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Numerical test of finite-barrier corrections for the hopping rate in the underdamped regime

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It is shown that the large differences, which have been found in the underdamped regime, between analytical calculations and exact numerical results for the hopping rate in a periodic potential are essentially due to finite-barrier effects. In fact, if finite-barrier corrections are taken into account, the analytical results turn out to be in quite good agreement with the exact ones in the full damping range below the turnover point.

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Recently, there has been considerable interest in the problem of finite-barrier corrections (FBC's) to the escape rate of a classical particle, coupled to a thermal bath, from a potential well. Analytical FBC's to Kramers's high-friction formula [1] have been obtained by Pollak and Talkner [2] and by Mel'nikov [3]; at low friction, analytical FBC's to the Mel'nikov-Meshkov result [4,5] have been obtained by Mel'nikov [3].

The high-friction FBC's have been tested [6] against exact numerical results [7,8]. The corrections were obtained for a single symmetric well, while the numerical results concerned the hopping rate in a periodic cosine potential. However, in the regime above the turnover, it has been shown that the quantitative discrepancies (which are never very large, at maximum of 13% in the case of a cosine potential with a barrier $U_0=4k_BT$) between the numerical results and Kramers's formula are essentially explained by the FBC's.

In the underdamped regime, discrepancies between analytical and numerical results are much larger [8,7] and still, to our knowledge, unexplained. In fact, if the numerical results are compared to the analytical formula for the escape rate from a symmetric well without taking into account the FBC's, differences of the order of 50% are present at low potential barriers.

In this Rapid Communication the numerical hopping rate in a periodic potential will be compared to the analytical escape rate from a symmetric well; in the latter result the FBC's will be taken into account. The aim of the work is to check whether the above-mentioned discrepancies are due to the FBC's also in the regime below the turnover, which is of great importance, for instance, in atomic surface diffusion [9].

The inverse lifetime (i.e., the escape rate) $1/\tau$ of a Brownian particle in a deep symmetric potential well $U(x)$ can be written in the form

$$\frac{1}{\tau}=\frac{\Omega}{\pi}A\exp\left(-\frac{U_0}{k_BT}\right), \tag{1}$$

where U_0 is the height of the potential barriers confining the particle to the well, T is the temperature, and Ω is the frequency of small oscillations at the bottom of the well. The other details of the potential shape as well as the mechanism of activation are absorbed into the coefficient A. Equation (1) differs from the traditional definition of $1/\tau$ by the factor 2, which accounts for two paths of escape out of a symmetric potential well. To calculate A, one needs to solve the Fokker-Planck equation

$$\frac{p}{m}\frac{\partial f}{\partial x}-\frac{dU(x)}{dx}\frac{\partial f}{\partial p}=\gamma\frac{\partial}{\partial p}\left(mk_BT\frac{\partial f}{\partial p}+pf\right) \tag{2}$$

with appropriate boundary conditions. A detailed discussion of this procedure can be found in the literature [5,10]. Aiming at introduction of the essential quantities in a heuristic fashion, we consider here the case of a very weak friction when, following Kramers, one can exploit the energy diffusion equation

$$\frac{\partial}{\partial\varepsilon}\,\delta(\varepsilon)\left(k_BT\frac{\partial f}{\partial\varepsilon}+f\right)=0, \tag{3}$$

where $\delta(\varepsilon)$ is the energy loss for the particle with a total energy ε during its motion between the turning points $\pm x_1(\varepsilon)$ $[U(x_1)=\varepsilon]$,

$$\delta(\varepsilon)=\gamma S(\varepsilon)=\gamma\int_{-x_1(\varepsilon)}^{x_1(\varepsilon)}\{2m[\varepsilon-U(x)]\}^{1/2}dx. \tag{4}$$

The energy $\varepsilon=0$ corresponds to the top of the potential barriers. Since the particles with positive energies escape out of the potential well, Eq. (3) must be solved with the boundary condition $f(0)=0$, which gives

$$f(\varepsilon)=\frac{\Omega}{2\pi k_BT}\exp\left(-\frac{\varepsilon+U_0}{k_BT}\right)\int_\varepsilon^0\frac{d\varepsilon}{\delta(\varepsilon)}\exp\left(\frac{\varepsilon}{k_BT}\right)\times\left[\int_0^{U_0}\frac{d\varepsilon'}{\delta(-\varepsilon')}\exp\left(-\frac{\varepsilon'}{k_BT}\right)\right]^{-1}. \tag{5}$$

