# Kramers' theory for diffusion on a periodic potential 

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#### Abstract

Kramers' turnover theory, based on the dynamics of the collective unstable normal mode (also known as PGH theory) is extended to motion of a particle on a periodic potential interacting bilinearly with a dissipative harmonic bath. This is achieved by considering the small parameter of the problem to be the deviation of the collective bath mode from its value along the reaction coordinate, defined by the unstable normal mode. With this change, the effective potential along the unstable normal mode remains periodic, albeit with a renormalized mass, or equivalently a renormalized lattice length. Using second order classical perturbation theory this not only enables the derivation of the hopping rates and the diffusion coefficient, but also the derivation of finite barrier corrections to the theory. The analytical results are tested against numerical simulation data for a simple cosine potential, Ohmic friction, and different reduced barrier heights.


## I. Introduction

[^0]The classical theory of surface diffusion on a periodic potential is well understood. For a particle whose motion is governed by a generalized Langevin equation, in the limit of weak damping, the diffusion coefficient diverges as $1 / \gamma$ where $\gamma$ is the friction coefficient. The divergence is a result of the fact that when the friction is weak, the rate of escape of the particle from a given well goes as $\gamma^{1}$ but the mean squared path length goes as $\gamma^{-2}$. An escaping particle will cross many barriers before being retrapped in a well, since its motion is almost ballistic. Conversely, in the strong friction limit, the rate of escape of the particle goes as $1 / \gamma$ and the mean squared path length is that of a single jump, since in the strong damping limit, an escaping particle is immediately retrapped in the adjacent well. The diffusion coefficient is thus a monotonically decreasing function of the friction strength.

Multiple hops in surface diffusion have been observed experimentally ${ }^{2-4}$ and numerically. ${ }^{5-8}$ The challenge of deriving an expression valid for any friction strength was met by Mel'nikov ${ }^{9}$ who showed how, with the use of a master equation, a Gaussian probability kernel for the exchange of energy of the particle with the bath and the Wiener Hopf method one may derive explicit expressions for the hopping probabilities and the diffusion coefficient when the escape is dominated by the energy exchange of the particle with the bath. In the moderate to strong damping limit, where energy exchange is rapid and spatial diffusion sets in, he multiplied the expression for the diffusion coefficient with the Kramers-Grote-Hynes spatial diffusion factor ${ }^{1,10}$ for the rate. The resulting theory was tested against numerical simulation in Ref. ${ }^{8}$

A related problem is known as Kramers' turnover theory. ${ }^{11,12}$ Kramers derived expressions for the escape rate in the energy and spatial diffusion limits, but not for the whole range of friction strengths. This problem was solved in two steps. Mel'nikov and Meshkov (MM) ${ }^{13}$ solved the problem for the energy diffusion limit, Pollak, Grabert and Hänggi (PGH) ${ }^{14}$ solved it for the whole range of friction. The PGH method employed a Hamiltonian formalism and considered the dynamics along the unstable collective mode, defined by the dynamics in the vicinity of the parabolic barrier. Mel'nikov extended his approach to periodic potentials. ${ }^{9}$ The original PGH formalism was not well suited to this problem, since the effective potential for the motion along
the unstable mode was not periodic. The first challenge dealt with in this paper is the extension of the PGH method to periodic potentials, that is to surface diffusion.

A second challenge is to derive finite barrier corrections for the diffusion. Pollak and Talkner ${ }^{15}$ derived the leading order correction term to the Kramers-Grote-Hynes expression for the rate in the spatial diffusion limited regime, which gives corrections of the order of $k_{B} T / V^{\ddagger}$ ( $T$ is the temperature, $V^{\ddagger}$ is the barrier height). Mel'nikov ${ }^{16}$ then derived finite barrier corrections for the energy diffusion limited regime. These were extended to the PGH formalism only recently, both in its old form ${ }^{17}$ as well as in its more modern formulation. ${ }^{18}$ However, to date, neither MM nor PGH have derived finite barrier corrections for the energy diffusion limited regime of motion on a periodic potential. This is the second challenge addressed in this paper.

In Section II we review the classical perturbation theory which underlies our revised PGH theory, as described in Ref. ${ }^{18}$ Then in Section III we apply the formalism to the problem of diffusion on a periodic potential, deriving explicit formulae for the hopping distribution and the diffusion coefficient. In Section IV we introduce finite barrier corrections and derive them for the hopping distribution and thus also for the diffusion coefficient. The analytic results of Section III and IV are then tested against numerical simulation data in Section V. The paper ends with a Discussion of the results and further extensions.

## II. Perturbation theory for surface diffusion

## II. 1 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:

$$
\begin{equation*}
M \ddot{q}+\frac{d V(q)}{d q}+M \int_{0}^{t} d t^{\prime} \gamma\left(t-t^{\prime}\right) \dot{q}\left(t^{\prime}\right)=F(t) . \tag{2.1}
\end{equation*}
$$

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

$$
\begin{equation*}
\left\langle F(t) F\left(t^{\prime}\right)\right\rangle=M k_{B} T \gamma\left(t-t^{\prime}\right) . \tag{2.2}
\end{equation*}
$$

$\gamma(t)$ is the friction function, $k_{B}$ is Boltzmann's constant and $T$ is the temperature. The potential is assumed to be periodic, with a well at $q=0+n l, \quad n=0, \pm 1, \pm 2, \ldots$ and $l$ is the distance between subsequent wells (lattice length). The wells are separated by barriers, located at $q=q^{\ddagger}+n l$, $n=0, \pm 1, \pm 2, \ldots$. The barrier heights are $V^{\ddagger}$. The wells are characterized with the harmonic frequency $\omega_{a}$ and the barriers with parabolic barrier (imaginary) frequency $\omega^{\ddagger}$. Without loss of generality, the potential may be written as

$$
\begin{equation*}
V(q)=-\frac{1}{2} M \omega^{\ddagger 2} q^{2}+V_{1}(q) \tag{2.3}
\end{equation*}
$$

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 $\rho$ and $p_{\rho}$ 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:

$$
\begin{equation*}
H=\frac{p_{\rho}^{2}}{2}-\frac{1}{2} \lambda^{\ddagger 2} \rho^{2}+V_{1}(q)+\frac{1}{2} \sum_{j=1}^{N}\left[p_{y_{j}}^{2}+\lambda_{j}^{2} y_{j}^{2}\right] \tag{2.4}
\end{equation*}
$$

where $\lambda_{j}$ denoted the frequency of the $j$-th normal mode. $\lambda^{\ddagger}$ denotes the unstable normal mode barrier frequency and it may be obtained through the Kramers-Grote-Hynes relation: ${ }^{1,10}$

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

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

$$
\begin{equation*}
\sqrt{M} q=u_{00} \rho+u_{1} \sigma \tag{2.6}
\end{equation*}
$$

with

$$
\begin{equation*}
u_{1} \sigma=\sum_{j=1}^{N} u_{j 0} y_{j} \tag{2.7}
\end{equation*}
$$

and

$$
\begin{equation*}
u_{1}^{2}=1-u_{00}^{2}=\sum_{j=1}^{N} u_{j 0}^{2} \tag{2.8}
\end{equation*}
$$

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 $u_{j 0}$ 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: ${ }^{14}$

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

The normal mode "friction kernel" is defined as:

$$
\begin{equation*}
K\left(t-t^{\prime}\right)=\sum_{j=1}^{N} \frac{u_{j 0}^{2}}{\lambda_{j}^{2}} \cos \left[\lambda_{j}\left(t-t^{\prime}\right)\right] . \tag{2.10}
\end{equation*}
$$

Using properties of the normal mode transformation (see for example Eq. 2.17 of Ref. ${ }^{19}$ ) one may readily express the Laplace transform of the kernel as

$$
\begin{equation*}
\hat{K}(s)=\left(\frac{s u_{00}^{2}}{\lambda^{\ddagger 2}\left(s^{2}-\lambda \ddagger 2\right)}+\frac{s+\hat{\gamma}(s)}{\omega^{\ddagger 2}\left(\omega^{\ddagger 2}-s^{2}-\hat{\gamma}(s) s\right)}\right) \tag{2.11}
\end{equation*}
$$

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

$$
\begin{equation*}
\Upsilon(\lambda)=\frac{\pi}{2} \sum_{j=1}^{N} \frac{u_{j 0}^{2}}{\lambda_{j}}\left[\delta\left(\lambda-\lambda_{j}\right)-\delta\left(\lambda+\lambda_{j}\right)\right] \tag{2.12}
\end{equation*}
$$

so that:

$$
\begin{equation*}
\Upsilon(\lambda)=\lambda \operatorname{Re}[\hat{K}(i \lambda)]=\frac{\lambda \operatorname{Re}[\hat{\gamma}(i \lambda)]}{\left(\omega^{\ddagger 2}+\lambda^{2}\right)^{2}+\lambda^{2} \hat{\gamma}(i \lambda) \hat{\gamma}(-i \lambda)} . \tag{2.13}
\end{equation*}
$$

## II. 2 The zero-th order motion

When the damping is weak, one may assume that the projection of the system coordinate onto the stable normal modes is small so that the parameter $u_{1}$ (Eq. 2.8) may be considered as the small parameter for the dynamics. However, if, as in PGH theory, one naively considers the zero-th order motion as being determined by setting $u_{1}=0$ in the Hamiltonian, then the potential for the motion along the unstable mode $-\frac{1}{2} \lambda^{\ddagger 2} \rho^{2}+V_{1}\left(u_{00} \rho\right)$ is no longer periodic and the perturbation theory will fail as one moves away from the primary well. To overcome this difficulty, following the derivation in Ref. ${ }^{18}$ we rewrite the Hamiltonian as:

$$
\begin{align*}
H= & \frac{p_{\rho}^{2}}{2}+V\left(\frac{u_{00} \rho+u_{1} \sigma}{\sqrt{M}}\right) \\
& +\frac{1}{2} \omega^{\ddagger 2}\left(u_{00} \rho+u_{1} \sigma\right)^{2}-\frac{1}{2} \lambda^{\ddagger 2} \rho^{2}+\frac{1}{2} \sum_{j=1}^{N}\left[p_{y_{j}}^{2}+\lambda_{j}^{2} y_{j}^{2}\right] . \tag{2.14}
\end{align*}
$$

We then define $\sigma^{*}(\rho)$ by demanding that

$$
\begin{equation*}
\omega^{\ddagger 2}\left(u_{00} \rho+u_{1} \sigma^{*}\right)^{2}=\lambda^{\ddagger 2} \rho^{2} \tag{2.15}
\end{equation*}
$$

and redefine the coordinate $\sigma$ by using the notation

$$
\begin{equation*}
u_{1} \sigma=u_{1} \sigma^{*}+u_{1} \Delta \sigma \tag{2.16}
\end{equation*}
$$

so that the "small" deviation from $u_{1} \sigma^{*}$ is:

$$
\begin{equation*}
u_{1} \Delta \sigma=u_{1} \sigma+\left(u_{00}-\frac{\lambda^{\ddagger}}{\omega^{\ddagger}}\right) \rho . \tag{2.17}
\end{equation*}
$$

