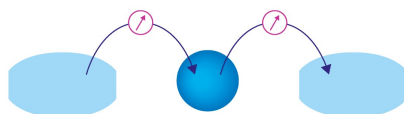
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Thermally activated traversal of an energy barrier of arbitrary shape

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(Received 16 July 1996; accepted 18 September 1996)

The thermally activated escape of a Brownian particle over an arbitrarily shaped potential barrier is considered. Based on an approximate solution of the corresponding Fokker–Planck equation a rate expression is given. It agrees in the limiting case of high friction with the rate following from the corresponding Smoluchowski equation and, in the limit of weak friction with the rate obtained from transition state theory. For a parabolic barrier the approximate rate expression deviates less than 16% from the known result. The results for cusp shaped and quartic barriers agree with known expressions which have been obtained by other means. Estimates of the rates from numerical simulations are compared with the approximate rate expressions for the cusp and quartic barrier.

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I. INTRODUCTION

An important step in many processes in physics, chemistry and biology is the change of a system from one stationary state to another by crossing a barrier located between the two states.^{1–3} The necessary energy to cross this barrier is supplied by a surrounding medium. At the same time the medium exerts a drag on the system taking away energy. Kramers,⁴ in his famous paper in 1940 modeled this process in terms of a Langevin equation which describes the motion of a particle under the combined influence of a potential $U(x)$ and a bath. For a particle in one dimension with mass weighted coordinate $x(t)$ at time t the Langevin equation reads

$$\ddot{x}(t) = -U'(x(t)) - \gamma \dot{x}(t) + \xi(t), \quad (1.1)$$

where dot and prime denote the derivatives with respect to time and position, respectively, γ denotes the friction constant and $\xi(t)$ a Gaussian white random force. The latter has zero mean and its strength relates to the friction constant via the Einstein relation

$$\langle \xi(t) \rangle = 0, \quad \langle \xi(t) \xi(s) \rangle = 2\gamma k_B T \delta(t-s), \quad (1.2)$$

where k_B is the Boltzmann constant, T the temperature of the bath and $\delta(t)$ the Dirac δ -function. An equivalent description can be given in terms of the Fokker–Planck equation^{4,5} which governs the time evolution of the probability density $p(x, v, t)$ of finding the particle at time t at the phase space point x, v . It reads

$$\begin{aligned} \frac{\partial}{\partial t} p(x, v, t) = & \left\{ -\frac{\partial}{\partial x} v + \frac{\partial}{\partial v} (U'(x) + \gamma v) \right. \\ & \left. + \gamma k_B T \frac{\partial^2}{\partial v^2} \right\} p(x, v, t). \end{aligned} \quad (1.3)$$

For a potential with a metastable well the escape rate Γ can always be expressed by Γ_{TST} following from classical transition state theory (TST) and a transmission factor κ which is at most unity

$$\Gamma = \kappa \Gamma_{\text{TST}}. \quad (1.4)$$

For the escape out of a potential well leading over a barrier of height E^\ddagger above the bottom of the well the TST rate reads

$$\Gamma_{\text{TST}} = \sqrt{\frac{k_B T}{2\pi}} \frac{\exp\{-E^\ddagger/(k_B T)\}}{\int_{-\infty}^0 dx \exp\{-(U(x) - U(x_0))/(k_B T)\}}, \quad (1.5)$$

where the barrier is located at $x=0$ and the bottom of the well at $x_0 < 0$. For sufficiently low temperatures, or high barriers, the TST rate becomes

$$\Gamma_{\text{TST}}^{T \rightarrow 0} = \frac{2\pi}{\omega_0} e^{-E^\ddagger/k_B T}, \quad (1.6)$$

where ω_0 is the frequency at the bottom of the well, i.e., $\omega_0^2 = U''(x_0)$. For a potential with a parabolic barrier Kramers⁴ constructed a stationary current carrying probability density describing a steady flow of particles out of the well which is continuously replenished. The decay rate follows from this solution as the ratio of the flux at the barrier to the population of the well. The resulting transmission factor κ strongly deviates from unity in both limits of weak and strong system-bath coupling i.e., for small and large friction γ , respectively. For low friction the suppression of the rate relative to the TST value is caused by the slow diffusion of energy which is the rate limiting step as long as $\gamma < \gamma_0 = (k_B T \omega_0)/(2\pi E^\ddagger)$. In the present paper we will only consider the intermediate to large friction regime with $\gamma > \gamma_0$. In this regime, for a parabolic barrier Kramers obtained the following expression for the transmission factor:⁴

$$\kappa_{\text{pb}} = \sqrt{\left(\frac{\gamma}{2\omega_b}\right)^2 + 1} - \frac{\gamma}{2\omega_b} \quad (1.7)$$

