Quantum Effects in Barrier Dynamics

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Abstract

The dynamics near the top of a potential barrier is studied in the temperature region where quantum effects become important. The time evolution of the density matrix of a system that deviates initially from equilibrium in the vicinity of the barrier top but is in local equilibrium away from the barrier top is determined. Explicit results are given for a range of parameters where the nonequilibrium state is not affected by anharmonicities of the barrier potential except for the barrier height. In particular, for a system confined initially to one side of the barrier the relaxation to a quasi-stationary flux state is determined. The associated rate constant is evaluated and the relation to other rate formulas is discussed in detail.

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I. INTRODUCTION

The dynamics of systems hindered by a potential barrier plays an important role in almost all areas of physics and chemistry. The reaction coordinate which describes the transition across the barrier typically interacts with many degrees of freedom. In the classical region, i.e. for high temperatures, the generalized Langevin equation for the reaction coordinate usually provides an adequate description of the barrier dynamics. Based on these stochastic methods, Kramers flux over population approach enables a detailed investigation of the escape process across the barrier [1].

A corresponding formulation of escape processes in the presence of quantum mechanical effects is available only since recently [2,3]. In the classical region where the barrier is crossed by thermally activated processes only the barrier height and the curvature of the potential at the barrier top and the well minimum are relevant for the rate constant [4]. In this article we study a region where quantum effects lead to large deviations from classical rate constants but where the harmonic approximation for the barrier potential is still sufficient to determine the dynamics of the nonequilibrium state. This allows for analytical results. We extend earlier results on quasi–stationary states of systems with large barriers to include the short time dynamics and the relaxation to a quasi–stationary flux state. Furthermore, the approach will be used to determine time correlation functions of population or flux operators associated with the escape process. This provides the connection with other familiar rate formulas.

The article is organized as follows. In section II we give a brief outline of the formalism and collect results which are of relevance in the following. In section III the time evolution of an initial state which is in nonequilibrium near the top of the barrier is investigated. In section IV these results are applied to determine expectation values, as e.g. the average flux across the barrier, and the flux-flux correlation function. The results are illustrated by an explicit example. Finally, the relation to other approaches of quantum rate theory is discussed.
II. DYNAMICS NEAR THE BARRIER TOP

In this section we collect some results on the description of dissipative systems that are needed in the following sections and introduce basic notation.

A. Dynamics of dissipative systems

The stochastic motion of a classical particle of mass $M$ moving in a potential field $V(q)$ coupled to a heat bath environment is described by the generalized Langevin equation

$$M \ddot{q}(t) + M \int_0^t dt' \gamma(t - t') \dot{q}(t') + \frac{d^2V(q)}{dq^2} = \xi(t).$$

(1)

Here, the stochastic force $\xi(t)$ and the nonlocal damping kernel $\gamma(t - t')$ are connected by the fluctuation–dissipation theorem

$$\langle \xi(t)\xi(t') \rangle = k_B T M \gamma(|t - t'|)$$

(2)

where $T$ is the temperature of the environment and $k_B$ denotes the Boltzmann constant. In this paper we consider systems where $V(q)$ has a smooth potential barrier. Then, near the barrier top the barrier potential can be approximated by the potential of an inverted harmonic oscillator. Assuming that the barrier top is at $q = 0$ and $V(0) = 0$, the barrier potential may be written as

$$V(q) = -\frac{1}{2} M \omega_0^2 q^2.$$  

(3)

