A study of Kramers' turnover theory in the presence of exponential memory friction

Reuven Ianconescu

Chemical Physics Department, Weizmann Institute of Science, 76100 Rehovoth, Israel and Shenkar College of Engineering and Design, Ramat Gan, Israel

Eli Pollak

Chemical Physics Department, Weizmann Institute of Science, 76100 Rehovoth, Israel

Abstract

Originally, the challenge of solving Kramers' turnover theory was limited to Ohmic friction, or equivalently, motion of the escaping particle governed by a Langevin equation. Mel'nikov and Meshkov (J. Chem. Phys. **85**, 1018 (1986)) (MM) presented a solution valid for Ohmic friction. The turnover theory was derived more generally and for memory friction by Pollak, Grabert and Hänggi (J. Chem. Phys. **91**, 4073 (1989)) (PGH). Mel'nikov proceeded to also provide finite barrier corrections to his theory (Phys. Rev. E, **48**, 3271 (1993)). Finite barrier corrections were derived only recently within the framework of PGH theory (J. Chem. Phys., **140** 154108, (2014)). A comprehensive comparison between MM and PGH theory including finite barrier corrections and using Ohmic friction showed that the two methods gave quantitatively similar results and were in quantitative agreement with numerical simulation data. In the present paper we extend the study of the turnover theories to exponential memory friction. By comparing with numerical simulation, we find that PGH theory is rather accurate, even in the strong friction long memory time limit, while MM theory fails. However, inclusion of finite barrier corrections to PGH theory leads to failure in this limit. The long memory time invalidates the fundamental assumption that consecutive traversals of the well are independent of each other. Why PGH theory without finite barrier corrections remains accurate is a puzzle.

I. INTRODUCTION

In 1940, Kramers [1] considered the rate of escape of a particle trapped in a well separated from a different well or a continuum by a barrier. The dynamical model he considered was equivalent to motion of the particle governed by a Langevin equation at temperature T in which the friction is "Ohmic". Kramers solved the problem separately for weak friction and for moderate to strong damping. In the weak friction limit he showed that the rate increases linearly with the friction coefficient. In the strong damping limit it decreases inversely with the friction coefficient. However, he did not provide a full solution for the whole friction range, this became known as the Kramers turnover problem.

Kramers' approach was generalized to include memory friction in the spatial diffusion limited regime by Grote and Hynes [2] and in the underdamped, energy diffusion limited regime by Carmeli and Nitzan [3]. However, these authors also, did not solve the Kramers turnover problem without or with memory in the friction.

Only in 1986 Mel'nikov and Meshkov (MM) [4, 5], using a master equation approach, derived an expression, valid for any value of the damping. The theory was further considered also in Ref. [6]. Although MM considered expressly the Langevin equation, their expression may be extended also to include memory friction. To date, MM theory has not been tested in the presence of memory friction. This is one of the central issues in the present paper. We find that MM theory significantly overestimates the rate in the strong friction long memory time limit.

A few years later, the Kramers turnover problem in the presence of memory friction was solved [7, 8]. Earlier, Pollak [9] used the equivalence of the generalized Langevin equation and its representation by a Hamiltonian in which the system is bilinearly coupled to a bath of harmonic oscillators to show that Kramers' spatial diffusion limited regime is just the rate predicted by variational transition state theory. This was achieved by noting that around the barrier top, the Hamiltonian is a quadratic form which may be diagonalized. The optimal reaction coordinate is the unstable normal mode. The solution to Kramers turnover problem described in Ref. [8], known as PGH theory, was based on consideration of the dynamics along the unstable normal mode instead of the physical system coordinate, as performed in MM theory.

Both MM and PGH theory were based on the conditional probability kernel for the particle initiated at the barrier with energy E to return to it with energy E':

$$P_0\left(E'|E\right) = \frac{1}{\sqrt{4\pi k_B T \Delta E}} \exp\left(-\frac{\left(E' - E + \Delta E\right)^2}{4k_B T \Delta E}\right). \tag{1.1}$$

The main physical quantity which needs to be determined is the average energy loss ΔE for motion from the barrier to the well and back. In MM theory it is determined by the physical motion of the particle, in PGH theory it is found from the motion along the unstable normal mode, from the barrier to the well and back. In both theories the rate expression is a product of three terms, the "standard" transition state theory expression for the rate, the depopulation factor which depends on the energy loss and accounts for the energy exchange with the bath, and a spatial diffusion factor which reduces to Kramers theory in the spatial diffusion limited regime and Langevin dynamics.

Both theories were tested numerically in the presence of Ohmic friction [10–12]. Our most recent extensive numerical tests [13] for the escape rate from a cubic potential showed that both theories were of comparable accuracy over the whole friction range, provided that the barrier was a factor of five or so larger than the thermal energy (k_BT).

The next step in the development of the theory was to include finite barrier corrections. In the spatial diffusion limited regime these were derived for memory friction in Ref. [14]. Mel'nikov [15], derived finite barrier corrections for the rate in the presence of Ohmic friction for the energy diffusion limited regime. A first numerical test of this improved turnover theory was given in Ref. [11], showing that the finite barrier corrections significantly improved the accuracy of the theory. In this case though, Mel'nikov's expression is valid only for Ohmic friction and is not readily extended to memory friction.

Finite barrier corrections for PGH theory in the energy diffusion regime were only recently derived. The temperature dependence of the PGH energy loss was considered in Ref. [16], while the energy dependence of the energy loss was treated in Ref. [13] where these results were used to formulate finite barrier corrections to the turnover theory. A numerical study for a cubic potential and Ohmic friction showed that for reduced barrier heights of 7 or more, the finite barrier theories in both the MM and PGH formulation are quite close to each other, leading to errors of only a few percent over the entire friction regime.

Numerical tests of PGH theory in the presence of memory friction have also been undertaken. Indeed, the original formulation of PGH theory came from a challenge presented by the numerical calculations of Straub, Borkovec and Berne [17]. They found, using exponential memory friction, that even when the friction coefficient (defined as the time integral of the time dependent friction) was large, long memory times could again reduce the rate constant. One of the successes of PGH theory was that it accounted reasonably well for this observation. In PGH theory, in the long memory time limit, the depopulation factor was again reduced from unity to low values.

PGH theory in the presence of memory friction was further tested against numerical simulation data in Ref. [18] with rates obtained from the reactive flux methodology [19]. These tests, using a cubic potential and exponential memory friction, indicated that in the presence of long memory times and large friction, PGH theory underestimates the numerically exact rates by factors of 2 or even more. The second purpose of the present work is to provide a careful numerical test of PGH theory in the presence of memory friction. We find excellent agreement between PGH theory and numerical simulation data. For the extensive range of parameters considered, we find that the accuracy of PGH theory is at worst 15%.

Finally, we consider finite barrier corrections in the presence of memory friction. For weak damping and short memory, the finite barrier corrections provide an improvement, as might be expected, since in this parameter range, the friction is Ohmic like. However, in the strong friction long memory limit, we find that the finite barrier corrections fail. As suggested earlier by Farago and Peyrard [20], in this limit, for energies below the barrier, the Markovian assumption that one traversal from the barrier to the well and back is independent of the previous traversal, fails due to the long memory time.

The paper is organized as follows. In section II we describe the numerical method used for solution of the barrier crossing rate in the presence of exponential memory friction for a cubic potential. The numerical results serve as benchmarks for comparison with theory. In section III we review the PGH and MM theories for the rate in the presence of memory friction and compare them with each other and the numerical simulation results. We find that PGH theory is superior to MM theory in the strong friction long memory time limit. In section IV we consider finite barrier corrections within the PGH approach. We end with a summary and discussion.