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The lifetime is then defined by the expression

$$\frac{1}{\tau}=-k_BT\delta(\varepsilon)\frac{df(\varepsilon)}{d\varepsilon}\Bigg|_{\varepsilon=0}$$
$$=\frac{\Omega}{2\pi}\exp\left(-\frac{U_0}{k_BT}\right)\left[\int_0^{U_0}\frac{d\varepsilon'}{\delta(-\varepsilon')}\exp\left(-\frac{\varepsilon'}{k_BT}\right)\right]^{-1}. \quad (6)$$

The quantity $\delta(\varepsilon)$ is then expanded in small ε and the upper limit of integration in Eq. (6) is put equal to ∞, neglecting exponentially small terms $\propto\exp[-U_0/(k_BT)]$. The expansion for $\delta(\varepsilon)$ gives

$$\delta(\varepsilon)\approx\delta+\frac{\gamma}{\omega}\varepsilon\left(\ln\frac{U_0}{k_BT}+C_U+1+\ln 2-\ln\frac{|\varepsilon|}{k_BT}\right), \quad (7)$$

where

$$\delta\equiv\delta(0)\equiv\gamma S, \quad (8)$$

$$S=\int_{-x_1}^{x_1}[-2mU(x)]^{1/2}dx, \quad (9)$$

ω is defined by the curvature of the barrier top, $\omega=[-U''(x_1)/m]^{1/2}$,

$$C_U\equiv\int_{-x_1}^{x_1}dx\left\{\frac{m\omega}{[-2mU(x)]^{1/2}}-\frac{1}{|x|}\right\}+\ln\frac{m\omega^2x_1^2}{U_0}, \quad (10)$$

and $x_1\equiv x_1(\varepsilon=0)$ is the position of the barrier top. With these definitions, for the preexponential factor A one gets

$$A(\gamma/\omega,k_BT/U_0)$$
$$\approx\Delta-\frac{k_BT}{U_0}\frac{U_0}{\omega S}\left[\Delta\ln\frac{U_0}{k_BT}+\Delta(C_U+2+\ln 2-C)\right], \quad (11)$$

where

$$\Delta=\frac{\delta}{k_BT}. \quad (12)$$

It is seen that the shape of the potential enters this expression through two coefficients, $U_0/\omega S$ and C_U. In the case of a cosine potential, one has

$$\frac{U_0}{\omega S}=\frac{1}{4}, \quad (13)$$

$$C_U=3\ln 2. \quad (14)$$

Equation (11) holds in the limit of small Δ and in the lowest order in k_BT/U_0. The logarithmic term is due to the slowing down of the particle motion near the top of the barrier; the other terms do not have a straightforward interpretation.

Generalization of Eq. (11) to the case of arbitrary Δ gives [3]

$$A(\gamma/\omega,k_BT/U_0)\approx A_0(\Delta)-\frac{k_BT}{U_0}\frac{U_0}{\omega S}\left[A_1(\Delta)\ln\frac{U_0}{T}+B_1(\Delta)\right], \quad (15)$$

where the functions A_0 and A_1 are defined by the relations

$$A_0(\Delta)=\exp\left\{\frac{1}{\pi}\int_0^\infty\frac{\ln\{1-\exp[-\Delta(\lambda^2+1/4)]\}d\lambda}{\lambda^2+1/4}\right\}, \quad (16)$$

$$A_1(\Delta)=A_0(\Delta)\left\{\int\frac{d\lambda}{2\pi}\frac{\Delta}{\exp[\Delta(\lambda^2+1/4)]-1}\right\}^2. \quad (17)$$

The function $B_1(\Delta)$ depends on the coefficient C_U,

$$B_1(\Delta)=(\Delta/2)[1-I(\Delta)]^2$$
$$+(C_U+1+\ln 2-C)A_1(\Delta)+D(\Delta), \quad (18)$$

whereas the new functions $I(\Delta)$ and $D(\Delta)$ are defined by

$$I(\Delta)\equiv A_0^{1/2}(\Delta)\int\frac{d\lambda}{2\pi}\frac{ig(\lambda)}{(\lambda+i/2)G_-(\lambda)}, \quad (19)$$