Within the range of coordinates where this form of the potential is valid, the classical barrier dynamics can be determined exactly by means of the Langevin equation (1). In particular, the dynamics near the barrier top depends on local features of the barrier potential only and is not affected by anharmonicities. However, when the temperatures is lowered quantum effects become important and the barrier dynamics may depend on global features of the potential field.
The dynamics of a quantum statistical system is determined by the time evolution of the corresponding density matrix. Starting at $t = 0$ from a general initial state $W_0$ of the entire system composed of the Brownian particle and the heat bath, one has

$$W(t) = \exp(-iHt/\hbar)W_0\exp(iHt/\hbar)$$

(4)

where $H$ contains the Hamiltonians of the system, the environmental degrees of freedom, and a system-environment coupling. We shall assume that the state $W_0$ is out of thermal equilibrium due to a preparation affecting the degrees of freedom of the Brownian particle only. Since we are interested in the dynamics of the particle only, the time evolution of the reduced density matrix $\rho(t) = \text{tr}_R W(t)$ will be considered, where $\text{tr}_R$ is the trace over the reservoir. To eliminate the environmental degrees of freedom it is convenient to employ the path integral approach [4,5]. The environmental degrees of freedom can be integrated out exactly if the heat bath consists of harmonic oscillators which are coupled linearly to the coordinate of the particle. In the limit of infinitely many bath oscillators with a continuous frequency spectrum this model causes dissipation and in the classical limit the generalized Langevin equation (1) is recovered. The details of the path integral representation of the reduced density matrix and explicit calculations are given elsewhere [8]. As a result, the position representation of the time dependent reduced density matrix is found to read

$$\rho(q_f, q'_f, t) = \int dq_i dq'_i d\bar{q} d\bar{q}' \ J(q_f, q_f, t, q_i, q_i, \bar{q}, \bar{q}') \ \lambda(q_i, q_i, \bar{q}, \bar{q}').$$

(5)

Here, $J(q_f, q_f, t, q_i, q_i, \bar{q}, \bar{q}')$ denotes the propagating function represented as a 3-fold path integral where two path integrals are in real time arising from the two time-dependent operators in (4) and one in imaginary time describes system–bath correlations in the initial state. Since for the parabolic barrier (3) the propagating function is given explicitly below, we omit here its general form and refer to [8]. Equation (5) determines the time evolution of the density matrix starting from the initial state

$$\rho(q_f, q'_f, 0) = \int d\bar{q} \ d\bar{q}' \ \lambda(q_f, \bar{q}, q'_f, \bar{q}') \rho_\beta(\bar{q}, \bar{q}'),$$

(6)
where \( \rho_\beta = \text{tr}_R(W_\beta) \). Here, \( W_\beta \) is the equilibrium density matrix of the entire system and 
\( \lambda(q_f, \bar{q}, q'_f, \bar{q}') \) is a preparation function describing the deviation from thermal equilibrium.
In an initial state of the form (5) the system and the bath are correlated. Hence, the customary assumption that the initial density matrix \( W_0 \) factorizes into the density matrix of the particle and the canonical density matrix of the unperturbed heat bath is avoided. This is a crucial point since (5) allows for the investigation of the dynamics of realistic physical systems also for short times where preparation effects are important.

**B. Reduced density matrix for an inverted harmonic oscillator**

In [2] we have shown that anharmonicities of the barrier potential are always essential for very low temperatures. Here, we investigate the region of high to intermediate temperatures where the parabolic approximation (5) for the barrier potential is sufficient but quantum effects may be important.

For the harmonic potential (3) the path integrals involved in the propagating function can be solved exactly. The explicit calculation is performed in [4]. One finds

\[
\rho(x_f, r_f, t) = \int \! d x_i \, d r_i \, d \bar{x} \, d \bar{r} \, J(x_f, r_f, t, x_i, r_i, \bar{x}, \bar{r}) \, \lambda(x_i, r_i, \bar{x}, \bar{r})
\]

where we have introduced sum and difference coordinates

\[
x = q - q', \quad r = (q + q')/2
\]

for \( q_f, q'_f \) and \( q_i, q'_i \) as well as for \( \bar{q}, \bar{q}' \), respectively. For the propagating function one obtains

\[
J(x_f, r_f, t, x_i, r_i, \bar{x}, \bar{r}) = \frac{1}{Z} \frac{1}{4\pi |A(t)|} \frac{1}{\sqrt{\omega_0^2 h\beta|\Lambda|}} \sqrt{\frac{M}{2\pi h^2 \beta}} \left( \prod_{n=1}^{\infty} \nu_n^2 u_n \right)
\times \exp \left( \frac{i}{\hbar} \Sigma_\beta(\bar{x}, \bar{r}) + \frac{i}{\hbar} \Sigma_t(x_f, r_f, t, x_i, r_i, \bar{x}, \bar{r}) \right).
\]