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where $\omega_b^2 = -U''(0)$ denotes the barrier frequency.

Kramers also considered the case of a symmetric cusp shaped barrier which is of particular importance for charge transfer reactions.^{6,7} In this case he gave the transmission factor only in the asymptotic limit of large friction where he found⁴

$$\kappa_{\text{cusp}}^{\gamma \rightarrow \infty} = \frac{a}{\gamma} \sqrt{\frac{\pi}{2k_B T}} \quad (1.8)$$

where a denotes the absolute value of the derivative of the potential at one side of the cusp. Within the regime of intermediate friction when γ becomes smaller than $a\sqrt{\pi/(2k_B T)}$ the rate approaches the TST value (1.6). There are various attempts in the literature to bridge these limiting cases for a cusp shaped barrier^{8–11} but exact results are presently not known.¹²

The situation is similar for all other shapes of barriers except for parabolic ones. For small friction the TST rate is approached. In the large friction limit in which the Fokker-Planck equation can be approximated by a Smoluchowski equation^{4,5} the transmission factor for an arbitrarily shaped barrier can be expressed in terms of the potential near the barrier. It reads

$$\kappa^{\gamma \rightarrow \infty} = \frac{\sqrt{2\pi k_B T}}{\gamma \int_{\text{barrier}} dx \exp\{(U(x) - U(0))/(k_B T)\}}, \quad (1.9)$$

where the integral has to be extended over the region around the top of the barrier which is assumed to lie at $x=0$. The result for the cusp (1.8) follows from Eq. (1.9) in the asymptotic limit $T \rightarrow 0$ when the integral in Eq. (1.9) can be restricted to a small vicinity of the top of the barrier where the potential can be approximated by linear pieces. No asymptotically exact results for low temperatures in the whole regime of intermediate to large friction are known for nonparabolic barriers. For quartic barriers an approximate expression is known which interpolates both limits of small and large friction.¹ In this paper a formula is derived that interpolates between these limits for arbitrary shapes of barriers.

II. APPROXIMATE RATE EXPRESSION

Following Kramers, we look for a current carrying stationary solution $\rho(x, v)$ of the Fokker-Planck equation (1.3) of the form

$$\rho(x, v) = \zeta(x, v) p_{\text{eq}}(x, v), \quad (2.1)$$

where $p_{\text{eq}}(x, v) = \exp\{-(v^2/2 + U(x))/(k_B T)\}$ denotes the (not normalized) equilibrium distribution and $\zeta(x, v)$ is the so-called Kramers function which is unity in the initial well and rapidly decreases to zero beyond the barrier. Once the Kramers function is known one can calculate the rate as the ratio of the current which flows over the barrier to the population of the well. This yields the following expression for the transmission factor in terms of the Kramers function

$$\kappa = - \int_{-\infty}^{\infty} dv \frac{\partial \zeta(0, v)}{\partial v} \exp\left\{-\frac{v^2}{2k_B T}\right\}. \quad (2.2)$$

From the fact that $\rho(x, v)$ and $p_{\text{eq}}(x, v)$ are stationary solutions of the Fokker-Planck equation one obtains the following equation for the Kramers function from (1.3):

$$\left\{ -v \frac{\partial}{\partial x} + (U'(x) - \gamma v) \frac{\partial}{\partial v} + \gamma k_B T \frac{\partial^2}{\partial v^2} \right\} \zeta(x, v) = 0. \quad (2.3)$$