The full Hamiltonian may now be rewritten as:

$$
\begin{align*}
H= & \frac{p_{\rho}^{2}}{2}+V\left[\frac{1}{\sqrt{M}}\left(\frac{\lambda^{\ddagger}}{\omega^{\ddagger}} \rho+u_{1} \Delta \sigma\right)\right]+\frac{1}{2} \sum_{j=1}^{N}\left[p_{y_{j}}^{2}+\lambda_{j}^{2} y_{j}^{2}\right] \\
& +\omega^{\ddagger} \lambda^{\ddagger} \rho u_{1} \Delta \sigma+\frac{1}{2} \omega^{\ddagger 2} u_{1}^{2} \Delta \sigma^{2} \tag{2.18}
\end{align*}
$$

and $u_{1} \Delta \sigma$ is readily identified as the "small parameter" of the problem. Setting it equal to zero now implies that the potential along the unstable normal mode is $V\left(\frac{1}{\sqrt{M}} \frac{\lambda^{\ddagger}}{\omega^{\ddagger}} \rho\right)$ and this zero-th order potential is periodic, albeit with a renormalized lattice length

$$
\begin{equation*}
\frac{l_{\rho}}{\sqrt{M}}=\frac{\omega^{\ddagger}}{\lambda^{\ddagger}} l \geq l . \tag{2.19}
\end{equation*}
$$

For a parabolic barrier potential one readily finds that:

$$
\begin{equation*}
V_{p b}\left[\frac{1}{\sqrt{M}}\left(\frac{\lambda^{\ddagger}}{\omega^{\ddagger}} \rho+u_{1} \Delta \sigma\right)\right]+\omega^{\ddagger} \lambda^{\ddagger} \rho u_{1} \Delta \sigma+\frac{1}{2} \omega^{\ddagger 2} u_{1}^{2} \Delta \sigma^{2}=-\frac{1}{2} \lambda^{\ddagger 2} \rho^{2} \tag{2.20}
\end{equation*}
$$

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.

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

$$
\begin{align*}
H_{\rho} & =\frac{p_{\rho}^{2}}{2}+V\left(\frac{\lambda^{\ddagger}}{\sqrt{M} \omega^{\ddagger}} \rho\right) \\
& =\frac{p_{\rho}^{2}}{2}-\frac{1}{2} \lambda^{\ddagger 2} \rho^{2}+V_{1}\left(\frac{\lambda^{\ddagger}}{\sqrt{M} \omega^{\ddagger}} \rho\right) . \tag{2.21}
\end{align*}
$$

Close to any barrier top, the zero-th order barrier remains the same as before, it is quadratic in the unstable mode coordinate. The central difference between this representation and the "stan-
dard" PGH formalism is that 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 $M \omega^{\ddagger 2} / \lambda^{\ddagger 2} \geq M$, or in other words, friction has led to a heavier effective mass. The zero-th order dynamics of the bath is that of a collection of uncoupled stable harmonic oscillators.

## II. 3 First order perturbation theory

To first order the Hamiltonian is expanded as:

$$
\begin{equation*}
H=H_{\rho}+V_{1}^{\prime}\left(\frac{\lambda^{\ddagger}}{\sqrt{M} \omega^{\ddagger}} \rho\right) \frac{u_{1} \Delta \sigma}{\sqrt{M}}+\frac{1}{2} \sum_{j=1}^{N}\left[p_{y_{j}}^{2}+\lambda_{j}^{2} y_{j}^{2}\right] \tag{2.22}
\end{equation*}
$$

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

$$
\begin{equation*}
\ddot{y}_{j_{t}, 1}=-\lambda_{j}^{2} y_{j_{t}, 1}-\frac{u_{j 0}}{\sqrt{M}} V_{1}^{\prime}\left(\frac{\lambda^{\ddagger}}{\sqrt{M} \omega^{\ddagger}} \rho_{t, 0}\right) . \tag{2.23}
\end{equation*}
$$

This is a forced oscillator equation of motion which is readily solved

$$
\begin{equation*}
y_{j_{t}, 1}=-\frac{u_{j 0}}{\sqrt{M}} \int_{-\infty}^{t} d t^{\prime} \frac{\sin \left[\lambda_{j}\left(t-t^{\prime}\right)\right]}{\lambda_{j}} V_{1}^{\prime}\left(\frac{\lambda^{\ddagger}}{\sqrt{M} \omega^{\ddagger}} \rho_{t^{\prime}, 0}\right) . \tag{2.24}
\end{equation*}
$$

Using the notation $\beta=1 /\left(k_{B} T\right)$, following the PGH methodology, the (reduced) energy gained by the bath as the unstable mode traverses from one barrier over the well to the adjacent barrier is given by:

$$
\begin{equation*}
\delta \equiv \frac{\beta}{2 M} \int_{-\infty}^{\infty} d t \int_{-\infty}^{\infty} d t^{\prime} V_{1}^{\prime}\left(\frac{\lambda^{\ddagger} \rho_{t, 0}}{\sqrt{M} \omega^{\ddagger}}\right) \frac{\partial^{2} K\left(t-t^{\prime}\right)}{\partial t \partial t^{\prime}} V_{1}^{\prime}\left(\frac{\lambda^{\ddagger} \rho_{t^{\prime}, 0}}{\sqrt{M} \omega^{\ddagger}}\right) . \tag{2.25}
\end{equation*}
$$

This may then be recast in the more convenient form:

$$
\begin{equation*}
\delta=\frac{\beta}{2 \pi M} \int_{-\infty}^{\infty} d \lambda \lambda \Upsilon(\lambda)\left|\int_{-\infty}^{\infty} d t \exp (-i \lambda t) V_{1}^{\prime}\left(\frac{\lambda^{\ddagger} \rho_{t, 0}}{\sqrt{M} \omega^{\ddagger}}\right)\right|^{2} . \tag{2.26}
\end{equation*}
$$

## II. 4 Second order perturbation theory

In anticipation of the derivation in the next section of finite barrier corrections to the hopping rates and the diffusion coefficient, it is necessary to consider the change in time up to second order in $u_{1}$ of the bath energy defined as:

$$
\begin{equation*}
E_{B, t}=\frac{1}{2} \sum_{j=1}^{N}\left[p_{y_{j}, t}^{2}+\lambda_{j}^{2} y_{j, t}^{2}\right] . \tag{2.27}
\end{equation*}
$$

The exact equation of motion for the j -th bath stable mode oscillator is:

$$
\begin{equation*}
\frac{d^{2} y_{j_{t}}}{d t^{2}}=-\lambda_{j}^{2} y_{j_{t}}-V_{1}^{\prime}\left(\frac{1}{\sqrt{M}}\left(\frac{\lambda^{\ddagger}}{\omega^{\ddagger}} \rho_{t}+u_{1} \Delta \sigma_{t}\right)\right) \frac{u_{j 0}}{\sqrt{M}} \tag{2.28}
\end{equation*}
$$

so that to second order:

$$
\begin{equation*}
\frac{d^{2} y_{j_{t}, 2}}{d t^{2}}=-\lambda_{j}^{2} y_{j_{t}, 2}-V_{1}^{\prime \prime}\left(\frac{\lambda^{\ddagger}}{\sqrt{M} \omega^{\ddagger}} \rho_{t}\right) \frac{u_{j 0}}{\sqrt{M}}\left(\frac{\lambda^{\ddagger}}{\sqrt{M} \omega^{\ddagger}} \rho_{t, 1}+\frac{1}{\sqrt{M}} u_{1} \Delta \sigma_{t, 0}\right) . \tag{2.29}
\end{equation*}
$$

This is again a forced oscillator equation of motion, which is readily solved, provided that the first order correction to the unstable mode motion, $\rho_{t, 1}$, is known.

The exact equation of motion for the unstable mode is:

$$
\begin{equation*}
\frac{d^{2} \rho_{t}}{d t^{2}}=\lambda^{\ddagger 2} \rho_{t}-\frac{u_{00}}{\sqrt{M}} V_{1}^{\prime}\left(\frac{1}{\sqrt{M}}\left(\frac{\lambda^{\ddagger}}{\omega^{\ddagger}} \rho_{t}+u_{1} \Delta \sigma_{t}\right)\right) \tag{2.30}
\end{equation*}
$$

so that the first order equation is:

$$
\begin{equation*}
\frac{d^{2} \rho_{t, 1}}{d t^{2}}=\lambda^{\ddagger 2} \rho_{t, 1}-\frac{u_{00}}{M} V_{1}^{\prime \prime}\left(\frac{1}{\sqrt{M}} \frac{\lambda^{\ddagger}}{\omega^{\ddagger}} \rho_{t, 0}\right)\left(\frac{\lambda^{\ddagger}}{\omega^{\ddagger}} \rho_{t, 1}+u_{1} \Delta \sigma_{t, 0}\right) . \tag{2.31}
\end{equation*}
$$

This parametric forced oscillator equation of motion may be solved using energy conserving per-
turbation theory. ${ }^{18}$ One readily finds that:

$$
\begin{equation*}
\rho_{t, 1}=\quad-p_{\rho_{t}, 0} \int_{-\infty}^{t} d t^{\prime} \frac{1}{p_{\rho_{t^{\prime}, 0}^{2}}^{2}} \int_{-\infty}^{t^{\prime}} d t^{\prime \prime} \frac{1}{\sqrt{M}} u_{1} \sigma_{t^{\prime \prime}, 0}\left[\frac{d}{d t^{\prime \prime}} V_{1}^{\prime}\left(\frac{\lambda^{\ddagger}}{\sqrt{M} \omega^{\ddagger}} \rho_{t^{\prime \prime}, 0}\right)\right] . \tag{2.32}
\end{equation*}
$$

and we ignored a term which is of order $u_{00}-\frac{\lambda^{\ddagger}}{\omega^{\ddagger}}$ since this is second order in $u_{1}$.
As described in Ref., ${ }^{17}$ it is then a matter of some algebra to show that to second order the average energy lost by the system as it traverses from one unstable mode barrier to the next is a sum of two terms:

$$
\begin{equation*}
\beta\left\langle E_{B}\right\rangle_{\infty}-\beta\left\langle E_{B}\right\rangle_{-\infty} \equiv \delta-\beta D E_{2} \equiv \delta(1-\mu) \tag{2.33}
\end{equation*}
$$

and this defines the expansion parameter $\mu$ to be used below. The first term $\delta$ is the average energy lost to the bath at $T=0$ and is given in Eqs. 2.25 and 2.26. The temperature dependent contribution which expresses the fact that the thermal bath will transfer energy to the system is readily found to be:

