Kramers' Turnover Theory: Improvement and Extension to Low Barriers

Eli Pollak [†] and Reuven Ianconescu[*,†]

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

‡*Shenkar College of Engineering and Design, Ramat Gan, Israel*

E-mail: eli.pollak@weizmann.ac.il

Abstract

Kramers' turnover theory as derived by Pollak, Grabert and Hänggi (PGH) suffers from a few drawbacks. The energy loss in PGH theory is not a monotonic function of the friction. Secondly, the theory is not applicable to surface diffusion, since the effective potential for the system does not conserve the periodicity of the potential. Thirdly, when the reduced barrier height is low, it is rather inaccurate. In this paper, we present a modification of PGH theory which alleviates these drawbacks. We also introduce a finite barrier correction term which takes into consideration that the energy interval of the escaping particle is bounded from below. The resulting theory is tested for motion on a cubic potential and relatively low reduced barriers.

Keywords: rate theory; Kramers' turnover theory ; PGH theory; Classical perturbation theory.

Introduction

The Kramers' turnover problem[1,2] for the influence of friction on the rate of escape of a particle from a potential well was seemingly solved over twenty years ago. First, Mel'nikov and Meshkov (MM) provided a framework valid for Ohmic friction.[3,4] Pollak realized that Kramers' expression in the spatial diffusion limited regime is identical to variational transition state theory.[5] Grabert and Pollak, Grabert and Hanggi (PGH) then used the normal mode representation of the dissipative Hamiltonian in the vicinity of the barrier to derive a continuum limit expression which was valid for any value of the friction, provided that the barrier height was much greater than the thermal energy $\left(V^{\ddagger} \gg k_B T\right)$.[6,7]

The theory was further refined to include in it the effect of a finite barrier, first in the spatial diffusion limit[8] then in the weakly damped to moderately damped regime within the Melnikov-Meshkov formulation[9] and lately also within the PGH formalism.[10,11] Our recent studies have demonstrated that the quality of both approaches is similar in the presence of Ohmic friction. Why then another paper, on a topic which seems to have been exhausted?

Only lately has it been demonstrated that the Kramers turnover may be observed in a "real" chemical system. Garcia-Muller et al[12,13] have shown this for the isomerization of LiCN to LiNC in the presence of an Ar solvent. They observed good agreement between numerical estimates of the rate and PGH theory, even though the reduced barrier height $V^{\ddagger}/k_B T$ was relatively low, in both cases studied by these authors it was 0.44 and 1.43. It is therefore of some practical interest to understand how limiting is the formal mathematical theory which imposes the condition of large reduced barriers for the PGH turnover theory to be valid.

But there are additional reasons for wanting to take a renewed look at theory. As already noted in Ref.,[14] in PGH theory the energy loss from the system to the bath is not a monotonic function of the friction strength, as it is in the MM formulation. This seems to be a bit nonphysical, one would expect that increasing the friction would always increase the energy loss to the surrounding. Of course, when the friction becomes large, the perturbation theory

which underlies the theory for the depopulation factor is no longer valid. However, a theory which combines the rigor of the PGH derivation and in which the energy loss is a monotonic function of the energy, would perhaps be preferable. This is one of the first results of the new approach to be presented in this paper.

A second drawback which has not been addressed previously is that in the derivation of the turnover expression, the lower limit for the energy is taken to be minus infinity. As long as $V^{\ddagger} \gg k_B T$ corrections to this assumption are exponentially small, of the order of $\exp\left(-V^{\ddagger}/k_B T\right)$. But when the reduced barrier height is of the order of unity, this simplifying assumption has to be corrected. Such a correction of the turnover theory is considered in the present paper.

A third drawback is that to date, PGH theory was never applied to the diffusion problem and with good reason. If one follows the PGH formalism, then although the system potential is periodic, the effective potential for the unstable mode is not. This result seems unphysical, challenging us to come up with a better formulation. The new PGH formalism presented here formally overcomes this difficulty.

The modification of PGH theory is not the first one to be attempted. It is of special interest to note the modified PGH theory proposed by Reese and Tucker.[15] They used a mean field approach for the motion along the unstable mode, in which the force is determined by a thermally averaged collective bath mode coordinate. They introduced this correction to account for reaction path curvature. In our present theory, the change in the equation of motion for the unstable mode is not temperature dependent, so that implementation is much simpler than the theory of Reese and Tucker.

Drozdov and Brey[16] suggested that the energy loss which is central to all turnover theories should not be computed from perturbation theory but from the zero-temperature generalized Langevin equation. However implementing this within the turnover theory formalism of MM or PGH is not derived, but taken as an ansatz. More recently, Mazo et al have considered separately in some detail finite barrier effects both in the underdamped[17] and in the spatial

diffusion limited regime of moderate to strong damping[18] however these authors do not relate directly to the turnover theories of MM and PGH.

The paper is structured as follows. In Section II we provide a brief review of PGH theory with finite barrier corrections. The improved formalism is then presented in Section III with finite barrier corrections that take into consideration the fact that the energy does not extend to minus infinity. Finally, in Section IV we consider the example of escape from a cubic potential, comparing theory with precise numerical simulation. We find that for a reduced barrier height of 4, over a range of four decades of the reduced friction coefficient, the error is at most 8 percent and typically, it is two percent or less. For a reduced barrier height of 2 the error over the same friction range, goes from an underestimate of 52 percent at low friction to an underestimate of 7 percent in the high friction range. The theory is most accurate in the turnover region, with the underestimate reaching less than 4 percent. We end in Section V with a discussion of the results, noting the limitations of the present approach when considering memory friction.

A brief review of PGH theory

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

$$\langle F(t)\,F(t')\rangle = Mk_BT\gamma(t-t')\,. \tag{2.2}$$

$\gamma(t)$ 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.[19] 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 denoted the frequency of the j-th normal mode. $\lambda^{\ddagger}$ denotes the unstable normal mode barrier frequency and it may be obtained with the Kramers-Grote-Hynes relation:[1,20]

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

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

$$\sqrt{M}q = u_{00}\rho + u_1\sigma \tag{2.6}$$

with

$$u_1\sigma = \sum_{j=1}^{N} u_{j0}y_j \tag{2.7}$$

and

$$u_1^2 = 1 - u_{00}^2 = \sum_{j=1}^{N} u_{j0}^2 \tag{2.8}$$

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:[7]

$$u_{00}^2 = \left[1 + \frac{1}{2}\left(\frac{\hat{\gamma}\left(\lambda^{\ddagger}\right)}{\lambda^{\ddagger}} + \frac{\partial \hat{\gamma}(s)}{\partial s}|_{s=\lambda^{\ddagger}}\right)\right]^{-1}. \tag{2.9}$$

Finally, the assumption of weak coupling between the system and the bath is expressed as:[7]

$$u_1^2 \ll 1. \tag{2.10}$$

The normal mode "friction kernel" is defined as:

$$K(t-t') = \sum_{j=1}^{N} \frac{u_{j0}^2}{\lambda_j^2} \cos\left[\lambda_j (t-t')\right]. \tag{2.11}$$

Using properties of the normal mode transformation (see for example Eq. 2.17 of Ref.[19]) one may readily express the Laplace transform (denoted by a "hat") of the kernel as

$$\hat{K}(s) = \left(\frac{s u_{00}^2}{\lambda^{\ddagger 2}\left(s^2 - \lambda^{\ddagger 2}\right)} + \frac{s + \hat{\gamma}(s)}{\omega^{\ddagger 2}\left(\omega^{\ddagger 2} - s^2 - \hat{\gamma}(s)\, s\right)}\right) \tag{2.12}$$

so that it is known in the continuum limit. Moreover, the spectral density of the stable modes is defined as:

$$I(\lambda) = \frac{\pi}{2} \sum_{j=1}^{N} \frac{u_{j0}^2}{\lambda_j} [\delta(\lambda - \lambda_j) - \delta(\lambda + \lambda_j)] \tag{2.13}$$

so that:

$$I(\lambda) = \lambda Re\left[\hat{K}(i\lambda)\right] = \frac{\lambda Re\left[\hat{\gamma}(i\lambda)\right]}{\left(\omega^{\ddagger 2} + \lambda^2\right)^2 + \lambda^2 \hat{\gamma}(i\lambda)\, \hat{\gamma}(-i\lambda)}. \tag{2.14}$$

The rate expression

In Kramers' turnover theory the rate factorizes as a product of three terms. One, is the "standard" transition state theory expression for the rate:

$$\Gamma_{TST} = \frac{\exp\left(-\beta V^{\ddagger}\right)}{(2\pi M\beta)^{1/2}\int_{-\infty}^{\infty} dq \exp\left(-\beta V\left(q\right)\right)\theta\left(-q\right)}. \tag{2.15}$$

The second factor is the spatial diffusion factor, better known as the Kramers-Grote-Hynes transmission factor[20]

$$\kappa_{SD}^{0} = \frac{\lambda^{\ddagger}}{\omega^{\ddagger}} \tag{2.16}$$

where the superscript 0 has been added to denote that this is the expression without finite barrier corrections. The spatial diffusion transmission factor is unity in the weak damping limit and goes to zero inversely with the damping strength in the strong damping limit.