In order to find an approximate solution of this equation we first introduce a scaled velocity $u = v/\gamma$ having the dimension of a coordinate. Next we replace the potential at the actual point x by its value at the shifted point $x - u$. Properly correcting this substitution we obtain as a still exact equation for the Kramers function

$$\begin{aligned} -u \left(\frac{\partial}{\partial x} + \frac{\partial}{\partial u} \right) \zeta(x, u) + \frac{1}{\gamma^2} \left[U'(x - u) \frac{\partial}{\partial u} + k_B T \frac{\partial^2}{\partial u^2} \right] \zeta(x, u) \\ = \frac{1}{\gamma^2} [U'(x - u) - U'(x)] \frac{\partial \zeta(x, u)}{\partial u}. \end{aligned} \quad (2.4)$$

Since the range of velocities which mainly contribute to the integral in Eq. (2.2) is essentially bounded by a Gaussian weight a displacement by u lying within this range becomes vanishingly small for large values of the damping constant and consequently the right hand side of Eq. (2.2) becomes negligible. This leads to the following simplified equation for the Kramers function:

$$\begin{aligned} u \left(\frac{\partial}{\partial x} + \frac{\partial}{\partial u} \right) \zeta(x, u) = \frac{1}{\gamma^2} \left[U'(x - u) \frac{\partial}{\partial u} \right. \\ \left. + k_B T \frac{\partial^2}{\partial u^2} \right] \zeta(x, u). \end{aligned} \quad (2.5)$$

Obviously there is a solution of the approximate equation (2.5) that depends on $z = x - u$ only and also fulfills the asymptotic conditions saying that the Kramers function approaches unity in the initial well and zero beyond the barrier. This solution reads

$$\zeta(x, v) = A \int_{x-v/\gamma}^{\infty} dz \exp\{U(z)/(k_B T)\}, \quad (2.6)$$

where A is determined by normalization

$$A = \left[\int_{-\infty}^{\infty} dz \exp\{U(z)/(k_B T)\} \right]^{-1}. \quad (2.7)$$

In fact, the integration in the last equation has to be restricted to the barrier region with a lower limit at, say, x_0 and the upper limit at a value beyond the barrier from where the recrossing probability of a particle with zero initial velocity can safely be ignored.

Using the approximate Kramers function (2.6) we obtain the following expression for the transmission factor (2.2):

$$\kappa = \frac{\int_{-\infty}^{\infty} dx \exp\{[U(x) - \gamma^2 x^2/2]/(k_B T)\}}{\int_{-\infty}^{\infty} dx \exp\{U(x)/(k_B T)\}}, \quad (2.8)$$

where both integrals are restricted to the barrier region. When the barrier is sufficiently high, or equivalently, the temperature sufficiently low, the potential in the integrals can

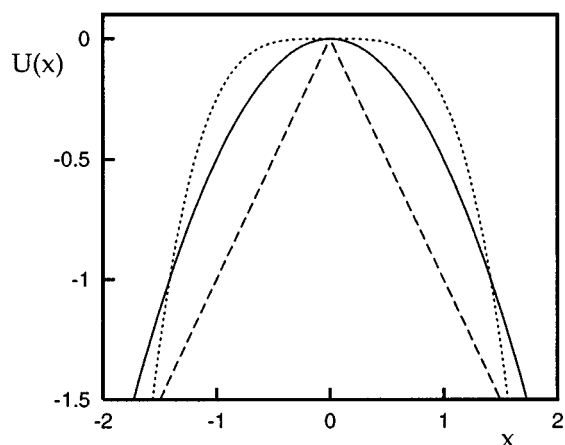


FIG. 1. Different shapes of the potential $U(x)$ in the vicinity of the top of the barrier according to Eq. (2.9) for a cusp shaped barrier, $\alpha=1$, (dashed line), parabolic barrier, $\alpha=2$, (solid line) and a quartic barrier, $\alpha=4$, (dotted line). The strength of the potential is always $a=1$.