$$
\begin{align*}
& \beta D E_{2}=-\frac{1}{M} \int_{-\infty}^{\infty} d t \frac{d V_{1}^{\prime}\left(\frac{\lambda^{\ddagger}}{\sqrt{M} \omega^{\ddagger}} \rho_{t}\right)}{d t} \int_{-\infty}^{t} d t^{\prime} \frac{1}{p_{\rho_{t^{\prime}, 0}^{2}}^{2}} \int_{-\infty}^{t^{\prime}} d t^{\prime \prime} \frac{\partial K\left(t^{\prime \prime}-t\right)}{\partial t} \frac{d V_{1}^{\prime}\left(\frac{\lambda^{\ddagger}}{\sqrt{M} \omega^{\ddagger}} \rho_{t^{\prime \prime}, 0}\right)}{d t^{\prime \prime}} \\
= & \frac{2}{\pi} \int_{0}^{\infty} d \lambda \Upsilon(\lambda)\left(\int_{-\infty}^{\infty} d t X(t) \cos \left[\lambda_{j} t\right]\left[\frac{d}{d t} V_{1}^{\prime}\left(\frac{\lambda^{\ddagger}}{\sqrt{M} \omega^{\ddagger}} \rho_{t}\right)\right]\right) \\
& \cdot\left(\int_{-\infty}^{\infty} d t^{\prime \prime} \sin \left[\lambda_{j} t^{\prime \prime}\right]\left[\frac{d}{d t^{\prime \prime}} V_{1}^{\prime}\left(\frac{\lambda^{\ddagger}}{\sqrt{M} \omega^{\ddagger}} \rho_{t^{\prime \prime}, 0}\right)\right]\right) \tag{2.34}
\end{align*}
$$

where the last two lines are a more convenient form for computational purposes, since one integration has been carried out. Here, we used the notation

$$
\begin{equation*}
X(t)=\int^{t} d t^{\prime} \frac{1}{p_{\rho_{t^{\prime}, 0}}^{2}}=-X(-t) \tag{2.35}
\end{equation*}
$$

A second aspect is that in principle the energy loss derived thus far is only at the barrier energy. In principle though the energy loss is energy dependent. As shown in Ref. ${ }^{17}$ this implies that to
second order in the coupling between the system and the bath and to lowest order in the expansion in energy $(\varepsilon=\beta E)$, the average energy loss is

$$
\begin{equation*}
\beta\langle\Delta E\rangle=\delta(1-\mu+\mu \varepsilon) . \tag{2.36}
\end{equation*}
$$

This relation lies at the heart of the finite barrier corrections to the hopping rates and the diffusion coefficient.

## III. Turnover theory for surface diffusion

The $j$-th well is bounded by two barriers, one from the left and the other from the right. $f_{j}^{+}(\varepsilon)$ denotes the flux of particles at reduced energy $\varepsilon$ approaching the right barrier of the $j$-th well moving from left to right while $f_{j}^{-}(\varepsilon)$ denotes the flux of particles approaching the left barrier of the $j$-th well, moving from right to left. Following the derivation of Melnikov ${ }^{9}$ and as also described in Ref. ${ }^{20}$ one has that at steady state, the flux $f_{j}^{+}(\varepsilon)$ is the sum of the flux $f_{j}^{-}\left(\varepsilon^{\prime}\right)$ reflected from the barrier with reflection probability $R\left(\varepsilon^{\prime}\right)$ returning to the right barrier with energy $\varepsilon$ and the flux of particles coming from the adjacent well, approaching the $j-1$ barrier and transmitted through it with transmission probability $T\left(\varepsilon^{\prime}\right)$ then reaching the right barrier with energy $\varepsilon$. The steady state equation is thus

$$
\begin{equation*}
f_{j}^{+}(\varepsilon)=\int_{-\infty}^{\infty} d \varepsilon^{\prime} P\left(\varepsilon \mid \varepsilon^{\prime}\right)\left[f_{j}^{-}\left(\varepsilon^{\prime}\right) R\left(\varepsilon^{\prime}\right)+f_{j-1}^{+}\left(\varepsilon^{\prime}\right) T\left(\varepsilon^{\prime}\right)\right] \tag{3.1}
\end{equation*}
$$

where $P\left(\varepsilon \mid \varepsilon^{\prime}\right)$ is the conditional probability that a particle initiated at say the left barrier with energy $\varepsilon^{\prime}$ will arrive at the adjacent barrier with energy $\varepsilon$. Within the turnover formalism, the kernel is the Gaussian

$$
\begin{equation*}
P_{0}\left(\varepsilon \mid \varepsilon^{\prime}\right)=\frac{1}{\sqrt{4 \pi \delta}} \exp \left[-\frac{\left(\varepsilon-\varepsilon^{\prime}+\delta\right)^{2}}{4 \delta}\right] \tag{3.2}
\end{equation*}
$$

where the zero subscript is used to denote that this kernel implies that the average energy lost upon one traversal from left to right (or equally from right to left) is $\delta$. It does not include in it effects
such as the energy and temperature dependence of the average energy loss, used below to derive finite barrier corrections to the turnover theory. Importantly, it obeys detailed balance.

The reflection and transmission coefficients are the quantum parabolic barrier estimates

$$
\begin{equation*}
R(\varepsilon)=\frac{1}{1+\exp (a \varepsilon)}, T(\varepsilon)=\frac{\exp (a \varepsilon)}{1+\exp (a \varepsilon)}, a=\frac{2 \pi}{\hbar \beta \lambda^{\ddagger}} \tag{3.3}
\end{equation*}
$$

In this paper we consider exclusively the classical dynamics so that at the end of the derivation we take the limit that $\hbar \rightarrow 0$, or equivalently $a \rightarrow \infty$.

The boundary conditions on the fluxes are that initially the particle is located in the $j=0$ well with a thermal distribution so that

$$
\begin{equation*}
f_{j}^{ \pm}(\varepsilon)_{\varepsilon \rightarrow-\infty}=\delta_{j 0} \frac{C}{2 \pi \hbar \beta} \exp (-\varepsilon) \tag{3.4}
\end{equation*}
$$

where $\delta_{j 0}$ is the Kronecker "delta" function. In the spatial diffusion limited regime, only nearest neighbor hops are allowed. The coefficient $C$ is chosen so that in this limit, the rate of escape from the initial well is just twice the spatial diffusion rate $\left(\Gamma_{s d}\right)$ for escape over one of the two adjacent barriers. Or more formally

$$
\begin{equation*}
C=\Gamma_{s d} \sin \left(\frac{\pi}{a}\right) \frac{2 \pi}{\lambda^{\ddagger}} \tag{3.5}
\end{equation*}
$$

The spatial diffusion escape rate is

$$
\begin{equation*}
\Gamma_{s d}=\Gamma_{T S T} \frac{\lambda^{\ddagger}}{\omega^{\ddagger}} \kappa_{F B} . \tag{3.6}
\end{equation*}
$$

where $\Gamma_{T S T}$ is the escape rate estimate without taking frictional effects into account, that is

$$
\begin{equation*}
\Gamma_{T S T}=\frac{2 \exp \left(-\beta V^{\ddagger}\right)}{(2 \pi M \beta)^{1 / 2} \int_{-\infty}^{\infty} d q \exp (-\beta V(q)) \theta\left(q+\frac{l}{2}\right) \theta\left(\frac{l}{2}-q\right)} \tag{3.7}
\end{equation*}
$$

where the factor of two in the numerator comes from the fact that the particle can escape from the well in either direction. We assumed that the initial well of the periodic surface is located at $q=0$.
$\kappa_{F B}$ is the finite barrier correction to the rate in the spatial diffusion limited regime, as given in Ref. ${ }^{15}$

From the symmetry of the periodic potential we note that

$$
\begin{equation*}
f_{j}^{ \pm}(\varepsilon)=f_{-j}^{\mp}(\varepsilon) \tag{3.8}
\end{equation*}
$$

The rate of trapping in the j -th well is by definition:

$$
\begin{equation*}
\Gamma_{j}=\int_{-\infty}^{\infty} d \varepsilon T(\varepsilon)\left[f_{j-1}^{+}(\varepsilon)+f_{j+1}^{-}(\varepsilon)-f_{j}^{-}(\varepsilon)-f_{j}^{+}(\varepsilon)\right] \tag{3.9}
\end{equation*}
$$

The turnover theory for surface diffusion is then aimed at deriving an explicit expression for the rates $\Gamma_{j}$ for any value of the friction.

For this purpose one defines the discrete Fourier transform

$$
\begin{equation*}
N(\varepsilon, k)=R(\varepsilon) \sum_{j=-\infty}^{\infty} \exp \left[i\left(j+\frac{1}{2}\right) k\right] f_{j}^{+}(\varepsilon) \tag{3.10}
\end{equation*}
$$

The double sided Laplace transform is defined as

$$
\begin{equation*}
\tilde{g}(i s)=\int_{-\infty}^{\infty} d \varepsilon \exp (-\varepsilon s) g(\varepsilon) \tag{3.11}
\end{equation*}
$$

Using the fact that $P_{0}\left(\varepsilon \mid \varepsilon^{\prime}\right)=P_{0}\left(\varepsilon-\varepsilon^{\prime}\right)$ we use the definition of the discrete Fourier transform and the integral equation 3.1 to find that

$$
\begin{equation*}
\tilde{N}(i s, k)+\tilde{N}[i(s-a), k]=\exp (i k) \tilde{P}_{0}(i s)(\tilde{N}[i(s-a), k]+\tilde{N}(i s,-k)) \tag{3.12}
\end{equation*}
$$

We then note that

$$
\begin{equation*}
\tilde{P}_{0}(i s)=\exp \left[\delta\left(s^{2}+s\right)\right] \tag{3.13}
\end{equation*}
$$

is real and

$$
\begin{equation*}
\operatorname{Re}[\tilde{N}(i s,-k)]=\operatorname{Re}[\tilde{N}(i s, k)] \tag{3.14}
\end{equation*}
$$

while

$$
\begin{equation*}
\operatorname{Im}[\tilde{N}(i s,-k)]=-\operatorname{Im}[\tilde{N}(i s, k)] . \tag{3.15}
\end{equation*}
$$

Separating the real and imaginary parts in Eq. 3.12 and rearranging leads to the relatively simple result (Eq. 2.13 of Ref. ${ }^{20}$ ):

$$
\begin{equation*}
\operatorname{Im} \tilde{N}[i(s-a), k]=-G(i s, k) \operatorname{Im} \tilde{N}(i s, k) \tag{3.16}
\end{equation*}
$$

with

$$
\begin{equation*}
G(i s, k)=\frac{1-\tilde{P}_{0}^{2}(i s)}{1+\tilde{P}_{0}^{2}(i s)-2 \tilde{P}_{0}(i s) \cos (k)} . \tag{3.17}
\end{equation*}
$$

Solution of the integral equation 3.16 will then lead to the desired hopping rates. To see this, we use the Fourier representation of the Kronecker delta function:

$$
\begin{equation*}
\delta_{l, j}=\frac{1}{2 \pi} \int_{0}^{2 \pi} d k \exp [i(l-j) k] \tag{3.18}
\end{equation*}
$$

to note that:

$$
\begin{equation*}
\frac{1}{2 \pi} \int_{0}^{2 \pi} d k \exp \left(-i\left(l+\frac{1}{2}\right) k\right) \tilde{N}(-i a, k)=\int_{-\infty}^{\infty} d \varepsilon T(\varepsilon) f_{l}^{+}(\varepsilon) \tag{3.19}
\end{equation*}
$$