The third factor, known as the depopulation factor accounts for the finite rate of exchange of energy between the system and the bath. It is determined completely by the average energy lost $\langle \Delta E \rangle$ to the bath, as the system traverses from the barrier over the well and back to the barrier. Introducing the reduced energy loss

$$\delta = \beta \langle \Delta E \rangle, \quad \beta = \frac{1}{k_B T}, \tag{2.17}$$

the depopulation factor, is then given by the expression

$$\Upsilon^{0} = \exp\left(\frac{1}{2\pi}\int_{-\infty}^{\infty} d\tau \frac{\ln\left[1-\tilde{P}^{0}\left(\tau-\frac{i}{2}\right)\right]}{\tau^{2}+\frac{1}{4}}\right) \tag{2.18}$$

where we used the notation:

$$\tilde{P}^{0}\left(\tau-\frac{i}{2}\right) = \exp\left[-\delta\left(\tau^{2}+\frac{1}{4}\right)\right] \tag{2.19}$$

and here too the superscript 0 serves to remind us that these are the expressions without finite barrier corrections. In the underdamped limit, the energy loss $\delta \ll 1$ and $\Upsilon^0 \simeq \delta$, in the strong damping limit, the energy loss becomes large and the depopulation factor goes to unity. The full turnover expression for the rate is then

$$\Gamma^0 = \Gamma_{TST}\kappa_{SD}^0\Upsilon^0 \tag{2.20}$$

and here too the superscript is used to denote that this is the result without finite barrier corrections.

Finite barrier corrections

Finite barrier corrections in the spatial diffusion limited regime have been derived by Pollak and Talkner (Eq. 4.4 of Ref.[8]). The spatial diffusion factor for a cubic potential is:

$$\frac{\kappa_{SD}}{\kappa_{SD}^0} = 1 + \frac{1}{36\beta V^{\ddagger}\chi^2}\left(2 - 3\chi - \frac{6\left(\chi+1\right)\lambda^{\ddagger 6}}{\pi^2 u_{00}^4}\int_{-\infty}^{\infty} d\lambda \int_{-\infty}^{\infty} d\lambda' \frac{I\left(\lambda\right) I\left(\lambda'\right)}{\lambda\lambda'\left[\lambda^{\ddagger 2} + \left(\lambda+\lambda'\right)^2\right]}\right) \tag{2.21}$$

and the "nonlinearity parameter" χ is:

$$\chi^{-1} = \frac{u_{00}^2\omega^{\ddagger 2}}{\lambda^{\ddagger 2}} - 1. \tag{2.22}$$

Finite barrier corrections to the depopulation factor have been recently derived within the PGH formalism.[10,11] Following Mel'nikov,[9] one considers, using perturbation theory, the temperature and energy dependence of the energy loss to leading order. Taking the barrier energy to be the zero of the energy of the system and using ε to denote the reduced energy in terms of $k_B T$, the average energy loss is expanded as:[11]

$$\beta\left\langle \Delta E_B \right\rangle \simeq \delta\left(1 - \mu + \mu\varepsilon\right). \tag{2.23}$$

An expression for the expansion parameter μ will be given in the next Section. The finite barrier corrected depopulation factor is then:

$$\Upsilon = \Upsilon^0 \exp\left(-\mu\Phi^2(\delta)\left[1+\frac{\delta+2}{8}\right]+\frac{\mu(\delta-2)}{4}\Phi(\delta)\right) \tag{2.24}$$

with

$$\Phi(\delta) = \frac{\delta}{2\pi}\int_{-\infty}^{\infty} d\tau \frac{\tilde{P}^0\left(\tau-\frac{i}{2}\right)}{1-\tilde{P}^0\left(\tau-\frac{i}{2}\right)}. \tag{2.25}$$

A new PGH theory

The modified theory

The normal mode Hamiltonian may be rewritten exactly as:

$$H = \frac{p_\rho^2}{2} + V\left(\frac{u_{00}\rho+u_1\sigma}{\sqrt{M}}\right) + \frac{1}{2}\omega^{\ddagger 2}\left(u_{00}\rho+u_1\sigma\right)^2 - \frac{1}{2}\lambda^{\ddagger 2}\rho^2 + \frac{1}{2}\sum_{j=1}^{N}\left[p_{y_j}^2+\lambda_j^2 y_j^2\right]. \tag{3.1}$$

In the "standard" PGH theory one assume that the coupling parameter u_1 is the small parameter of the problem so that to zero-th order the motion of the unstable mode is governed by the Hamiltonian

$$H_{\rho,PGH} = \frac{p_\rho^2}{2} + V\left(\frac{u_{00}\rho}{\sqrt{M}}\right) + \frac{1}{2}\left(\omega^{\ddagger 2}u_{00}^2 - \lambda^{\ddagger 2}\right)\rho^2. \tag{3.2}$$

The effective potential appearing here is qualitatively different from the potential $V(q)$, for example, the barrier height for escape now becomes dependent on the friction. Or, even if $V(q)$ is a periodic potential, the potential governing the unstable mode motion is no longer periodic due to the quadratic term.

To overcome these difficulties we define a coordinate $\sigma^*(\rho)$ by demanding that

$$\omega^{\ddagger 2}\left(u_{00}\rho+u_1\sigma^*\right)^2 = \lambda^{\ddagger 2}\rho^2. \tag{3.3}$$

Using then the notation

$$u_1\sigma = u_1\sigma^* + u_1\Delta\sigma \tag{3.4}$$

so that:

$$u_1\Delta\sigma = u_1\sigma + \left(u_{00} - \frac{\lambda^\ddagger}{\omega^\ddagger}\right)\rho \tag{3.5}$$

we have that the exact Hamiltonian is:

$$H = \frac{p_\rho^2}{2} + V\left[\frac{1}{\sqrt{M}}\left(\frac{\lambda^\ddagger}{\omega^\ddagger}\rho + u_1\Delta\sigma\right)\right] + \omega^\ddagger\lambda^\ddagger\rho u_1\Delta\sigma + \frac{1}{2}\omega^{\ddagger 2}u_1^2\Delta\sigma^2 + \frac{1}{2}\sum_{j=1}^{N}\left[p_{y_j}^2 + \lambda_j^2 y_j^2\right]. \tag{3.6}$$

We will then consider the "small parameter" to be $u_1\Delta\sigma$.