be approximated by its local behavior in the vicinity of the top of the barrier. We assume that it is given by an algebraic form

$$U(x) = -\frac{a}{\alpha}|x|^\alpha \quad \text{for } x \text{ near the barrier,} \quad (2.9)$$

where a is a positive parameter and α the order of the maximum of the potential describing the top of the barrier, see Fig. 1. Using this form of the potential in Eq. (2.8) one can perform the integral in the denominator and obtains for the transmission factor

$$\kappa_\alpha = \frac{\alpha^{1-1/\alpha}}{q\Gamma(1/\alpha)} \int_0^\infty du \exp\{-(u^2/2 + u^\alpha/(\alpha q^\alpha))\}, \quad (2.10)$$

where $\Gamma(z)$ is the gamma-function and

$$q = \frac{\gamma}{\sqrt{k_B T}} \left(\frac{k_B T}{a} \right)^{1/\alpha} \quad (2.11)$$

is a single, dimensionless parameter which is determined by the order of the maximum and local strength of the potential, the friction constant, and temperature. It is given by the ratio between the thermal length-scale of the potential, $(k_B T/a)^{1/\alpha}$, and the dissipative length-scale $\sqrt{k_B T}/\gamma$. Note that the dependence of q on temperature changes qualitatively at $\alpha=2$ when the barrier is parabolic. For $\alpha < 2$ the parameter q increases whereas for $\alpha > 2$ it decreases with increasing temperature. For large values of γ the parameter q is also large. In the limit $q \rightarrow \infty$ the integral in Eq. (2.10) is dominated by its Gaussian contribution. Taking into account first order corrections in $q^{-\alpha}$ one obtains the following expression:

$$\kappa_\alpha^{q \rightarrow \infty} = \frac{\alpha^{1-1/\alpha}}{q\Gamma(1/\alpha)} \sqrt{\frac{\pi}{2}} \left(1 - \frac{2^{\alpha/2} \Gamma((\alpha+1)/2)}{\alpha \Gamma(1/2)} q^{-\alpha} + \mathcal{O}(q^{-2\alpha}) \right). \quad (2.12)$$

The leading term coincides with the transmission factor resulting from the corresponding Smoluchowski equation in steepest descent approximation (1.9).

In the opposite limit, for small values of q , the quadratic term $u^2/2$ in Eq. (2.10) is small compared to $|u|^\alpha/(\alpha q^\alpha)$. An asymptotic evaluation of the integral yields for the transmission factor

$$\kappa_\alpha^{q \rightarrow 0} = 1 - \frac{\alpha^{2/\alpha} \Gamma(3/\alpha)}{2\Gamma(1/\alpha)} q^2 + \mathcal{O}(q^4). \quad (2.13)$$

Here the leading term coincides with the value predicted by transition state theory. It hence goes to the correct value in the limit of small friction. This is rather surprising since the assumptions leading to the approximate Kramers function (2.6) are only justified in the opposite limit of large friction. The reason for the unexpected success can be seen in the fact that the approximate Kramers function (2.6) approaches a step function in the limit of vanishing friction as does the correct Kramers function. The different orientations of both step functions do not affect the value of the flux over population expression of the transmission factor. Therefore, Eq. (2.10) represents an interpolating formula for the transmission factor from large to small values of the friction constant for different forms of the potential in the vicinity of the barrier.

Following an idea of Calef and Wolynes⁹ we yet give another simple interpolating formula for the transmission factor over a barrier of the form (2.9). Comparing the strong damping limits of the transmission factor over a parabolic barrier, $\kappa_{pb}^{\gamma \rightarrow \infty} = \omega_b/\gamma$, with the leading term of the transmission factor (2.12) over a barrier of the order α , we introduce an effective parabolic barrier frequency $\omega_\alpha = \lim_{\gamma \rightarrow \infty} (\gamma \kappa_\alpha)$ which reads in terms of the original parameters

$$\omega_\alpha = \left(\frac{a}{\alpha k_B T} \right)^{1/\alpha} \frac{\alpha}{\Gamma(1/\alpha)} \sqrt{\frac{\pi k_B T}{2}}. \quad (2.14)$$