From Eq. 3.9 one then finds that:

$$
\begin{equation*}
\Gamma_{j}=-\frac{2}{\pi} \int_{0}^{2 \pi} d k \cos (j k) \sin \left(\frac{k}{2}\right) \operatorname{Im}[\tilde{N}(-i a, k)] \tag{3.20}
\end{equation*}
$$

It remains then to solve the integral equation 3.16, this follows the same steps as in the Ap-
pendix of Ref. ${ }^{21}$ Using the notation

$$
\begin{equation*}
\tilde{N}_{2}(i s, k)=-\frac{\sin \left[\frac{k}{2}\right]}{2 \sin \left[\frac{\pi(s+1)}{a}\right]} \Gamma_{s d} \sin \left(\frac{\pi}{a}\right) \tag{3.21}
\end{equation*}
$$

implies that

$$
\begin{equation*}
\tilde{N}_{2}[i(s-a), k]=-\tilde{N}_{2}(i s, k) . \tag{3.22}
\end{equation*}
$$

This is then rewritten as:

$$
\begin{equation*}
\operatorname{Im} \tilde{N}(i s, k)=\tilde{N}_{1}(i s, k) \tilde{N}_{2}(i s, k) \tag{3.23}
\end{equation*}
$$

so that the integral equation takes the form:

$$
\begin{equation*}
\tilde{N}_{1}[i(s-a), k]=G(i s, k) \tilde{N}_{1}(i s, k) \tag{3.24}
\end{equation*}
$$

## Defining

$$
\begin{equation*}
\tilde{g}(i s, k)=\ln \tilde{N}_{1}(i s, k) \tag{3.25}
\end{equation*}
$$

we then have that:

$$
\begin{equation*}
\tilde{g}[i(s-a), k]-\tilde{g}(i s, k)=\ln G(i s, k) . \tag{3.26}
\end{equation*}
$$

This equation is then readily solved (see the Appendix of Ref. ${ }^{21}$ ):

$$
\begin{equation*}
\tilde{g}(i s, k)=\frac{1}{2 i a} \int_{z-i \infty}^{z+i \infty} d y \ln G(i y, k)\left[\cot \left(\frac{\pi(s-y)}{a}\right)+\cot \left(\frac{\pi(y+1)}{a}\right)\right] . \tag{3.27}
\end{equation*}
$$

Choosing $z=-1 / 2$ and shifting the contour such that $i y=\tau-i / 2$ gives

$$
\begin{equation*}
\tilde{g}(-i a, k)=\frac{1}{a} \int_{-\infty}^{\infty} d \tau \ln G\left(\tau-\frac{i}{2}, k\right) \frac{\sin \frac{\pi}{a}}{\left[\cosh \left(2 \frac{\pi \tau}{a}\right)-\cos \frac{\pi}{a}\right]} . \tag{3.28}
\end{equation*}
$$

From Eq. 3.20 one then obtains the central result:

$$
\begin{equation*}
\Gamma_{j}=-\frac{\Gamma_{s d}}{\pi} \int_{0}^{2 \pi} d k \cos (j k) \sin ^{2}\left(\frac{k}{2}\right) \exp \left(\frac{1}{a} \int_{-\infty}^{\infty} d \tau \ln G\left(\tau-\frac{i}{2}, k\right) \frac{\sin \frac{\pi}{a}}{\left[\cosh \left(2 \frac{\pi \tau}{a}\right)-\cos \frac{\pi}{a}\right]}\right) \tag{3.29}
\end{equation*}
$$

and this is precisely Eq. 2.15 of Ref. ${ }^{20}$
The diffusion coefficient is given in terms of the partial rates as:

$$
\begin{equation*}
D=\frac{1}{2} l^{2} \sum_{j=-\infty}^{\infty} j^{2} \Gamma_{j} \tag{3.30}
\end{equation*}
$$

Noting the discrete Fourier representation of the Dirac "delta" function

$$
\begin{equation*}
\sum_{m=-\infty}^{\infty} \delta(k+2 m \pi)=\frac{1}{2 \pi} \sum_{j=-\infty}^{\infty} \exp (i j k)=\frac{1}{2 \pi} \sum_{j=-\infty}^{\infty} \cos (j k) \tag{3.31}
\end{equation*}
$$

so that:

$$
\begin{equation*}
\sum_{j=-\infty}^{\infty} j^{2} \cos (j k)=-2 \pi \sum_{m=-\infty}^{\infty} \frac{d^{2} \delta(k+2 m \pi)}{d k^{2}} \tag{3.32}
\end{equation*}
$$

one derives the explicit expression for the diffusion coefficient:

$$
\begin{equation*}
D=\frac{1}{2} \Gamma_{s d} l^{2} \exp \left(\frac{1}{a} \int_{-\infty}^{\infty} d \tau \ln \left[\frac{1+\tilde{P}_{0}\left(\tau-\frac{i}{2}\right)}{1-\tilde{P}_{0}\left(\tau-\frac{i}{2}\right)}\right] \frac{\sin \frac{\pi}{a}}{\left[\cosh \left(2 \frac{\pi \tau}{a}\right)-\cos \frac{\pi}{a}\right]}\right) \tag{3.33}
\end{equation*}
$$

and this is formally the same as Eq. 2.16 of Ref. ${ }^{20}$
All the expressions derived thus far are valid in a semiclassical limit, in which the temperature is above the crossover temperature between deep tunneling and thermal activation. ${ }^{11}$ Their classical limit, which is of interest in this paper, is obtained by letting $a \rightarrow \infty$. This implies that the hopping rates are:

$$
\begin{equation*}
\Gamma_{j} \rightarrow-\frac{\Gamma_{s d}}{\pi} \int_{0}^{2 \pi} d k \cos (j k) \sin ^{2}\left(\frac{k}{2}\right) \exp \left(\frac{1}{2 \pi} \int_{-\infty}^{\infty} d \tau \ln G\left(\tau-\frac{i}{2}, k\right) \frac{1}{\left[\tau^{2}+\frac{1}{4}\right]}\right) \tag{3.34}
\end{equation*}
$$

and the diffusion coefficient is:

$$
\begin{equation*}
D \rightarrow \frac{1}{2} \Gamma_{s d} l^{2} \exp \left(\frac{1}{2 \pi} \int_{-\infty}^{\infty} d \tau \ln \left[\frac{1+\tilde{P}_{0}\left(\tau-\frac{i}{2}\right)}{1-\tilde{P}_{0}\left(\tau-\frac{i}{2}\right)}\right] \frac{1}{\left[\tau^{2}+\frac{1}{4}\right]}\right) . \tag{3.35}
\end{equation*}
$$

The difference between these results and those of Refs. ${ }^{9}$ and ${ }^{20}$ is in the evaluation of the energy loss. In contrast to the MM energy loss ${ }^{13}$ which diverges linearly with the friction, or the "standard" PGH energy loss ${ }^{14}$ which is not monotonic with the increase of friction, in the present theory the energy loss is given in Eqs. 2.25 and 2.26. This expression gives an energy loss which increases monotonically with the friction, reaching a constant in the high friction limit. It is also valid for memory friction provided that the memory time does not become too long.

## IV. Finite barrier corrections to the turnover theory for surface

## diffusion

The conditional probability kernel $P_{0}\left(\varepsilon \mid \varepsilon^{\prime}\right)$ implies that the averaged (reduced) energy loss is $\delta$ or it is equivalent to setting the expansion parameter $\mu$ in Eq. 2.36 to zero. Finite barrier corrections, that is correction terms of the order of $1 /\left(\beta V^{\ddagger}\right)$ to the rate coming from the energy exchange with the bath are obtained when considering the energy exchange dynamics to first order in $\mu$. ${ }^{16}$ This means that the conditional probability kernel has to satisfy three conditions. The first is normalization

$$
\begin{equation*}
\int_{-\infty}^{\infty} d \varepsilon^{\prime} P\left(\varepsilon^{\prime} \mid \varepsilon\right)=1 \tag{4.1}
\end{equation*}
$$

the second is that it gives the correct averaged energy loss, that is:

$$
\begin{equation*}
\delta(1-\mu+\mu \varepsilon)=\int_{-\infty}^{\infty} d \varepsilon^{\prime}\left(\varepsilon-\varepsilon^{\prime}\right) P\left(\varepsilon^{\prime} \mid \varepsilon\right) \tag{4.2}
\end{equation*}
$$

The third condition is that it obeys detailed balance. This means that if we write

$$
\begin{equation*}
P\left(\varepsilon^{\prime} \mid \varepsilon\right)=P_{0}\left(\varepsilon^{\prime} \mid \varepsilon\right) \Delta P\left(\varepsilon^{\prime}, \varepsilon\right) \tag{4.3}
\end{equation*}
$$

the correction term $\Delta P\left(\varepsilon^{\prime}, \varepsilon\right)$ must be symmetric with respect to exchange of $\varepsilon^{\prime}$ with $\varepsilon$.
The conditions given in Eqs. 4.1 and 4.2 are actually four conditions, not only two, since the equalities must hold for any value of the energy $\varepsilon$. As shown in previous work (in Eq. 2.46 of Ref. ${ }^{17}$ the minus sign before the $\left(\varepsilon-\varepsilon^{\prime}\right)^{4}$ term should be a plus sign ) this means that to lowest order in $\mu$

$$
\begin{align*}
\Delta P\left(\varepsilon^{\prime}, \varepsilon\right)= & 1+\frac{\mu}{2}+\frac{\mu \delta}{4}\left[3-\frac{\left(\varepsilon-\varepsilon^{\prime}\right)^{2}}{\delta^{2}}\right] \\
& -\mu \frac{\left(\varepsilon+\varepsilon^{\prime}\right)}{64 \delta^{2}}\left[\left(12+12 \delta+\delta^{2}\right)\left[\delta(2+\delta)-2\left(\varepsilon-\varepsilon^{\prime}\right)^{2}\right]+\frac{(2+\delta)\left(\varepsilon-\varepsilon^{\prime}\right)^{4}}{\delta}\right] \tag{4.4}
\end{align*}
$$

Some tedious integrations show that indeed this form obeys the conditions of Eqs. 4.1 and 4.2. To derive the finite barrier corrected expression to the hopping rates one follows the same route as described in the previous section, except that it becomes somewhat more involved.