Note that for a parabolic barrier potential:

$$\begin{aligned} & V_{pb}\left[\frac{1}{\sqrt{M}}\left(\frac{\lambda^\ddagger}{\omega^\ddagger}\rho + u_1\Delta\sigma\right)\right] + \omega^\ddagger\lambda^\ddagger\rho u_1\Delta\sigma + \frac{1}{2}\omega^{\ddagger 2}u_1^2\Delta\sigma^2 \\ = & -\frac{1}{2}\omega^{\ddagger 2}\left(\frac{\lambda^\ddagger}{\omega^\ddagger}\rho + u_1\Delta\sigma\right)^2 + \omega^\ddagger\lambda^\ddagger\rho u_1\Delta\sigma + \frac{1}{2}\omega^{\ddagger 2}u_1^2\Delta\sigma^2 \\ = & -\frac{1}{2}\lambda^{\ddagger 2}\rho^2 \end{aligned} \tag{3.7}$$

in other words, for a parabolic barrier we regain the separable dynamics of the normal modes. Any coupling between the unstable mode and the stable modes necessarily comes from the nonlinear part of the potential. This also means that the Hamiltonian may be recast as:

$$H = \frac{p_\rho^2}{2} - \frac{1}{2}\lambda^{\ddagger 2}\rho^2 + V_1\left(\frac{1}{\sqrt{M}}\left(\frac{\lambda^\ddagger}{\omega^\ddagger}\rho + u_1\Delta\sigma\right)\right) + \frac{1}{2}\sum_{j=1}^{N}\left[p_{y_j}^2 + \lambda_j^2 y_j^2\right]. \tag{3.8}$$

The zero-th order dynamics of the unstable normal mode will then be determined by the

zero-th order unstable mode Hamiltonian

$$\begin{aligned} H_\rho &= \frac{p_\rho^2}{2} + V\left(\frac{\lambda^\ddagger}{\sqrt{M}\omega^\ddagger}\rho\right) \\ &= \frac{p_\rho^2}{2} - \frac{1}{2}\lambda^{\ddagger 2}\rho^2 + V_1\left(\frac{\lambda^\ddagger}{\sqrt{M}\omega^\ddagger}\rho\right) \end{aligned} \tag{3.9}$$

in other words, close to the barrier top, the zero-th order barrier remains the same as before, it is quadratic in the unstable mode coordinate. The central differences between this representation and the previous one is that the added quadratic term has been eliminated and the argument of the nonlinear part of the potential has changed from $u_{00}\rho/\sqrt{M}$ to $\lambda^\ddagger\rho/\left(\sqrt{M}\omega^\ddagger\right)$. This means that the shape of the potential has not changed, only the effective mass of the motion is now $M\omega^{\ddagger 2}/\lambda^{\ddagger 2}$, or in other words, friction has led to a heavier effective mass. The zero-th order dynamics of the bath remains the same as a collection of uncoupled harmonic oscillators.

Following the "standard" PGH formalism, the Hamiltonian is then expanded to first order in $u_1\Delta\sigma$:

$$H \simeq H_\rho + V_1'\left(\frac{\lambda^\ddagger}{\sqrt{M}\omega^\ddagger}\rho\right)\frac{u_1\Delta\sigma}{\sqrt{M}} + \frac{1}{2}\sum_{j=1}^{N}\left[p_{y_j}^2 + \lambda_j^2 y_j^2\right] \tag{3.10}$$

where the prime denotes differentiation with respect to the argument. The first order equation of motion for the j-th bath oscillator is then:

$$\ddot{y}_{j_t,1} = -\lambda_j^2 y_{j_t,1} - \frac{u_{j0}}{\sqrt{M}}V_1'\left(\frac{\lambda^\ddagger}{\sqrt{M}\omega^\ddagger}\rho_{t,0}\right) \tag{3.11}$$

so that $y_{j_t,1}$ is obtained as the solution for a forced harmonic oscillator:

$$y_{j_t,1} = -\frac{u_{j0}}{\sqrt{M}}\int_{-\infty}^{t} dt' \frac{\sin\left[\lambda_j\left(t-t'\right)\right]}{\lambda_j} V_1'\left(\frac{\lambda^\ddagger}{\sqrt{M}\omega^\ddagger}\rho_{t',0}\right). \tag{3.12}$$

The reduced average energy gained by the bath as the unstable mode traverses from the

barrier over the well and back to the barrier is given by:

$$\delta \equiv \frac{\beta}{2M}\int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' V_1'\left(\frac{\lambda^{\ddagger}\rho_{t,0}}{\sqrt{M}\omega^{\ddagger}}\right)\frac{\partial^2 K\left(t-t'\right)}{\partial t \partial t'} V_1'\left(\frac{\lambda^{\ddagger}\rho_{t',0}}{\sqrt{M}\omega^{\ddagger}}\right). \tag{3.13}$$

Using the definition of the spectral density of normal modes, this may then be recast in the more convenient form:

$$\delta = \frac{\beta}{2\pi M}\int_{-\infty}^{\infty} d\lambda \lambda I(\lambda)\left|\int_{-\infty}^{\infty} dt \exp\left(-i\lambda t\right) V_1'\left(\frac{\lambda^{\ddagger}\rho_{t,0}}{\sqrt{M}\omega^{\ddagger}}\right)\right|^2. \tag{3.14}$$

These last two expression lie at the heart of the "improved" PGH theory, the form is similar to the "old" PGH expression for the energy loss, it differs however, since the argument of the force in the old theory $\frac{u_{00}\rho_{t,0}}{\sqrt{M}}$ is replaced by $\frac{\lambda^{\ddagger}\rho_{t,0}}{\sqrt{M}\omega^{\ddagger}}$ in the new theory and the equation of motion governing the zero-th order dynamics of the unstable mode has also been modified.

Similarly, following the derivation as presented in Ref.[11] but using the new perturbation theory formulation, one readily finds that the expansion parameter μ (Eq. 2.23) is given by:

$$\mu = -\frac{1}{\delta}\int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' \frac{dV_1'\left(\frac{\lambda^{\ddagger}\rho_{t,0}}{\sqrt{M}\omega^{\ddagger}}\right)}{dt}\frac{\partial K\left(t'-t\right)}{\partial t}\frac{dV_1'\left(\frac{\lambda^{\ddagger}\rho_{t',0}}{\sqrt{M}\omega^{\ddagger}}\right)}{dt'}\int_{t'}^{t} dt'' \frac{1}{p^2_{\rho_{t''},0}}. \tag{3.15}$$

The only difference between this expression and the analogous one given in Ref.[11] is as before when considering the energy loss, the argument of the force is now $\frac{\lambda^{\ddagger}}{\sqrt{M}\omega^{\ddagger}}\rho_t$ instead of $\frac{u_{00}}{\sqrt{M}}\rho_t$, and the zero-th order trajectory is governed by the modified zero-th order Hamiltonian (Eq. 3.9). It is worthwhile to recast this expression in terms of the spectral density of the normal modes. Using the notation

$$X\left(t\right) = \int^{t} dt' \frac{1}{p^2_{\rho_{t'},0}}, \tag{3.16}$$

one finds after some manipulations that:

$$\mu = -\frac{2}{\pi\delta}\int_0^\infty d\lambda I(\lambda)\int_{-\infty}^{\infty} dtX(t)\cos(\lambda t)\frac{dV_1'\left(\frac{\lambda^\ddagger\rho_{t,0}}{\sqrt{M}\omega^\ddagger}\right)}{dt}\int_{-\infty}^{\infty} dt\sin(\lambda t)\frac{dV_1'\left(\frac{\lambda^\ddagger\rho_{t,0}}{\sqrt{M}\omega^\ddagger}\right)}{dt}. \tag{3.17}$$

Finite barrier correction to the transition kernel

The derivation of finite barrier corrections to the depopulation factor were predicated on the assumption that the energy of the particle varies from $-\infty$ to ∞. This is not precise, since the reduced energy of the unstable mode cannot be lower than the bottom of the well in which the particle is trapped. To account for this, one must limit the (reduced) energy integration to the interval $\left[-\beta V^\ddagger, \infty\right]$. More specifically, in the absence of finite barrier corrections, the (reduced) energy transfer probability kernel for the particle initiated at the barrier with (reduced) energy ε to return to the barrier with energy ε' is the Gaussian kernel:

$$P^0(\varepsilon'|\varepsilon) = \frac{1}{\sqrt{4\pi\delta}}\exp\left(-\frac{(\varepsilon'-\varepsilon+\delta)^2}{4\delta}\right). \tag{3.18}$$

The two sided Laplace transform of this kernel is:

$$\begin{aligned}\tilde{P}^0(is) &= \int_{-\infty}^{\infty} d\varepsilon'\exp(-s\varepsilon')P^0(\varepsilon'|\varepsilon) \\ &= \exp\left[\delta\left(s^2+s\right)\right]\end{aligned} \tag{3.19}$$

where explicitly the integration is over the real axis, that is $[-\infty,\infty]$. This was then used in Eq. 2.18 for the depopulation factor and in Eq. 2.25 for the finite barrier correction to it.