$$D(\Delta)\equiv A_0(\Delta)\Delta\frac{i\pi}{2}\int\int\ln|\lambda-\lambda'|\mathrm{sgn}(\lambda-\lambda')\frac{d^2}{d\lambda d\lambda'}$$
$$\times\frac{g(\lambda)+g(\lambda')}{G_+(\lambda)G_-(\lambda')}\frac{d\lambda}{2\pi}\frac{d\lambda'}{2\pi}, \quad (20)$$

where $g(\lambda)=\exp[-\Delta(\lambda^2+1/4)]$ and

$$\ln G_\pm(\lambda)=\pm\int\frac{d\lambda'}{2\pi i}\frac{\ln[1-g(\lambda')]}{\lambda'-\lambda\mp i0}. \quad (21)$$

Let us consider a cosine potential of amplitude $U_0/2$, period a, and small-oscillation frequency Ω. In this case, $\omega=\Omega=[2\pi^2U_0/(ma^2)]^{1/2}$ and

$$\Delta=\frac{4\gamma U_0}{k_BT\omega}. \quad (22)$$

The exact rate r_j in a periodic potential can be numerically calculated by the Fourier analysis of the width of the quasielastic peak of the dynamic structure factor [7,8]. The numerical rate can be compared then to different analytical approximations: the Mel'nikov and Meshkov result without FBC's, denoted as r_m [which corresponds to Eq. (1) with A set equal to A_0, as given by Eq. (16)]; the Kramers result with FBC's, denoted as r_k [in this case A is given by Eq. (11)], which is expected to be valid in the extremely underdamped limit; the Mel'nikov result with FBC's, denoted as r_{fb} [in this case A is given by Eq. (15)], which should be valid in the whole region below the turnover. Up to now, the FBC's have not been calculated in other analytical approaches such as the turnover theories by Büttiker, Harris, and Landauer (BHL) [11] and Pollak, Grabert, and Hänggi (PGH) [12,13]. In Figs. 1 and 2 the exact results for the hopping rate r_j (triangles) are compared to r_m, r_k, and r_{fb}; in Figs. 3 and 4 the relative differences C and C_m, defined by

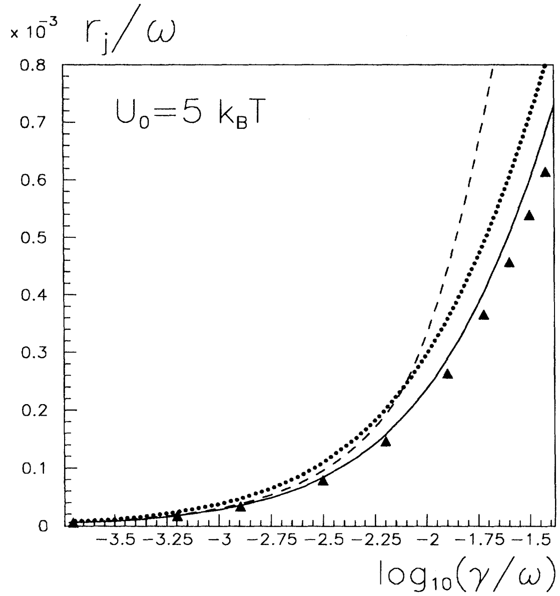

FIG. 1. Numerical hopping rate r_j (triangles); Mel'nikov-Meshkov rate r_m (dotted line) without finite-barrier corrections; Kramers's extremely underdamped result r_k with finite-barrier corrections (dashed line); Mel'nikov result r_{fb} with finite-barrier corrections (full line). All the above quantities are reported as functions of the friction at a fixed potential barrier of $5k_BT$.

$$C=\frac{r_{fb}-r_j}{r_j}, \quad C_m=\frac{r_m-r_j}{r_j}, \tag{23}$$

are shown as functions of γ/ω. It results clearly that the introduction of the FBC's improves largely the agreement between numerical and analytical results. We remark that, at $\gamma\to 0$, both BHL [11] and PGH [13] theories tend to the