As shown in the Appendix, the final result, using the notations

$$
\begin{equation*}
\varphi(i s, k) \equiv \frac{\tilde{P}_{0}(i s)}{\left[1-\tilde{P}_{0}^{2}(i s)\right]}\left(\cos k-\frac{2 \tilde{P}_{0}(i s) \sin ^{2} k}{1+\tilde{P}_{0}^{2}(i s)-2 \tilde{P}_{0}(i s) \cos (k)}\right) \tag{4.5}
\end{equation*}
$$

and

$$
\begin{equation*}
\Phi(\delta, k)=\frac{\delta}{2 \pi} \int_{-\infty}^{\infty} d \tau \varphi(\tau-i / 2, k) \tag{4.6}
\end{equation*}
$$

is

$$
\begin{align*}
\Gamma_{j}= & -\frac{\Gamma_{s d}}{\pi} \int_{0}^{2 \pi} d k \cos (j k) \sin ^{2}\left(\frac{k}{2}\right) \exp \left(\frac{1}{2 \pi} \int_{-\infty}^{\infty} d \tau \ln G\left(\tau-\frac{i}{2}, k\right) \frac{1}{\left[\tau^{2}+\frac{1}{4}\right]}\right) \\
& \cdot \exp \left[\mu\left(\frac{2-\delta}{2} \Phi(\delta, k)-\left(\frac{\delta}{2}+5\right) \Phi^{2}(\delta, k)\right)\right] \tag{4.7}
\end{align*}
$$

It is instructive to study the underdamped limit of the function $\Phi(\delta, k)$. One readily finds that

$$
\begin{equation*}
\lim _{\delta \rightarrow 0} \Phi(\delta, k)=-\frac{1}{2}, \quad k \neq 0 \tag{4.8}
\end{equation*}
$$

On the other hand,

$$
\begin{equation*}
\lim _{\delta \rightarrow 0} \Phi(\delta, 0)=\lim _{\delta \rightarrow 0} \Phi(\delta, 2 \pi)=\frac{1}{2} \tag{4.9}
\end{equation*}
$$

In other words in the underdamped limit, the function has a discontinuity at the edges of the $k$ interval. For the hopping rates, this implies that

$$
\begin{equation*}
\lim _{\delta \rightarrow 0} \Gamma_{j}=\lim _{\delta \rightarrow 0} \Gamma_{j}^{(0)}(\delta) \exp \left(-\frac{7}{4} \mu\right) \tag{4.10}
\end{equation*}
$$

where $\Gamma_{j}^{(0)}(\delta)$ are the hopping rates as obtained without finite barrier corrections, that is as in Eq. 3.34 .

From the definition of the diffusion coefficient (Eq. 3.30) one then finds that the finite barrier correction for the diffusion coefficient in the underdamped limit is:

$$
\begin{equation*}
\lim _{\delta \rightarrow 0} D=D^{(0)} \exp \left(-\frac{7}{4} \mu\right) \tag{4.11}
\end{equation*}
$$

where $D^{(0)}$ is the diffusion coefficient without finite barrier corrections (Eq. 3.35).

In the overdamped limit

$$
\begin{align*}
\lim _{\delta \rightarrow \infty} \Phi(\delta, k) & =\frac{\delta}{2 \pi} \cos k \int_{-\infty}^{\infty} d \tau \exp \left[-\delta\left(\tau^{2}+\frac{1}{4}\right)\right] \\
& =\frac{\sqrt{\delta} \cos k}{2 \sqrt{\pi}} \exp \left[-\frac{\delta}{4}\right] \rightarrow 0 \tag{4.12}
\end{align*}
$$

so that the finite barrier correction to the rates and the diffusion coefficient which comes from the depopulation factor, goes to unity. It is in fact instructive to study this limit in some more detail. When the energy loss is sufficiently large $(\delta \gg 1)$ one also notes that:

$$
\begin{equation*}
\frac{1}{2 \pi} \int_{-\infty}^{\infty} d \tau \ln G\left(\tau-\frac{i}{2}, k\right) \frac{1}{\left[\tau^{2}+\frac{1}{4}\right]}=4 \cos (k) \frac{\exp \left(-\frac{\delta}{4}\right)}{\sqrt{\pi \delta}}+O\left[\exp \left(-\frac{\delta}{2}\right)\right] \tag{4.13}
\end{equation*}
$$

This then implies that to leading order in $\exp \left(-\frac{\delta}{4}\right)$ :

$$
\begin{align*}
\Gamma_{j}= & -\delta_{j, 0} \Gamma_{s d}\left[1-\frac{\exp \left(-\frac{\delta}{4}\right)}{2 \sqrt{\pi \delta}}\left(\frac{\mu \delta(2-\delta)}{4}+4\right)\right] \\
& +\left(\delta_{j, 1}+\delta_{j,-1}\right) \Gamma_{s d}\left[\frac{1}{2}-\frac{\exp \left(-\frac{\delta}{4}\right)}{2 \sqrt{\pi \delta}}\left(\frac{\mu \delta(2-\delta)}{4}+4\right)\right] \\
& +\left(\delta_{j, 2}+\delta_{j,-2}\right) \Gamma_{s d}\left[\frac{\exp \left(-\frac{\delta}{4}\right)}{4 \sqrt{\pi \delta}}\left(\frac{\mu \delta(2-\delta)}{4}+4\right)\right] \tag{4.14}
\end{align*}
$$

implying that to this order only single and double hops contribute.
This exponential hopping limit without the finite barrier corrections has been studied in some detail in Refs. ${ }^{22,23}$ For our purposes here we note that a consequence of the assumption that $\delta \gg 4$ is that if $\mu \delta^{2}-16>0$ then $\Gamma_{ \pm 2}$ is negative, which is of course an unphysical result. In this limit the perturbation theory in $\mu$ is no longer valid so that the negative value is not a failing of the finite barrier correction theory. But it does point out that one must employ the finite barrier correction with care. To compute the diffusion coefficient for any value of the friction when including the finite barrier correction we then employed the following strategy. On the one hand, the outgoing
rate from the initial well $--\Gamma_{0}$ must equal the sum of all incoming rates $\Gamma_{j}, j \neq 0$. On the other hand we set any incoming rate which is negative, equal to 0 . To assure the proper normalization we then renormalize the rates such that (noting that $\Gamma_{j}=\Gamma_{-j}$ )

$$
\begin{equation*}
\bar{\Gamma}_{j}=-\Gamma_{j} \theta\left(\Gamma_{j}\right) \frac{\Gamma_{0}}{2 \sum_{j=1}^{\infty} \Gamma_{j} \theta\left(\Gamma_{j}\right)}, \quad j \neq 0 \tag{4.15}
\end{equation*}
$$

where $\bar{\Gamma}_{j}$ denotes the renormalized rate into the j -th well and $\theta(x)$ is the unit step function. This assures that indeed $-\Gamma_{0}=2 \sum_{j=1}^{\infty} \bar{\Gamma}_{j}$. The renormalized diffusion coefficient is then obtained from the relationship

$$
\begin{equation*}
\bar{D}=\frac{1}{2} l^{2} \sum_{j=-\infty}^{\infty} j^{2} \bar{\Gamma}_{j} \tag{4.16}
\end{equation*}
$$

In the numerical examples studied below we find that the renormalization is close to unity for almost all values of the friction. Negative values are obtained only when the rates are in any case negligibly small.

A final word of caution. In the absence of finite barrier corrections, one employs the trigonometric representation of the Dirac "delta" function (Eq. 3.31) to obtain a direct expression for the diffusion coefficient (Eq. 3.33) by performing two integrations by parts. Formally, one may suggest to use the same strategy also when including the finite barrier correction. The resulting expression, when ignoring terms such as $k \frac{\partial \Phi(\delta, k)}{\partial k}$ and $k^{2} \frac{\partial^{2} \Phi(\delta, k)}{\partial k^{2}}$ gives the expression:

$$
\begin{equation*}
D=D_{0} \exp \left[\mu\left(\frac{2-\delta}{2} \Phi(\delta, 0)-\left(\frac{\delta}{2}+5\right) \Phi^{2}(\delta, 0)\right)\right] \tag{4.17}
\end{equation*}
$$

where $D_{0}$ is the diffusion coefficient in the absence of finite barrier corrections as given in Eq. 3.33. However, this has two drawbacks, one is that it implicitly includes the negative rates, when they occur. Secondly, due to the discontinuity of the function $\Phi(\delta, k)$ in the limit that $k$ is finite and $\delta \rightarrow 0$ this result is no longer correct in this limit. We shall see below that Eq. 4.17 is useful as long as $\delta$ is not too small.

## V Application to a periodic potential with Ohmic friction

## V. 1 Properties and integrals for Ohmic friction

For Ohmic friction $(\gamma(t)=2 \gamma \delta(t))$ the spectral density of the normal modes is:

$$
\begin{equation*}
\Upsilon(\lambda)=\frac{\lambda \gamma}{\left(\omega^{\ddagger 2}+\lambda^{2}\right)^{2}+\lambda^{2} \gamma^{2}} \tag{5.1}
\end{equation*}
$$

We also note the following identities and notation:

$$
\begin{align*}
\lambda^{\ddagger} & =\frac{\sqrt{\gamma^{2}+4 \omega^{\ddagger 2}}-\gamma}{2}  \tag{5.2}\\
\lambda_{1} & =\frac{\gamma+\sqrt{\gamma^{2}+4 \omega^{\ddagger 2}}}{2}  \tag{5.3}\\
\mu_{\gamma}^{2} & =\frac{\lambda_{1}^{2}}{\lambda^{\ddagger 2}} \tag{5.4}
\end{align*}
$$

where $\lambda^{\ddagger}$ and $\lambda_{1}$ are the roots of the Kramers-Grote-Hynes equation (2.5).
Following Ref. ${ }^{21}$ we also use the notation

$$
\begin{align*}
M_{4}\left(\mu_{\gamma}\right) & =\int_{-\infty}^{\infty} d \bar{\lambda} \frac{\left(\bar{\lambda}^{2}+1\right) \bar{\lambda}^{4}}{\left(\bar{\lambda}^{2}+\mu_{\gamma}^{2}\right) \sinh ^{2}(\bar{\lambda} \pi)} \\
& =\frac{2}{5 \pi}-\frac{\mu_{\gamma}^{2}}{3 \pi}+\frac{2}{\pi} \mu_{\gamma}^{3}\left(\mu_{\gamma}^{2}-1\right) \psi^{\prime}\left(\mu_{\gamma}\right)-\frac{2}{\pi} \mu_{\gamma}^{2}\left(\mu_{\gamma}^{2}-1\right)-\frac{1}{\pi} \mu_{\gamma}\left(\mu_{\gamma}^{2}-1\right) \tag{5.5}
\end{align*}
$$

with

$$
\begin{equation*}
\psi^{\prime}\left(\mu_{\gamma}\right)=\sum_{n=0}^{\infty} \frac{1}{\left(\mu_{\gamma}+n\right)^{2}} \tag{5.6}
\end{equation*}
$$

In the weak damping limit

$$
\begin{equation*}
\lim _{\mu_{\gamma} \rightarrow 1} M_{4}\left(\mu_{\gamma}\right)=\frac{1}{15 \pi} \tag{5.7}
\end{equation*}
$$

and conversely, in the strong damping limit

$$
\begin{equation*}
\lim _{\mu_{\gamma} \rightarrow \infty} \mu_{\gamma}^{2} M_{4}\left(\mu_{\gamma}\right)=\frac{4}{35 \pi} \tag{5.8}
\end{equation*}
$$