If one limits the integration to the interval $\left[-\beta V^\ddagger, \infty\right]$ one has that:

$$\begin{aligned}\tilde{P}(is;\varepsilon) &= \int_{-\beta V^\ddagger}^{\infty} d\varepsilon'\exp(-s\varepsilon')P^0(\varepsilon'|\varepsilon) \\ &= \frac{1}{2}\exp\left[\delta\left(s^2+s\right)\right]\exp(-s\varepsilon)\,\mathrm{erfc}\left(\frac{-\beta\mathrm{V}^\ddagger-\varepsilon+\delta+2\delta\mathrm{s}}{2\sqrt{\delta}}\right).\end{aligned} \tag{3.20}$$

Expanding this expression about $\varepsilon = 0$ and considering only the zero-th order term gives:

$$\tilde{P}\left(\tau - \frac{i}{2}\right) \equiv \tilde{P}\left(\tau - \frac{i}{2}; \varepsilon = 0\right). \tag{3.21}$$

In the limit that $\beta V^{\ddagger} \to \infty$ the erfc term tends to 2 and we have regained the "standard" kernel. The finite barrier correction is then obtained by replacing the kernel $\tilde{P}^0\left(\tau - \frac{i}{2}\right)$ in Eqs. 2.18 and 2.25 with the corrected kernel $\tilde{P}\left(\tau - \frac{i}{2}\right)$. We will refer below to the corrected kernel as the "EXP" correction, indicating that the correction is exponentially dependent on the reduced barrier height.

As already noted, this "EXP" correction is significant only when the reduced barrier height is of the order of unity. In the underdamped limit, where the energy loss $\delta \to 0$ the erfc term again tends to 2 irrespective of the value of $\beta V^{\ddagger}$, so that this correction becomes insignificant. Conversely, in the strong friction limit δ becomes very large such that $\tilde{P}^0\left(\tau - \frac{i}{2}\right)$ becomes very small, and again this correction becomes insignificant. It is important mainly in the turnover region.

Application to a cubic potential with Ohmic friction

For Ohmic friction

$$\gamma(t) = 2\gamma\delta(t) \tag{4.1}$$

where $\delta(t)$ is the Dirac "delta" function, the spectral density of normal modes is:

$$I(\lambda) = \frac{\lambda\gamma}{\left(\omega^{\ddagger 2} + \lambda^2\right)^2 + \lambda^2\gamma^2}. \tag{4.2}$$

For the cubic potential

$$V(q) = -\frac{M\omega^{\ddagger^2}}{2} q^2 \left(1 + \frac{q}{q_0}\right) \tag{4.3}$$

the barrier is located at $q = 0$ and the well at $q = -2q_0/3$, The barrier height is thus

$$V^{\ddagger} = \frac{2M\omega^{\ddagger^2} q_0^2}{27}. \tag{4.4}$$

The time dependence of the coordinate for the trajectory initiated at $t \to -\infty$ at the barrier towards the well and returning to the barrier as $t \to \infty$ is:

$$q_t = -\frac{q_0}{\cosh^2\left(\frac{\omega^{\ddagger} t}{2}\right)}. \tag{4.5}$$

The potential energy governing the motion of the unstable mode is (Eq. 3.9):

$$V(\rho) = -\frac{\lambda^{\ddagger 2}\rho^2}{2}\left(1 + \frac{\lambda^{\ddagger}}{\omega^{\ddagger}\sqrt{M}q_0}\rho\right) \tag{4.6}$$

so that the "effective" q_0 is:

$$q_{0,NEW} = \frac{\omega^{\ddagger}\sqrt{M}}{\lambda^{\ddagger}} q_0 \tag{4.7}$$

and the time dependence for the unstable mode is:

$$\rho_{t,0,NEW} = -\frac{\omega^{\ddagger}\sqrt{M}q_0}{\lambda^{\ddagger}\cosh^2\left(\frac{\lambda^{\ddagger}}{2}t\right)}. \tag{4.8}$$

In the old theory

$$V_{PGH}(\rho) = -\frac{\lambda^{\ddagger 2}\rho^2}{2}\left(1 + \frac{\omega^{\ddagger^2}}{\lambda^{\ddagger 2}q_0}\frac{u_{00}^3\rho}{\sqrt{M}}\right) \tag{4.9}$$

so that the "effective" q_0 is

$$q_{0,PGH} = \frac{\lambda^{\ddagger 2}\sqrt{M}}{\omega^{\ddagger^2}u_{00}^3} \tag{4.10}$$

and the time dependence for the unstable mode is:

$$\rho_{t,0,PGH} = -\frac{\lambda^{\ddagger 2}\sqrt{M}q_0}{\omega^{\ddagger^2}u_{00}^3\cosh^2\left(\frac{\lambda^{\ddagger}}{2}t\right)} \tag{4.11}$$

and

$$\frac{q_{0,PGH}}{q_{0,NEW}} = \frac{\lambda^{\ddagger 3}}{\omega^{\ddagger^3} u_{00}^3}. \tag{4.12}$$

Using Eq. 3.14 it is a matter of some algebra to show that the "new" energy loss is:

$$\delta = 108\pi\beta V^{\ddagger}\nu\left(\nu - 1\right) M_4\left(\nu\right) \tag{4.13}$$

where the friction dependent parameter ν is the ratio of the two solutions of the Kramers equation (Eq. 2.5)

$$\nu = \frac{\gamma + \sqrt{\gamma^2 + 4\omega^{\ddagger 2}}}{\sqrt{\gamma^2 + 4\omega^{\ddagger 2}} - \gamma} \tag{4.14}$$

and[14]

$$M_4\left(\nu\right) = \frac{2}{5\pi} - \frac{\nu^2}{3\pi} + \frac{2}{\pi}\nu^3\left(\nu^2 - 1\right)\psi'\left(\nu\right) - \frac{2}{\pi}\nu^2\left(\nu^2 - 1\right) - \frac{1}{\pi}\nu\left(\nu^2 - 1\right) \tag{4.15}$$

with

$$\psi'\left(\nu\right) = \sum_{n=0}^{\infty}\frac{1}{\left(\nu + n\right)^2}. \tag{4.16}$$

The result for the new energy loss (Eq. 4.13) should be compared with the "standard" PGH result

$$\delta_{PGH} = \frac{27\pi}{4}\beta V^{\ddagger} M_4\left(\nu\right)\left(\nu - 1\right)\frac{\left(\nu + 1\right)^4}{\nu^3} \tag{4.17}$$

and the MM result:

$$\delta_{MM} = \frac{36\left(\nu - 1\right)}{5\sqrt{\nu}}\beta V^{\ddagger} = \frac{36}{5}\beta V^{\ddagger}\frac{\gamma}{\omega^{\ddagger}}. \tag{4.18}$$

From Eqs. 4.13 and 4.17 one readily finds that

$$\frac{\delta}{\delta_{PGH}} = \frac{16\nu^4}{\left(\nu + 1\right)^4} = \left(\frac{\omega^{\ddagger 4} u_{00}^4}{\lambda^{\ddagger 4}}\right)^2 \tag{4.19}$$

In the weak damping limit $\frac{\omega^{\ddagger 4} u_{00}^4}{\lambda^{\ddagger 4}} \to 1$ so that the new and old energy losses are identical and both reduce to the MM result in this limit.

In the strong damping limit $\nu \simeq \frac{\gamma^2}{\omega^{\ddagger 2}}$ and $\lim_{\nu\to\infty} \nu^2 M_4(\nu) = \frac{4}{35\pi}$ so that:

$$\lim_{\gamma\to\infty} \delta = \frac{432}{35}\beta V^{\ddagger}. \tag{4.20}$$

The energy loss does not diverge, however it is a factor of 16 larger than the energy loss found in the "standard" PGH theory. More generally, for Ohmic friction the parameter $1 \leq \nu \leq \infty$ so that for any value of the friction $\delta \geq \delta_{PGH}$.

In Fig. 1 we plot the three energy losses as a function of the reduced friction $(\gamma/\omega^{\ddagger})$ with $\beta V^{\ddagger} = 1$ (the magnitude of the barrier is trivial for this purpose, since all three energy losses scale linearly with the reduced barrier height).

One notes that while the MM energy loss goes linearly to infinity, the new energy loss is practically identical to the MM energy loss for $\gamma/\omega^{\ddagger} \leq 1$, diverging from it only for higher values, but increasing monotonically with the friction strength. This good agreement implies that the two theories will give results which are quite close to each other for any value of the friction. This is shown in Fig. 2 where we plot the ratio of the depopulation factor obtained with the new theory to the MM result as a function of the friction strength, for $\beta V^{\ddagger} = 4$ and 2.