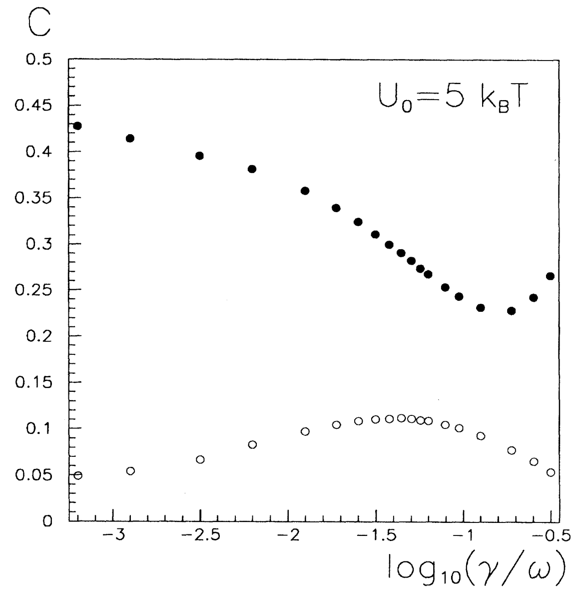

FIG. 3. Relative differences C (open circles) and C_m (black dots), as defined in Eq. (23), in the case of a barrier of $5k_BT$.

same limit as r_m; their difference from the exact result is more than 40% at $U_0=5k_BT$. This fact shows that the largest part of the difference between r_m and the exact results is due to the FBC's. Even at rather high barriers such as $16k_BT$, in the friction regime below the turnover point, a quantitative comparison between different analytical approaches [4,11–13] may be meaningful only if the FBC's are introduced in the analytical calculations. As far as we know, the low-friction FBC's have been introduced up to now only in the framework of the Mel'nikov-Meshkov approach. The extremely underdamped result r_k gives good estimates to the

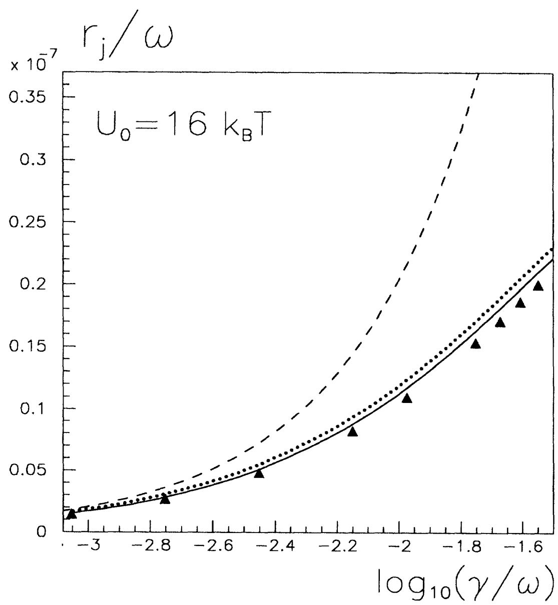

FIG. 2. The same as in Fig. 1, but for a barrier of $16k_BT$.

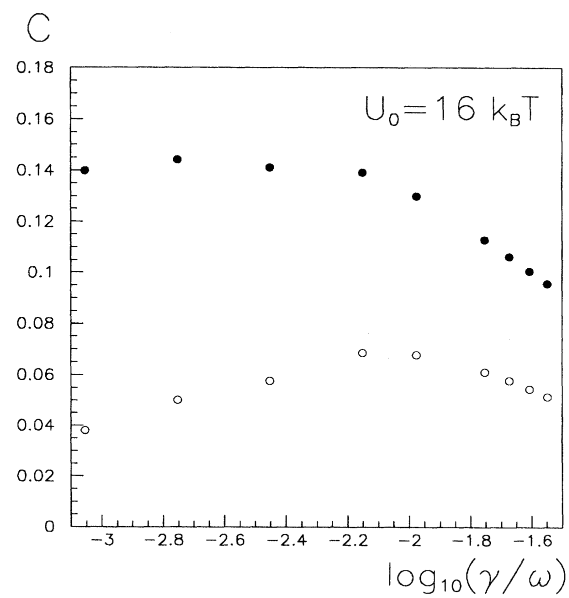

FIG. 4. The same as in Fig. 3, but for a barrier of $16k_BT$.

hopping rate only at $\gamma/\omega < 10^{-2}$; on the contrary, r_{fb} is a very reliable estimate in the full friction range below the turnover.

We can conclude that the hopping rate in a periodic potential is very well approximated in any friction regime by the escape rate from a single symmetric well. If finite-barrier corrections are not taken into account, the quantitative differences between the analytical results and the exact ones are rather large in the underdamped regime; only a qualitative agreement is obtained. If finite-barrier corrections are introduced, the quantitative agreement becomes quite good, showing that other possible effects are essentially negligible.

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