II. NUMERICAL SOLUTION

In this section we describe the numerical computation of the escape rate of a particle with mass M from a cubic potential

$$V\left(q\right)=-\frac{M\omega^{\ddagger^2}}{2}q^2\left(1+\frac{q}{q_0}\right), \tag{2.1}$$

with parabolic barrier frequency $\omega^{\ddagger}$ and barrier height

$$V^{\ddagger}=\frac{2M\omega^{\ddagger^2}q_0^2}{27}. \tag{2.2}$$

Following in the footsteps of Ref. [17] we use the exponential friction function

$$\gamma(t)=\frac{\gamma}{\tau}\exp(-|t|/\tau), \tag{2.3}$$

where γ is the friction coefficient in the sense that $\int_0^\infty dt\gamma(t)=\gamma$ and τ is the memory time. The friction function may also be written as the Fourier transform of a spectral density $J(\omega)$ such that:

$$\gamma(t)=\frac{2}{\pi}\int_0^\infty d\omega\frac{J(\omega)}{\omega}\cos(\omega t). \tag{2.4}$$

For the exponential friction function one readily finds that:

$$J(\omega)=\frac{\omega\gamma}{1+\tau^2\omega^2}. \tag{2.5}$$

Instead of varying the two friction function parameters (γ,τ) separately, following Ref. [17] we will keep the constant relation

$$\frac{\gamma}{\tau}=\frac{3\omega^{\ddagger 2}}{4}, \tag{2.6}$$

and vary only the single parameter γ. This implies that when the friction coefficient γ is very small the memory time is also small, so that in the small friction limit the friction behaves as Ohmic friction. Conversely, the large friction limit is also the long memory time limit.

The numerical computations have been implemented as described in Ref. [13], using the same high quality random generator [21], with period of 3.138×10^{57}. We employ the following units: $q_0=1$, $M=1$ and $V^{\ddagger}=1$. The frequency is then $\omega^{\ddagger}=\sqrt{27/2}$. Trajectories are initiated from the Boltzmann distribution in the well, as described in Ref. [13].

The dynamics is evolved from the Generalized Langevin Equation (GLE):

$$M\ddot{q}+\frac{dV\left(q\right)}{dq}+M\int_0^t dt'\gamma\left(t-t'\right)\dot{q}\left(t'\right)=F\left(t\right), \tag{2.7}$$

where $F(t)$ is a Gaussian random force with zero mean and correlation function

$$\langle F(t) F(t') \rangle = M k_B T \gamma (t - t') . \tag{2.8}$$

The Langevin dynamics is carried out using a 4th order Runge Kutta algorithm, with a time step $dt = \frac{1}{50} \frac{2\pi}{\omega^\ddagger}$. This time step limits the memory interval τ (see Eq. (2.4)), so that τ cannot be much smaller than dt. This means according to Eq. (2.6) that $\gamma/\omega^\ddagger$ cannot be much smaller than 0.1. We calculated the escape rates for $\gamma/\omega^\ddagger \geq 0.056234$. For lower values of $\gamma/\omega^\ddagger$ we use the Ohmic friction approximation results computed in Ref. [13], since the memory time scales with the magnitude of the friction coefficient and in this small friction limit, the friction function is essentially Ohmic. The random force is treated using the procedure explained in Ref. [22]. Each trajectory is propagated until it escapes the well, using the escape criterion $q > 0.452 q_0$, at which point the potential energy of the particle is $-2V^\ddagger$.

The sample size used for a given value of the friction and memory time is $N_0 = 500,000$. The rate constant is obtained as in Ref. [13] by fitting the time dependent population remaining in the well $N(t)$ to the exponential form $N_0 \exp(-\Gamma t)$ using a least squares estimate, where Γ is the escape rate. This is performed for the time interval $t_{\max}/20 < t < t_{\max}/5$, where $t_{\max}$ is the escape time of the last particle which remained in the well. The ratio of the standard deviation σ_Γ to the rate Γ as estimated from the linear regression error formula is a few parts per million.

Escape rates have been computed for the reduced barrier height $\beta V^\ddagger = 10$, and the range $0.056234 \leq \gamma/\omega^\ddagger \leq 1000$. They are normalized by Γ_{TST}, defined as:

$$\Gamma_{TST} = \frac{\exp\left(-\beta V^\ddagger\right)}{(2\pi M \beta)^{1/2} \int_{-\infty}^{\infty} dq \exp\left(-\beta V(q)\right) \theta(-q)} . \tag{2.9}$$

This choice eliminates the error induced by assuming that the reactants partition function is the harmonic one. For a cubic potential with $\beta V^\ddagger = 10$ as used in Ref. [18] the harmonic approximation induces an overestimate of the rate by a factor of 1.015. The normalized rates

$$\kappa \equiv \frac{\Gamma}{\Gamma_{TST}} \tag{2.10}$$

are presented in table I, together with the analytic results which are developed in the next sections.

TABLE I: Transmission factors for a cubic potential with $\beta V^\ddagger = 10$, $\Gamma_{TST} = 2.6134 \times 10^{-5}$. For $\gamma/\omega^\ddagger < 0.056234$ the rates are calculated with Ohmic friction only. The columns show the numerical results and the analytic results obtained by the PGH method (section II), the MM method (section III) and the PGH method with energy diffusion finite barrier corrections (section IV B), and the PGH method with spatial diffusion finite barrier corrections (section IV C).

$\gamma/\omega^\ddagger$	$\lambda^\ddagger/\omega^\ddagger$	κ numeric	κ PGH	κ MM	κ_{ED}	κ_{SD}
0.001	0.99950	0.050734	0.057665	0.057704	0.906082	1.00000
0.001333521	0.99933	0.065745	0.074224	0.074323	0.908838	1.00000
0.001778279	0.99911	0.084785	0.095054	0.095309	0.912145	1.00000
0.002371373	0.99882	0.10872	0.120986	0.121419	0.916026	1.00000
0.003162277	0.99843	0.13806	0.152889	0.153592	0.920501	1.00000
0.004216965	0.99791	0.17492	0.191602	0.192734	0.925598	1.00000
0.005623413	0.99721	0.21931	0.237821	0.239614	0.931360	1.00000
0.007498942	0.99629	0.27256	0.291962	0.294746	0.937828	1.00000
0.01	0.99508	0.33249	0.353961	0.358184	0.945025	1.00000
0.013335	0.99347	0.40372	0.423068	0.429302	0.952940	1.00000
0.017783	0.99135	0.47945	0.497681	0.506587	0.961507	1.00000
0.023714	0.98857	0.56305	0.575180	0.587420	0.970570	1.00000
0.031623	0.98493	0.64735	0.652042	0.668106	0.979863	1.00000
0.042170	0.98022	0.7261	0.724102	0.744058	0.988975	0.99999
0.056234	0.97414	0.79398	0.787113	0.810333	0.997357	0.99999
0.1	0.95664	0.89859	0.873088	0.897697	1.009489	0.99995
0.31623	0.89167	0.88585	0.882036	0.890416	1.011462	0.99956
1.0	0.78512	0.78713	0.781469	0.785115	1.013662	0.99639
3.1623	0.66819	0.63158	0.646954	0.668160	1.066207	0.97721
10.0	0.57960	0.41692	0.446774	0.577090	0.906476	0.90104
31.623	0.53109	0.21171	0.221695	0.484200	0.288056	0.74430
100.0	0.51074	0.088841	0.088945	0.325820	0.070779	0.59591
316.23	0.50350	0.032899	0.032434	0.166784	0.028307	0.51883
1000.0	0.50112	0.01158	0.011284	0.069974	0.018544	0.49430