When we replace the frequency ω_b by ω_α in the parabolic barrier transmission factor (1.7) we obtain the following expression:

$$\kappa_\alpha^{CW} = \sqrt{\left(\frac{\gamma \Gamma(1/\alpha)}{2\alpha} \right)^2 \left(\frac{\alpha k_B T}{a} \right)^{2/\alpha} \frac{2}{\pi k_B T} + 1} - \frac{\gamma \Gamma(1/\alpha)}{2\alpha} \left(\frac{\alpha k_B T}{a} \right)^{1/\alpha} \sqrt{\frac{2}{\pi k_B T}} \quad (2.15)$$

$$= \sqrt{\frac{\Gamma(1/\alpha)^2}{2\pi \alpha^{2-2/\alpha} q^2 + 1}} - \frac{\Gamma(1/\alpha)}{(2\pi)^{1/2} \alpha^{1-1/\alpha} q}, \quad (2.16)$$

where, in the second line, the original parameters are expressed in terms of the single parameter q . By construction, this rate expression gives correct results for weak and strong friction and else interpolates between these limits. For a cusp shaped potential, $\alpha=1$, it coincides with the formula of Calef and Wolynes.⁹

Still another interpolation formula is given by the inverse of the sum of the inverse rates for small and large damping, reading¹

$$\kappa_{\alpha}^{\text{int}} = (1 + (\kappa^{\gamma \rightarrow \infty})^{-1})^{-1}. \quad (2.17)$$

By construction, it also approaches the correct limiting behavior for both weak and strong damping.

III. COMPARISON OF THE INTERPOLATING FORMULAE WITH EXACT AND NUMERICAL RESULTS

For a parabolic barrier, i.e., $\alpha = 2$, the parameter q reads $q = \gamma/\omega_b$, where $\omega_b = a^{1/2}$ denotes the barrier frequency. Performing the integral in Eq. (2.10) one obtains for the transmission factor

$$\kappa_2 = (1 + \gamma^2/\omega_b^2)^{-1/2}. \quad (3.1)$$

This expression has to be compared with Eq. (1.7), see Fig. 2. The interpolating formula (3.1) approaches the correct limits both for vanishing and large friction. In between it is always larger than the exact result with a maximal deviation of less than 16% at $\gamma = \omega_b/\sqrt{2}$.

The interpolation formula κ_2^{int} is always smaller than the true transmission factor κ_{pb} . Its absolute relative deviation from the exact transmission factor is larger than the respective deviation of the interpolation formula (3.1), see Fig. 2.

For other values of α exact results for the transmission factor are not known. Therefore we compare the interpolating formulae for a cusp shaped and a quartic barrier with $\alpha = 1$ and $\alpha = 4$, respectively, for which one can analytically determine the interpolating formula (2.10) with the results from numerical simulations. From Eq. (2.10) one obtains for the cusp

$$\kappa_1 = \sqrt{\frac{\pi}{2}} \frac{1}{q} \exp\{1/(2q^2)\} \text{erfc}\{1/(\sqrt{2}q)\}, \quad (3.2)$$

where $\text{erfc}\{z\} = 2/\sqrt{\pi} \int_z^\infty dt \exp\{-t^2\}$ denotes the complementary error function. Note that this result coincides with the formula given in Ref. 10. For a quartic barrier one finds

$$\kappa_4 = \frac{q \exp\{q^4/8\}}{\Gamma(1/4)} K_{1/4}(q^4/8), \quad (3.3)$$

where $K_{1/4}(x)$ denotes the modified Bessel function of the second type.¹³ This expression coincides with the rate formula for a quartic barrier given in Ref. 1.

As starting point for the numerical evaluation of the transmission factor we use the expression

$$\kappa = -\frac{1}{k_B T} \int_{-\infty}^{\infty} dv \, v \pi(0, v) \exp\left\{-\frac{v^2}{2k_B T}\right\}, \quad (3.4)$$

where the function $\pi(x, v)$ denotes the splitting probability^{14,15} with which a trajectory starting at the point (x, v) reaches the reactant state before it approaches the product state beyond the barrier. The reactant and the product states correspond to small regions in phase space surrounding the initial and final locally stable states, respectively. The splitting probability and the Kramers function are closely related to each other. One follows from the other by means of a time reversal transformation.¹⁶ Hence,