## V. 2 Turnover theory for the cosine potential

We consider the periodic potential

$$
\begin{equation*}
V(q)=-\frac{V^{\ddagger}}{2} \cos \left(\frac{2 \pi q}{l}\right) \tag{5.9}
\end{equation*}
$$

such that $V^{\ddagger}$ is the barrier height for escape. The barrier frequency is then:

$$
\begin{equation*}
\omega^{\ddagger 2}=\frac{2 \pi^{2} V^{\ddagger}}{M l^{2}} \tag{5.10}
\end{equation*}
$$

To derive an analytic expression for the energy losses, we note that the time dependence of the trajectory moving under the influence of the periodic potential (Eq. 5.9) initiated at one barrier $(q=-l / 2)$ at $t=-\infty$, reaching the adjacent barrier $(q=l / 2)$ at the time $t=\infty$ is

$$
\begin{equation*}
\tan \left(\frac{\pi q_{t}}{2 l}\right)=\exp \left(\omega^{\ddagger} t\right) . \tag{5.11}
\end{equation*}
$$

Similarly, for the effective Hamiltonian for the unstable mode motion

$$
\begin{equation*}
H_{\rho}=\frac{p_{\rho}^{2}}{2}+\frac{V^{\ddagger}}{2} \cos \left(\frac{2 \pi \lambda^{\ddagger} \rho}{\sqrt{M} \omega^{\ddagger} l}\right) \tag{5.12}
\end{equation*}
$$

we have that the trajectory is

$$
\begin{equation*}
\tan \left(\frac{\pi \rho_{t}}{2 l_{\rho}}\right)=\exp \left(\lambda^{\ddagger} t\right) \tag{5.13}
\end{equation*}
$$

and we used the renormalized lattice length as given in Eq. 2.19.
In the Mel'nikov Meshkov (MM) formulation ${ }^{13}$ one finds that the energy loss is

$$
\begin{equation*}
\delta_{M M}=\beta M \gamma \int_{-\infty}^{\infty} d t\left(\frac{d q_{t}}{d t}\right)^{2}=4 \beta V^{\ddagger} \frac{\gamma}{\omega^{\ddagger}} . \tag{5.14}
\end{equation*}
$$

For the theory presented in this paper, we find, using Eq. 2.26 that the energy loss is

$$
\begin{equation*}
\delta=2 \beta V^{\ddagger}\left(\mu_{\gamma}-1\right)\left[2 \mu_{\gamma}+\left(1-\mu_{\gamma}^{2}\right) \sum_{k=0}^{\infty} \frac{1}{\left(\frac{\mu_{\gamma}+1}{2}+k\right)^{2}}\right] \tag{5.15}
\end{equation*}
$$

and this function is a monotonically increasing function of the friction coefficient. In the small friction limit this energy loss is identical to the MM estimate:

$$
\begin{equation*}
\lim _{\gamma \rightarrow 0} \delta=4 \beta V^{\ddagger} \frac{\gamma}{\omega^{\ddagger}}=\delta_{M M} \tag{5.16}
\end{equation*}
$$

In the large friction limit:

$$
\begin{equation*}
\lim _{\gamma \rightarrow \infty} \delta=\frac{16}{3} \beta V^{\ddagger} \tag{5.17}
\end{equation*}
$$

This is not identical to the MM result, which diverges.

## V. 3 Finite barrier corrections for the cosine potential

## V.3.1 Corrections due to the energy exchange process

The main effort goes into estimation of the expansion parameter $\mu$ (Eq. 2.36). The symmetry of motion here is different than in the cubic potential, the zero-th order motion along the unstable mode is antisymmetric in time. Using the notation of Eq. 2.35 we note that for the periodic cosine potential:

$$
\begin{equation*}
X(t)=\frac{\pi^{2}}{4 \omega^{\ddagger 2} M l^{2} \lambda^{\ddagger}}\left[\sinh \left(2 \lambda^{\ddagger} t\right)+2 \lambda^{\ddagger} t\right] . \tag{5.18}
\end{equation*}
$$

After some lengthy algebra we then find that (see Eq. 2.34)

$$
\begin{equation*}
\beta D E_{2}=4 \mu_{\gamma}\left(\mu_{\gamma}-1\right)\left(\mu_{\gamma} \psi^{\prime}\left(\frac{\mu_{\gamma}+1}{2}\right)-1-\frac{\left(1-\mu_{\gamma}^{2}\right)}{4} \psi^{\prime \prime}\left(\mu_{\gamma}\right)\right) \tag{5.19}
\end{equation*}
$$

The limits are then

$$
\begin{equation*}
\lim _{\gamma \rightarrow 0} \beta D E_{2}=\frac{4 \gamma}{\omega^{\ddagger}}\left(\frac{\pi^{2}}{6}-1\right) \tag{5.20}
\end{equation*}
$$

and

$$
\begin{equation*}
\lim _{\gamma \rightarrow \infty} \beta D E_{2}=\frac{16}{3} \tag{5.21}
\end{equation*}
$$

These results are roughly half the results that one finds for the cubic oscillator, and this makes sense, since here we have only half a period, in the sense that the particle traverses over the well only once rather than twice as in the cubic case. Furthermore

$$
\begin{equation*}
\lim _{\gamma \rightarrow 0} \mu=\lim _{\gamma \rightarrow 0} \frac{\beta D E_{2}}{\delta}=\frac{1}{\beta V_{0}}\left(\frac{\pi^{2}}{6}-1\right) \simeq \frac{0.64}{\beta V^{\ddagger}} \tag{5.22}
\end{equation*}
$$

so that the finite barrier correction to the diffusion coefficient in the underdamped limit is $\exp \left(-\frac{7}{4} \mu\right) \simeq$ $\exp \left(-\frac{7}{6 \beta V^{\ddagger}}\right)$.

## V.3.2 Finite barrier correction in the spatial diffusion limit

The potential is separated into a parabolic part and a nonlinear correction as in Eq. 2.3. Following Ref., ${ }^{15}$ due to the symmetry of the potential about the bottom of the well, for the lowest order correction, one only needs to average over the symmetric part, as follows:

$$
\begin{align*}
\left\langle V_{1 s}\right\rangle & =\sqrt{\frac{\beta \chi^{2} \omega^{\ddagger 2} \Omega^{2}}{2 \pi}} \int_{-\infty}^{\infty} d x \exp \left(-\beta \omega^{\ddagger 2} \chi^{2} x^{2}\right) V_{1}(x) \\
& =-\frac{V^{\ddagger}}{2}\left\{1-\exp \left[-\frac{1}{\beta V^{\ddagger} \chi}\right]-\frac{1}{\beta V^{\ddagger} \chi}\right\} \tag{5.23}
\end{align*}
$$

and the nonlinearity parameter for Ohmic friction is:

$$
\begin{equation*}
\chi=\frac{\lambda_{1}+\lambda^{\ddagger}}{\lambda_{1}-\lambda^{\ddagger}}=\frac{\sqrt{4 \omega^{\ddagger}+\gamma^{2}}}{\gamma} . \tag{5.24}
\end{equation*}
$$

The spatial diffusion FBC is then to leading order:

$$
\begin{equation*}
\kappa_{F B}=1-\beta\left\langle V_{1 s}\right\rangle \simeq 1-\frac{1}{4 \beta V^{\ddagger} \chi^{2}}+O\left(\frac{1}{\beta^{2} V^{\ddagger^{2}}}\right) . \tag{5.25}
\end{equation*}
$$

## V. 4 Numerical results

For the model computations presented below, we chose $l=1, V^{\ddagger}=1, M=1$ so that the barrier frequency is (cf. Eq. 5.10) $\omega^{\ddagger}=\sqrt{2 \pi^{2}} \sim 4.4429$. The numerical calculations described here use a high quality random number generator, ${ }^{24}$ having a period of $3.138 \times 10^{57}$, as described in Ref. ${ }^{17}$ One initiates trajectories trapped in an initial well with a Boltzmann distribution

$$
\begin{equation*}
P(p, q ; \beta)=\exp \left[-\beta\left(\frac{p^{2}}{2 M}+V(q) \Pi(q / l)\right)\right] \tag{5.26}
\end{equation*}
$$

where $V(q)$ is given in Eq. 5.9, $\Pi(x)$ is the rectangular function, i.e. 1 for $|x| \leq 1 / 2$ and 0 otherwise, and $l$ is the lattice length. The initial momentum $p$ is thus a Gaussian random variable with 0 average and $M / \beta$ variance. The initial coordinate $q$ is determined through the same 2 step rejection procedure, described in, ${ }^{17}$ adapted for the periodic potential.

Trajectories are propagated using a 4th order Runge-Kutta algorithm, with a time step of $\frac{1}{50} \frac{2 \pi}{\omega^{\ddagger}}$. The random force is taken into account using the procedure explained in. ${ }^{25}$ Trajectories are propagated for a time that is sufficiently long such that one observes diffusional motion, that is $\left\langle q^{2}\right\rangle$ becomes a linear function of time. In practice, this meant that they were propagated for a time which was at least $10 / \Gamma_{T S T}$ (with $\Gamma_{T S T}$ defined in Eq. (3.7)).

The diffusion coefficient is determined by averaging over 500,000 trajectories. The last third of the time interval, is fit by minimizing the least square distance of the data from a linear dependence on time. The slope of this line, divided by 2 is the numerical result for the diffusion coefficient.

In Figure 1 we first plot the dependence of the finite barrier correction expansion parameter $\mu$ defined in Eq. (2.33) on the reduced friction coefficient $\gamma / \omega^{\ddagger}$. Since $\mu$ scales as $1 /\left(\beta V^{\ddagger}\right)$ ), the figure displays $\beta V^{\ddagger} \mu$ or equivalently it shows $\mu$ for $\beta V^{\ddagger}=1$. The condition for validity of the


Figure 1: The dependence of the finite barrier correction expansion parameter $\mu$ on the reduced friction coefficient $\gamma / \omega^{\ddagger}$. For further details see the text.
finite barrier correction to the diffusion coefficient is that $\mu \ll 1$. This condition is not met, for low reduced barriers.