III. PGH AND MM THEORY WITH EXPONENTIAL FRICTION

A. Preliminaries

For a general one dimensional GLE, the potential is assumed to have a well at q_a with frequency ω_a and a barrier at $q = 0$ with frequency $\omega^\ddagger$ which separates the well from a continuum of a different well. The potential is separated into a parabolic barrier and a nonlinearity $V_1(q)$:

$$V(q) = -\frac{1}{2}M\omega^{\ddagger 2}q^2 + V_1(q). \tag{3.1}$$

Without the nonlinearity the Hamiltonian equivalent of the GLE (Eq. 2.7) has a quadratic form and may be diagonalized [9, 23]. The (unstable) mass weighted normal mode and associated momentum are denoted as ρ and p_ρ respectively. The stable (mass weighted) bath normal mode coordinates and momenta are denoted as y_j and p_{y_j} respectively. The system coordinate q is expressed in terms of the normal modes as

$$\sqrt{M}q = u_{00}\rho + \sum_{j=1}^{N} u_{j0}y_j \tag{3.2}$$

where u_{j0} is the projection of the system coordinate onto the j-th stable normal mode and u_{00} is the projection on the unstable normal mode. It is expressed in the continuum limit as [8]:

$$u_{00}^2 = \left[1 + \frac{1}{2}\left(\frac{\hat{\gamma}\left(\lambda^\ddagger\right)}{\lambda^\ddagger} + \frac{\partial\hat{\gamma}(s)}{\partial s}|_{s=\lambda^\ddagger}\right)\right]^{-1}. \tag{3.3}$$

where $\hat{\gamma}(s)$ denotes the Laplace transform of the time dependent friction at the frequency s. The barrier frequency $\lambda^\ddagger$ associated with the unstable normal mode is given by the Kramers-Grote-Hynes relation [1, 2]:

$$\lambda^{\ddagger 2} + \hat{\gamma}\left(\lambda^\ddagger\right)\lambda^\ddagger = \omega^{\ddagger 2}. \tag{3.4}$$

PGH theory is predicated on the assumption of weak coupling between the system and the bath. This is expressed through the "small parameter" [8]:

$$u_1^2 = 1 - u_{00}^2 \ll 1. \tag{3.5}$$

The normal mode friction kernel (we use here a definition which is slightly different from that of Ref. [24]) is defined as

$$K(t) = \sum_{j=1}^{N} \frac{u_{j0}^2}{\lambda_j^2}\cos(\lambda_j t). \tag{3.6}$$

Its Laplace transform may be expressed in the continuum limit through the relation [24]:

$$\hat{K}(s) = \left(\frac{su_{00}^2}{\lambda^{\ddagger 2}\left(s^2 - \lambda^{\ddagger 2}\right)} + \frac{s + \hat{\gamma}\left(s\right)}{\omega^{\ddagger 2}\left(\omega^{\ddagger 2} - s^2 - \hat{\gamma}\left(s\right)s\right)}\right). \tag{3.7}$$

The spectral density of the normal modes defined as [24]:

$$I\left(\lambda\right) = \frac{\pi}{2}\sum_{j=1}^{N}\frac{u_{j0}^2}{\lambda_j}\left[\delta\left(\lambda - \lambda_j\right) - \delta\left(\lambda + \lambda_j\right)\right] \tag{3.8}$$

is related to the normal mode friction kernel through the relation

$$I\left(\lambda\right) = \lambda \mathrm{Re}\hat{\mathrm{K}}(\mathrm{i}\lambda) \tag{3.9}$$

B. The exponential friction kernel

The Laplace transform of Eq. (2.3) is

$$\hat{\gamma}(s) = \frac{\gamma}{1 + s\tau}, \tag{3.10}$$

so that from Eq. 3.3 we find:

$$u_{00}^2 = \left[1 + \frac{\gamma}{2\lambda^{\ddagger}(1 + \lambda^{\ddagger}\tau)^2}\right]^{-1}. \tag{3.11}$$

The normal mode barrier frequency $\lambda^{\ddagger}$ is obtained as the only real-positive solution of the Kramers-Grote-Hynes relation (3.4). In the long memory time large friction limit (using Eq. 2.6) one obtains:

$$\lambda_{\infty}^{\ddagger} = \frac{\omega^{\ddagger}}{2} + \frac{3}{2\tau} + \mathrm{O}\left(\frac{1}{\tau^2}\right). \tag{3.12}$$

From Eqs. 3.7, 3.9 and 3.10 one finds that the spectral density of normal modes is

$$I(\lambda) = \frac{\gamma\lambda}{\left[\left(\omega^{\ddagger 2} + \lambda^2\right)^2 + \lambda^2\left[\left(\omega^{\ddagger 2} + \lambda^2\right)\tau - \gamma\right]^2\right]} \tag{3.13}$$

and here we have not yet used the relation given in Eq. 2.6.

C. The depopulation factor

1. *PGH theory*

The depopulation factor is determined by the conditional probability $P_0\left(E'|E\right)$ that the system originates at the barrier with energy E and returns to it with energy E'. Introducing the dimensionless energy variable $\varepsilon = \beta E$ and energy loss variable $\delta = \beta \Delta E$ the normalized Gaussian conditional probability given in Eq. 1.1 is written as:

$$P_0\left(\varepsilon'|\varepsilon\right) = \frac{1}{\sqrt{4\pi\delta}} \exp\left(-\frac{\left(\varepsilon' - \varepsilon + \delta\right)^2}{4\delta}\right). \tag{3.14}$$

The subscript 0 notes that this is the kernel without finite barrier corrections.

The average energy lost by the particle is obtained by considering the zero-th order solution ($\rho_{0,t}$) for the motion of the unstable mode which is governed by the zero-th order equation of motion

$$\ddot{\rho}_{0,t} - \lambda^{\ddagger 2}\rho_{0,t} = -\frac{u_{00}}{\sqrt{M}} V_1'\left(\frac{u_{00}\rho_{0,t}}{\sqrt{M}}\right) \equiv F_{PGH}(t). \tag{3.15}$$

The (reduced) average energy lost by the unstable mode as it goes through one cycle, starting at $t = -\infty$ at the barrier top ($\rho = 0$) and returning to the barrier top at time $t = \infty$ is:

$$\delta_{PGH} \equiv \frac{\beta}{2M} \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' V_1'\left(\frac{u_{00}\rho_{0,t}}{\sqrt{M}}\right) \frac{\partial^2 K\left(t - t'\right)}{\partial t \partial t'} V_1'\left(\frac{u_{00}\rho_{0,t'}}{\sqrt{M}}\right). \tag{3.16}$$

Using the spectral density of normal modes enables a rewriting of the expression of the energy loss in the more convenient form

$$\delta_{PGH} = \frac{\beta}{2\pi u_{00}^2} \int_{-\infty}^{\infty} d\lambda \lambda I(\lambda) f(\lambda) \tag{3.17}$$

where $f(\lambda)$ is

$$f(\lambda) = \left| \int_{-\infty}^{\infty} dt \exp(i\lambda t) F_{PGH}(t) \right|^2, \tag{3.18}$$

and $F_{PGH}(t)$ is the force acting on the unstable normal mode (Eq. 3.15). For the cubic potential one readily finds [24]:

$$f(\lambda) = \frac{216\pi^2}{u_{00}^2} V^{\ddagger} \left(\frac{\lambda^{\ddagger}}{u_{00}\omega^{\ddagger}}\right)^6 \frac{\lambda^2\left(\lambda^2 + \lambda^{\ddagger 2}\right)^2}{\lambda^{\ddagger 6}} \frac{1}{\sinh^2\left(\frac{\pi\lambda}{\lambda^{\ddagger}}\right)}. \tag{3.19}$$

In the strong damping long memory time limit one then finds that the energy loss reduces to

$$\lim_{\gamma\to\infty} \delta_{PGH} = \frac{81}{32} \beta V^{\ddagger} \frac{\omega^{\ddagger}}{\gamma}. \tag{3.20}$$

In this limit, the energy loss vanishes and the depopulation factor will also vanish.

