Finite Barrier Corrections to the PGH solution of Kramers' turnover theory

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Abstract

In his seminal paper of 1940 (Physica **7**, 284 (1940)), Kramers derived expressions for the rate of crossing a barrier in the underdamped limit of weak friction and the moderate to strong friction limit where the rate limiting step is the spatial diffusion of the particle across the barrier. The challenge of obtaining a uniform expression for the rate, valid for all damping strengths is known as Kramers' turnover theory. Two different solutions have been presented. Mel'nikov and Meshkov (J. Chem. Phys. **85**, 1018 (1986)) (MM) considered the motion of the particle, treating the friction as a perturbation parameter. Pollak, Grabert and Hanggi (J. Chem. Phys. **91**, 4073 (1989)) (PGH), considered the motion along the unstable mode which is separable from the bath in the barrier region. The two theories differ in the way an energy loss parameter is estimated. In this paper, we show that previous numerical attempts to resolve the quality of the two approaches were incomplete and that at least for a cubic potential with Ohmic friction, the agreement of both expressions with numerical simulation is quite similar over a large range of friction strengths and temperatures. In a later paper (Phys. Rev. E, **48**, 3271 (1993)), Melnikov improved his theory by introducing finite barrier corrections which took into account the energy dependence of the energy loss of the particle. We note that previous tests of these finite barrier corrections were also incomplete as they did not employ the exact rate expression, but a harmonic approximation to it. The central part of this present paper, is to include finite barrier corrections also within the PGH formalism. Tests on a cubic potential demonstrate that finite barrier corrections significantly improve the agreement of both MM and PGH theories when compared with numerical simulations.

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I. INTRODUCTION

The theory for the rate of escape of a particle trapped in a potential well whose motion is subject to a Gaussian random force and associated frictional force has intrigued the Physics and Chemistry communities for well over a century. It is arguably the simplest model for an activated barrier crossing in the presence of a thermal liquid (with temperature T), in which the source of the random force is the motion of the surrounding liquid molecules. In 1940, Kramers [1] defined and solved this problem in two limits. Assuming that the barrier height ($V^{\ddagger}$) is much larger than the thermal energy (k_BT) he showed that in the underdamped limit, when the friction is weak, the rate increases linearly with increasing friction. When the friction is strong, the rate decreases inversely with the friction strength and it reaches a maximum in between. Kramers did not manage to derive an expression for the rate which is valid for the whole range of friction. This challenge became known as the Kramers turnover problem.

In 1986, Mel'nikov and Meshkov (MM) [2, 3] introduced into the problem the concept of a conditional probability for the particle initiated at the barrier with energy E to return to it with energy E'. Using perturbation theory with the friction strength as the small parameter they used a Gaussian expression for the kernel:

$$P_0\left(E'|E\right) = \frac{1}{\sqrt{4\pi k_BT\Delta E}} \exp\left(-\frac{\left(E'-E+\Delta E\right)^2}{4k_BT\delta E}\right) \tag{1.1}$$

where ΔE denotes the average energy lost by the particle to the bath as it traverses from the barrier to the well and back. This kernel has the important property that it obeys detailed balance. They then wrote down a master equation for the energy flow and upon solving it in steady state, derived an expression for a so called depopulation factor which went smoothly from the weak damping limit where it was linear in the friction strength to unity for strong damping. The full rate expression was then written as a product of three terms, the "standard" transition state theory expression for the rate, the depopulation factor, and Kramers' spatial diffusion factor which went from unity at weak damping to being inversely proportional to the damping when the friction was strong. A further justification for the MM theory may be found in Ref. [4].

Mel'nikov and Meshkov's rate expression was then tested against numerical simulation [5, 6]. The test showed that the MM expression for the rate, provided that the barrier height was 5 times or more greater then the thermal energy, was accurate within $\sim 20\%$ or less over the whole range of damping. Mel'nikov went further, and improved his expression by incorporating a leading order finite barrier correction term [7]. A numerical test of his improved expression showed that the leading order term reduced the error in the analytic expression by an additional factor ~ 4 [6]. Mel'nikov's finite barrier correction was derived for the depopulation factor, by noting that the average energy loss ΔE depends in principle on the initial energy of the particle. For the moderate to strong friction limit, he rederived the finite barrier correction to the rate obtained previously by Pollak and Talkner [23] by taking into account dynamical recrossings of the transition state.

Kramers' paper assumed that the friction was "Ohmic" with white noise. In reality, in a liquid, due to the fact that the molecular time scales of a liquid are of the same order of time scales as motion of the reacting species, one expects that the frictional force would be characterized by at least one memory time. This necessitated the introduction of memory friction to the model of activated barrier crossing. Grote and Hynes proceeded to solve the Kramers rate problem in the presence of memory friction, in the spatial diffusion limited regime [8], that is in the regime of moderate to strong friction. Carmeli and Nitzan [9] did the same for the underdamped regime.

The turnover problem in the presence of memory friction was then solved in a few steps. Pollak [10] realised in 1986 that Kramers' problem in the spatial diffusion limit may be derived using variational transition state theory. His derivation was based on the known equivalence of the generalized Langevin equation dynamics to the dynamics derived from a Hamiltonian description in which the system is bilinearly coupled to a harmonic bath. Around the barrier top, the Hamiltonian is a quadratic form and so can be diagonalized. The normal modes are composed of an unstable collective mode and stable bath modes. Grabert [11], using the discretized oscillator model derived a generalization of Mel'nikov and Meshkov's turnover theory by considering the dynamics of the unstable normal mode, instead of the system coordinate. The continuum limit version of this theory was then presented in Ref. [12] and is known as PGH theory. It is also based on a Gaussian energy transfer kernel as in Eq. 1.1 except that now the energy stands for the energy in the unstable mode and the energy loss is the energy lost by the unstable mode as it goes through one traversal from the barrier to the well region and back.

The MM and PGH expressions for the rate are very similar, the only difference being in the average energy loss. In MM theory it is the energy lost by the original system motion to the physical bath, while in PGH theory it is the energy lost by the collective unstable mode motion to the bath of stable normal modes. For Ohmic friction, in the underdamped limit, both energy losses are identical and both theories give the same answer as obtained by Kramers in 1940. In the strong friction limit the two theories give slightly different results. The system energy loss diverges as the friction is increased indefinitely and the MM depopulation factor goes to unity. In PGH theory, the unstable mode energy loss tends to a large constant so that the depopulation factor in this limit is slightly less than unity.

Numerical tests were undertaken to determine numerically, which theory is more accurate. Simulations on a cubic potential seemingly showed that especially in the intermediate region with moderate friction, PGH theory is more accurate. A first goal of the present study is to undertake highly accurate numerical simulations and compare the numerically exact results with those predicted by the MM and PGH theories. We will show that both previous simulations, that is the test using a cubic potential given in Ref. [5] as well as the tests of MM theory without and with finite barrier corrections [6] were incomplete. In both cases, the authors used for the theoretical estimate the harmonic expression for the partition function of the reactants. In reality, one should use the exact partition function of the reactants and for a finite barrier height this makes a difference. This analysis then invalidates the conclusion of Ref. [5] that PGH theory is more accurate than MM theory in the turnover region. The finite barrier expansion of Mel'nikov is even more accurate than presented in Ref. [6].

Both in MM theory as well as in PGH theory, the average energy lost to the bath was assumed to be temperature independent. This is not so. As shown by Pollak and Ankerhold [13] the average energy loss appearing in PGH theory is temperature dependent and as might be expected it decreases as the temperature increases. Increasing the bath temperature gives some energy back to the unstable mode. This then leads to a finite barrier correction to the PGH rate expression. The reduced energy loss leads to a reduction of the depopulation factor.

When considering the same for the MM formalism, one finds that for Ohmic friction the average energy deposited by the bath at finite temperature diverges. In the PGH formalism, one considers the motion of the unstable mode and when the motion is slow in the vicinity of the barrier the unstable mode is decoupled from the bath so that the bath cannot feed it any energy. This is not the case when considering the motion in the system coordinate which is coupled to the bath even in the vicinity of the barrier. This then leads to the nonphysical divergence. Mel'nikov, in his theoretical derivation of finite barrier corrections did not explicitly consider the temperature dependence of the energy loss.

When comparing the PGH and MM theories with finite barrier corrections, one notes that Mel'nikov considered the effect of the energy dependence of the energy loss, while thus far this was not carried out for the PGH theory approach. This is the main objective of this paper. In Section II we derive the full finite barrier correction expression for PGH theory which includes the dependence of the energy loss on both the temperature of the bath and the energy of the unstable mode. Then, in Section III we compare the resulting PGH and MM expressions, including finite barrier corrections with numerical simulations. We end with a discussion, noting that following the semiclassical version of PGH theory as presented in Ref. [16] it should be straightforward to also derive finite barrier corrections to the semiclassical extension of PGH theory.

II. FINITE BARRIER CORRECTIONS TO PGH THEORY

A. Preliminaries

The classical dynamics of the generic system is that of a particle with mass M and coordinate q whose classical equation of motion is a Generalized Langevin Equation (GLE) of the form:

$$M\ddot{q} + \frac{dV(q)}{dq} + M\int_0^t dt'\gamma(t-t')\dot{q}(t') = F(t). \tag{2.1}$$

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

$$\langle F(t) F(t')\rangle = M k_B T \gamma(t-t'). \tag{2.2}$$

$\gamma(t)$ is the friction function, k_B is Boltzmann's constant and T is the temperature. The potential is assumed to have a well at q_a with frequency ω_a and a barrier at $q = 0$ which separates the well from a continuum. The harmonic (imaginary) frequency at the barrier top is denoted as $\omega^{\ddagger}$. The potential is then written as

$$V(q) = -\frac{1}{2}M\omega^{\ddagger 2}q^2 + V_1(q) \tag{2.3}$$

and $V_1(q)$ is termed the nonlinear part of the potential function.