Numerical results are provided in Table 1. The accuracy of the numerical results is a function of both the (reduced) barrier height and the magnitude of the (reduced) friction coefficient. The more rare the event, the larger is the sample needed. For the results presented in the Table the typical accuracy for $\beta V^{\ddagger}=8$ is a few ppms for $\gamma / \omega^{\ddagger}>5.6 \mathrm{e}-3$ but this degrades to several tens of ppm for lower friction. For $\beta V^{\ddagger}=5$ the accuracy is $\sim 10 \mathrm{ppm}$ for $\gamma / \omega^{\ddagger}>5.6 \mathrm{e}-3$ and it degrades to several tens of ppm up to 100 ppm for lower friction. The typical accuracy for $\beta V^{\ddagger}=2$ is several tens of ppm for $\gamma / \omega^{\ddagger}>5.6 \mathrm{e}-3$ and it degrades to several hundreds of ppm for lower values. For this low gap size, we didn't go below $\gamma / \omega^{\ddagger}=3.16 \mathrm{e}-3$, as the accuracy would further degrade to
several thousands of ppm.
Table 1: Numerical results for the diffusion coefficient for the periodic potential defined in Eq. 5.9, for three reduced gap sizes $\beta V^{\ddagger}=2,5,8$. The dimensions are determined by the specific choice of the parameters used, that is $M=1, l=1, V^{\ddagger}=1$.

| $\gamma / \omega^{\ddagger}$ | $\beta V^{\ddagger}=2$ | $\beta V^{\ddagger}=5$ | $\beta V^{\ddagger}=8$ |  | $\gamma / \omega^{\ddagger}$ | $\beta V^{\ddagger}=2$ | $\beta V^{\ddagger}=5$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $\beta V^{\ddagger}=8$ |  |  |  |  |  |  |  |
| 0.001 |  | 0.40241 | 0.013297 | 0.13335 | 0.20100 | 0.0066898 | $2.8135 \mathrm{e}-04$ |
| 0.001333 |  | 0.29606 | 0.010768 | 0.17783 | 0.16384 | 0.0057339 | $2.4904 \mathrm{e}-04$ |
| 0.001778 |  | 0.23261 | 0.0080552 | 0.23713 | 0.13490 | 0.0049773 | $2.2390 \mathrm{e}-04$ |
| 0.002371 |  | 0.17127 | 0.0060088 | 0.31623 | 0.11161 | 0.0043764 | $2.0505 \mathrm{e}-04$ |
| 0.003162 | 4.1367 | 0.13647 | 0.0046123 | 0.42169 | 0.093474 | 0.0038979 | $1.8837 \mathrm{e}-04$ |
| 0.004216 | 3.4371 | 0.10222 | 0.0036115 | 0.56234 | 0.078326 | 0.0034983 | $1.7348 \mathrm{e}-04$ |
| 0.005623 | 2.7983 | 0.078927 | 0.0027971 | 0.74989 | 0.065765 | 0.0031218 | $1.5835 \mathrm{e}-04$ |
| 0.007498 | 2.2317 | 0.061136 | 0.0021455 | 1.0 | 0.054527 | 0.0027418 | $1.3980 \mathrm{e}-04$ |
| 0.01 | 1.7556 | 0.046946 | 0.0016649 | 1.33352 | 0.044333 | 0.0023430 | $1.2041 \mathrm{e}-04$ |
| 0.013335 | 1.3449 | 0.036913 | 0.0013339 | 1.7783 | 0.035368 | 0.0019483 | $1.0047 \mathrm{e}-04$ |
| 0.017783 | 1.0346 | 0.028818 | 0.0010550 | 2.37137 | 0.027683 | 0.0015657 | $8.1308 \mathrm{e}-05$ |
| 0.023714 | 0.81920 | 0.022661 | $8.4046 \mathrm{e}-04$ | 3.1623 | 0.021368 | 0.0012313 | $6.4423 \mathrm{e}-05$ |
| 0.031623 | 0.63062 | 0.018198 | $6.7706 \mathrm{e}-04$ | 4.21696 | 0.016267 | $9.5327 \mathrm{e}-04$ | $5.0003 \mathrm{e}-05$ |
| 0.042170 | 0.49536 | 0.014553 | $5.5091 \mathrm{e}-04$ | 5.0 | 0.013814 | $8.0492 \mathrm{e}-04$ | $4.2584 \mathrm{e}-05$ |
| 0.056234 | 0.38944 | 0.011730 | $4.5442 \mathrm{e}-04$ | 6.0 | 0.011580 | $6.8036 \mathrm{e}-04$ | $3.5861 \mathrm{e}-05$ |
| 0.074989 | 0.31209 | 0.0096163 | $3.8123 \mathrm{e}-04$ | 7.0 | 0.009964 | $5.8544 \mathrm{e}-04$ | $3.0863 \mathrm{e}-05$ |
| 0.1 | 0.24938 | 0.0079304 | $3.2522 \mathrm{e}-04$ | 8.0 | 0.008748 | $5.1270 \mathrm{e}-04$ | $2.7088 \mathrm{e}-05$ |

The numerical results are compared with the theoretical results in Figs. 2-4 where we show the diffusion coefficient as a function of the reduced friction for the reduced barrier heights of $\beta V^{\ddagger}=2,5$ and 8 respectively. In each Figure we plot the numerically exact diffusion coefficient, the diffusion coefficient without any finite barrier correction (FBC), as obtained from Eq. (3.35) with $\kappa_{F B}=1$, and the diffusion coefficient obtained by including both the energy and spatial diffusion finite barrier corrections as obtained from Eq. (4.16) and $\kappa_{F B}$ from Eq. (5.25). In each Figure, the left panel shows the diffusion coefficients and the right panel the error of the analytic diffusion coefficients relative to the numerically exact result defined as:

$$
\begin{equation*}
\Delta \kappa=\frac{\kappa_{i}-\kappa_{N}}{\kappa_{N}} \tag{5.27}
\end{equation*}
$$

where $\kappa_{i}$, is the analytic estimate obtained without or with the FBC , while $\kappa_{N}$ is the numerically


Figure 2: Diffusion coefficients for the reduced gap $\beta V^{\ddagger}=2$ : The left panel compares the analytic diffusion coefficients with and without FBC's to the numerically exact diffusion coefficient. The right panel shows the relative errors (see Eq. (5.27)). The units are as in Table 1.


Figure 3: Diffusion coefficients for the reduced gap $\beta V^{\ddagger}=5$. The notation is as in Fig. 2.

One notes that (as expected) the analytical results improve systematically with increasing barrier height. At the same time, the finite barrier correction significantly improves the accuracy of the estimate. For the lowest barrier $\beta V^{\ddagger}=2$ the error even with the finite barrier correction becomes significant, especially in the underdamped limit. The quantitative failure in this limit was also found when considering escape from a cubic potential, as may be seen in Fig. 5 of Ref. ${ }^{18}$


Figure 4: Diffusion coefficients for the reduced gap $\beta V^{\ddagger}=8$. The notation is as in Fig. 2.

However, for the cubic potential, the analytic theory underestimates the rate, while here it overestimates the diffusion coefficient. It is remarkable though that already for a reduced barrier height as low as $\beta V^{\ddagger}=5$ the error with finite barrier corrections is less than $10 \%$ for any value of the friction coefficient.

Thus far the analytical estimate for the diffusion coefficient with finite barrier corrections was obtained by the discrete summation as given in Eq. (4.16). One may also formally carry out the summation analytically and use the result given in Eq. (4.17), keeping in mind that this compact analytic result is valid provided that the reduced energy loss $\delta$, is not too small. To obtain a better feeling for the accuracy of the analytically summed expression (Eq. (4.17)) we compare in figure 5 between the numerically summed and renormalized form of Eq. (4.16) with the analytically summed result (Eq. (4.17)). As may be discerned from the Figure, the results are close to each other provided that the reduced friction coefficient is larger than $\sim 0.003$, for which the reduced energy loss is $\delta \sim 0.63$. For smaller values of the friction coefficient the summed result is more accurate. For a larger reduced barrier height of $\beta V^{\ddagger}=8$, the lines cross at $\gamma / \omega^{\ddagger} \sim 0.002$, for which $\delta \sim 0.56$. We conclude, that except for the underdamped limit defined as the limit for which the reduced energy loss is much smaller than unity, one may safely use the analytically summed result.


Figure 5: The relative errors $(\Delta \kappa)$ for the analytically summed diffusion coefficient (Eq. 4.17, denoted as 'formula') and the numerically summed form (Eq. 4.16, denoted as 'summing') plotted as a function of the reduced friction coefficient.

## VI. Discussion

In this paper we considered the motion of a particle moving on a periodic potential influenced by friction and Gaussian thermal noise. Two central results are derived. The first is a uniform expression for the diffusion coefficient, valid for any value of the friction based on the normal mode representation of the dynamics. This result is the periodic potential analog of the modified PGH turnover theory for the escape rate, as presented in Ref. ${ }^{18}$

The second result is the derivation of finite barrier corrections to the diffusion coefficient for any value of the reduced friction coefficients. Such finite barrier corrections were considered previously only for escape from a potential well, but not for diffusion on a periodic lattice. Numerical
simulation results demonstrated than indeed the finite barrier corrections improve the accuracy of the zero-th order results, while at the same time showing that for reduced barrier heights of the order of 5 or greater, the theory is quantitative (with an error of at most $20 \%$ ), even without the finite barrier corrections. Even for a reduced barrier as low as 2, we found that the turnover theory does a reasonable job in predicting the diffusion coefficient.

The theory presented here may be expanded in a few directions. We have not considered memory friction. In this context, as noted already in Ref. ${ }^{18}$ the present perturbation expansion underlying the theory is not valid when the memory time becomes too long. In other words, the turnover problem in the presence of long memory and periodic potentials remains open. On the other hand, one may use the formalism presented here with memory friction and the results should be valid for not too long memory times. There is thus interest to employ the present work in this limit and test its validity.

A second, not less interesting aspect of the theory is its extension to quantum mechanics. The expressions presented here were derived under the assumption of incoherent tunneling between adjacent barriers at temperatures which are above the crossover temperature between deep tunneling and thermal activation. ${ }^{11}$ As discussed in Ref. ${ }^{20}$ such a theory may lead to unexpected results, such that the quantum diffusion coefficient becomes smaller than the classical due to above barrier quantum reflection. This warrants the further study of the theory presented here, in the semiclassical limit.

A third aspect is dimensionality. The theory presented here was limited to one dimensional diffusion. As already noted in the Introduction, such one dimensional diffusion has been observed experimentally. ${ }^{2,3}$ However, the challenge of deriving a multidimensional theory of surface diffusion remains open ${ }^{22}$ especially since in most cases, surface diffusion is not limited to one dimensional channels.

The results presented in this paper, together with previous results for the rate of escape from a potential well ${ }^{18}$ suggest that the linear response theory which lies at the heart of the turnover theory ${ }^{11}$ is valid, even when the barrier height for escape is of the order of the thermal energy,
provided that one accounts for anharmonicity in the potential. This has implications for recent measurements on the transit time distribution between folded and unfolded states of proteins and nucleic acids and the residence time in each of the two states. ${ }^{26}$ In these experiments, the proteins are stretched using optical tweezers such that the equilibrium populations of the folded and unfolded states are approximately equal. The transit time distribution between the two states is then measured and fit to a theoretical distribution based only on assuming a parabolic barrier whose height is large compared to the thermal energy. ${ }^{27,28}$ The resulting fits are inconsistent since they imply much too low barriers ( a fraction of the thermal energy). The present theory suggests that here too, finite barrier corrections and the methodology presented in this paper could go a long way in resolving the discrepancy.

Finally we note that the formalism used here is applicable to many additional phenomena of interest, whose underlying dynamics is described by a master equation who's structure is similar to that of Eq. 3.1. These include ${ }^{29}$ the theory of sticking and desorption from surfaces, ionic hopping in solids, cascade capture of electrons in semiconductors and Josephson systems.