In MM theory, with time dependent friction, the reduced energy loss is given by the expression

$$\delta_{MM} = M \int_{-\infty}^{\infty} dt \int_{-\infty}^{t} dt' \dot{q}_{0,t} \gamma \left(t - t'\right) \dot{q}_{0,t'}. \tag{3.21}$$

The zero-th order motion of the system obeys the unperturbed equation of motion:

$$M\ddot{q}_{0,t} = -\frac{dV\left(q_{0,t}\right)}{dq_{0,t}} \equiv F(t). \tag{3.22}$$

The MM energy loss can also be rewritten in the more convenient form in terms of the spectral density as [24]

$$\delta_{MM} = \frac{M\beta}{\pi} \int_{0}^{\infty} d\omega \frac{J\left(\omega\right)}{\omega} \left| \int_{-\infty}^{\infty} dt \exp\left(i\omega t\right) \dot{q}_{0,t} \right|^2. \tag{3.23}$$

For the cubic potential given in Eq. (2.1), the solution for the zero-th order equation of motion for the system coordinate at the barrier energy is [24]:

$$q_{0,t} = -\frac{q_0}{\cosh^2\left(\frac{\omega^{\ddagger}}{2}t\right)} \tag{3.24}$$

so that (see Eq. 3.982.1 of Ref. [25] and Eq. 2.5):

$$\delta_{MM} = \frac{16\pi M\beta q_0^2}{\omega^{\ddagger 4}} \int_{0}^{\infty} d\omega \frac{J\left(\omega\right)}{\omega} \frac{\omega^4}{\sinh^2\left(\frac{\pi\omega}{\omega^{\ddagger}}\right)}. \tag{3.25}$$

For Ohmic friction ($J(\omega) = \gamma\omega$) this gives the known result [4]:

$$\delta_{MM}(\text{Ohmic}) = \frac{36\gamma}{5\omega^{\ddagger}}\beta V^{\ddagger}. \tag{3.26}$$

For exponential memory (using Eqs. 4.373.4 and 8.363.8 of Ref. [25]) one finds after some algebra that:

$$\delta_{MM} = 36\frac{\gamma}{\omega^{\ddagger}}\frac{\beta V^{\ddagger}}{\omega^{\ddagger 2}\tau^2}\left[1 + \frac{6}{\omega^{\ddagger}\tau}\left(\frac{1}{\omega^{\ddagger}\tau} + \frac{1}{2} - \frac{1}{\tau^2\omega^{\ddagger 2}}\Psi_1(1/(\omega^{\ddagger}\tau)\right)\right] \tag{3.27}$$

where $\Psi_1(z) \equiv \frac{d^2}{dz^2}\ln\Gamma(z)$ is the trigamma function. In the Appendix we show that this expression reduces correctly to the Ohmic expression in the limit of short memory. In the strong friction long memory time limit (keeping $\frac{\gamma}{\tau}$ constant (see Eq. (2.6))) noting that $\lim_{z\to 0} z^2\Psi_1(z) = 1$ we find that

$$\lim_{\gamma\to\infty} \delta_{MM} = 36\beta V^{\ddagger}\frac{\omega^{\ddagger}}{\gamma} \tag{3.28}$$

In other words, the MM energy loss will vanish in the large friction, long memory time limit. This implies that also in MM theory, in this limit, the rate will vanish due to the infinitely slow energy relaxation. However, the MM coefficient (36) in the energy loss factor is $\frac{384}{27} = 14\frac{3}{16}$ times larger than the numerical factor in the PGH energy loss in this limit (Eq. 3.20) implying that the MM depopulation factor will be ~ 14 times larger than the PGH depopulation factor.

3. *The depopulation factor*

The depopulation factor is obtained by solution of the steady state expression for the flux of particles $f(\varepsilon)$ hitting the barrier, when considered in the energy of the unstable normal mode for PGH theory and when considered in the particle energy for MM theory. This solution is described in some detail in the Appendix of Ref. [24]. Here we just bring the final expression for the depopulation factor, valid for both PGH and MM theory:

$$\Upsilon_0 = \exp\left(\frac{1}{2\pi}\int_{-\infty}^{\infty} d\tau \frac{\ln\left[1-\tilde{P}_0\left(\tau-\frac{i}{2}\right)\right]}{\tau^2+\frac{1}{4}}\right). \tag{3.29}$$

where the tilde notation signifies the Fourier transform of a function $g(\varepsilon)$

$$\tilde{g}\left(\tau-\frac{i}{2}\right) = \int_{-\infty}^{\infty} d\varepsilon \exp\left(i\left(\tau-\frac{i}{2}\right)\varepsilon\right) g(\varepsilon). \tag{3.30}$$

so that

$$\tilde{P}_0\left(\tau-\frac{i}{2}\right) = \exp\left(-\delta\left[\frac{1}{4}+\tau^2\right]\right). \tag{3.31}$$

As before, the zero subscript is used to note that Eq. 3.29 is the result without finite barrier corrections.

In both theories, the rate of escape is the product of three terms:

$$\Gamma = \frac{\lambda^{\ddagger}}{\omega^{\ddagger}}\Upsilon\Gamma_{TST} \tag{3.32}$$

where Γ_{TST} is defined in Eq. (2.9). At this point the only practical difference between PGH and MM theory is in the definition of the reduced energy loss δ, given by Eq. 3.21 for MM theory and Eq. 3.16 for PGH theory.

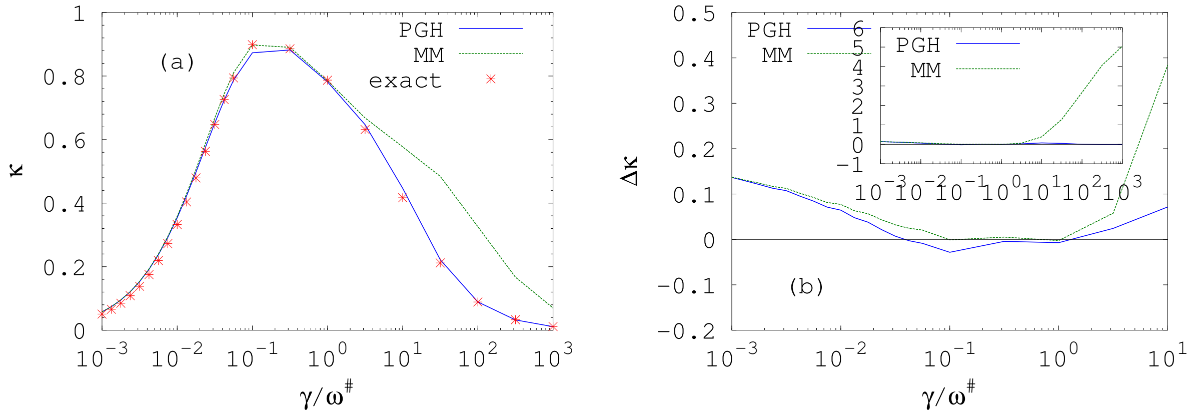

FIG. 1: A comparison of PGH and MM theories (without finite barrier corrections) with numerically exact simulation results for the cubic potential and exponential memory friction. The transmission factors as defined in Eq. 2.10 are plotted in panel (a) of the figure as functions of the reduced friction coefficient. The associated relative errors $\Delta\kappa$ (Eq. 3.33) are plotted in panel (b) in a smaller range of the reduced friction coefficient, while the full range is shown in the inset.