When one ignores the nonlinear part of the potential the resulting Hamiltonian has a quadratic form and may be diagonalized [15]. We denote the (unstable) mass weighted normal mode and momentum as ρ and p_ρ respectively and the stable bath normal mode coordinates and momenta as y_j and p_{y_j} respectively. The full Hamiltonian may then be expressed as:

$$H = \frac{p_\rho^2}{2} - \frac{1}{2}\lambda^{\ddagger 2}\rho^2 + V_1(q) + \frac{1}{2}\sum_{j=1}^{N}\left[p_{y_j}^2 + \lambda_j^2 y_j^2\right] \tag{2.4}$$

where λ_j denotes the frequency of the j-th normal mode. $\lambda^\ddagger$ denotes the unstable normal mode barrier frequency and it is obtained from the Kramers-Grote-Hynes relation [1, 8]:

$$\lambda^{\ddagger 2} + \hat{\gamma}\left(\lambda^\ddagger\right)\lambda^\ddagger = \omega^{\ddagger 2} \tag{2.5}$$

where $\hat{\gamma}(s)$ stands for the Laplace transform of the time dependent friction. The system coordinate q is expressed in terms of the normal modes as

$$\sqrt{M}q = u_{00}\rho + \sum_{j=1}^{N} u_{j0} y_j \tag{2.6}$$

so that the nonlinear part of the potential $V_1(q)$ couples the motion of the unstable normal mode to that of the stable normal modes. The matrix element u_{j0} is the projection of the system coordinate on the j-th normal mode. The projection of the system coordinate on the unstable mode u_{00} is given by the relation [12]:

$$u_{00}^2 = \left[1 + \frac{1}{2}\left(\frac{\hat{\gamma}\left(\lambda^\ddagger\right)}{\lambda^\ddagger} + \frac{\partial\hat{\gamma}(s)}{\partial s}|_{s=\lambda^\ddagger}\right)\right]^{-1}. \tag{2.7}$$

Finally, the assumption of weak coupling between the system and the bath is expressed as [12]:

$$u_1^2 = 1 - u_{00}^2 \ll 1. \tag{2.8}$$

B. The depopulation factor

The depopulation factor is determined by the conditional probability $P_0(E'|E)$ that the system originates at the barrier with energy E and returns to it with energy E'. We will simplify the ensuing expressions by using dimensionless energy variables (with $\beta = 1/(k_B T)$)

$$\varepsilon = \beta E. \tag{2.9}$$

In PGH theory as well as in MM theory, the normalized conditional probability is the Gaussian given in Eq. 1.1 which is written in reduced variables as:

$$P_0\left(\varepsilon'|\varepsilon\right) = \frac{1}{\sqrt{4\pi\delta}}\exp\left(-\frac{\left(\varepsilon' - \varepsilon + \delta\right)^2}{4\delta}\right). \tag{2.10}$$

The subscript 0 anticipates the development below in which we allow for energy and temperature dependence of the energy loss. In PGH theory, the temperature independent (reduced) energy loss is given by the expression:

$$\delta_{PGH} \equiv \frac{\beta}{2M}\int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' V_1'\left(\frac{u_{00}\rho_{0,t}}{\sqrt{M}}\right)\frac{\partial^2 K\left(t-t'\right)}{\partial t \partial t'}V_1'\left(\frac{u_{00}\rho_{0,t'}}{\sqrt{M}}\right). \tag{2.11}$$

where $\rho_{0,t}$ is the time dependent solution for the trajectory obeying the unperturbed equation of motion

$$\ddot{\rho}_{0,t} - \lambda^{\ddagger 2}\rho_{0,t} = -\frac{u_{00}}{\sqrt{M}}V_1'\left(\frac{u_{00}\rho_{0,t}}{\sqrt{M}}\right) \tag{2.12}$$

initiated at the barrier energy $\varepsilon = 0$ and asymptotically close to the top of the barrier so that it traverses once over the well and comes back to the barrier. The period of this motion diverges. In MM theory, the reduced energy loss is given by the expression

$$\delta_{MM} = M\int_{-\infty}^{\infty} dt \int_{-\infty}^{t} dt' \dot{q}_{0,t}\gamma\left(t-t'\right)\dot{q}_{0,t'} \tag{2.13}$$

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

$$M\ddot{q}_{0,t} = -\frac{dV\left(q_{0,t}\right)}{dq_{0,t}} \tag{2.14}$$

The normal mode "friction kernel" is defined as:

$$K\left(t-t'\right) = \sum_{j=1}^{N}\frac{u_{j0}^2}{\lambda_j^2}\cos\left[\lambda_j\left(t-t'\right)\right]. \tag{2.15}$$

Using properties of the normal mode transformation (see for example Eq. 2.17 of Ref. [15]) one may readily express the Laplace transform (denoted by a "hat") of the kernel as

$$\hat{K}\left(s\right) = \left(\frac{su_{00}^2}{\lambda^{\ddagger 2}\left(s^2 - \lambda^{\ddagger 2}\right)} + \frac{s + \hat{\gamma}\left(s\right)}{\omega^{\ddagger 2}\left(\omega^{\ddagger 2} - s^2 - \hat{\gamma}\left(s\right)s\right)}\right) \tag{2.16}$$

so that it is known in the continuum limit.

The depopulation factor is obtained by solution of the steady state expression for the flux of particles $f\left(\varepsilon\right)$ hitting the barrier, when considered in the energy of the unstable normal mode. It is simpler to consider a quantum mechanical like version of the steady state expression by allowing particles to be transmitted through the barrier and reflected when above the barrier. We thus define

$$R\left(\varepsilon\right)=\frac{1}{1+\exp\left(\alpha\varepsilon\right)},\quad T\left(\varepsilon\right)=1-R\left(\varepsilon\right) \tag{2.17}$$

with

$$\alpha=\frac{2\pi}{\hbar\beta\lambda^{\ddagger}}. \tag{2.18}$$

The classical limit is then obtained by allowing $\alpha\rightarrow\infty$.

The steady state equation for the flux of particle hitting the barrier per unit time is:

$$f\left(\varepsilon'\right)=\int_{-\infty}^{\infty}d\varepsilon P\left(\varepsilon'|\varepsilon\right)R\left(\varepsilon\right)f\left(\varepsilon\right). \tag{2.19}$$

The boundary condition for the flux is that at substantial energy below the top of the barrier it is thermally distributed:

$$f\left(\varepsilon\right)_{\varepsilon\rightarrow-\infty}\rightarrow C\exp\left(-\varepsilon\right). \tag{2.20}$$

with

$$C=\frac{1}{\left(2\pi M\beta\right)^{1/2}\int_{-\infty}^{\infty}dq\exp\left(-\beta V\left(q\right)\right)\theta\left(-q\right)}\frac{\lambda^{\ddagger}}{\omega^{\ddagger}} \tag{2.21}$$

The rate is then given as the flux transmitted through the barrier that is:

$$\Gamma=\int_{-\infty}^{\infty}d\varepsilon T\left(\varepsilon\right)f\left(\varepsilon\right)\equiv\frac{\lambda^{\ddagger}}{\omega^{\ddagger}}\Upsilon\frac{\exp\left(-\beta V^{\ddagger}\right)}{\left(2\pi M\beta\right)^{1/2}\int_{-\infty}^{\infty}dq\exp\left(-\beta V\left(q\right)\right)\theta\left(-q\right)} \tag{2.22}$$

and this defines the dimensionless depopulation factor Υ. The heart of the theory is then to find a solution for the steady state flux $f\left(\varepsilon\right)$.

As shown in detail in the Appendix of Ref. [16] the steady state equation may be solved by Fourier transform. The Fourier transform of a function $g\left(\varepsilon\right)$ is defined such that

$$\tilde{g}\left(\tau-\frac{i}{2}\right)=\int_{-\infty}^{\infty}d\varepsilon\exp\left(i\left(\tau-\frac{i}{2}\right)\varepsilon\right)g\left(\varepsilon\right). \tag{2.23}$$

For example, for the zero-th order conditional probability given in Eq. 2.10 one finds that:

$$\tilde{P}_0\left(\tau-\frac{i}{2}\right)=\exp\left(-\delta\left[\frac{1}{4}+\tau^2\right]\right). \tag{2.24}$$

The solution of the steady state equation in the classical limit that $\alpha\rightarrow\infty$ is then found to be:

$$\Upsilon_0=\exp\left(\frac{1}{2\pi}\int_{-\infty}^{\infty}d\tau\frac{\ln\left[1-\tilde{P}_0\left(\tau-\frac{i}{2}\right)\right]}{\tau^2+\frac{1}{4}}\right). \tag{2.25}$$

At this point the only practical difference between the PGH and Melnikov theories is in the evaluation of the energy loss.

C. Finite barrier corrections

1. *Correction due to the finite temperature of the bath*

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

$$\delta_{PGH}(\beta) = \delta_{PGH}(1-\mu_\beta) \tag{2.26}$$

where the minus sign was used to assure that the expansion parameter μ_β is positive. The temperature dependent correction was found to be:

$$\mu_\beta \equiv -\frac{1}{\delta_{PGH} M}\int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt'' \frac{d}{dt}\left[V_1'\left(\frac{u_{00}\rho_{0,t}}{\sqrt{M}}\right)\right] \frac{dK(t-t'')}{dt}\frac{d}{dt}\left[V_1'\left(\frac{u_{00}\rho_{0,t''}}{\sqrt{M}}\right)\right]\int_{t''}^{t} dt' \frac{\theta(t-t'')}{\dot{\rho}_{0,t'}^2} \tag{2.27}$$

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

To take the effect of bath temperature into consideration one modifies the conditional transition probability. However, it must also obey the detailed balance property that is that

$$P(\varepsilon|\varepsilon')\exp(-\varepsilon') = P(\varepsilon'|\varepsilon)\exp(-\varepsilon) \tag{2.28}$$

implying that the correction terms must be symmetric with respect to interchange of ε and ε'. To lowest order, the probability kernel corrected for the effect of temperature was shown to be [13]:

$$P_\beta(\varepsilon'|\varepsilon) \simeq P_0(\varepsilon'|\varepsilon)\left(1+\frac{\mu_\beta}{4}\left[2+\delta_{PGH}-\frac{(\varepsilon'-\varepsilon)^2}{\delta_{PGH}}\right]\right). \tag{2.29}$$

One readily verifies that this distribution is normalised and that the average energy lost is given as in Eq. 2.26.

The depopulation factor resulting from the temperature dependence of the energy loss was then shown to take the form:

$$\begin{aligned}\Upsilon_\beta &= \exp\left(\frac{1}{2\pi}\int_{-\infty}^{\infty} d\tau \frac{\ln\left[1-\tilde{P}_\beta\left(\tau-\frac{i}{2}\right)\right]}{\tau^2+\frac{1}{4}}\right)\\ &\simeq \Upsilon_0 \exp\left(-\mu_\beta\left[1-\mathrm{erf}\left(\frac{\sqrt{\delta_{\mathrm{PGH}}}}{2}\right)\right]\right)\end{aligned} \tag{2.30}$$

where the similarity on the second line is obtained in the limit that $\tilde{P}_{\beta}\left(\tau-\frac{i}{2}\right)\ll 1$ and we note that in Eq. 4.18 of Ref. [13] the factor of two in the exponent of the second expression on the right hand side is incorrect. The thermal energy of the bath reduces the energy loss so that the depopulation factor is diminished, the energy diffusion rate which would lead to reaction is decreased.