The PGH energy loss is always lower than the other two and has an un-physical maximum which reflects the competition between the increasing coupling to the bath, which increases the energy loss and the lowering of the effective barrier height for the zero-th order motion in the PGH formalism. As noted, in the new theory, the barrier height remains unchanged so that the energy loss always increases with increasing friction and the un-physical maximum is removed.

It is a matter of some algebra, noting that (see Eq. 3.16)

$$X(t) = \frac{2\cosh^5\left(\frac{\lambda^{\ddagger}}{2}t\right) + 5\cosh^3\left(\frac{\lambda^{\ddagger}}{2}t\right) - 15\cosh\left(\frac{\lambda^{\ddagger}}{2}t\right) + 15\left(\frac{\lambda^{\ddagger}}{2}t\right)\sinh\left(\frac{\lambda^{\ddagger}}{2}t\right)}{4\lambda^{\ddagger}M\omega^{\ddagger 2}q_0^2\sinh\left(\frac{\lambda^{\ddagger}}{2}t\right)} \tag{4.21}$$

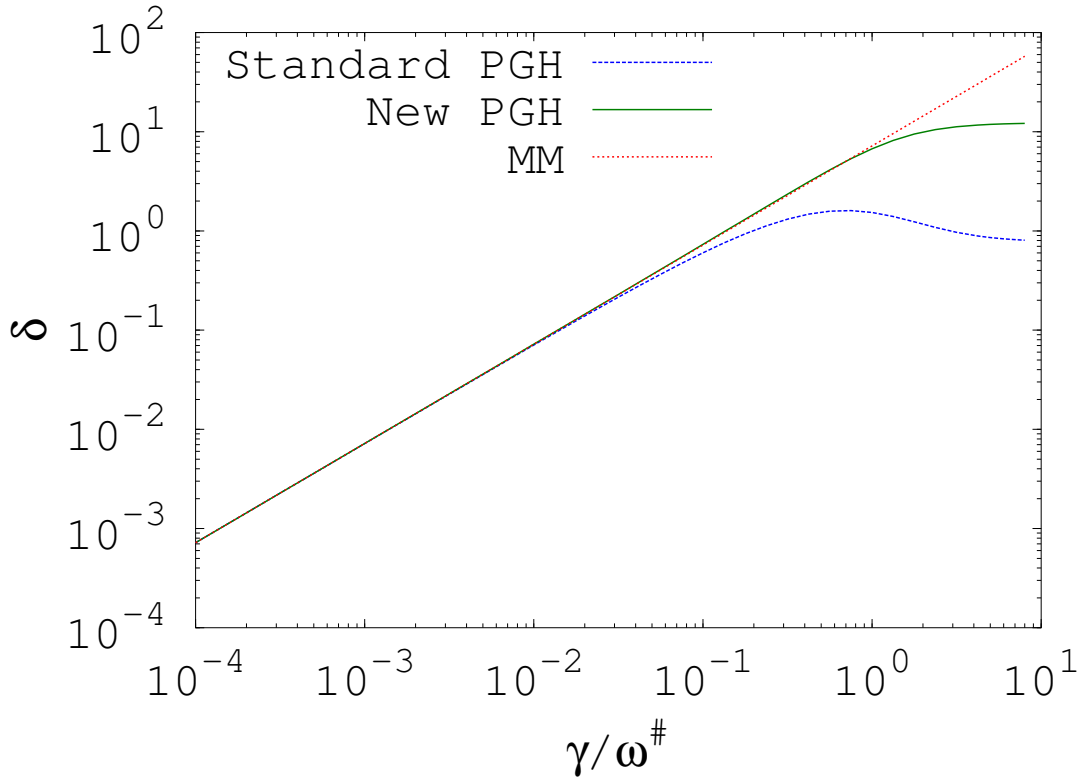


Figure 1: (color online) The reduced energy loss δ is shown as a function of the reduced friction ($\gamma/\omega^{\ddagger}$) for "standard" PGH theory (blue, dashed line), the new PGH theory (green, solid line) and MM theory (red, straight dotted line). Note that the NEW PGH estimate agree with the MM estimate for $\delta \leq 10$ and increases monotonically, while the PGH estimate starts decreasing when $\gamma/\omega^{\ddagger} \simeq 1$.

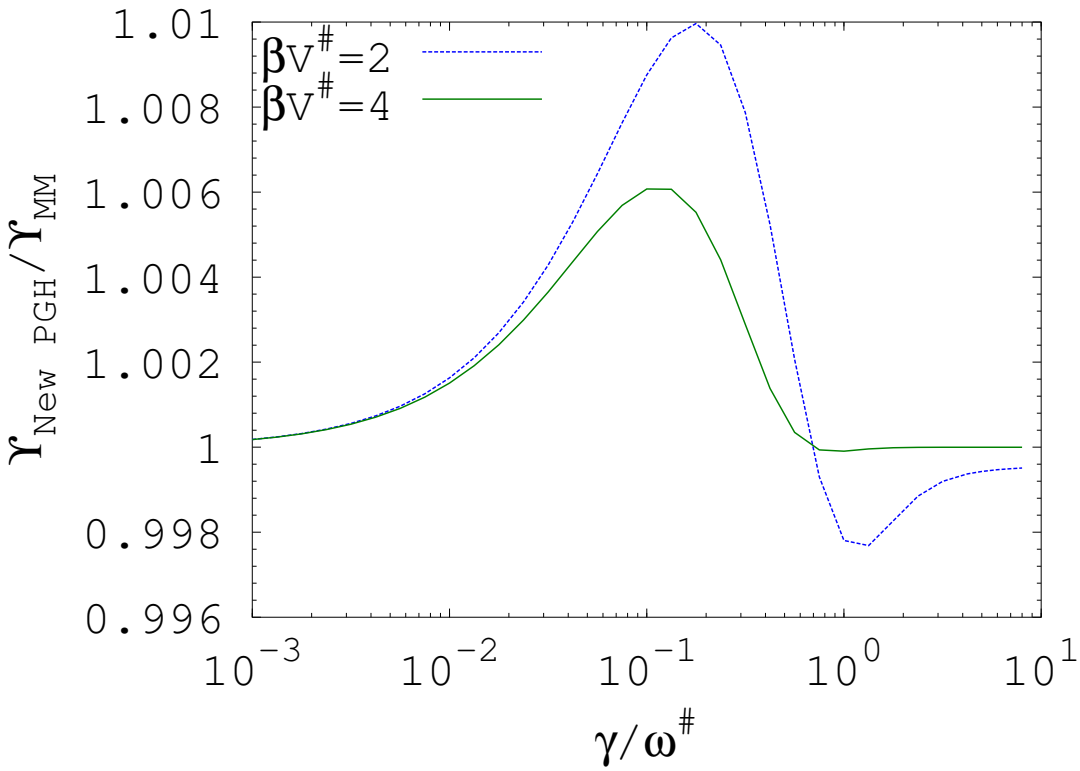


Figure 2: The ratio between the depopulation factor obtained from the new PGH theory and the depopulation factor obtained from MM theory for $\beta V^{\ddagger} = 4$ and $\beta V^{\ddagger} = 2$. The two estimates are very close to each other over the whole friction range.

to find that the finite barrier correction parameter (Eq. 3.15) is

$$\mu = \frac{1}{\delta}\left(-5\nu\left(6\nu^5 - 9\nu^3 - 3\nu^2 + 2\nu + 4\right) + 60\left(\nu - 1\right)\nu^5\left(\nu^2 - 1\right)\sum_{k=0}^{\infty}\frac{1}{\left(\nu + k\right)^3}\right). \tag{4.22}$$

In the underdamped regime, one readily finds that

$$\lim_{\gamma\to 0}\mu = \frac{25}{36\beta V^{\ddagger}} \tag{4.23}$$

implying that especially for low barriers, one cannot neglect the finite barrier corrections. Conversely, in the strong damping limit

$$\lim_{\gamma\to\infty}\mu = \frac{175}{216\beta V^{\ddagger}}. \tag{4.24}$$

The ratio of the strong to weak friction limit is $7/6 \simeq 1$. The correction parameter is thus almost a constant over the whole friction range.