$$\pi(x, v) = \zeta(x, -v). \quad (3.5)$$

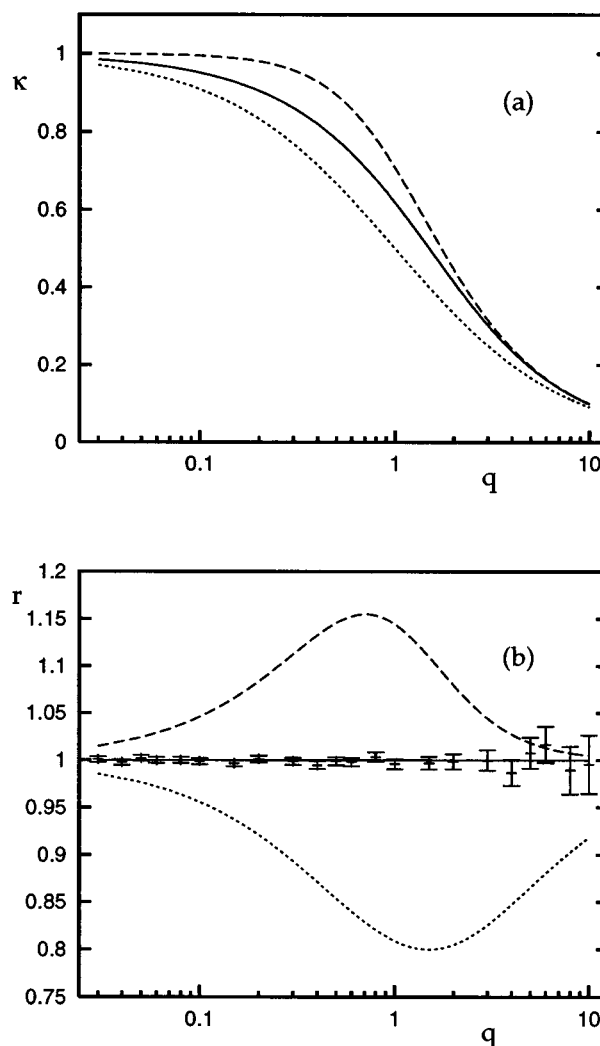


FIG. 2. (a) The transmission factor for a parabolic barrier as a function of $q = \gamma/\omega_b$. The solid line shows the exact result κ_{pb} , see Eq. (1.7), the dashed line represents the interpolating formula κ_2 , see Eq. (3.1), and the dotted line gives the formula κ_2^{int} , see Eq. (2.17). (b) The ratios $r = \kappa_2 / \kappa_{\text{pb}}$ (dashed line) and $r = \kappa_2^{\text{int}} / \kappa_{\text{pb}}$ (dotted line) as a function of q . The single points with error bars show the ratio $r = \kappa_2^{\text{sim}} / \kappa_{\text{pb}}$ for simulations of the transmission factor κ_2^{sim} . The error bars indicate the respective statistical error. The absolute statistical deviations of the simulated rates are approximately independent of the value of q . As the rate decreases with increasing q , the relative errors of the simulated rates and transmission factors increase with increasing q .

Using this identity one easily sees that the expressions (2.2) and (3.4) for the transmission factor are identical.

The numerical simulation is based on the Langevin equation (1.1). We started 10^6 trajectories at $x = 0$ with initial velocities from the thermal distribution and determined whether the trajectories approached the region in phase space corresponding to reactants rather than the opposite product well. The random variable $\chi(v)$ taking the values 1 in the former and 0 in the latter case yields the splitting probability $\pi(0, v)$ when averaged over different realizations of the Langevin equation (1.1) starting from $x = 0$ and v . In order to avoid finite barrier corrections we used the local form of the

TABLE I. Transmission factor for a cusp shaped barrier ($\alpha=1$) for different values of $q=\sqrt{k_B T}\gamma/a$ obtained from a numerical simulation of 10^6 trajectories starting at the top of the barrier. The statistical error estimated as two standard deviations is smaller than 0.0034 for all q .