D. Comparison between theory and numerical results

In Figure 1 we compare the (normalized, see Eq. 2.10) escape rates obtained via PGH and MM theory with the numerically exact results in panel (a) and their accuracy $\Delta\kappa_i$ defined as

$$\Delta\kappa_i = \frac{\kappa_i - \kappa_{ex}}{\kappa_{ex}}, \quad i = \mathrm{MM}, \mathrm{PGH} \tag{3.33}$$

in panel (b). One notes that PGH is accurate for the full range of friction values, while MM theory is only qualitative correct in the long memory time limit. The error in PGH theory is less than 15% in the whole range, while the error in the MM result reaches a factor of five. These results imply that even though PGH theory is unwieldy relative to MM theory, it is the theory of choice, especially in the presence of memory friction. One also notes that the magnitude of the friction and the memory need not be very large for the differences between the two theories to emerge.

IV. FINITE BARRIER CORRECTIONS TO THE PGH SOLUTION

A. Finite barrier corrections to the PGH depopulation factor

In Ref. [13] we considered the temperature and energy dependence of the PGH energy loss, noting that as the temperature of the bath is increased, the bath will also transfer energy back to the system. The energy loss was then expanded to leading order as:

$$\delta\left(\beta,\varepsilon\right)=\delta\left(1-\mu+\mu\varepsilon\right) \tag{4.1}$$

and the expansion parameter is given by:

$$\begin{aligned}\mu &\equiv -\frac{1}{u_{00}^2\delta}\int_{-\infty}^{\infty}dt\int_{-\infty}^{\infty}dt''\frac{dF_{PGH}(t)}{dt}\frac{dK\left(t-t''\right)}{dt}\frac{dF_{PGH}(t'')}{dt''}\theta\left(t-t''\right)\int_{t''}^{t}\frac{dt'}{\dot{\rho}_{0,t'}^2}\\ &= -\frac{2}{\pi u_{00}^2\delta}\int_0^{\infty}d\lambda'\mathrm{Im}\left[\mathrm{g}\left(\lambda'\right)\sigma\left(-\lambda'\right)\right]\mathrm{I}(\lambda')\end{aligned} \tag{4.2}$$

where $\theta(x)$ is the unit step function and

$$g\left(\lambda\right) = \int_{-\infty}^{\infty}dt\exp\left(i\lambda t\right)\frac{dF_{PGH}(t)}{dt} \tag{4.3}$$

$$\sigma\left(\lambda\right) = \int_{-\infty}^{\infty}dt\exp\left(i\lambda t\right)Q\left(t\right)\frac{dF_{PGH}(t)}{dt} \tag{4.4}$$

$$Q\left(t\right) = \int^{t}\frac{dt'}{\dot{\rho}_{0,t'}^2}. \tag{4.5}$$

Inclusion of the expansion given in Eq. 4.1 to lowest order leads to a finite barrier correction to the depopulation factor:

$$\kappa_{ED}=\exp\left[-\mu\left(\Phi^2(\delta)\left(1+\frac{\delta+2}{8}\right)-\Phi(\delta)\frac{\delta-2}{4}\right)\right], \tag{4.6}$$

where the subscript ED is used to note that this is the correction to the depopulation factor which accounts for the energy diffusion dominated dynamics. The function $\Phi(\delta)$ is

$$\begin{aligned}\Phi\left(\delta\right) &\equiv \frac{\delta}{2\pi}\int_{-\infty}^{\infty}d\tau\frac{\tilde{P}_0\left(\tau-\frac{i}{2}\right)}{1-\tilde{P}_0\left(\tau-\frac{i}{2}\right)}\\ &= \frac{\delta}{2\pi}\int_{-\infty}^{\infty}d\tau\frac{1}{\exp\left(\delta\left(\tau^2+\frac{1}{4}\right)\right)-1}.\end{aligned} \tag{4.7}$$

and the finite barrier corrected depopulation factor is:

$$\Upsilon=\Upsilon_0\kappa_{ED}, \tag{4.8}$$

B. Application to the cubic potential with exponential memory friction

For the cubic potential, the unperturbed motion of the trajectory initiated at the barrier and returning after infinite time to the barrier, along the unstable mode is given by:

$$\rho_{0,t} = -\frac{\lambda^{\ddagger 2}\sqrt{M} q_0}{u_{00}^3 \omega^{\ddagger 2} \cosh^2(\lambda^\ddagger t/2)}, \tag{4.9}$$

With some straightforward algebra (and use of Maple) one finds:

$$g(\lambda) = -i\frac{4\pi\sqrt{M} q_0}{u_{00}^3 \omega^{\ddagger 2}} \frac{\lambda^2\left(\lambda^{\ddagger 2}+\lambda^2\right)}{\sinh\left(\frac{\pi\lambda}{\lambda^\ddagger}\right)} \tag{4.10}$$

$$Q(t) = \frac{u_{00}^6 \omega^{\ddagger 4}}{4M\lambda^{\ddagger 7} q_0^2}\left[\frac{2\cosh^5\left(\frac{\lambda^\ddagger t}{2}\right)+5\cosh^3\left(\frac{\lambda^\ddagger t}{2}\right)+15\frac{\lambda^\ddagger t}{2}\sinh\left(\frac{\lambda^\ddagger t}{2}\right)-15\cosh\left(\frac{\lambda^\ddagger t}{2}\right)}{\sinh\left(\frac{\lambda^\ddagger t}{2}\right)}\right] \tag{4.11}$$

$$\sigma(\lambda) = -\frac{3\omega^{\ddagger^2} u_{00}^3 \pi}{2q_0\sqrt{M}\lambda^{\ddagger 2}}\delta(\lambda) + \frac{15\pi^2\omega^{\ddagger^2} u_{00}^3}{2q_0\sqrt{M}\lambda^{\ddagger 7}} \frac{\lambda^2\left(\lambda^{\ddagger 2}+\lambda^2\right)\cosh\left(\frac{\pi\lambda}{\lambda^\ddagger}\right)}{\sinh^2\left(\frac{\pi\lambda}{\lambda^\ddagger}\right)} \tag{4.12}$$

where $\delta(\lambda)$ is the Dirac "delta" function. Inserting these results into Eq. 4.2 and using Eq. 3.13 the expression for the expansion parameter μ reduces to the quadrature:

$$\mu = \frac{270\pi\omega^{\ddagger 6}}{u_{00}^2\delta\lambda^{\ddagger 6}}\frac{\gamma}{\omega^\ddagger}\int_0^\infty dx \frac{1}{\sinh^2\left(\frac{\omega^\ddagger}{\lambda^\ddagger}\pi x\right)}\left(\frac{d}{dx}\left[\frac{x^5\left(\frac{\lambda^{\ddagger 2}}{\omega^{\ddagger 2}}+x^2\right)^2}{9\left(1+x^2\right)^2+\frac{\gamma^2}{\omega^{\ddagger 2}}x^2\left(1+4x^2\right)^2}\right]\right). \tag{4.13}$$

One notices that in the strong friction long memory time limit, the expansion parameter will go to a constant, independent of the friction strength. Explicitly, one finds in this limit that:

$$\lim_{\gamma\to\infty}\mu \simeq \frac{80}{3\beta V^\ddagger}. \tag{4.14}$$

In other words, the correction does not vanish in this limit.

