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Numerical test of finite-barrier corrections for the hopping rate in a periodic potential

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It is demonstrated that a recent finite-barrier expansion for jump rates accounts quantitatively for the observed discrepancy between numerically determined exact rates and the Kramers estimates of these rates.

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There has been recent interest in the hopping rate of a particle in a periodic potential which is coupled to a heat bath. Ferrando, Spadacini, and Tommei [1] have obtained a numerical solution for the jump rate out of one of the wells as a function of the damping and the height of the barrier separating between wells. They have also compared the numerical solution with their analytical solution for the escape rate of a particle trapped between two symmetrically displaced barriers. The analytic theory is an extension of the Kramers [2] turnover theory developed by Mel'nikov and Meshkov [3] and by Pollak, Grabert, and Hänggi [4,5].

There is very good qualitative agreement between the exact numerical results of Ferrando, Spadacini, and Tommei and the analytic theory. However, there is also a noticeable quantitative discrepancy which becomes larger as the barrier height is lowered. One can think of a few reasons for this difference. The theory used is really correct only for a particle in a single well trapped between two barriers. It is not "exact" for the periodic potential. It is also true that the Kramers turnover theory is really an asymptotic theory valid only for high barriers. The fact that agreement between theory and numerical experiment improves as the barrier height increases suggests the latter possibility.

The purpose of this Rapid Communication is to quantify this assertion and show that the recent finite-barrier expansions for the decay rate developed in Refs. [6–9] leads to excellent agreement between the theoretical expression and the numerical result. The finite-barrier expansion for the decay rate has thus far been developed only for the moderate to strong damping regime also known as the spatial diffusion regime so that this paper will deal only with this range. Finite-barrier expansions for the rate in the low-damping-energy diffusion regime are not known.

The hopping dynamics of the particle with mass m, coordinate x, moving under the influence of the potential $U(x)$ are assumed to be governed by the Langevin equation:

$$m\ddot{x}+\frac{dU(x)}{dx}+m\eta\dot{x}=\xi(t)\,. \tag{1}$$

The Gaussian random force has zero mean and is δ-correlated at temperature T with the friction η $[\langle\xi(t)\xi(\tau)\rangle=2mk_BT\eta\delta(t-\tau)]$. Ferrando, Spadacini, and Tommei [1] use the symmetric infinite chain potential

$$U(x)=-A\cos\left[\frac{2\pi x}{a}\right], \tag{2}$$

which has wells at $x/a=0,\pm1,\pm2,\ldots$ and barriers at $x/a=\pm\frac{1}{2},\pm\frac{3}{2},\pm\frac{5}{2},\ldots$. The height of the barrier relative to the well bottom is

$$V^{\ddagger}=2A\,. \tag{3}$$

The barrier frequency $\omega^{\ddagger}$ is seen to be

$$\omega^{\ddagger}=\frac{2\pi}{a}\left[\frac{A}{m}\right]^{1/2}. \tag{4}$$

Ferrando, Spadacini, and Tommei also define a reduced barrier parameter g and friction constant γ as

$$g\equiv\tfrac{1}{4}\beta V^{\ddagger},\quad \gamma\equiv\frac{\eta}{\omega^{\ddagger}}\left[\frac{\beta V^{\ddagger}}{2}\right]^{1/2}. \tag{5}$$

The expression for the rate of escape of a particle trapped in a bimetastable potential (one well, two symmetric barriers, and equal barrier and well frequencies) derived in Ref. [1] is

$$\Gamma_0=\frac{\omega^{\ddagger}}{\pi}e^{-\beta V^{\ddagger}}\frac{\lambda^{\ddagger}}{\omega^{\ddagger}}\Upsilon\,. \tag{6}$$

The Kramers [2] friction-dependent barrier frequency $\lambda^{\ddagger}$ is

$$\frac{\lambda^{\ddagger}}{\omega^{\ddagger}}=(\alpha^2+1)^{1/2}-\alpha,\quad \alpha\equiv\frac{\eta}{2\omega^{\ddagger}}=\frac{\gamma}{2^{3/2}g^{1/2}}\,. \tag{7}$$

The depopulation factor Υ [3–5] is unity in the spatial diffusion regime and so need not be considered any further here.