2. *Correction due to the energy dependence of the energy loss*

Mel'nikov derived finite barrier corrections to the rate by introducing an energy dependence to the energy loss. Here, we show how the same may be estimated within the framework of PGH theory. The energy dependent energy loss is found by considering the zero-th order motion for the unstable mode, when initiated at time $t=0$ at the inner turning point of motion on the effective potential $-\frac{1}{2}\lambda^{\ddagger 2}\rho^2+V_1\left(u_{00}\rho\right)$ at energy ε/β and integrated to the time $t\left(\varepsilon\right)$ at which it either arrives at the outer turning point close to the barrier top ($\varepsilon/\beta<0$) or the barrier top ($\rho=0$) for energies above the barrier top ($\varepsilon/\beta\geq 0$). The energy dependent energy loss is then

$$\delta_{PGH}\left(\varepsilon\right)\equiv\frac{\beta}{2M}\int_{-t(\varepsilon)/2}^{t(\varepsilon)/2}dt\int_{-t(\varepsilon)/2}^{t(\varepsilon)/2}dt'V_1'\left(\frac{u_{00}\rho_{0,t}}{\sqrt{M}}\right)\frac{\partial^2K\left(t-t'\right)}{\partial t\partial t'}V_1'\left(\frac{u_{00}\rho_{0,t'}}{\sqrt{M}}\right) \tag{2.31}$$

Following Mel'nikov, we expand the energy loss about its value at the barrier energy, using the notation

$$\delta_{PGH}\left(\varepsilon\right)\simeq\delta_{PGH}\left(1+\mu_{\varepsilon}\varepsilon\right). \tag{2.32}$$

As shown in Appendix A, one finds that the expansion coefficients for the effect of temperature and energy are identical:

$$\mu\equiv\mu_{\beta}=\mu_{\varepsilon}. \tag{2.33}$$

The coefficient μ_{ε} is then positive, this is not surprising since typically the energy loss is an increasing function of the energy.

There is a qualitative difference between the energy dependence of the energy loss when considering the unstable mode and the system coordinate. Melnikov, who considers the system coordinate finds that the energy derivative of the energy loss diverges at the barrier energy, due to the infinite time it takes the unperturbed trajectory to return to the barrier.

In PGH theory, the energy loss of the unstable mode comes as a result of the nonlinearity of the potential which vanishes in the barrier region. As a result the energy derivative of the energy loss does not diverge, and the theory simplifies considerably.

As in the case of the correction due to the thermal motion of the bath, the conditional probability kernel has to conform to the principle of detailed balance, yet at the same time lead to an energy dependent energy loss. Guided especially by Eq. 81 in Mel'nikov's derivation [7] we expand the kernel as:

$$P_\varepsilon\left(\varepsilon'|\varepsilon\right) = P_0\left(\varepsilon'|\varepsilon\right)\left[a_0 + a_1\frac{\left(\varepsilon+\varepsilon'\right)}{2} + a_2\frac{\left(\varepsilon+\varepsilon'\right)}{2}\left(\varepsilon-\varepsilon'\right)^2 + a_3\frac{\left(\varepsilon+\varepsilon'\right)}{2}\left(\varepsilon-\varepsilon'\right)^4\right]. \tag{2.34}$$

The four coefficients are determined from the normalization condition

$$\int_{-\infty}^{\infty} d\varepsilon' P_\varepsilon\left(\varepsilon'|\varepsilon\right) = 1 \tag{2.35}$$

and the known average energy loss

$$\delta_{PGH}\left(1+\mu_\varepsilon\varepsilon\right) = \int_{-\infty}^{\infty} d\varepsilon' P_\varepsilon\left(\varepsilon'|\varepsilon\right)\left(\varepsilon-\varepsilon'\right). \tag{2.36}$$

With some algebra one finds that (for the sake of brevity we suppress from here on the PGH subscript for the energy loss δ)

$$\frac{P_\varepsilon\left(\varepsilon'|\varepsilon\right)}{P_0\left(\varepsilon'|\varepsilon\right)} = 1+\frac{\mu\delta}{2}\left\{1-\frac{\left(\varepsilon+\varepsilon'\right)}{32\delta^3}\left[\left(12+12\delta+\delta^2\right)\left[\delta\left(2+\delta\right)-2\left(\varepsilon-\varepsilon'\right)^2\right]-\frac{\left(2+\delta\right)\left(\varepsilon-\varepsilon'\right)^4}{\delta}\right]\right\}. \tag{2.37}$$

The Fourier transform of this kernel is readily found to be

$$\begin{aligned}\frac{\tilde{P}_\varepsilon\left(is\right)}{\tilde{P}_0\left(is\right)} &= 1+\mu\delta s^2\left[\left(3+2s\right)+\frac{\delta\left(\delta+2\right)\left(2s+1\right)\left(s+1\right)^2}{4}\right]\\ &\quad -\mu\delta\varepsilon s\left(s+1\right)\left[\frac{s\delta}{2}\left(s+1\right)+s^2+s-1\right].\end{aligned} \tag{2.38}$$

As shown in Appendix B this then leads to the depopulation factor

$$\Upsilon_\varepsilon = \Upsilon_0\exp\left(-\mu\Phi^2\left(\delta\right)\left[1+\frac{\delta+2}{8}\right]+\frac{\mu\left(\delta+2\right)}{4}\Phi\left(\delta\right)\right) \tag{2.39}$$

where

$$\Phi\left(\delta\right) = \frac{\delta}{2\pi}\int_{-\infty}^{\infty} d\tau\frac{1}{\exp\left(\delta\left(\tau^2+\frac{1}{4}\right)\right)-1}. \tag{2.40}$$

As shown by Mel'nikov the small and large energy loss limits of the function $\Phi(\delta)$ are

$$\Phi(\delta) \simeq 1 - 0.407\sqrt{\delta}, \quad \delta \ll 1 \tag{2.41}$$

$$\Phi(\delta) \simeq \frac{1}{2}\sqrt{\frac{\delta}{\pi}} \exp\left(-\frac{\delta}{4}\right), \quad \delta \gg 1. \tag{2.42}$$

This implies that

$$\Upsilon_\varepsilon \simeq \Upsilon_0 \exp\left(-\frac{3\mu}{4}\right), \quad \delta \ll 1 \tag{2.43}$$

$$\Upsilon_\varepsilon \simeq \Upsilon_0 \left[1 + \frac{\mu\delta^{3/2}}{8\sqrt{\pi}} \exp\left(-\frac{\delta}{4}\right)\right] \quad \delta \gg 1. \tag{2.44}$$

In PGH theory, the energy dependence of the energy loss lowers the rate in the weak damping region but increases it (albeit by an exponentially small amount) in the strong damping region.

3. *Finite barrier corrections to the PGH turnover theory*

As may be inferred from Appendix B, the two processes, that is the effects of temperature of the bath and energy dependence of the energy loss are to first order in the perturbation theory additive. The energy kernel is given to first order as

$$\begin{aligned}\frac{P(\varepsilon'|\varepsilon)}{P_0(\varepsilon'|\varepsilon)} &= 1 + \frac{\mu}{4}\left[2 + \delta - \frac{(\varepsilon' - \varepsilon)^2}{\delta}\right] \\ &+ \frac{\mu\delta}{2}\left\{1 - \frac{(\varepsilon + \varepsilon')}{32\delta^3}\left[\left(12 + 12\delta + \delta^2\right)\left[\delta(2+\delta) - 2(\varepsilon - \varepsilon')^2\right] - \frac{(2+\delta)(\varepsilon - \varepsilon')^4}{\delta}\right]\right\}\end{aligned} \tag{2.45}$$

and one may readily ascertain that it is normalized and that the average energy loss is

$$\langle \Delta\varepsilon \rangle = \delta(1 - \mu + \mu\varepsilon). \tag{2.46}$$

Following the derivation in Appendix B one then finds that to first order in the parameter μ the depopulation factor is given by the product of the two separate depopulation factors:

$$\Upsilon = \frac{\Upsilon_\beta \Upsilon_\varepsilon}{\Upsilon_0}. \tag{2.47}$$

This is the central result of this paper. In the next Section we will compare this result with numerical simulations on a cubic oscillator potential.

It is of interest to consider the limits of this expression for small energy loss. In this limit, noting that the expansion parameter

$$\mu \simeq \frac{\alpha}{\beta V^{\ddagger}} + \mathrm{O}\left(\delta\right) \tag{2.48}$$

where α is a constant of order unity ($\alpha = 25/36$ for a cubic potential) one readily finds that to leading order

$$\Upsilon_{PGH} \simeq \delta\left[1 - \frac{7}{4}\frac{\alpha}{\beta V^{\ddagger}}\right], \quad \delta \ll 1. \tag{2.49}$$

This should be compared with the result obtained by Mel'nikov [7]

$$\Upsilon_M \simeq \delta\left[1 - \frac{1}{\beta\omega^{\ddagger}S}\left(\ln 2\beta V^{\ddagger} + C_U + 2 - C\right)\right], \quad \delta \ll 1 \tag{2.50}$$

where $\beta\omega^{\ddagger}S$ depends on the form of the potential and is of the order of $5\beta V^{\ddagger}$ (for the cubic potential it is $36\beta V^{\ddagger}/5$), $C \simeq 0.5772$ is the Euler number and C_U is also a constant which depends on the potential ($C_U = 3\ln 6$ for the cubic potential). This underdamped limit for the cubic potential is considered further in the next Section.

In the overdamped limit one finds that

$$\ln \Upsilon_0 \simeq -\frac{2}{\sqrt{\pi\delta}}\exp\left(-\frac{\delta}{4}\right), \quad \delta \gg 1.$$

For the PGH depopulation factor with finite barrier corrections one then has that

$$\ln\frac{\Upsilon_{PGH}}{\Upsilon_0} \simeq \frac{\mu}{2\sqrt{\pi\delta}}\exp\left(-\frac{\delta}{4}\right)\left[\frac{\delta^2}{4} - 1\right], \quad \delta \gg 1.$$

In the limit of large friction, the PGH energy loss does not diverge as does the MM energy loss. The finite barrier corrections then imply that in this large friction limit, the depopulation factor is numerically larger than unity by an exponentially small amount. In principle, the depopulation factor cannot be larger than unity. In this large friction limit the PGH expression with finite barrier corrections gives a nonphysical result. Of course, one should remember that in this limit the perturbation theory is no longer valid, so this does not imply an essential failure of the theory.