Here,
\[ \Sigma_\beta(\bar{x}, \bar{r}) = i \frac{M}{2\Lambda} \bar{r}^2 + i \frac{M\Omega}{2} \bar{x}^2 \]  

is the well-known minimal imaginary-time action of a damped inverted harmonic oscillator at inverse temperature \( \beta = 1/k_B T \) where

\[ \Lambda = \frac{1}{\hbar \beta} \sum_{n=-\infty}^{\infty} u_n \]  

and

\[ \Omega = \frac{1}{\hbar \beta} \sum_{n=-\infty}^{\infty} \left( |\nu_n| \hat{\gamma}(|\nu_n|) - \omega_0^2 \right) u_n. \]  

Furthermore,

\[ \nu_n = \frac{2\pi n}{\hbar \beta} \]  

are Matsubara frequencies and

\[ u_n = \left( \nu_n^2 + |\nu_n| \hat{\gamma}(|\nu_n|) - \omega_0^2 \right)^{-1}. \]  

\( \hat{\gamma}(z) \) denotes the Laplace transform of the macroscopic damping kernel \( \gamma(s) \) which is determined by the spectral density \( I(\omega) \) of the heat bath

\[ \gamma(s) = \frac{2}{M} \int_0^\infty \frac{d\omega}{\pi} \frac{I(\omega)}{\omega} \cos(\omega s). \]  

We note that for a harmonic oscillator the functions \( \Lambda \) and \( \Omega \) correspond to the variance of the position and of the momentum, respectively. However, for a barrier there is no obvious physical meaning since e.g. for high temperatures one has \( \Lambda < 0 \). When the temperature is lowered \( |\Lambda| \) becomes smaller and vanishes for the first time at a critical temperature \( T_c \). As seen from (9) and (10) this leads to a divergence of the propagating function. Hence, as already discussed in [2], the harmonic approximation is limited to temperatures above the critical temperature \( T_c \). For temperatures near and below \( T_c \) anharmonicities of the barrier potential field are always essential [3].

Apart from the pre–exponential factor the time dependence of the propagating function is contained in the second part of the exponent of (9). One finds [2]
Hence, the dynamics at a parabolic barrier is essentially determined by the functions $A(t)$ and $S(t)$. They are given by the Laplace transforms of

$$
\hat{A}(z) = -\frac{\hbar}{2M} \left( z^2 + z\gamma(z) - \omega_0^2 \right)^{-1}.
$$

and

$$
\hat{S}(z) = \frac{2}{\hbar\beta} \sum_{n=-\infty}^{\infty} \frac{z}{z^2 - \nu_n^2} \left( \hat{A}(z) - \hat{A}(\nu_n) \right).
$$

Within the harmonic approximation the above formulas (17)–(18) determine the time evolution of the density matrix near the top of a potential barrier starting from an initial state with a deviation from thermal equilibrium described by the preparation function $\lambda(x_i, r_i, \bar{x}, \bar{r})$.

### III. DYNAMICS OF THE ESCAPE PROCESS

Now, we consider a system in a metastable state which may decay by crossing a potential barrier. We imagine that the system starts out from a potential well to the left of the barrier. Metastability means that the barrier height $V_b$ is much larger than other relevant energy scales of the system such as $k_BT$ and $\hbar\omega_0$, where $\hbar\omega_0$ is the excitation energy in the well of the
inverted potential. In the temperature region where anharmonicities can be neglected, i.e. for temperatures sufficiently above $T_c$, the time evolution of an initial nonequilibrium state near the barrier top can be calculated with the propagating function (9). In particular, for a system prepared at $t = 0$ in thermal equilibrium in the metastable well, the relaxation to the quasi–stationary state with constant flux across the barrier can be investigated. This will be done in this section. The stationary flux state was already determined in [2] by evaluating the propagating function in the large time limit. These investigations are extendend in the following to include the short time dynamics and the relaxation to the quasi–stationary state. Firstly, in III A we introduce the initial preparation. Then, in III B we determine the time dependent density matrix, and in III C the relaxation to stationary nonequilibrium state is investigated.