In Figure 2 we plot μ as a function of $\gamma/\omega^\ddagger$. One notes that as long as $\gamma/\omega^\ddagger \leq 1$, μ remains small. However it increases as the friction increases beyond this limit, already indicating that the finite barrier correction will become large.

In panel (a) of Figure 3 we compare the results obtained for PGH with and without finite barrier corrections for the depopulation factor, with the numerical results. The relative error (see Eq. 3.33) is plotted in panel (b). For short memory, the finite barrier corrections significantly decrease the PGH error. For long memory, the finite barrier correction is big and the resulting estimate is poor.

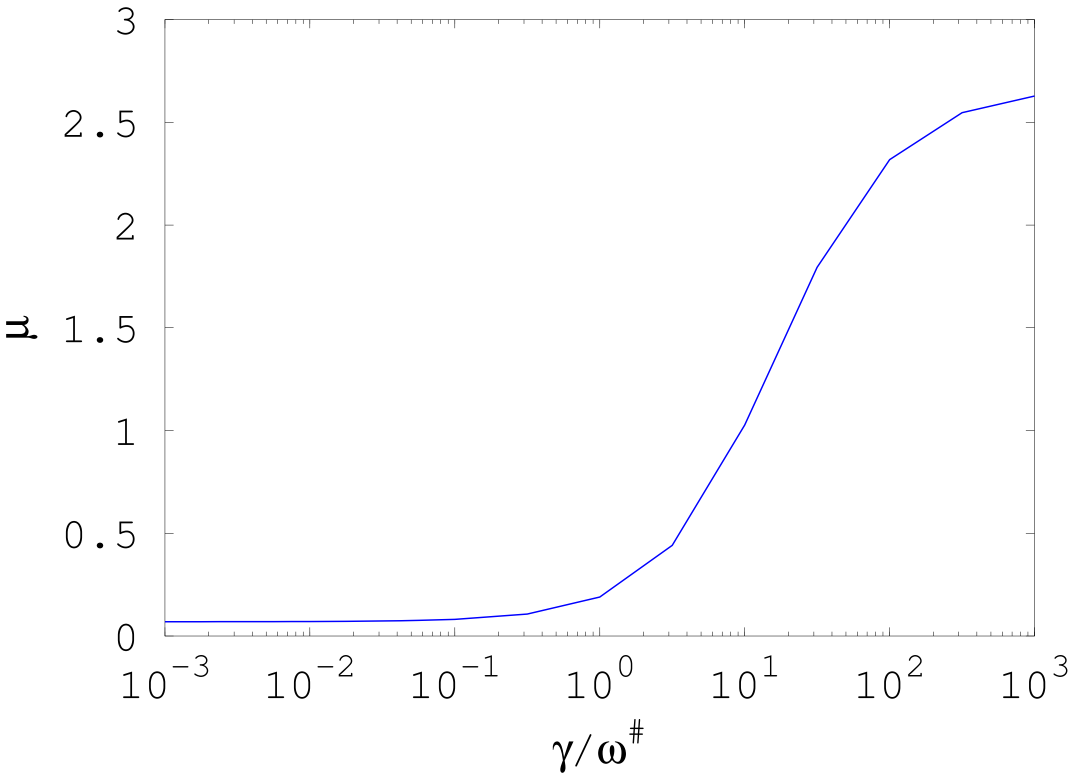

FIG. 2: The dependence of the energy derivative μ on the reduced friction coefficient $\gamma/\omega^{\ddagger}$ for $\beta V^{\ddagger} = 10$ keeping the ratio between the friction and the memory time fixed, as in Eq. 2.6. In the large friction long memory time limit μ approaches the asymptotic value of $\frac{26\frac{2}{3}}{\beta V^{\ddagger}}$, which is $2\frac{2}{3}$ for the parameters used in this paper.

As noted by Farago and Peyrard [20] both PGH and MM theory are predicated on a Markovian assumption with regards to the motion to and from the barrier top. The assumption is that each cycle from the barrier top to the well and back is independent of the previous cycle. However, this assumption would break down if the memory time is longer than the period of one cycle. As we shall show below, this condition breaks down in the strong friction long memory time limit considered in this paper.

To leading order in ε, the cycle time (period) for the unperturbed motion of the unstable mode (Eq. 3.15) is readily found to be [15]:

$$T(\varepsilon) = \frac{1}{\lambda^{\ddagger}} \left[\ln 2 + 3 \ln 6 + \ln \left(\left(\frac{\lambda^{\ddagger}}{\omega^{\ddagger} u_{00}} \right)^{6} \frac{\beta V^{\ddagger}}{-\varepsilon} \right) \right]. \tag{4.15}$$

The typical escape energy is the standard deviation of the energy loss $\sqrt{2\delta}/\beta$. The cycle

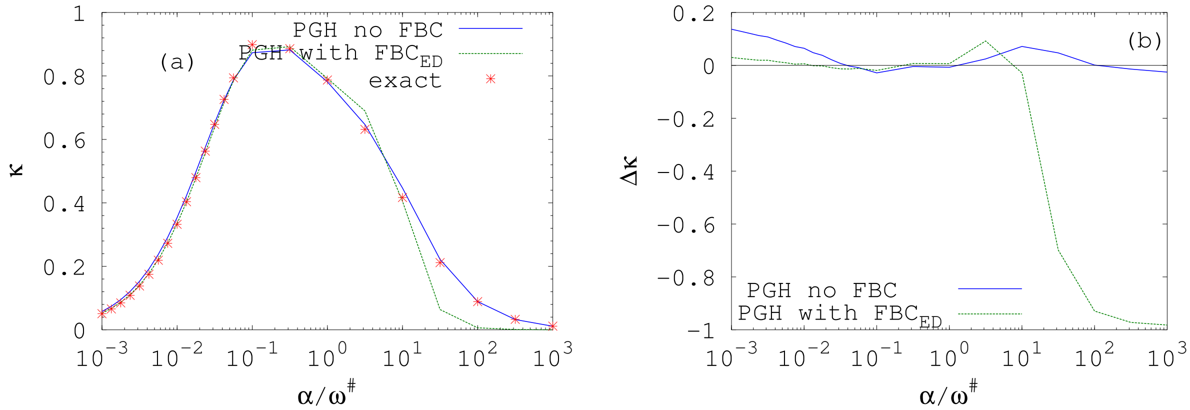

FIG. 3: Comparison of PGH theory with and without energy diffusion finite barrier corrections (FBC_{ED}) with numerically exact simulation results for the cubic potential and exponential memory friction. The transmission factors are plotted in panel (a) of the figure as functions of the reduced friction coefficient. The associated relative errors are plotted in panel (b) of the figure for the same conditions.

time at the reduced energy $\varepsilon = -\sqrt{2\delta}$ is then:

$$T(\varepsilon = -\sqrt{2\delta}) = \frac{1}{\lambda^{\ddagger}}\left[\ln 2 + 3\ln 6 + \ln\left(\left(\frac{\lambda^{\ddagger}}{\omega^{\ddagger}u_{00}}\right)^{6}\frac{\beta V^{\ddagger}}{\sqrt{2\delta}}\right)\right]. \tag{4.16}$$

In Fig. 4 we plot the (reduced) cycle time $\omega^{\ddagger}T(\varepsilon = -\sqrt{2\delta})$ and the reduced memory time ($\omega^{\ddagger}\tau$) as functions of the reduced friction coefficient $\gamma/\omega^{\ddagger}$. As is evident from the Figure, the memory time becomes larger than the cycle time at about $\gamma/\omega^{\ddagger} = 6$. Inspection of Fig. 3 shows that this is the point at which the finite barrier correction starts to increase significantly. In the same parameter region, the expansion parameter μ approaches unity, it is no long a "small" parameter and so the perturbation theory on which the finite barrier corrections to the depopulation factor are predicated is no longer valid.