q	$\kappa_1(q)$	q	$\kappa_1(q)$
0.1	0.9966	1	0.7769
0.15	0.9929	1.5	0.6300
0.2	0.9875	2	0.5229
0.3	0.9760	3	0.3816
0.4	0.9527	4	0.2965
0.5	0.9271	5	0.2399
0.6	0.9003	6	0.2028
0.8	0.8379	8	0.1538
		10	0.1223

potential in the vicinity of the top of the barrier (2.9) and counted a trajectory as reactive when it had reached a positive value of x with less energy $v^2/2 + U(x)$ than $6k_B T$ below the top of the barrier and as nonreactive when it was below the same energy at a negative value of x . Finally, the integral in Eq. (3.4) was evaluated as the mean value of $v\chi(v)$. Note that the method of reactive flux^{1,17} leads to a different Monte Carlo simulation of the transmission factor (3.4). For a cusp shaped barrier the method of the reactive flux was used by Starobinets *et al.*¹²

Figure 2(b) shows the ratio between the simulated and the exact rates for parabolic barriers. The relative statistical error of the simulated rates is less than 4%.

Table I shows the results of this simulation for cusp shaped barriers with different values of the dimensionless parameter $q=\sqrt{k_B T}\gamma/a$. The results agree with the findings of Starobinets *et al.*¹² within the statistical errors. The ratios of the interpolating formulae κ_1^{CW} , Eq. (2.16), κ_1^{int} , Eq. (2.17), and κ_1 , Eq. (3.2), to the results of the simulation are shown in Fig. 3. We find that the interpolating formulae give results that are smaller than the numerically exact transmission factor. They deviate strongest for q -values of the order unity. The maximal relative errors are 13% and 16% for κ_1^{CW} and κ_1 , respectively, while κ_1^{int} deviates up to 28% from the numerically exact rate.

Table II and Fig. 4 show the corresponding results of the simulation for a quartic barrier. Here the interpolating for-

TABLE II. Transmission factor for a quartic barrier ($\alpha=4$) for different values of $q=\gamma/(ak_B T)^{1/4}$ obtained from a numerical simulation of 10^6 trajectories starting at the top of the barrier. The statistical error estimated as two standard deviations is smaller than 0.0034 for all q .

q	$\kappa_4(q)$	q	$\kappa_4(q)$	q	$\kappa_4(q)$
0.01	0.9835	0.1	0.9049	1	0.5438
0.015	0.9770	0.15	0.8700	1.5	0.4474
0.02	0.9725	0.2	0.8425	2	0.3732
0.03	0.9614	0.3	0.7907	3	0.2795
0.04	0.9524	0.4	0.7414	4	0.2221
0.05	0.9440	0.5	0.7039	5	0.1814
0.06	0.9375	0.6	0.6669	6	0.1564
0.08	0.9198	0.8	0.6034	8	0.1188
				10	0.0968

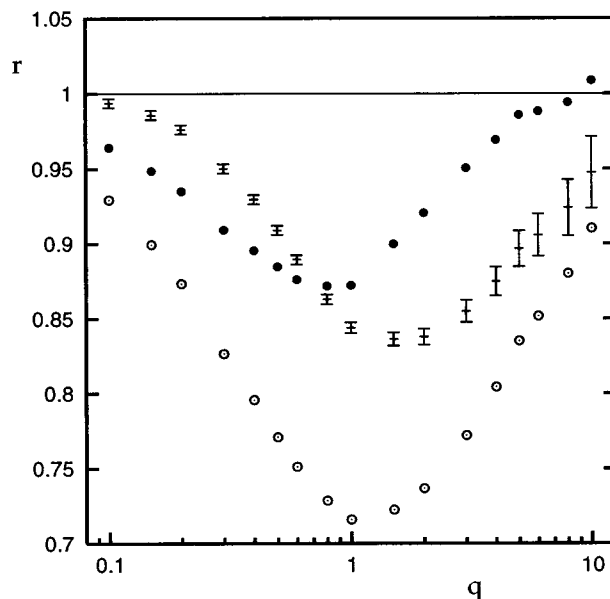


FIG. 3. The ratios $\kappa_1/\kappa_1^{\text{sim}}$ (crosses), $\kappa_1^{\text{CW}}/\kappa_1^{\text{sim}}$ (full circles), and κ_1^{int} (open circles) for different values of $q=\sqrt{k_B T}\gamma/a$ for a cusp shaped barrier. The values of κ_1^{sim} are taken from Table I, κ_1 and κ_1^{CW} are given by Eqs. (3.2) and (2.16), respectively. The error bars reflect the statistical error of the simulation. For the sake of clarity they are shown only for the ratio with κ_1 . The error bars are the same for the other two ratios.