In Fig. 3 we consider the quality of the improved theory. We compare the theoretical transmission factor without finite barrier corrections, defined as

$$\kappa^0 = \frac{\Gamma^0}{\Gamma_{TST}} = \kappa^0_{SD}\Upsilon^0 \tag{4.25}$$

where the spatial diffusion factor is the Kramers-Grote-Hynes expression (Eq. 2.16) and Υ^0 is the depopulation factor without finite barrier corrections, as given in Eq. 2.18 with numerically exact simulations (solid circles). The numerics were carried out as described in Ref.[11] and are highly accurate (error of $1 \cdot 10^{-6}$). We checked that the numerically computed results are independent of the initial condition chosen. They are compared with three different theories. The solid line shows the result based on the improved formulation of PGH theory for the energy loss (Eq. 4.13), the dashed line is based on the "standard" PGH theory where the energy loss is given by Eq. 4.17 and the dotted line is the result of MM

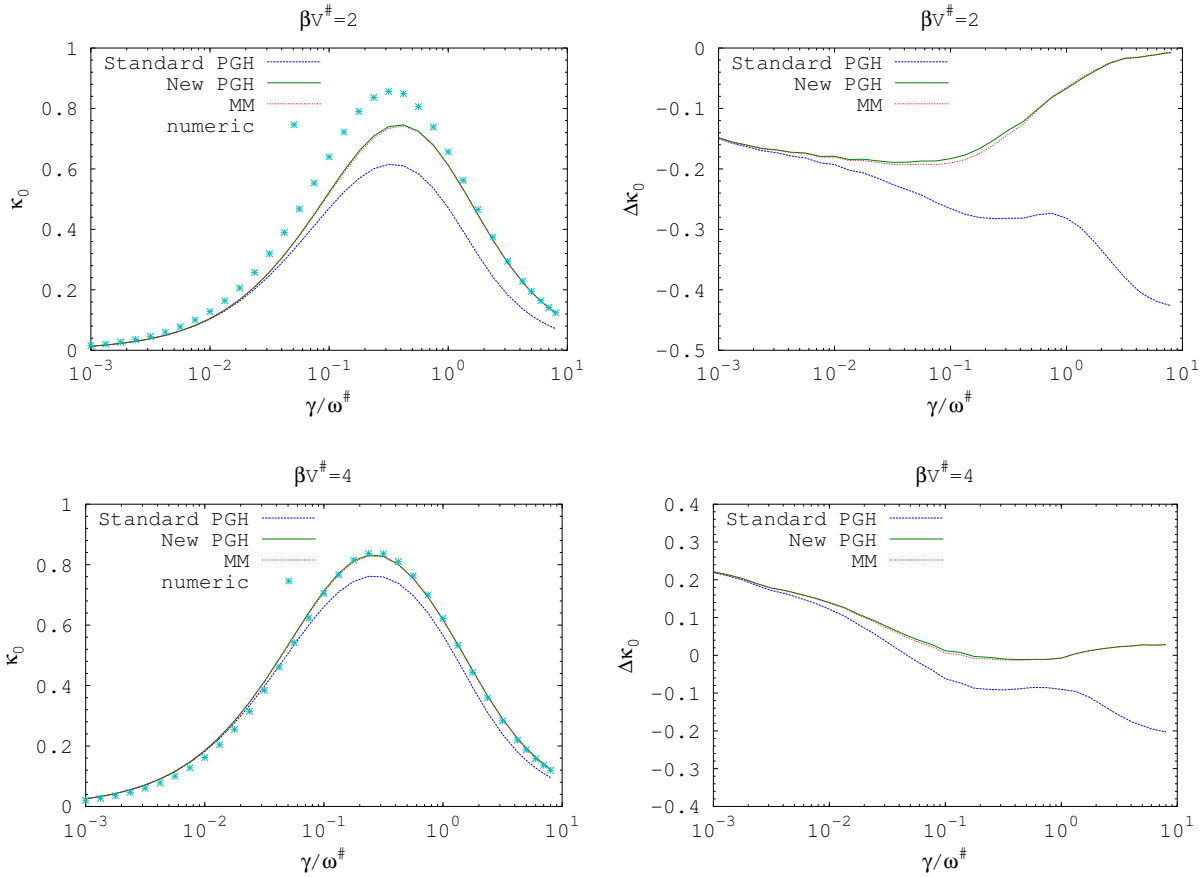


Figure 3: (color online) Transmission factors and relative errors without finite barrier corrections for the standard PGH theory (blue, dashed line), new PGH theory (green, solid line) and MM theory (red, dotted line), for $\beta V^{\ddagger} = 2$ (upper panels) and 4 (lower panels). The green asterisks denote the numerically exact transmission factors. Note that MM theory and the new PGH theory are almost identical and more accurate than the "standard" PGH theory.

theory (energy loss given by Eq. 4.18). The left panels show the results for the transmission factor for $\beta V^{\ddagger} = 2$ (upper panel) and $\beta V^{\ddagger} = 4$ (lower panel) as functions of the reduced friction coefficient. The right panels show the relative errors of the various estimates, defined as

$$\Delta\kappa_i^0 = \frac{\kappa_i^0 - \kappa_{ex}}{\kappa_{ex}}, \quad i = MM, PGH, NEW. \tag{4.26}$$

In all cases, MM and the new PGH theory are very close to each other, as already noted above, their respective energy losses are very similar in the range of friction for which the depopulation factor is significantly different from unity. In comparison, the "standard" PGH theory is much less accurate, especially in the moderate to strong friction range, this is due to the lack of monotonicity of the PGH energy loss as a function of the damping, which leads to a depopulation factor in the strong damping limit which is $0.743, 0.539$ for $\beta V^{\ddagger} = 4, 2$ respectively, while for the new PGH, the depopulation factor in this limit tends to $0.9999993, 0.9995$ respectively. The MM depopulation factor tends to unity in both cases, since the MM energy loss diverges in the strong friction limit.

These results already imply that the modified turnover theory is superior to the "standard" PGH theory, in the moderate to strong damping regimes. The relative errors are however, not negligible, already for a reduced barrier height of 4. As noted in our previous computations, the introduction of finite barrier corrections improves the estimates. However, a word of caution, the finite barrier corrected PGH results shown in Fig. 4 are based on ad-hoc corrected theory, both for the MM result as well as the PGH results, where we imposed the condition that the PGH energy loss function does not go down in the strong friction limit.

One of the central improvements of the modified PGH theory presented in this paper is that indeed the energy loss is a monotonically increasing function of the friction strength, and the resulting theory has no ad-hoc correction to it. Formally, it is thus also superior to the MM finite barrier corrected theory which also employs an ad-hoc correction term to extend it into the moderate to strong damping regime.

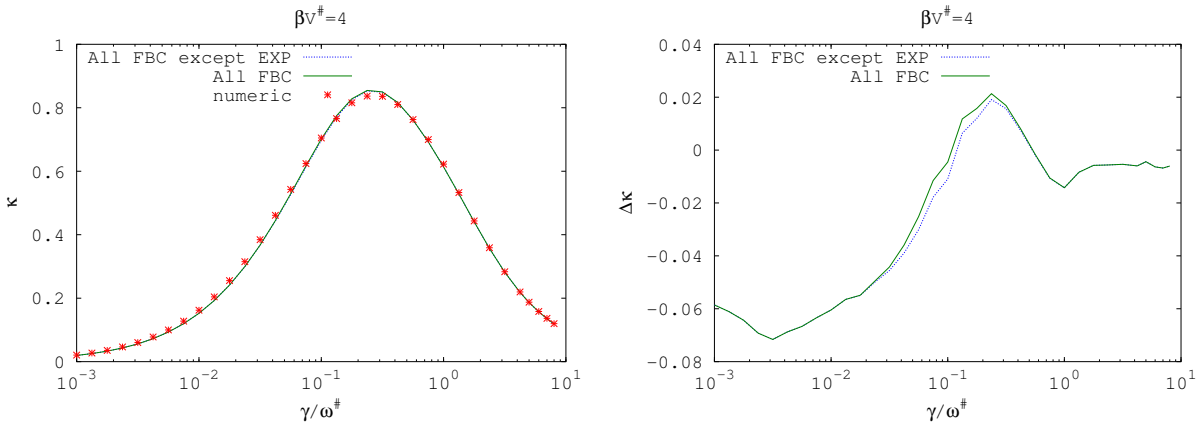


Figure 4: (color online) Finite barrier corrected transmission factors and relative errors for the new PGH theory for $\beta V^{\ddagger} = 4$. The solid, green line denotes the results when including all finite barrier corrections, including the EXP term, the dotted blue line shows the results including all finite barrier corrections, excluding the EXP correction to the transition probability kernel and the asterisks are the numerically exact results. For this barrier height the EXP correction is negligible, and the finite barrier corrected result is quite accurate over the whole friction range.