C. Spatial diffusion finite barrier corrections for the cubic potential

As already noted in the Introduction, finite barrier corrections are also found for the spatial diffusion factor. For a cubic potential, the factor is [14]:

$$\kappa_{SD} = 1 + \frac{1}{36\beta V^{\ddagger}\chi^3}\left[2 - 3\chi - \frac{6\left(\chi+1\right)^3\lambda^{\ddagger 6}}{\pi^2 u_{00}^4}\int_{-\infty}^{\infty}d\lambda\int_{-\infty}^{\infty}d\lambda'\frac{I\left(\lambda\right)I\left(\lambda'\right)}{\lambda\lambda'\left[\lambda^{\ddagger 2} + \left(\lambda+\lambda'\right)^2\right]}\right] \tag{4.17}$$

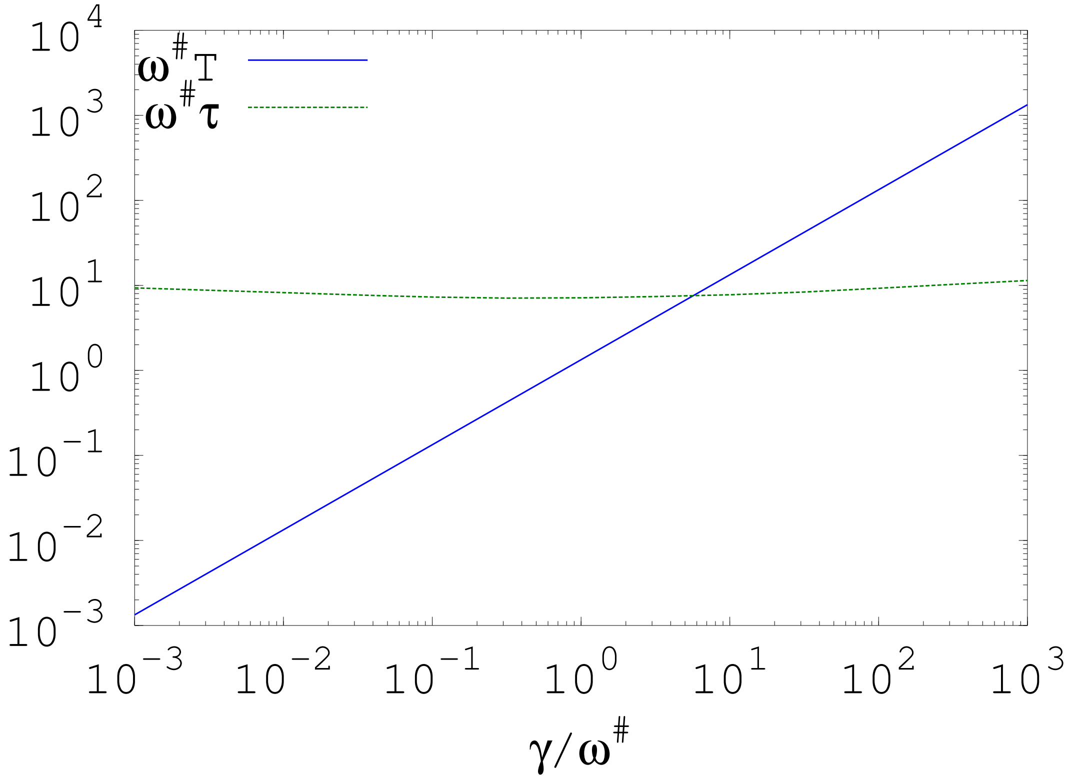

FIG. 4: Comparison of the cycle time for the unstable mode motion with the memory time. The memory time becomes larger than the cycle time at about $\gamma/\omega^{\ddagger} = 6$.

where

$$\frac{1}{\chi} = \frac{u_{00}^2 \omega^{\ddagger^2}}{\lambda^{\ddagger^2}} - 1. \tag{4.18}$$

For the exponential friction function in the strong friction long memory time limit one readily finds that

$$\lambda^{\ddagger^6} \int_{-\infty}^{\infty} d\lambda \int_{-\infty}^{\infty} d\lambda' \frac{I(\lambda)\, I(\lambda')}{\lambda\lambda' \left[\lambda^{\ddagger^2} + (\lambda + \lambda')^2\right]} \to \frac{9}{16}\pi^2 \tag{4.19}$$

so that in this limit the spatial diffusion correction is a constant:

$$\kappa_{SD} \to 1 - \frac{21}{4\beta V^{\ddagger}} \tag{4.20}$$

In Figure 5 we show the finite barrier correction for the spatial diffusion factor and its asymptotic value in the strong friction long memory time limit.

The rate estimate obtained by multiplication of the PGH expression for the transmission factor by the spatial diffusion finite barrier correction is shown and in Figure 6. Panel (a)

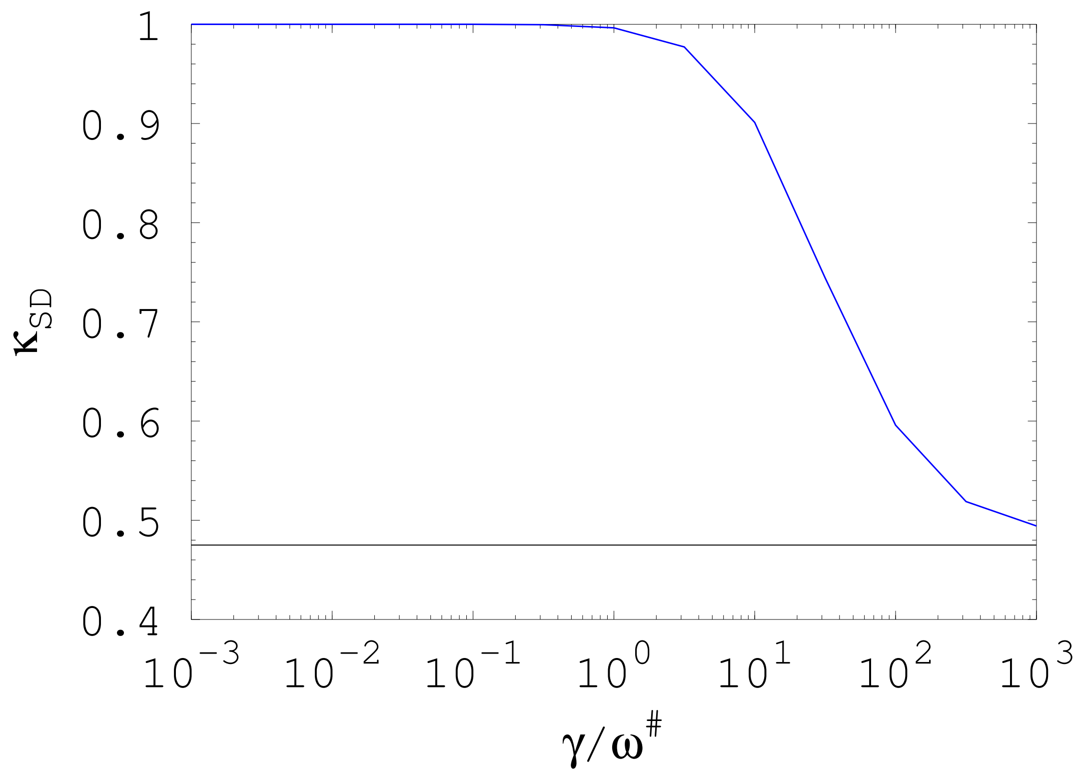

FIG. 5: The finite barrier correction for the spatial diffusion factor and its asymptotic value for in the strong friction long memory time limit.