mulae κ_4^{CW} and κ_1 give too large values for the rate compared to the numerical results. The maximal relative deviations occur again for q -values of the order of unity. In this case the interpolating formula κ_4 is with maximally 40%

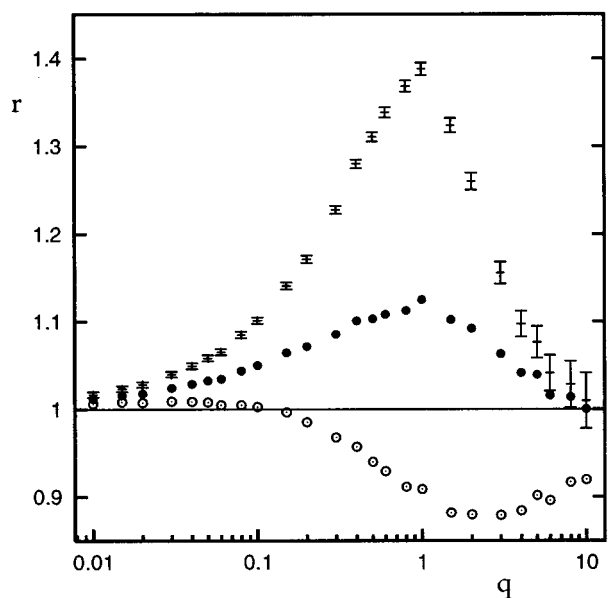


FIG. 4. The ratios $\kappa_4/\kappa_4^{\text{sim}}$ (crosses), $\kappa_4^{\text{CW}}/\kappa_4^{\text{sim}}$ (full circles), and κ_4^{int} (open circles) for different values of $q=\gamma/(ak_B T)^{1/4}$ for a quartic barrier. The values of κ_4^{sim} are taken from Table II, κ_4 and κ_4^{CW} are given by Eqs. (3.3) and (2.16), respectively. The error bars reflect the statistical error of the simulation. For the sake of clarity they are shown only for the ratio with κ_4 . The error bars are the same for the other two ratios.

considerably worse than κ_4^{CW} which has a maximal relative error of less than 12%. The interpolation formula κ_4^{int} is quite accurate for q -values smaller than 0.1. It is smaller than the numerically exact transmission factor from which it maximally deviates by 12% for $q \approx 2$.

IV. CONCLUSIONS

Based on an approximate solution of the Fokker–Planck equation we derived a formula for the transition rate over a potential barrier of arbitrary shape by means of the flux over population method. The resulting rate expression approaches the correct limiting behavior for both weak and strong friction. Comparison with known results for a parabolic barrier and from numerical simulations for cusp shaped barriers give maximal errors of 16% and for quartic barriers of 40%. A generalization of the Calef–Wolynes rate formula shows smaller deviations while the quality of $\kappa_\alpha^{\text{int}}$ strongly depends on the shape of the barrier.

In contrast to the interpolation formulae $\kappa_\alpha^{\text{CW}}$ and $\kappa_\alpha^{\text{int}}$ there are different possibilities to improve a rate formula that is based on a flux carrying solution of the Fokker–Planck solution. First, instead of the flux over population method one can use a Rayleigh quotient¹⁶ with the same approximate Kramers function as test function. Moreover, the Kramers function itself can systematically be improved by means of a perturbation theory based on Eq. (2.4). The approximate Kramers function (2.6) then serves as an unperturbed solution and the right hand side of Eq. (2.4) as perturbation which can be treated iteratively.

ACKNOWLEDGMENTS

The authors thank Professor Eli Pollak for many valuable discussions. Two of the authors (A.M.B. and V.Yu.Z.) acknowledge partial support of this work by the Russian Foundation of Basic Investigation (Grants No. 95-03-09133a and No. 96-03-32733). J.E. acknowledges support by the Deutsche Akademische Austausch Dienst.

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