A. Initial preparation

The initial nonequilibrium state at time $t = 0$ is described by the preparation function [2]

$$\lambda(x_i, r_i, \bar{x}, \bar{r}) = \delta(x_i - \bar{x})\delta(r_i - \bar{r})\Theta(-r_i) \quad (19)$$

so that the initial state is a thermal equilibrium state restricted to the left side of the barrier only. Then, according to (7), the dynamics is given by

$$\rho(x_f, r_f, t) = \int dx_i dr_i \tilde{J}(x_f, r_f, t, x_i, r_i) \Theta(-r_i) \quad (20)$$

with

$$\tilde{J}(x_f, r_f, t, x_i, r_i) = J(x_f, r_f, t, x_i, r_i, x_i, r_i). \quad (21)$$

In this case the time dependent part of the exponent in the propagating function (21) simplifies to read

$$\tilde{\Sigma}_t(x_f, r_f, t, x_i, r_i) = \Sigma_t(x_f, r_f, t, x_i, r_i, x_i, r_i) =$$
\[
x_f x_f \frac{\dot{A}(t)}{A(t)} + x_i x_i \frac{\hbar}{2 \Lambda(t)} - r_i x_i \frac{M S(t)}{2 \Lambda A(t)} + r_i x_f \frac{M^2}{\hbar} \left( \frac{\dot{S}(t)}{\Lambda} - \frac{S(t) \dot{A}(t)}{\Lambda A(t)} \right) \\
+ \frac{i}{2} x_i^2 M \left[ -\Omega + \frac{\hbar^2 \Lambda}{4 M^2 A(t)^2} \left( 1 - \frac{M^2 S(t)^2}{\hbar^2 \Lambda^2} \right) \right] \\
- i x_i x_f \frac{\hbar \Lambda}{2 A(t)^2} \left[ \dot{A}(t) \left( \frac{M^2 S(t)^2}{\hbar^2 \Lambda^2} - 1 \right) - A(t) \frac{S(t) \dot{S}(t) M^2}{\Lambda^2 \hbar^2} \right] \\
+ \frac{i}{2} x_f^2 M \left[ \Omega + \Lambda \frac{\dot{A}(t)^2}{A(t)^2} - \frac{M^2}{\hbar^2 \Lambda} \left( \dot{S}(t) - \frac{\dot{A}(t)}{A(t)} S(t) \right)^2 \right].
\] (22)

B. Time dependent density matrix

Since the exponents (10) and (22) in the propagating function are bilinear functions of the coordinates, the integrals in (20) are Gaussian and can be evaluated exactly. For large times this calculation is performed in detail in [2]. For arbitrary times we may proceed accordingly. After determining the extremum of the exponent in the propagating function (20) with respect to \(x_i\) and \(r_i\), one first evaluates the \(x_i\)-integral. Then, after simple manipulations of the remaining \(r_i\)-integral, the time dependent density matrix may be written in the form

\[
\rho(x_f, r_f, t) = \rho_\beta(x_f, r_f) g(x_f, r_f, t).
\] (23)