III. NUMERICAL TESTS

A. Previous tests

1. *Cubic potential*

The first numerical test of PGH theory did not include finite barrier corrections and compared the MM theory with PGH theory. Linkwitz et al [5], considered thermal escape for a particle of mass M over a barrier of a cubic potential

$$V(q) = -\frac{M\omega^{\ddagger 2}}{2} q^2 \left(1 + \frac{q}{q_0}\right) \tag{4.1}$$

with Ohmic friction. For this potential the barrier height is

$$V^{\ddagger} = \frac{2M\omega^{\ddagger 2} q_0^2}{27}. \tag{4.2}$$

In the intermediate damping regime, where the reduced friction coefficient $0.1 \leq \gamma/\omega^{\ddagger} \leq 1$ Linkwitz et al found that PGH theory agreed well with the numerical simulation results, while MM theory gave a result which was slightly too high (by about 3% when $\beta V^{\ddagger} = 8$ and ca. 6% for $\beta V^{\ddagger} = 5$).

Unfortunately, in their rate expression, they used a harmonic partition function for the reactants instead of the correct partition function which includes the full potential as in Eq. 2.22. For the cubic potential one readily finds that to leading order the partition function is larger than the harmonic estimate by the factor of $\left(1 + \frac{5}{36}\frac{1}{\beta V^{\ddagger}}\right)$. This implies that in fact the MM estimate for $\beta V^{\ddagger} = 5$ should be lowered by $1/36 \simeq 3\%$ while for $\beta V^{\ddagger} = 8$ it should be lowered by about 1.7% bringing it into better agreement with the numerical results. Their PGH estimate should be lowered by the same ratios, leading to the conclusion that the MM estimate is a bit higher than the numerical estimate while the PGH estimate is a bit lower. These numerical computations are not conclusive as to which theory is more accurate in the turnover region. The noise in the numerical results cannot distinguish between the two.

2. *Periodic potential*

Ferrando et al [6] tested the MM theory, without and with finite barrier corrections for a periodic cosine potential

$$V(q) = \frac{V^{\ddagger}}{2} \cos\left(2\pi \frac{q}{l}\right) \tag{4.3}$$

where l is the "lattice length". For Ohmic friction they find in the region $10^{-3} \leq \gamma/\omega^{\ddagger} \leq 10^{-1/2}$ that when $\beta V^{\ddagger} = 5$ the MM theory overestimates the numerical results by a factor varying from 1.45 in the low friction limit to 1.25 for $\gamma/\omega^{\ddagger} \simeq 10^{-1}$. In the same friction region, including Melnikov's finite barrier correction terms leads to a much smaller overestimate of 1.05 in the low friction regime reaching a maximal overestimate of 1.1 when $\gamma/\omega^{\ddagger} \leq 10^{-1.3}$. For $\beta V^{\ddagger} = 15$ the error without finite barrier corrections is reduced to the range of 1.14 to 1.1 while finite barrier corrections reduce the overestimate to the range of 1.04 to 1.07. As expected, increasing the reduced barrier height, reduces the error.

Unfortunately, here too the authors used a harmonic approximation to the partition function of reactants. To leading order the anharmonic partition function is larger than the harmonic by a factor of $1 + \frac{1}{4\beta V^{\ddagger}}$. This implies that for $\beta V^{\ddagger} = 5$ the theoretical estimates have to be reduced by 5% putting the finite barrier estimate almost in perfect agreement with the numerical estimate. For $\beta V^{\ddagger} = 15$, the theoretical estimates should be reduced by $1/60 \simeq 1.7\%$. Interestingly, this implies that the finite barrier correction of Mel'nikov is in better agreement with the numerics for the lower reduced barrier height.

B. Numerical tests for a cubic potential

1. *Numerical details*

All the numerical calculations described here use a high quality random generator from [24], having a period of 3.138×10^{57}.

The particles trapped in the well start in a Boltzmann distribution

$$\exp\left[-\beta\left(\frac{p^2}{2M} + V(q)\,\theta(-q)\right)\right] \tag{4.4}$$

where $V(q)$ is given in Eq. 2.22 and $\theta(-q)$ is the unit step function. Therefore, the starting momentum p is a gaussian random variable with 0 average and M/β variance, while for the starting position q, we use a 2 step rejection procedure, described below.

We first define the approximate harmonic potential

$$V_h(q) = -V^{\ddagger} + \frac{M\omega^{\ddagger 2}}{2}\left(q + \frac{2}{3}q_0\right)^2 \tag{4.5}$$

which satisfies $V_h(q) \leq V(q)$ for any $q \leq 0$, with equality for $q = -\frac{2}{3}q_0$. We choose q as a gaussian random variable with $-\frac{2}{3}q_0$ average and $\frac{2q_0^2}{9\beta V^\ddagger}$ variance, but reject all $q > 0$. After that we chose a random variable, uniformly distributed between 0 and $\exp[-\beta V_h(q)]$, and if the value of this variable is bigger than $\exp[-\beta V(q)]$, the above value of q is rejected.

So after having the initial position and momentum, we start the dynamics of the particle in the well. Each particle satisfies Langevin equation 2.1 with Ohmic friction, i.e $\gamma(t-t') = \gamma\delta(t-t')$.

The Langevin dynamics is carried out using a 4th order R-K algorithm, with a time step of $\frac{1}{50}\frac{2\pi}{\omega^\ddagger}$, and the random force is treated using the procedure explained in [25]. Each particle is let to run till it escapes the well, and the escape criterion is $q > .452q_0$, at which point the potential energy of the particle is $-2V^\ddagger$.

For each particle we monitor the total time it ran, and we run on each experiment $N_0 = 500,000$ particles, so we know how many particles $N(t)$ are still trapped after the time t. The function $N(t)$ is expected to behave like $N_0 \exp(-\Gamma t)$, if the number of particles left is not too small.

We therefore calculate $-\ln N$, which is expected to behave like $-\ln N_0 + \Gamma t$, and fit a straight line for this function in the interval $t_{\max}/20 < t < t_{\max}/5$, where $t_{\max}$ is the escape time of the last particle in the well. The line fit is chosen by least square distance error from the function, and the slope of this line is the measured escape rate Γ. The error (standard deviation) σ_Γ of this estimation is given by the simple linear regression error formula so that σ_Γ/Γ is few ppms for our sample size.

The numerical results for the escape rates for three reduced barrier heights ($\beta V^\ddagger = 4, 7, 10$) and for a range of reduced friction coefficients ($\gamma/\omega^\ddagger$) are shown in Table I. For each reduced barrier height we also give the value of Γ_{TST} in Eq. 4.7 to facilitate the comparison with the analytic results.

ELI, THIS SECTION BELOW WAS HERE, BUT DOESN'T BELONG TO THE NUMERICAL TESTS I THINK. HOWEVER, I USED THE DEFINITION OF GAMMA_TST, WHICH SHOULD PROBABLY BELONG TO A PREVIOUS SECTION.

For Ohmic friction ($\hat{\gamma}(s) = \gamma$) the matrix element

$$u_{00}^2 = \left(1 + \frac{\gamma}{2\lambda^\ddagger}\right)^{-1}$$

TABLE I: The numerical results for the escape rates for three reduced barrier heights $\beta V^\ddagger = 4, 7, 10$. The values of Γ_{TST} for those reduced barrier heights are 1.0198×10^{-2}, 5.2045×10^{-4} and 2.6134×10^{-5}, respectively.

$\gamma/\omega^\ddagger$	$\beta V^\ddagger = 4$	$\beta V^\ddagger = 7$	$\beta V^\ddagger = 10$	$\gamma/\omega^\ddagger$	$\beta V^\ddagger = 4$	$\beta V^\ddagger = 7$	$\beta V^\ddagger = 10$
0.0001	2.2348e-05	1.9617e-06	1.4474e-07	0.074989	6.3651e-03	3.9798e-04	2.2279e-05
0.0001778279	3.9682e-05	3.4659e-06	2.5834e-07	0.1	7.1873e-03	4.2965e-04	2.3253e-05
0.0003162277	6.9791e-05	6.0682e-06	4.5160e-07	0.133352	7.8109e-03	4.4828e-04	2.3654e-05
0.0005623413	1.2190e-04	1.0579e-05	7.7499e-07	0.17783	8.3173e-03	4.5623e-04	2.3571e-05
0.001	2.1061e-04	1.8239e-05	1.3259e-06	0.237137	8.5338e-03	4.5537e-04	2.3167e-05
0.001333521	2.7579e-04	2.3639e-05	1.7182e-06	0.31623	8.5246e-03	4.4239e-04	2.2298e-05
0.001778279	3.6091e-04	3.0673e-05	2.2158e-06	0.421697	8.2618e-03	4.2004e-04	2.1198e-05
0.002371373	4.7221e-04	3.9715e-05	2.8414e-06	0.56234	7.7798e-03	3.9289e-04	1.9760e-05
0.003162277	6.1463e-04	5.0946e-05	3.6080e-06	0.749894	7.1368e-03	3.5963e-04	1.8080e-05
0.004216965	7.9286e-04	6.5154e-05	4.5713e-06	1.0	6.3485e-03	3.2048e-04	1.6073e-05
0.005623413	1.0193e-03	8.2289e-05	5.7316e-06	1.333521	5.4333e-03	2.7709e-04	
0.007498942	1.3019e-03	1.0407e-04	7.1231e-06	1.7783	4.5212e-03	2.3146e-04	
0.01	1.6530e-03	1.2953e-04	8.6895e-06	2.371374	3.6598e-03	1.8764e-04	
0.013335	2.0809e-03	1.5998e-04	1.0551e-05	3.1623	2.8887e-03	1.4823e-04	
0.017783	2.6038e-03	1.9459e-04	1.2530e-05	4.216965	2.2396e-03	1.1529e-04	
0.023714	3.2128e-03	2.3465e-04	1.4715e-05	5.0	1.9105e-03	9.8535e-05	
0.031623	3.9193e-03	2.7636e-04	1.6918e-05	6.0	1.6115e-03	8.3174e-05	
0.042170	4.7029e-03	3.1829e-04	1.8976e-05	7.0	1.3906e-03	7.1241e-05	
0.056234	5.5358e-03	3.6143e-04	2.0849e-05	8.0	1.2209e-03	6.2826e-05	

and the unstable mode frequency is the smaller positive solution of the quadratic equation

$$\lambda^{\ddagger 2} + \lambda^\ddagger \gamma = \omega^{\ddagger^2}.$$

The symmetric in time kernel $K(t)$, is for positive t:

$$K(t) = \left\{ \frac{u_{00}^2}{2\lambda^{\ddagger^2}} \left(\exp\left(-\lambda^\ddagger t\right) - \frac{\lambda^\ddagger}{\lambda_1} \exp\left(-\lambda_1 t\right) + 1 + \frac{\lambda^\ddagger}{\lambda_1} \right) - \frac{1}{\omega^{\ddagger^2}} \right\}$$

with

$$\lambda_1 = \gamma + \lambda^\ddagger.$$

Therefore:

$$R\left(t-t'\right) \ = \ \frac{\partial^2 K\left(t-t'\right)}{\partial t \partial t'} = \frac{u_{00}^2}{2}\exp\left(-\lambda^{\ddagger}\left(t-t'\right)\right)\left(\frac{\gamma+\lambda^{\ddagger}}{\lambda^{\ddagger}}\exp\left(-\gamma\left(t-t'\right)\right)-1\right)$$