In Fig. 4 we consider the finite barrier corrected theory for $\beta V^{\ddagger} = 4$. The left panel presents a comparison between the numerically exact results and the finite barrier corrected transmission factor

$$\kappa = \kappa_{SD} \Upsilon$$

where κ_{SD} for the cubic potential was defined in Eq. 2.21 and its explicit form for the Ohmic friction is given in Eq. 4.12 of Ref.[8] The finite barrier corrected depopulation factor (Υ) was defined in Eq. 2.24. The numerically exact results are the solid circles, the solid line shows the theoretical results obtained using the finite barrier correction estimate (2.24) with the finite barrier corrected kernel as given in Eq. 3.21. The dotted line, is the same but replacing $\frac{1}{2}\mathrm{erfc}\left(\frac{-\beta \mathrm{V}^{\ddagger} - \mathrm{i}2\delta\tau}{2\sqrt{\delta}}\right)$ with unity in Eq. 3.21, that is ignoring the finite barrier correction to the kernel. The relative error is shown on the right panel. It is remarkable, that even though the reduced barrier is quite low, the error in the theoretical estimate is less than 8% and this only in the very weak damping regime. Secondly, there is hardly any difference between

the results based on the finite barrier corrected kernel (solid line) and the kernel without the correction (dotted line). As already noted, for $\beta V^{\ddagger} = 4$ this correction is very close to unity, since $\exp(-4) \simeq 0.018$.

The same comparison is presented in Fig. 5 but here, for $\beta V^{\ddagger} = 2$. The numerical results are given in Table 1. First one notes the relatively large error in the estimate for the rate

Table 1: Numerical escape rates for a cubic potential with two reduced barrier heights $\beta V^{\ddagger} = 2, 4$. The values of Γ_{TST} for the respective reduced barrier heights are 7.2961×10^{-2} and 1.0198×10^{-2}.

$\gamma/\omega^{\ddagger}$	$\beta V^{\ddagger} = 2$	$\beta V^{\ddagger} = 4$		$\gamma/\omega^{\ddagger}$	$\beta V^{\ddagger} = 2$	$\beta V^{\ddagger} = 4$	
0.001	1.1380e-03	2.1061e-04		0.133352	0.052664	7.8109e-03	
0.001333521	1.4997e-03	2.7579e-04		0.17783	0.057628	7.8109e-03	
0.001778279	1.9674e-03	3.6091e-04		0.237137	0.061017	8.5338e-03	
0.002371373	2.5785e-03	4.7221e-04		0.31623	0.062466	8.5246e-03	
0.003162277	3.3586e-03	6.1463e-04		0.421697	0.061958	8.2618e-03	
0.004216965	4.3710e-03	7.9286e-04		0.56234	0.058823	7.7798e-03	
0.005623413	5.6508e-03	1.0193e-03		0.749894	0.053887	7.1368e-03	
0.007498942	7.3090e-03	1.3019e-03		1.0	0.047874	6.3485e-03	
0.01	9.3355e-03	1.6530e-03		1.333521	0.040992	5.4333e-03	
0.013335	0.011928	2.0809e-03		1.7783	0.033965	4.5212e-03	
0.017783	0.015015	2.6038e-03		2.371374	0.027312	3.6598e-03	
0.023714	0.018805	3.2128e-03		3.1623	0.021493	2.8887e-03	
0.031623	0.023303	3.9193e-03		4.216965	0.016671	2.2396e-03	
0.042170	0.028422	4.7029e-03		5.0	0.014229	1.9105e-03	
0.056234	0.034117	5.5358e-03		6.0	0.011967	1.6115e-03	
0.074989	0.040379	6.3651e-03		7.0	0.010303	1.3906e-03	
0.1	0.046683	7.1873e-03		8.0	9.0473e-03	1.2209e-03	

in the underdamped regime. In this limit, the term $\frac{1}{2}\mathrm{erfc}\left(\frac{-\beta V^{\ddagger} - i2\delta\tau}{2\sqrt{\delta}}\right)$ may be ignored, for example, at $\gamma/\omega^{\ddagger} = 10^{-3}$, $\beta V^{\ddagger}/\left(2\sqrt{\delta}\right) \simeq 8.3$ so that the correction is exponentially small. Similarly $\Upsilon^{0}\left(\gamma/\omega^{\ddagger} = 10^{-3}\right) = 0.0130$ which is already 17% smaller than the numerically exact result for the transmission factor which is 0.0156. Incorporating the finite barrier correction as in Eq. 2.24 leads to a much worse estimate - 0.0075 and a relative underestimate of the rate by 52%. In this limit, the leading order finite barrier correction is insufficient. The supposedly small expansion parameter $\mu\left(\gamma/\omega^{\ddagger} = 10^{-3}\right) = 0.35$, which is of the order of unity. This quantitative failure in the underdamped limit and low barriers has already

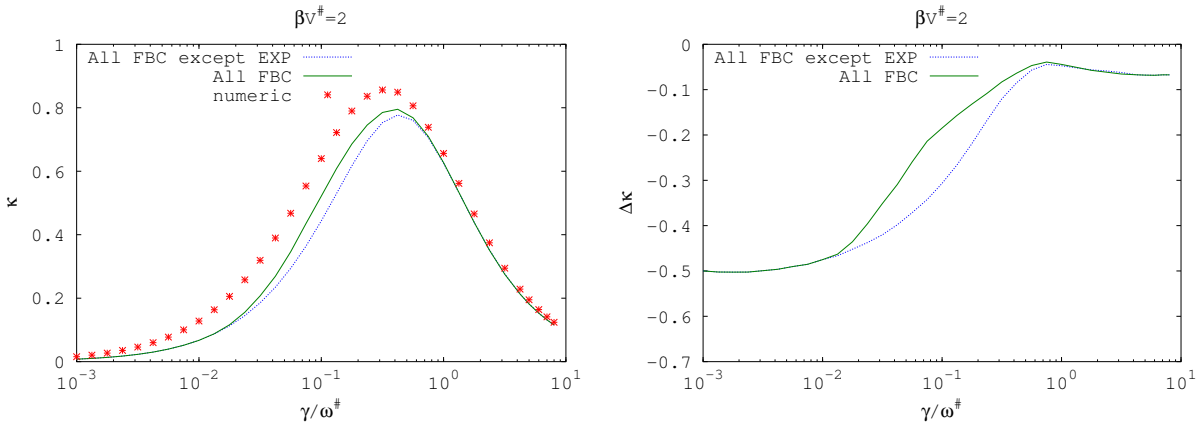


Figure 5: (color online) Finite barrier corrected transmission factors and relative errors for the new PGH theory for $\beta V^{\ddagger} = 2$. The notation is as in Fig. 4. Here, the EXP correction improves the agreement between theory and experiment especially in the turnover region.

been documented previously, as may be seen for example by inspection of Fig. 1 of Ref.[21] The more interesting result is that in the turnover region, the theory with full finite barrier corrections is quite accurate. For $\gamma/\omega^{\ddagger} \geq 0.25$ the error is less than 10%. Inclusion of the finite barrier correction to the kernel as in Eq. 3.21 helps, it significantly reduces the error in the estimate in this region. The finite barrier corrected theory predicts the location of the maximum in the transmission coefficient reasonably well.

Discussion

In this paper we have introduced a modified formulation for the PGH version of Kramers' turnover theory. Theoretical analysis as well as numerical experiment show that this theory is superior to the "standard" PGH formalism and the MM theory for a number of reasons. Compared to the "standard" PGH, the energy loss in the new formulation is a monotonically increasing function of the friction in the Ohmic case. There is no need to introduce an ad-hoc correction as done for example in Ref.[11] Secondly, in contrast to the "standard" PGH theory, the present formulation can also be applied to surface diffusion, since the zero-th

order motion along the unstable mode keeps the topological structure of the original system potential. Thirdly, the theory is superior to MM theory, especially when introducing finite barrier corrections. In the MM theory there is an essential breakdown of these corrections when the reduced friction is of the order of unity. This is removed in Mel'nikov's formulation by introducing an ad-hoc interpolation.[9] In our present formulation, this is not needed, the theory is well defined for any value of the friction coefficient, and moreover quite accurate, even for barriers as low as $\beta V^{\ddagger} = 4$.