The expression for the rate given in Eq. (6) is based on the first term of a steepest-descent estimate of the partition function for the particle trapped in the well and a steepest-descent estimate of the barrier dynamics and is thus denoted with a 0 subscript. The "large parameter" is the reduced barrier height $\beta V^{\ddagger}$. To obtain the first corrections for the well and barrier dynamics one must expand the potential around the well and the barrier, respectively:

TABLE I. Comparison between analytic finite-barrier corrections and numerically exact results for the hopping rate.

g [a]	γ [b]	Γ_0 [c]	Γ [d]	P_T [e]	P_N [f]
1	1.41	5.102×10^{-3}	4.721×10^{-3}	0.0749	0.0747
	2.00	4.268×10^{-3}	3.914×10^{-3}	0.0833	0.0829
	3.00	3.274×10^{-3}	2.951×10^{-3}	0.0956	0.0987
	4.47	2.389×10^{-3}	2.120×10^{-3}	0.1071	0.1126
	6.32	1.761×10^{-3}	1.548×10^{-3}	0.1146	0.1210
	8.16	1.388×10^{-3}	1.216×10^{-3}	0.1182	0.1239
	9.00	1.265×10^{-3}	1.106×10^{-3}	0.1194	0.1257
	9.50	1.201×10^{-3}	1.050×10^{-3}	0.1199	0.1257
	10.0	1.143×10^{-3}	9.986×10^{-4}	0.1204	0.1263
	10.5	1.091×10^{-3}	9.523×10^{-4}	0.1208	0.1271
	11.0	1.043×10^{-3}	9.101×10^{-4}	0.1211	0.1274
	14.1	8.188×10^{-4}	7.132×10^{-4}	0.1226	0.1290
4	1.41	7.916×10^{-8}	7.777×10^{-8}	0.0165	0.0176
	1.69	7.547×10^{-8}	7.412×10^{-8}	0.0169	0.0179
	2.58	6.515×10^{-8}	6.388×10^{-8}	0.0183	0.0195
	4.47	4.907×10^{-8}	4.795×10^{-8}	0.0216	0.0228
	6.32	3.872×10^{-8}	3.772×10^{-8}	0.0242	0.0258
	9.00	2.920×10^{-8}	2.837×10^{-8}	0.0268	0.0284
	10.0	2.667×10^{-8}	2.589×10^{-8}	0.0275	0.0293
	11.0	2.453×10^{-8}	2.380×10^{-8}	0.0280	0.0298
	14.1	1.957×10^{-8}	1.896×10^{-8}	0.0291	0.0312

[a] g is the reduced barrier height [cf. Eq. (5)].
[b] γ is the reduced friction constant [cf. Eq. (5)].
[c] Γ_0 is the escape rate of a particle trapped in bimetastable potential [cf. Eq. (6)].
[d] Γ is the numerically exact hopping rate in a periodic potential adapted from Ref. [1,16].
[e] P_T is the relative theoretical finite-barrier correction to the steepest-descent prediction for the rate [cf. Eqs. (6) and (13)].
[f] P_N is the numerically exact relative correction to the steepest-descent correction for the rate [cf. Eq. (14)] adapted from Ref. [1,16].

$$U(x)\simeq\begin{cases}\dfrac{1}{2}m\omega^{\ddagger 2}x^2\left[1-\dfrac{m\omega^{\ddagger 2}}{12A}x^2\right], & x\simeq 0, \quad (8)\\[2ex] V^{\ddagger}-\dfrac{1}{2}m\omega^{\ddagger 2}\left(x\pm\dfrac{a}{2}\right)^2\left[1-\dfrac{m\omega^{\ddagger 2}}{12A}\left(x\pm\dfrac{a}{2}\right)^2\right], & x\simeq\mp a. \quad (9)\end{cases}$$

In the Smoluchowski limit ($\alpha\gg 1$) the leading-order corrections for this potential have been derived previously by a number of authors [10–15], the result is

$$\Gamma_S\simeq\Gamma_0(\alpha\gg 1)\left[1-\frac{1}{8\beta}\left(\frac{U^{(4)}(x=a/2)}{[U^{(2)}(x=a/2)]^2}-\frac{U^{(4)}(x=0)}{[U^{(2)}(x=0)]^2}\right)\right], \tag{10}$$

where $U^{(n)}$ denotes the nth derivative of the potential.