For the cubic potential (Eq. 4.1) the potential energy governing the zero-th order motion of the unstable mode is:

$$V\left(\rho\right) = -\frac{\lambda^{\ddagger^2}\rho^2}{2} - \frac{\omega^{\ddagger^2}}{2}\frac{u_{00}^3\rho^3}{\sqrt{M}q_0}.$$

The unstable mode barrier energy is then

$$V_\rho^{\ddagger} = \frac{\lambda^{\ddagger^6}}{\omega^{\ddagger^6}u_{00}^6}V^{\ddagger}.$$

One readily notes that in the strong friction limit

$$V_\rho^{\ddagger} \rightarrow_{\gamma/\omega^{\ddagger}\gg 1} \frac{V^{\ddagger}}{8}. \tag{4.6}$$

This reduction of the barrier for the unstable mode motion has noticeable consequences, as discussed below. As shown in Ref. [16] the solution for the zero-th order equation of motion for the unstable mode (Eq. 2.21) at the barrier energy is:

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

2. A comparison of turnover theories without finite barrier corrections

The transition state theory rate expression, including Kramers' correction for the spatial diffusion limit is denoted as:

$$\Gamma_{TST} = \frac{\exp\left(-\beta V^{\ddagger}\right)}{\left(2\pi M\beta\right)^{1/2}\int_{-\infty}^{\infty}dq\exp\left(-\beta V\left(q\right)\right)\theta\left(-q\right)}. \tag{4.7}$$

A transmission coefficient is then defined as:

$$\kappa = \frac{\Gamma}{\Gamma_{TST}}.$$

In the absence of finite barrier corrections, the transmission coefficient is just the zero-th order depopulation factor, as given in Eqs. 2.24 and 2.25. We then denote $\kappa_{\rm ex}$, $\kappa_{\rm MM}$ and $\kappa_{\rm PGH}$ to denote respectively the numerically exact, the MM and the PGH transmission factors without barrier corrections, respectively. A comparison between the three transmission factors as a function of the reduced friction coefficient ($\gamma/\omega^{\ddagger}$) and for three reduced barrier heights ($\beta V^{\ddagger} = 4, 7, 10$) is plotted in Figure 1. Also plotted on the right side of the Figure, is the relative error of the MM and PGH expressions, defined as

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

for the three reduced barrier heights. From these plots it becomes evident, that at least for the cubic potential, especially in the turnover region MM theory is somewhat more accurate than the PGH one. On the other hand PGH theory does better in the low friction regime. In any case, both theories are rather accurate, with absolute errors of at most 20 percent.

The larger error of PGH theory for moderate to high friction has to do with the fact that the PGH energy loss is not a monotonic function of the friction, as shown in Figure 2. For low friction, the coupling to the bath increases and so does the energy loss. But as the friction is increased, as discussed above, the effective barrier height in the potential for the unstable mode decreases tending to 1/8 of the barrier height of the system potential (Eq. 4.6). The result is that at some point, the increase coming about from the stronger coupling to the bath is more than offset by the lowering of the barrier height, leading to the dependence on the friction as shown in Figure 2.

One can significantly improve the PGH result on an ad hoc basis, simply by removing the decrease in the PGH energy loss. That is if the energy loss reaches its maximum at some value of the friction, then for higher friction values, one retains this energy loss in the PGH expression for the depopulation factor. The resulting "ad hoc" PGH theory results are compared with the MM results in Figure 3. One notes the improvement for the low and moderate barrier heights ($\beta V^{\ddagger} = 4, 7$), however, for $\beta V^{\ddagger} = 10$ the temperature is low enough and the energy loss sufficiently large that the depopulation factor is exponentially close to unity and the ad-hoc correction makes little difference. At least for the cubic potential and for reduced barrier height of 10 or more one can safely say that PGH and MM theory are comparable in quality for the whole friction range.

For the cubic potential this then implies that

$$\Upsilon_{PGH} \simeq \delta \left[1 - \frac{5}{36\beta V^{\ddagger}} \frac{35}{4}\right], \quad \delta \ll 1$$

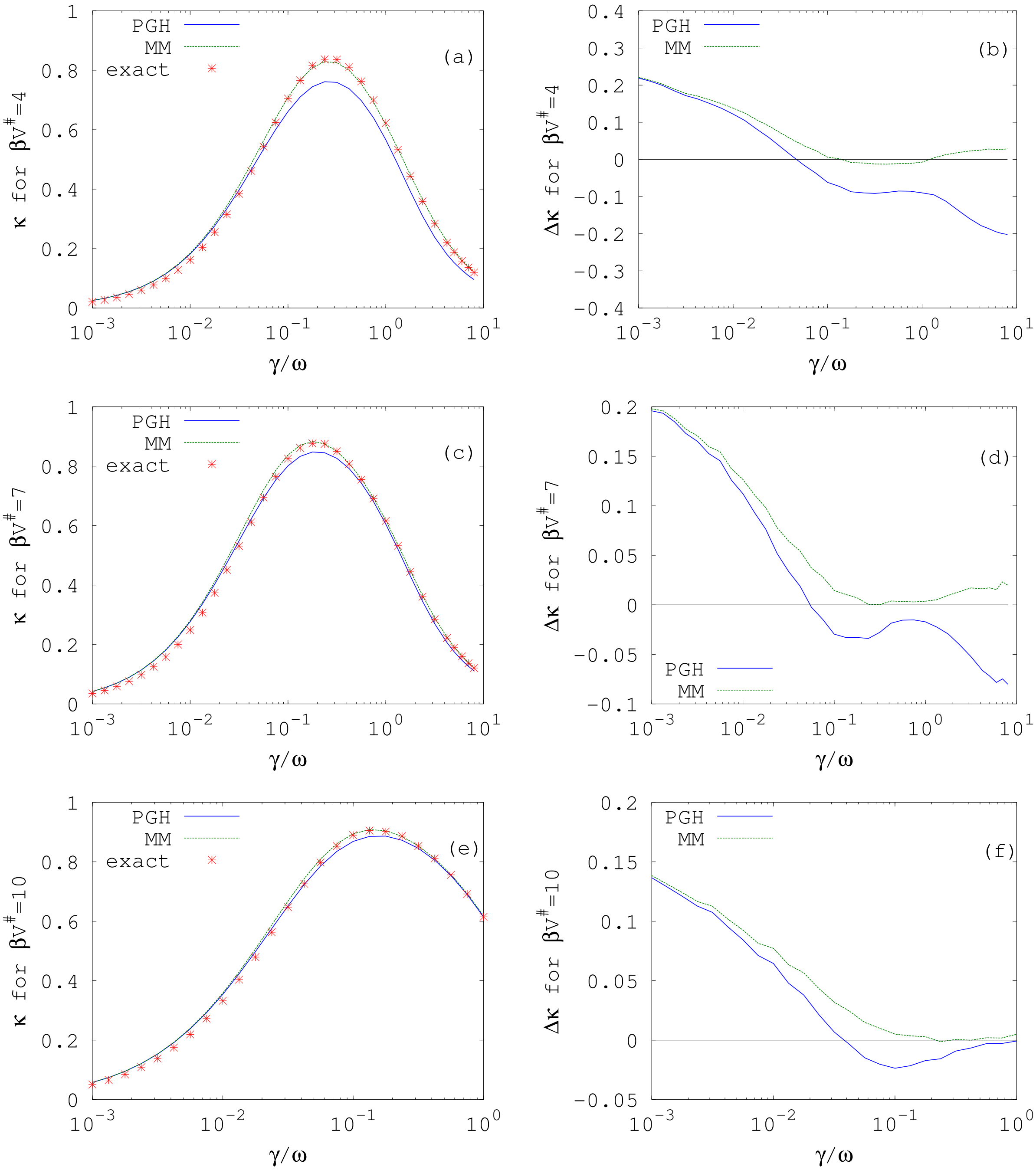

FIG. 1: The transmission factors and their relative errors as function of the reduced friction coefficients for three reduced barrier heights.

and

$$\Upsilon_{MM} \simeq \delta \left[1 - \frac{5}{36\beta V^{\ddagger}} \left(\ln 432\beta V^{\ddagger} + 2 - C \right) \right], \quad \delta \ll 1$$

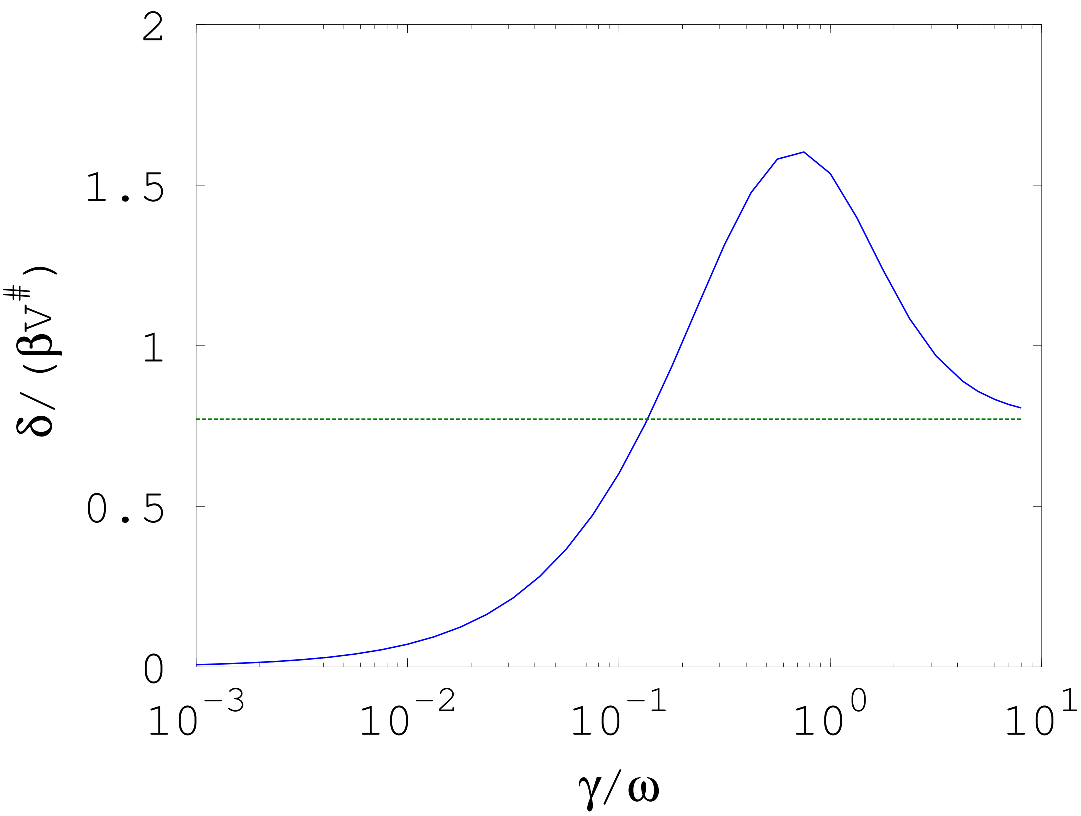

FIG. 2: The dimensionless PGH energy loss δ normalized by the reduced barrier height $\beta V^\ddagger$ as function of the reduced friction coefficient γ/ω. of the reduced friction coefficients for three reduced barrier heights.