## Acknowledgements

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

## APPENDIX A: Derivation of the finite barrier correction to the

## hopping rates

The purpose of this Appendix is to provide some detail on the derivation of the expression for the finite barrier corrected hopping rates, given in Eq. 4.7. From Eqs. 3.11,4.3 and 4.4 we note that

$$
\begin{equation*}
\tilde{P}(i s, \varepsilon)=\tilde{P}_{0}(i s)\left[1+\mu v_{1}(s)-\mu \varepsilon v_{2}(s)\right] \tag{A.1}
\end{equation*}
$$

with

$$
\begin{equation*}
v_{1}(s)=\frac{\delta s^{2}}{4} \delta(\delta+2)(2 s+1)(s+1)^{2}+2 \delta s^{2}(s+1)-\delta s \tag{A.2}
\end{equation*}
$$

and

$$
\begin{equation*}
v_{2}(s)=\delta s(s+1)\left[\frac{\delta+2}{2} s(s+1)-1\right] \tag{A.3}
\end{equation*}
$$

Anticipating the usual choice of contour, we also note that:

$$
\begin{align*}
& v_{1}\left(-i \tau-\frac{1}{2}\right)=\delta\left[2 i \tau^{3}+\frac{3}{2} i \tau-\frac{i \tau \delta(\delta+2)\left(\tau^{2}+\frac{1}{4}\right)^{2}}{2}+\left(\tau^{2}+\frac{1}{4}\right)+\frac{1}{2}\right]  \tag{A.4}\\
& v_{2}\left(-i \tau-\frac{1}{2}\right)=\delta\left(\tau^{2}+\frac{1}{4}\right)\left[\left(\tau^{2}+\frac{1}{4}\right)\left(\frac{\delta}{2}+1\right)+1\right] \tag{A.5}
\end{align*}
$$

The integral equation for the steady state fluxes, as given in Eq. 3.1 continues to be valid, except that one must use the full conditional probability $P\left(\varepsilon^{\prime} \mid \varepsilon\right)$ instead of the zero-th order (in $\mu$ ) probability $P_{0}\left(\varepsilon^{\prime} \mid \varepsilon\right)$. Noting that:

$$
\begin{equation*}
\int_{-\infty}^{\infty} d \varepsilon \exp (-s \varepsilon) N(\varepsilon, k) \varepsilon=-\frac{\partial \tilde{N}(i s, k)}{\partial s} \tag{A.6}
\end{equation*}
$$

one finds after some algebra that the integral equation to leading order in $\mu$ becomes:

$$
\begin{align*}
& \tilde{N}(i s, k)+\tilde{N}[i(s-a), k]=\tilde{P}_{0}(i s) \exp (i k)\left(\tilde{N}(i s,-k)\left[1+\mu v_{1}(s)\right]+\frac{\partial \tilde{N}(i s,-k)}{\partial s} \mu v_{2}(s)\right) \\
& +\tilde{P}_{0}(i s) \exp (i k)\left(\tilde{N}(i(s-a), k)\left[1+\mu v_{1}(s)\right]+\frac{\partial \tilde{N}(i(s-a), k)}{\partial s} \mu v_{2}(s)\right) \tag{A.7}
\end{align*}
$$

Using the symmetry relations given in Eqs. 3.14 and 3.15, noting that the same relations hold also for $\frac{\partial \tilde{N}(i s,-k)}{\partial s}$ and that $\tilde{P}_{0}(i s), v_{1}(s)$ and $v_{2}(s)$ are real allows us to replace the single equation A. 7 with two equations for the real and imaginary parts.

Defining the operator

$$
\begin{equation*}
\hat{O}(i s, k)=\left(1-\mu \frac{\tilde{P}_{0}(i s) \cos k}{\left[1-\tilde{P}_{0}(i s) \cos k\right]}\left[v_{1}(s)+v_{2}(s) \frac{\partial}{\partial s}\right]\right) \tag{A.8}
\end{equation*}
$$

and noting that to leading order in $\mu$

$$
\begin{equation*}
\hat{O}^{-1}(i s, k) \simeq 2-\hat{O}(i s, k) \tag{A.9}
\end{equation*}
$$

allows us to derive an equation for the imaginary part

$$
\begin{align*}
& \operatorname{Im} \tilde{N}(i s, k)+\operatorname{Im} \tilde{N}[i(s-a), k]=\frac{\tilde{P}_{0}(i s) \cos k-\tilde{P}_{0}^{2}(i s)}{\left[1-\tilde{P}_{0}(i s) \cos k\right]}[\operatorname{Im} \tilde{N}(i(s-a), k)-\operatorname{Im} \tilde{N}(i s, k)] \\
& -\tan ^{2} k\left[[1-\hat{O}(i s, k)] \frac{1}{\left[1-\tilde{P}_{0}(i s) \cos k\right]}\right][\operatorname{Im} \tilde{N}(i(s-a), k)-\operatorname{Im} \tilde{N}(i s, k)] \\
& +\left(\frac{\left[1-\tilde{P}_{0}(i s) \cos k\right]}{\cos ^{2} k}[1-\hat{O}(i s, k)]\right)[\operatorname{Im} \tilde{N}(i(s-a), k)-\operatorname{Im} \tilde{N}(i s, k)] \tag{A.10}
\end{align*}
$$

Using the ansatz as given in Eq. 3.23 with $\tilde{N}_{2}(i s, k)$ given in Eq. 3.21 , noting that

$$
\begin{equation*}
\frac{\partial \ln \tilde{N}_{2}(i s, k)}{\partial s}=-\frac{\pi}{a} \cot \left[\frac{\pi(s+1)}{a}\right]=\frac{\partial}{\partial s} \ln \tilde{N}_{2}(i(s-a), k) \tag{A.11}
\end{equation*}
$$

using the notation as in Eq. 4.5, keeping only up to linear terms in $\mu$ leads to the intermediate result:

$$
\begin{align*}
& \tilde{N}_{1}(i(s-a), k)=G(i s, k) \tilde{N}_{1}(i s, k) \\
& +\mu \frac{\left[1-\tilde{P}_{0}^{2}(i s)\right] \varphi(i s, k)}{\left[1-\tilde{P}_{0}(i s) \cos k\right]}\left[v_{1}(s)+v_{2}(s)\left(-\frac{\pi}{a} \cot \left[\frac{\pi(s+1)}{a}\right]+\frac{\partial}{\partial s}\right)\right]\left[\tilde{N}_{1}(i s, k)+\tilde{N}_{1}(i(s-a), k)\right] \\
& -\mu \sin ^{2} k \frac{G(i s, k) \tilde{P}_{0}^{2}(i s)}{\left[1-\tilde{P}_{0}^{2}(i s)\right]} \frac{\delta(2 s+1) v_{2}(s)}{\left[1-\tilde{P}_{0}(i s) \cos k\right]^{2}}\left[\tilde{N}_{1}(i s, k)+\tilde{N}_{1}(i(s-a), k)\right] . \tag{A.12}
\end{align*}
$$

We then use the notation as given in Eq. 3.25 expanding however with respect to $\mu$

$$
\begin{equation*}
\tilde{g}(i s, k)=\tilde{g}_{0}(i s, k)+\mu \tilde{g}_{1}(i s, k) \tag{A.13}
\end{equation*}
$$

such that $\tilde{g}_{0}(i s, k)$ is the solution in the absence of finite barrier corrections, that is, it is the solution
of Eq. 3.26 and has the property that

$$
\begin{equation*}
\tilde{g}_{0}(i(s-a), k)=\tilde{g}_{0}(i s, k) . \tag{A.14}
\end{equation*}
$$

To first order in $\mu$ we then have that:

$$
\begin{equation*}
\frac{\partial}{\partial s}\left[\tilde{N}_{1}(i s, k)+\tilde{N}_{1}(i(s-a), k)\right] \simeq\left[\frac{\partial \tilde{g}_{0}(i s, k)}{\partial s}\right]\left[\tilde{N}_{1}(i s, k)+\tilde{N}_{1}(i(s-a), k)\right] \tag{A.15}
\end{equation*}
$$

Inserting all these results into Eq. A. 12 and rearranging leads to:

$$
\begin{align*}
\frac{\tilde{N}_{1}(i(s-a), k)}{\tilde{N}_{1}(i s, k)}= & G(i s, k)\left(1+2 \mu \varphi(i s, k)\left[v_{1}(s)+v_{2}(s)\left(-\frac{\pi}{a} \cot \left[\frac{\pi(s+1)}{a}\right]+\frac{\partial \tilde{g}_{0}(i s, k)}{\partial s}\right)\right]\right) \\
& +\mu v_{2}(s) \frac{G(i s, k) \delta(2 s+1)}{\left[1-\tilde{P}_{0}(i s) \cos k\right]}\left(\varphi(i s, k)-\frac{\tilde{P}_{0}(i s) \cos k}{\left[1-\tilde{P}_{0}^{2}(i s)\right]}\right) \tag{A.16}
\end{align*}
$$

and this gives the desired analog of Eq. 3.26

$$
\begin{align*}
\mu \tilde{g}_{1}(i(s-a), k)-\mu \tilde{g}_{1}(i s, k)= & 2 \mu \varphi(i s, k)\left[v_{1}(s)+v_{2}(s)\left(-\frac{\pi}{a} \cot \left[\frac{\pi(s+1)}{a}\right]+\frac{\partial \tilde{g}_{0}(i s, k)}{\partial s}\right)\right] \\
& +\mu v_{2}(s) \frac{G(i s, k) \delta(2 s+1)}{\left[1-\tilde{P}_{0}(i s) \cos k\right]}\left(\varphi(i s, k)-\frac{\tilde{P}_{0}(i s) \cos k}{\left[1-\tilde{P}_{0}^{2}(i s)\right]}\right) \\
\equiv & L(i s, k) \tag{A.17}
\end{align*}
$$

whose solution is known: ${ }^{21}$

$$
\begin{equation*}
\mu \tilde{g}_{1}(i s, k)=\frac{1}{2 i a} \int_{z-i \infty}^{z+i \infty} d y L(i y, k)\left[\cot \left(\frac{\pi(s-y)}{a}\right)+\cot \left(\frac{\pi(y+1)}{a}\right)\right] . \tag{A.18}
\end{equation*}
$$

The remaining task is then to insert the explicit result for $L(i y, k)$ and change the contour to $z=-1 / 2$ and $i y=\tau-i / 2$ and take the classical limit that $a \rightarrow \infty$. One finds

$$
\begin{equation*}
\lim _{a \rightarrow \infty} \tilde{g}_{1}(-i a, k)=\frac{2-\delta}{2} \Phi(\delta, k)-\left(\frac{\delta}{2}+5\right) \Phi^{2}(\delta, k) \tag{A.19}
\end{equation*}
$$

with $\Phi(\boldsymbol{\delta}, k)$ defined as in Eq. 4.6. This then implies that the finite barrier corrected expression for the hopping rates is as given in Eq. 4.7.

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