Recently [6–9], this expression has been generalized for the entire spatial diffusion limit, the dependence on the damping appears only in the barrier dynamics. The resulting expression which is the central one used in this paper is

$$\Gamma\simeq\Gamma_0(\alpha)\left[1-\frac{1}{8\beta}\left(\frac{1}{\chi^2}\frac{U^{(4)}(x=a/2)}{[U^{(2)}(x=a/2)]^2}-\frac{U^{(4)}(x=0)}{[U^{(2)}(x=0)]^2}\right)\right], \tag{11}$$

where the dependence of the so-called nonlinearity parameter χ [8,9] on the damping is

$$\chi=\frac{(1+\alpha^2)^{1/2}}{\alpha}. \tag{12}$$

Combining Eqs. (5), (7), (11), and (12) one finds that the relative correction P_T to the steepest-descent estimate employed by Ferrando, Spadacini, and Tommei is

$$P_T\equiv\frac{\Gamma_0-\Gamma}{\Gamma_0}=\frac{1}{16g}\left(1+\frac{\gamma^2/8g}{1+\gamma^2/8g}\right). \tag{13}$$

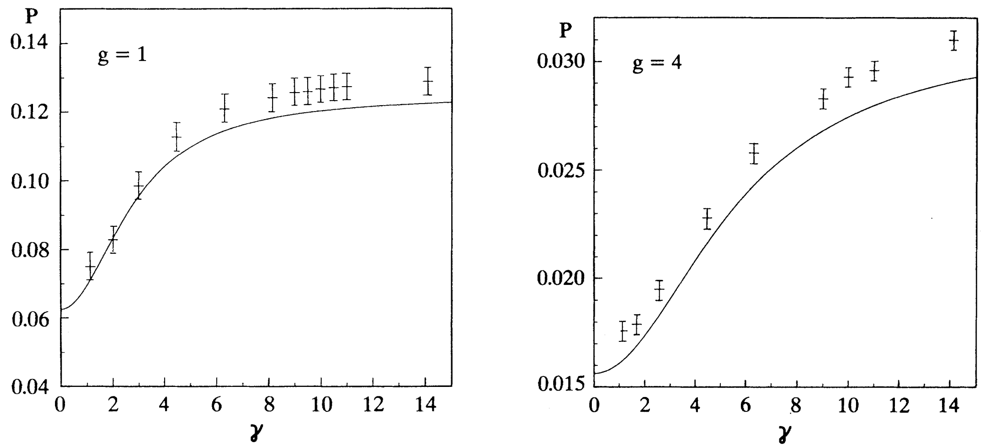

FIG. 1. Relative correction P_T as given by Eq. (13) (solid line) and numerically exact correction P_N as defined in Eq. (14) (crosses) as function of the reduced friction constant γ for reduced barrier heights $g=1$ and $g=4$. The error bars correspond to an uncertainty of the exact rate of 1% and 0.1% for $g=1$ and $g=4$, respectively.

The numerically exact results for the rate (Γ_N) and the steepest-descent estimate of Ferrando, Spadacini, and Tommei is presented in Table I. In Fig. 1 we compare the theoretical correction P_T to the numerically exact correction P_N defined as

$$P_N \equiv \frac{\Gamma_0 - \Gamma_N}{\Gamma_0} . \tag{14}$$

The excellent agreement between the numerical result and the predicted barrier height dependent correction term leads to the following conclusions: (a) The hopping rate in a periodic potential is quantitatively approximated by the decay rate of a particle trapped by two symmetric barriers. (b) The friction dependence of the first-order correction term in the asymptotic expansion has been verified from the numerically exact results. (c) There seems to be no practical need to include higher-order terms in the steepest-descent expansion for the rate in the spatial diffusion limit.

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