The two will then be identical when

$$\beta V^\ddagger = \frac{1}{432}\exp\left(\frac{27}{4}+C\right) \simeq 3.5.$$

$$\ln\Upsilon \simeq \frac{2}{\sqrt{\pi\delta}}\exp\left(-\frac{\delta}{4}\right)\left[\frac{175\delta^2}{432\beta V^\ddagger} - 1 - \frac{175}{108\beta V^\ddagger}\right], \quad \delta \gg 1.$$

Figure 4 we see the same comparison as in Figure 1, but using finite barrier corrections for both PGH and MM.

Figure 5 we see the same comparison as in Figure 4, only we use keep for PGH the energy loss constant from the friction it starts to decrease.

Although the MM results look better, one should remark that those results do manifest the theory described in [7], which may be summarized by Eq.15 in the above reference, but the ad hoc adjustment in Eq.146.

The MM theory in [7] (Eq.15) fails in the high friction region as one may see in Figure 6

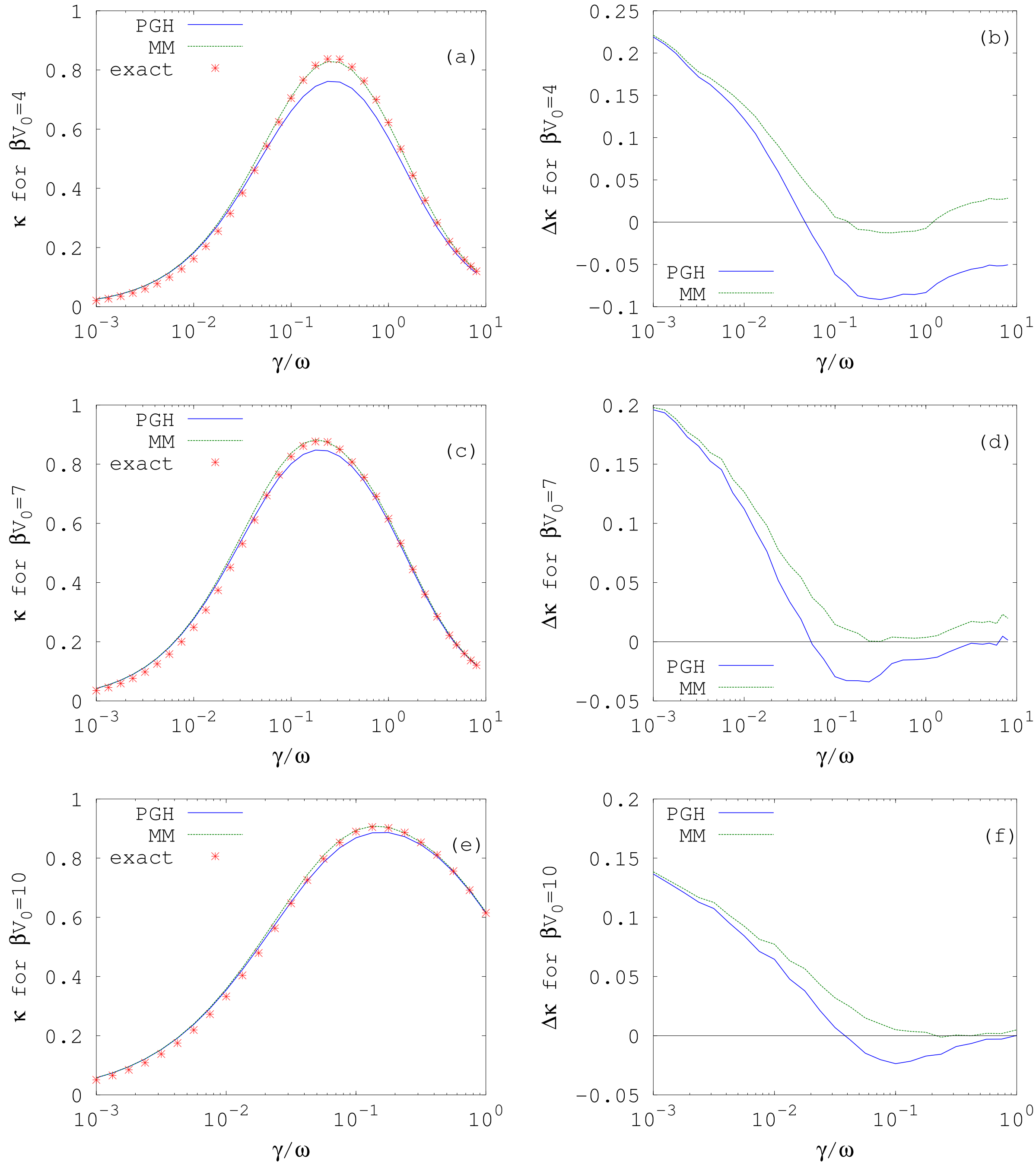

FIG. 3: The transmission factors and their relative errors as function of the reduced friction coefficients for three reduced barrier heights. The PGH results are corrected ad hoc.

IV. DISCUSSION

The central result of this paper is the derivation of finite barrier corrections to the PGH turnover theory for the rate of activated escape of a particle over a potential barrier. There

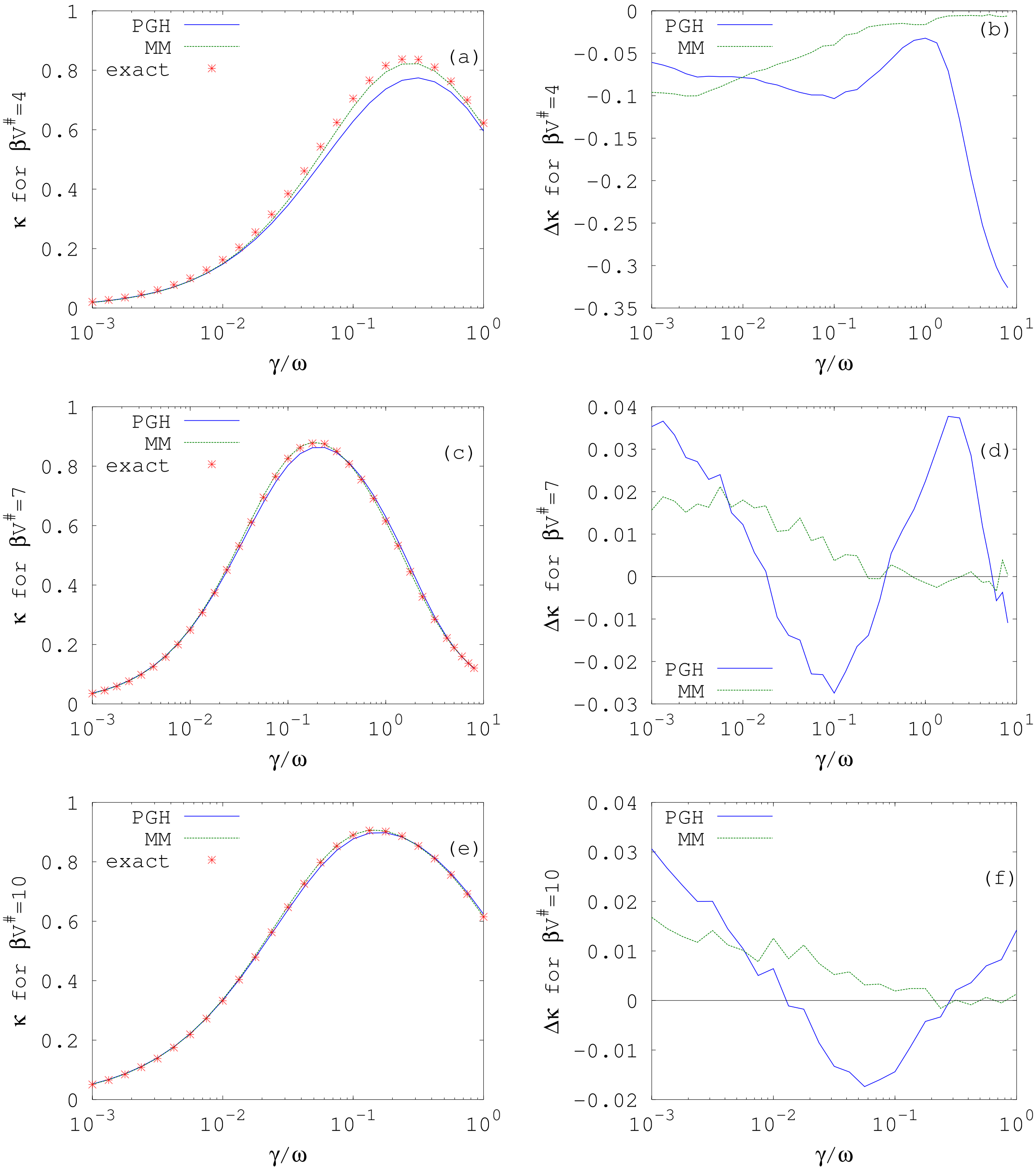

FIG. 4: The transmission factors and their relative errors as function of the reduced friction coefficients for three reduced barrier heights. All the results contain the finite barrier correction.

are differences between the PGH theory and the parallel theory of Melnikov. As already noted in Ref. [13] Melnikov's theory ignores the question of deposition of thermal energy to the particle during its traversal over the well. When considering the motion of the particle, this added energy diverges. Within the PGH formalism it is finite and not less important than the contribution coming from the energy dependence of the energy loss.

The finite barrier corrections derived by Mel'nikov in Ref. [7] and given in his Eq. 15 will lead to negative and thus nonphysical values of the transmission probability when the (reduced) friction coefficient is of the order of unity or larger. Ferrando et al [6] in their numerical tests of Melnikov's expression, used this version of the theory (see their Eq. 15). They only studied the theory in the region of (reduced) friction coefficient which is less than ca. 1/3. In this present paper, we mainly employed Melnikov's ad hoc corrected expression (Eq. 146) for the rate. It is this form which leads to the high accuracy of Melnikov's version of the turnover theory with finite barrier corrections.