We have also shown how one may introduce a finite barrier correction to the probability kernel which partially corrects for the fact that when the barrier is low, one must consider that the final energy cannot go to $-\infty$. This correction is of special importance in the turnover region. We showed that for $\beta V^{\ddagger} = 2$ the theory is qualitatively correct and is rather accurate in the turnover region. This supports the observations of Refs.[12,13] where they found a Kramers like turnover in the rate for the isomerization of LiCN in an Ar solvent even though the reduced barrier was quite low.

The inexorable conclusion is that the present version of PGH theory is the version to be used. However, this does not yet end all the challenges presented by the Kramers' turnover problem. PGH theory was invented to treat memory friction. All the expressions derived in this paper are expressed in terms of the time dependent friction and do not introduce explicitly the assumption that the friction is Ohmic. Yet, one must be careful. Consider the case of exponential memory friction

$$\gamma(t) = \frac{\gamma}{\tau} \exp\left(-\frac{t}{\tau}\right) \tag{5.1}$$

where γ is the friction coefficient, in the sense that when the memory time $\tau \to 0$ the time dependent friction $\gamma(t)$ becomes Ohmic friction with friction coefficient γ. Furthermore consider this same form, but keeping the ratio between the friction coefficient and the memory

time constant

$$\frac{\gamma}{\tau} = \alpha\omega^{\ddagger 2} \tag{5.2}$$

as discussed extensively in Refs.[22,23] Keeping the ratio parameter α fixed and less than unity one finds that in the strong friction long memory time limit, that is letting α stay fixed but allowing $\gamma \to \infty$ one finds that $u_{00}^2 \to 1$. This of course implies that $u_1^2 = 1 - u_{00}^2$ becomes small and as shown in Ref.[23] in this limit one may successfully apply the "standard" PGH theory. However, in this limit $\frac{\lambda^{\ddagger 2}}{\omega^{\ddagger 2}} \to 1 - \alpha$ so that $u_{00} - \frac{\lambda^{\ddagger}}{\omega^{\ddagger}} \to 1 - \sqrt{1-\alpha}$ and this is not necessarily small. But the turnover theory formulated in this paper, was predicated on the assumption that $u_1 \Delta\sigma$ (see Eq. 3.5) is small. In other words, in this limit, the present formulation of PGH theory is not valid, and it fails as badly as MM theory.[23] It thus remains a challenge to formulate a theory which is valid even in this strong friction long memory time limit. From a practical point of view though, for "typical" memory friction, one does not reach this high friction long memory time limit, and the present modified PGH theory should provide a good estimate for the activated rate of escape.

Further development of the present turnover theory would be to follow the development of Ref.[14] and include in the present reformulated theory also the quantum effects of quantum tunneling and quantum reflection as well as low temperature effects due to the quantization of the bath modes.

Acknowledgements

This work was supported by grants of the Minerva Foundation, Munich and the Israel Science Foundation. We take this opportunity to thank Professor Ronnie Kosloff for his stimulating and creative ideas which have served as a source of inspiration for many of us.

References

(1) Kramers H. A. Brownian Motion in a Field of Force and the Diffusion Model of Chemical Reactions. *Physica* **1950** *7* 284-304

(2) Hänggi, P.; Talkner, P.; Borkovec, M. Reaction-rate Theory: Fifty Years After Kramers. *Rev. Mod. Phys.* **1990**, *62* 251-341

(3) Mel'nikov V. I.; Meshkov S.V. Theory of Activated Rate Processes: Exact Solution of the Kramers Problem. *J. Chem. Phys.* **1986** *85* 1018-1027

(4) Mel'nikov V.I. The Kramers Problem: Fifty Years of Development. *Physics Reports* **1991** *209* 1-71

(5) Pollak, E. Theory of Activated Rate Processes: A New Derivation of Kramers' Expression. *J. Chem. Phys.* **1986** *85* 865-867.

(6) Grabert H. Escape From a Metastable well: The Kramers Turnover Problem. Phys. Rev. Lett. **1998** *61* 1683-1686 (1998).

(7) Pollak E.; Grabert H.; Hänggi P. Theory of Activated Rate Processes for Arbitrary Frequency Dependent Friction: Solution of the Turnover Problem, *J. Chem. Phys.* **1989** *91* 4073-4087

(8) Pollak E.; Talkner P. Activated Rate Processes: Finite Barrier Expansion for the Rate in the Spatial Diffusion Limit, *Phys. Rev. E* **1993** *47* 922-933

(9) Mel'nikov V.I. Activated Decay Rate: Finite-barrier Corrections *Phys. Rev. E*, **1994** *48* 3271-3284

(10) Pollak, E.; Ankerhold, J. Improvements to Kramers Turnover Theory. *J. Chem. Phys.* **2013**, *138* 164116(1-9)

(11) E. Pollak and R. Ianconescu, Finite Barrier Corrections to the PGH Solution of Kramers' Turnover Theory. *J. Chem. Phys.* **2014** *140* 154108(1-16)

(12) P.L. Garcia-Muller, F. Borondo, R. Hernandez and R.M. Benito, Solvent Induced Acceleration of the Rate of Activation of a Molecular Reaction *Phys. Rev. Lett.* **2008** *101* 178302(1-4)

(13) Garcia-Muller P.L.; Hernandez R.; Benito R.M.; Borondo F. Detailed Study of the Direct Numerical Observation of the Kramers Turnover in the LiNC→LiCN Isomerization Rate. *J. Chem. Phys.* **2012** *137* 204301(1-8)

(14) Rips I.; Pollak E. The Quantum Kramers' Model: Solution of the Turnover Problem. *Phys. Rev. A* **1990** *41* 5366-5382

(15) S.K. Reese and S.C. Tucker, Solventsolute Reaction Path Curvature Effects on Energy Transfer Corrections to the Solute Reaction Rate *J. Chem. Phys.* **1996** *105* 2263-2279

(16) Drozdov A.N.; Brey J.J. On the Role of the Energy Loss in Turnover Theories of Activated Rate Processes. *Chem. Phys.* **1998** *235* 147-156

(17) Mazo J.J.; Naranjo F.; Zueco D. Nonequilibrium Effects in the Thermal Switching of Underdamped Josephson Junctions. *Phys. Rev. B* **2010** *82* 094505(1-5)

(18) Mazo J.J.; Fajardo O. Y.; Zueco D. Thermal Activation at Moderate-to-high and High Damping: Finite Barrier Effects and Force Spectroscopy. *J. Chem. Phys.* **2013** *138* 104105(1-9)

(19) J.L. Liao and E. Pollak, Quantum Transition State Theory for Dissipative Systems. *Chem. Phys.* **2001** *268* 295-313

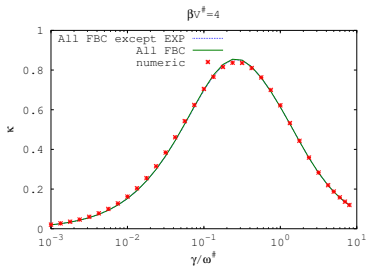
(20) Grote R.F.; Hynes J.T. The Stable States Picture of Chemical Reactions. II. Rate Constants for Condensed and Gas Phase Reaction Models. *J. Chem. Phys.* **1980** *73* 2715-2732

(21) Drozdov A.N.; Hayashi S. Self-similar Renormalization Approach to Barrier Crossing Processes *Phys. Rev. E* **1999** *60* 3804-3813

(22) Straub J.; Borkovec M.; Berne B.J. Non Markovian Activated Rate Processes: Comparison of Current Theories with Numerical Simulation Data. *J. Chem. Phys.* **1986** *84* 1788-1794

(23) Ianconescu R.; Pollak E. A Study of Kramers' Turnover Theory in the Presence of Exponential Memory Friction. *J. Chem. Phys.* **2015** *143* 104104(1-10)

TOC:


βV♯=4
All FBC except EXP
All FBC
numeric
κ
γ/ω♯
0
0.2
0.4
0.6
0.8
1
10−3
10−2
10−1
100
101