of the Figure shows the comparison with the numerically exact results, and the associated relative errors are shown in panel (b). Here too, one notes that a reduced friction value greater than 5 or so, the spatial diffusion finite barrier correction deteriorates the PGH estimate significantly, albeit, the disaster is not as large as the error resulting from using the energy diffusion finite barrier correction. In the strong friction long memory time limit one must consider the dynamics for an increasingly longer time. As in any time dependent perturbation theory, the longer the time the higher is the order of the perturbation that must be used. The finite barrier correction of Ref. [16] is predicated on the lowest order correction and so is no longer valid in this limit.

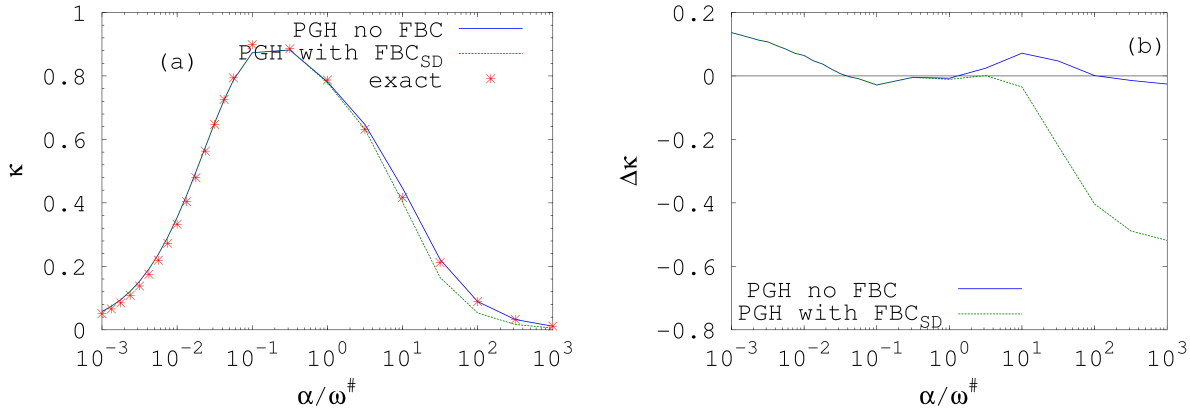

FIG. 6: Comparison of PGH theory with and without spatial diffusion finite barrier corrections (FBC$_{SD}$) with numerically exact simulation results for the cubic potential and exponential memory friction. The transmission factors are plotted in panel (a) of the figure as functions of the reduced friction coefficient. The associated relative errors are plotted in panel (b) of the figure for the same conditions.

VI. DISCUSSION

The results presented in this paper lead to a number of conclusions, puzzles and challenges. In a previous paper [13] we found that for Ohmic friction, MM theory and PGH theory are comparable. Here we found that MM theory fails in the large friction long memory time limit. This further supports our previous conclusion, based on the divergence of the expansion of the MM energy loss with respect to the bath temperature [16], that PGH theory is superior to MM theory. Here, we found that in the presence of exponential memory friction, PGH theory remains quite accurate over the whole range of friction coefficients considered. Thirdly, we found that the finite barrier corrections to the depopulation factor in PGH theory fail in the long memory time large friction limit, probably due to the fact that the memory time becomes longer than the cycle time of the unstable mode as it moves from the barrier to the well and back. Fourthly, we found that also the finite barrier corrections for the spatial diffusion factor fail.

These results present two puzzles. One, why does PGH theory do so well even in the long memory time large friction limit? Secondly, is there a way in which one could in practice correct for the failure of the Markovian assumption that two cycles of the particle are independent of each other. Similarly can one practically include higher order perturbation terms in the spatial diffusion finite barrier correction factor?

A number of additional challenges remain. For exponential memory friction, Reese and Tucker [18] have noted that PGH theory fails in the long memory time limit if the ratio of the damping constant to the memory time becomes unity or larger. The present work kept the ratio at 3/4 and so does not explore their parameter range. What happens to MM theory in this parameter range? Perhaps it is better than PGH theory? Reese et al have also noted [26] that if the frequency spectrum of the bath does not overlap well with the oscillator frequency at the well bottom, then the vibrational energy relaxation at the well bottom can become the rate determining step and here too both PGH and MM theories would fail, predicting a rate which is too large. For a typical potential, the energy range in which the frequency becomes substantially smaller than the harmonic frequency is close to the barrier top. Can one then use the expansion of the energy loss with respect to the energy to correct for this failure? We leave these questions for future work.

Acknowledgements

This work was supported by a grant of the Israel Science Foundation.

APPENDIX A: Ohmic limit of the MM energy loss

In this appendix we show that the MM energy loss in the presence of memory friction as given in Eq. (3.27) reduces to the correct Ohmic friction limit (Eq. 3.26) when the memory time is short. This is attained by using the asymptotic Stirling expansion [28] for the $\Gamma(z)$ function, for large z

$$\ln(\Gamma(z)) \sim \left(z - \tfrac{1}{2}\right)\ln(z) - z + \tfrac{1}{2}\ln(2\pi) + \sum_{n=1}^{\infty} \frac{B_{2n}}{2n(2n-1)z^{2n-1}}, \tag{A.1}$$

where B_j are the Bernoulli numbers. One must then include the first three terms in the expansion for large z

$$\Psi_1(z) \sim \frac{1}{z} + \frac{1}{2z^2} + \frac{B_2}{z^3} + \frac{B_4}{z^5}. \tag{A.2}$$

Setting $z = 1/(\omega^{\ddagger}\tau)$, we get for small $\omega^{\ddagger}\tau$

$$\delta_{MM} \simeq 36\frac{\gamma}{\omega^{\ddagger}}\frac{\beta V^{\ddagger}}{\omega^{\ddagger 2}\tau^2}\left[1 + \frac{6}{\omega^{\ddagger}\tau}\left(\frac{1}{\omega^{\ddagger}\tau} + \frac{1}{2} - \frac{1}{\tau^2\omega^{\ddagger 2}}(\omega^{\ddagger}\tau + \frac{1}{2}(\omega^{\ddagger}\tau)^2 + \right.\right. \tag{A.3}$$

$$\left.\left. B_2(\omega^{\ddagger}\tau)^3 + B_4(\omega^{\ddagger}\tau)^5)\right)\right] \quad . \tag{A.4}$$

Using $B_2 = 1/6$ and $B_4 = -1/30$, one regains the Ohmic result.

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