Within PGH theory, nonphysical results will be found when the reduced barrier height is less than 4. The depopulation factor will become complex. However, the theory is explicitly derived for large reduced barriers, so that this implies that when the reduced barrier becomes small, the leading order finite barrier correction is insufficient. A comparison of PGH and MM theories without finite barrier corrections with numerical results for a cubic oscillator, reveals that in the low friction limit PGH theory is somewhat better than MM theory while in the intermediate to strong friction regime, MM theory is more accurate. In the moderate to strong friction regime, the PGH depopulation factor does not go to unity, but a constant somewhat lower than unity. This results from the behavior of the PGH energy loss which reaches a maximum when the reduced friction is of order unity but then decreases with increase of friction, due to the decrease of the effective barrier height to reaction in the unstable normal mode potential. This decrease is not physical, as increasing the friction should increase the energy loss. Introducing an ad hoc correction to PGH theory by using the maximal value of the energy loss for all friction strengths above the point at which the energy loss becomes maximal significantly improves the quality of the PGH expression as compared to the numerical simulations. All this leads to the conclusion, that for Ohmic friction, in practice, the MM and PGH theories without finite barrier corrections are of similar quality.

Acknowledgements

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Appendix A: Energy derivative of the energy loss

The definition of the energy dependent energy loss is given in Eq. 2.31. At the barrier energy the initial and final condition is that the unstable mode coordinate tends to the barrier top. This implies that the surface terms in the energy derivative vanish giving the intermediate result:

$$\frac{d\delta_{PGH}(\varepsilon)}{d\varepsilon}|_{\varepsilon=0} = \left\{ \frac{\beta}{2M} \int_{-t(\varepsilon)/2}^{t(\varepsilon)/2} dt \int_{-t(\varepsilon)/2}^{t(\varepsilon)/2} dt' R(t-t') \frac{\partial}{\partial \varepsilon} \left[V_1' \left(\frac{u_{00}\rho_{\varepsilon,t}}{\sqrt{M}} \right) V_1' \left(\frac{u_{00}\rho_{\varepsilon,t'}}{\sqrt{M}} \right) \right] \right\}_{\varepsilon=0} . \tag{A.1}$$

We then have to find the dependence of the trajectory on the energy and we do this using perturbation theory. That is for $\varepsilon = 0$ we assume that the barrier energy trajectory $\rho_{0,t}$ is known so that

$$\rho_{E,t} = \rho_{0,t} + E\rho_{1,t} \tag{A.2}$$

and E is the actual energy (not the reduced energy). From energy conservation we have that:

$$E = \frac{1}{2} \left(\frac{d(\rho_{0,t} + E\rho_{1,t})}{dt} \right)^2 - \frac{1}{2} \lambda^{\ddagger^2} (\rho_{0,t} + E\rho_{1,t})^2 + V_1 \left(\frac{u_{00}(\rho_{0,t} + E\rho_{1,t})}{\sqrt{M}} \right). \tag{A.3}$$

Noting that the zero-th order trajectory is at energy $E = 0$ we then find to first order in E:

$$1 = \dot{\rho}_{0,t}\dot{\rho}_{1,t} - \rho_{1,t}\ddot{\rho}_{0,t}. \tag{A.4}$$

This first order in time derivative equation is readily solved:

$$\rho_{1,t} = \dot{\rho}_{0,t} \int_{t_i}^{t} dt' \frac{1}{\dot{\rho}_{0,t'}^2}. \tag{A.5}$$

We then find after some manipulation (using the symmetry in time of $K(t)$ and the zero-th order trajectory) the desired result, that is that:

$$\frac{d\delta_{PGH}(\varepsilon)}{d\varepsilon} = \mu_\beta \delta_{PGH} \tag{A.6}$$

where $\mu_\beta \equiv \mu$ is as given in Eq. 2.27.

APPENDIX B: Solution of the integral equation

In this Appendix we solve the integral equation 2.19 for the steady state flux of particles hitting the barrier per unit time including the correction for the energy dependence of the energy loss. Defining (see also Eq. 2.17)

$$N(\varepsilon) = R(\varepsilon) f(\varepsilon) \tag{B.1}$$

and Fourier transforming the integral equation gives:

$$\tilde{N}_\varepsilon(is) + \tilde{N}_\varepsilon(i(s-\alpha)) = \int_{-\infty}^{\infty} d\varepsilon \exp(-s\varepsilon) N_\varepsilon(\varepsilon) \tilde{P}_\varepsilon(is,\varepsilon) \tag{B.2}$$

where the ε subscript serves to remind that we are considering corrections due to the energy ependence of the energy loss. We note that

$$\int_{-\infty}^{\infty} d\varepsilon \exp(-s\varepsilon) N(\varepsilon)\varepsilon = -\frac{\partial \tilde{N}(is)}{\partial s}. \tag{B.3}$$

Using Eq. 2.38 we find that

$$\begin{aligned}\tilde{N}_\varepsilon(is) + \tilde{N}_\varepsilon(i(s-\alpha)) &= \tilde{N}_\varepsilon(is)\tilde{P}_0(is)\left\{1 + \mu_\varepsilon \delta s^2 \left[(3+2s) + \frac{\delta(\delta+2)(2s+1)(s+1)^2}{4}\right]\right\} \\ &+ \tilde{N}_\varepsilon(is)\tilde{P}_0(is)\mu_\varepsilon \delta s(s+1)\frac{\partial \ln \tilde{N}(is)}{\partial s}\left[\frac{s\delta}{2}(s+1) + s^2 + s - 1\right]\end{aligned} \tag{B.4}$$

Following the derivation in the Appendix of Ref. [16] we use the ansatz:

$$\tilde{N}_\varepsilon(is) = -\frac{\pi C}{\alpha \sin\left(\frac{\pi(s+1)}{\alpha}\right)} \tilde{N}_{r,\varepsilon}(is) \tag{B.5}$$

so that

$$\tilde{N}_\varepsilon(i(s-\alpha)) = \frac{\pi C}{\alpha \sin\left(\frac{\pi(s+1)}{\alpha}\right)} \tilde{N}_{r,\varepsilon}(i(s-\alpha)) \tag{B.6}$$

and

$$\frac{\partial \ln \tilde{N}_\varepsilon(is)}{\partial s} = \frac{\partial \ln \tilde{N}_{r,\varepsilon}(is)}{\partial s} - \frac{\pi \cos\left(\frac{\pi(s+1)}{\alpha}\right)}{\alpha \sin\left(\frac{\pi(s+1)}{\alpha}\right)} \to \frac{\partial \ln \tilde{N}_{r,\varepsilon}(is)}{\partial s} - \frac{1}{s+1} \tag{B.7}$$

where the rightarrow denotes the classical limit obtained with $\alpha \to \infty$. Introducing

$$\tilde{g}_\varepsilon(is) = \ln\left[\tilde{N}_{r,\varepsilon}(is)\right] \tag{B.8}$$

the integral equation then becomes:

$$\tilde{g}_\varepsilon\left(i\left(s-\alpha\right)\right)-\tilde{g}_\varepsilon\left(is\right) \;=\; \ln\left[1-\tilde{P}_0\left(is\right)\left\{1+\mu_\varepsilon\delta s\left(s+1\right)W\left(is\right)\right\}\right] \tag{B.9}$$

with

$$\begin{aligned} W\left(is\right) \;=\; & \left(s+1\right)+\frac{\delta\left(\delta+2\right)\left(2s+1\right)s\left(s+1\right)-2\delta s}{4} \\ & +\frac{\partial\tilde{g}\left(is\right)}{\partial s}\left(\frac{s\delta\left(s+1\right)}{2}+s^2+s-1\right) \end{aligned} \tag{B.10}$$

Expanding to first order in the coefficient μ_ε we get that:

$$\tilde{g}_\varepsilon\left(i\left(s-\alpha\right)\right)-\tilde{g}_\varepsilon\left(is\right)=\ln\left[1-\tilde{P}_0\left(is\right)\right]-\mu_\varepsilon\tilde{H}\left(is\right) \tag{B.11}$$

where

$$\tilde{H}\left(is\right)\equiv\frac{\tilde{P}_0\left(is\right)\delta s\left(1+s\right)}{1-\tilde{P}_0\left(is\right)}W\left(is\right). \tag{B.12}$$

As shown in the Appendix of Ref. [16], the solution of the integral equation is:

$$\begin{aligned} \tilde{g}_\varepsilon\left(is\right) \;=\; & \frac{1}{2\alpha i}\int_{z-i\infty}^{z+i\infty}dy\left[\ln\left[1-\tilde{P}_0\left(iy\right)\right]-\mu_\varepsilon\tilde{H}\left(iy\right)\right] \\ & \cdot\left(\cot\left[\frac{\pi\left(s-y\right)}{\alpha}\right]+\cot\left[\frac{\pi\left(1+y\right)}{\alpha}\right]\right) \end{aligned} \tag{B.13}$$

so that:

$$\tilde{g}_0\left(is\right) \;=\; \frac{1}{2\alpha i}\int_{z-i\infty}^{z+i\infty}dy\ln\left[1-\tilde{P}_0\left(iy\right)\right]\left(\cot\left[\frac{\pi\left(s-y\right)}{\alpha}\right]+\cot\left[\frac{\pi\left(1+y\right)}{\alpha}\right]\right). \tag{B.14}$$

where the subscript 0 denotes the function in the absence of the energy dependent part. This implies that:

$$\begin{aligned} \frac{\partial\tilde{g}_0\left(is\right)}{\partial s} \;=\; & -\frac{1}{2\alpha i}\int_{z-i\infty}^{z+i\infty}dy'\frac{1}{1-\tilde{P}_0\left(iy'\right)}\left[\frac{d}{dy'}\tilde{P}_0\left(iy'\right)\right]\cot\left(\pi\frac{s-y'}{\alpha}\right) \\ & \to -\frac{\delta}{2\pi i}\int_{z-i\infty}^{z+i\infty}dy'\frac{\tilde{P}_0\left(iy'\right)}{1-\tilde{P}_0\left(iy'\right)}\frac{2y'+1}{s-y'}. \end{aligned} \tag{B.15}$$

Putting it all together we then have:

$$\tilde{g}_\varepsilon\left(is\right) \;=\; \tilde{g}_0\left(is\right)-\frac{\mu_\varepsilon}{2\alpha i}\int_{z-i\infty}^{z+i\infty}dy\tilde{H}\left(iy\right)\left(\cot\left[\frac{\pi\left(s-y\right)}{\alpha}\right]+\cot\left[\frac{\pi\left(1+y\right)}{\alpha}\right]\right) \tag{B.16}$$

or:

$$\lim_{\alpha\to\infty}\tilde{g}_{\varepsilon}\left(-i\alpha\right) = \lim_{\alpha\to\infty}\tilde{g}_{0}\left(-i\alpha\right) - \mu_{\varepsilon}\Phi^{2}\left(\delta\right)\left[1+\frac{\delta+2}{8}\right] + \frac{\mu_{\varepsilon}\left(\delta+2\right)}{4}\Phi\left(\delta\right). \tag{B.17}$$

Here we used the change of variable and contour as in the Appendix of Ref. [16]:

$$iy = \tau - \frac{i}{2}; \tag{B.18}$$

and the notation

$$\begin{aligned}\Phi\left(\delta\right) &\equiv \frac{\delta}{2\pi}\int_{-\infty}^{\infty} d\tau \frac{\tilde{P}_0\left(\tau-\frac{i}{2}\right)}{1-\tilde{P}_0\left(\tau-\frac{i}{2}\right)} \\ &= \frac{\delta}{2\pi}\int_{-\infty}^{\infty} d\tau \frac{1}{\exp\left(\delta\left(\tau^2+\frac{1}{4}\right)\right)-1}.\end{aligned} \tag{B.19}$$

This result (Eq. B.17) was derived by using the symmetry in time of the Fourier transformed transition kernel to find that

$$\frac{\delta}{2\pi}\int_{-\infty}^{\infty} d\tau \frac{\tilde{P}_0\left(\tau-\frac{i}{2}\right)}{1-\tilde{P}_0\left(\tau-\frac{i}{2}\right)}\frac{\delta}{2\pi}\int_{-\infty}^{\infty} d\tau' \frac{\tilde{P}_0\left(\tau'-\frac{i}{2}\right)}{1-\tilde{P}_0\left(\tau'-\frac{i}{2}\right)}\frac{2\tau'}{\tau'-\tau} = \Phi^2\left(\delta\right) \tag{B.20}$$

and

$$0 = \frac{\delta}{2\pi}\int_{-\infty}^{\infty} d\tau \frac{\tilde{P}_0\left(\tau-\frac{i}{2}\right)}{1-\tilde{P}_0\left(\tau-\frac{i}{2}\right)}\frac{\delta}{2\pi}\int_{-\infty}^{\infty} d\tau' \frac{\tilde{P}_0\left(\tau'-\frac{i}{2}\right)}{1-\tilde{P}_0\left(\tau'-\frac{i}{2}\right)}\frac{2\tau^2\tau'}{\tau-\tau'}. \tag{B.21}$$

The depopulation factor is:

$$\Upsilon_{\varepsilon} = \exp\left(\tilde{g}_{\varepsilon}\left(-i\alpha\right)\right) \tag{B.22}$$

Inserting Eq. B.17 then gives the result for the depopulation factor as given in Eq. 2.39.

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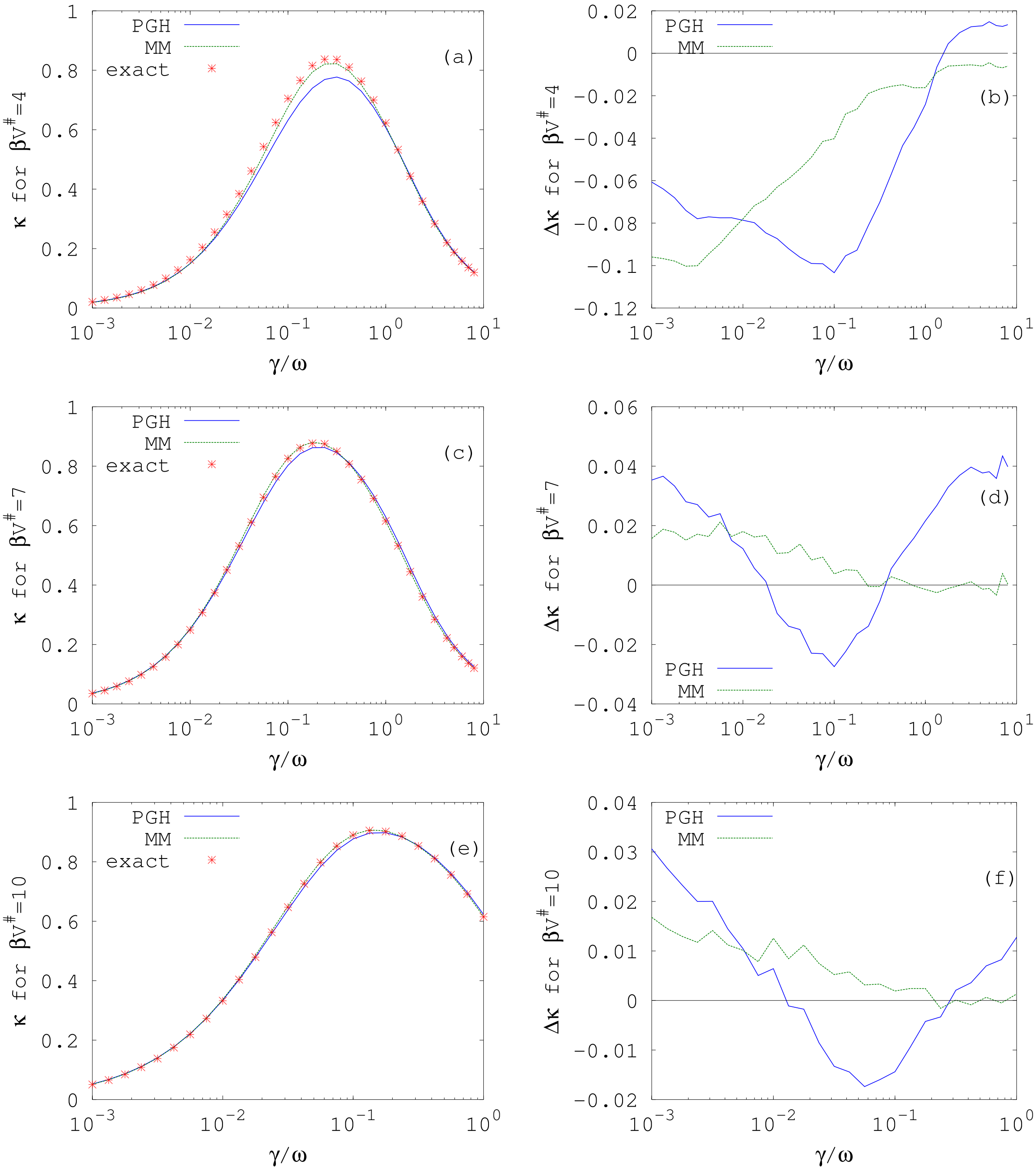

FIG. 5: The transmission factors and their relative errors as function of the reduced friction coefficients for three reduced barrier heights. All the results contain the finite barrier correction, and the PGH energy loss is kept constant from the friction it starts to decrease.

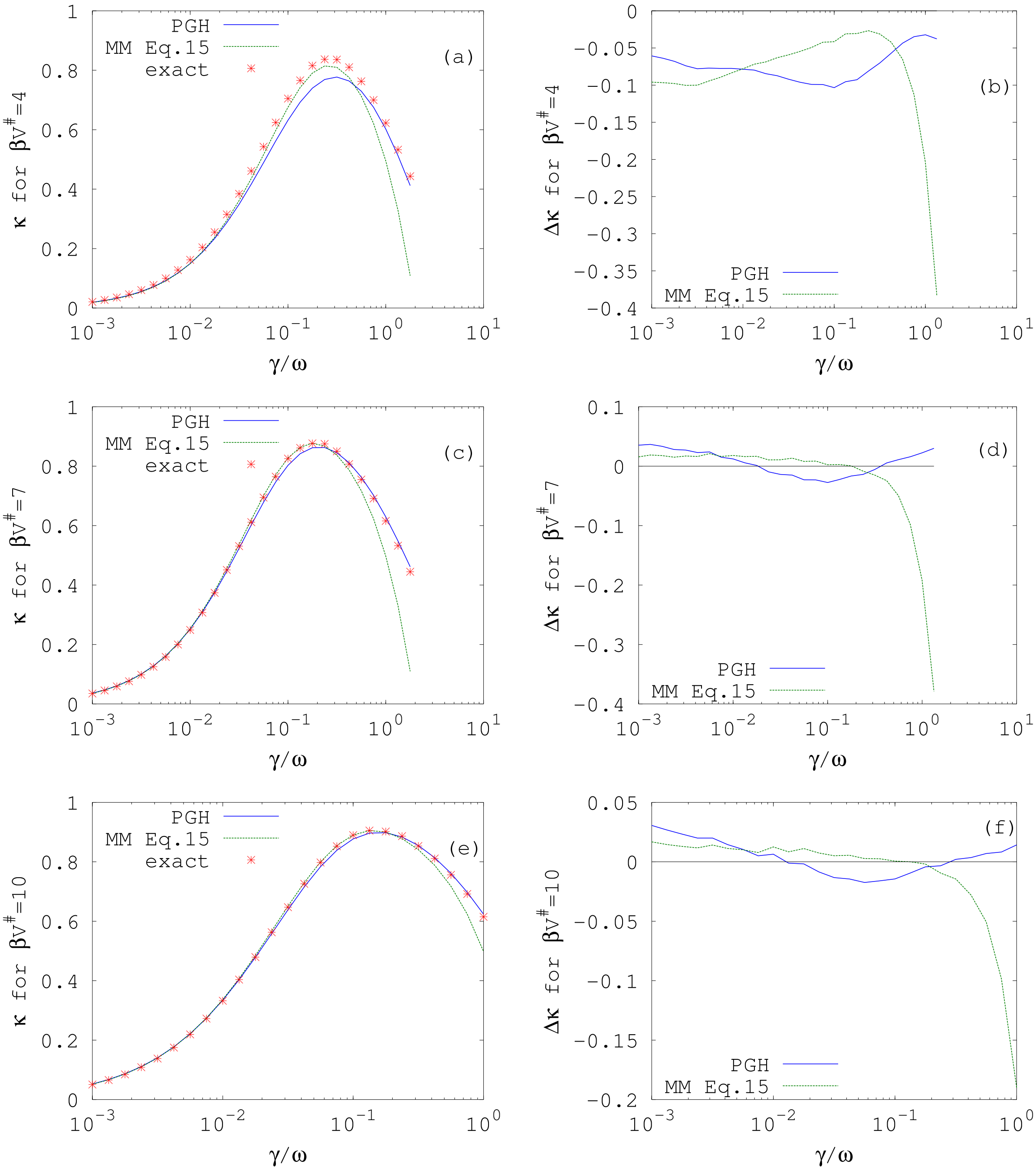

FIG. 6: The transmission factors and their relative errors as function of the reduced friction coefficients for reduced barrier height 7. The results contain the finite barrier correction, MM is based on result 15 and PGH uses its regular energy loss.