Here,

\[
\rho_\beta(x, r) = \frac{1}{Z} \frac{1}{\sqrt{\omega_0^2 \hbar \beta |\Lambda|}} \sqrt{\frac{M}{2 \pi \hbar^2 \beta}} \left( \prod_{n=1}^{\infty} \nu_n^2 u_n \right) \exp \left( \frac{i}{\hbar} \Sigma_\beta(x, r) \right)
\] (24)

is the equilibrium density matrix for an inverted harmonic oscillator and

\[
g(x, r, t) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{u(x, r, t)} dz \exp \left( -z^2 \right) = \frac{1}{2} \text{erfc} \left[ -u(x, r, t) \right]
\] (25)

is a form factor describing deviations from equilibrium with

\[
u(x, r, t) = \sqrt{\frac{M}{2 \hbar |\Lambda|}} \left( 1 - \frac{\hbar^2 \Lambda^2}{M^2 S(t)^2} \right)^{-1/2} \left( -r + i |\Lambda| \frac{\dot{S}(t)}{S(t)} x \right).
\] (26)

Clearly, the harmonic approximation is valid only for high enough temperatures. For temperatures near the critical temperature \(T_c\) where \(|\Lambda|\) vanishes, the above result becomes divergent.
C. Relaxation to stationary nonequilibrium state

Now, we investigate the dynamics of the density matrix (23) starting from the initial state at \( t = 0 \) in greater detail. Note that the time dependence of the form factor (23) is completely determined by the function \( S(t) \).

Firstly, let us consider small times \( \omega_0 t \ll 1 \). There, one has

\[
S(t) = \frac{\hbar \Lambda}{M} - \frac{\hbar \Omega}{2M} t^2 + \mathcal{O}(t^4)
\]  

which leads to

\[
1 - \frac{\hbar^2 \Lambda^2}{M^2 S(t)^2} = \frac{\Omega}{|\Lambda|} t^2 + \mathcal{O}(t^3).
\]  

Then, the function \( u(x, r, t) \), which gives the upper bound of integration in (25), reads

\[
u(x, r, t) = -r \sqrt{\frac{M}{2\hbar \Omega}} \frac{1}{t} + ix \sqrt{\frac{M \Omega}{2\hbar}} + \mathcal{O}(t).
\]  

Hence, using the asymptotic formula

\[
\int_{\mathbb{R}} dx \exp(-x^2) \simeq \frac{1}{2z} \exp(-z^2) \quad \text{for Re}\{z\} \to \infty
\]  

where Re denotes the real part, the leading order expression for the form factor (25) in the limit \( \omega_0 t \ll 1 \) is found to read for finite \( r \)

\[
g(x, r, t) = \Theta(-r) + \sqrt{\frac{\hbar \Omega}{2M \pi r}} t \exp \left( -\frac{Mr^2}{2\hbar \Omega t^2} + i \frac{Mx}{\hbar t} + \frac{M \Omega}{2\hbar} x^2 \right)
\]  

while for \( r = 0 \)

\[
g(x, 0, t) = \frac{1}{2} + \frac{1}{\sqrt{\pi}} \int_0^{ix\sqrt{M\Omega/2\hbar}} dz \exp(-z^2) + \mathcal{O}(t).
\]  

Clearly, for \( t \to 0^+ \) and \( r \neq 0 \) the form factor reduces to the \( \Theta \) function contained in the initial preparation (19) as expected. On the other hand, at \( r = 0 \) the \( t \to 0^+ \) limit differs from the \( t \to 0^- \) limit by an imaginary part due to the discontinuity of the \( \Theta \) function. Defining the width \( \Delta(t) \) in position space of the nonequilibrium state (23) as that value of \(|q|, q < 0\) where \( u(0, q, t) = 1 \), one gets
\[
\Delta(t) = \sqrt{\frac{2\hbar|\Lambda|}{M}} \left( 1 - \frac{\hbar^2 \Lambda^2}{M^2 S(t)^2} \right)^{1/2}.
\]

This reduces to \( \Delta(t) = \sqrt{2\hbar \Omega/Mt} \) for small times in accordance with (31).

In [2] we have shown that for large times the time evolution of the density matrix near the barrier top has a stationary solution. Here, we regain this result from (23). Evaluating the functions \( A(t) \) and \( S(t) \) for times larger than \( 1/\omega_R \) one gets to leading order an exponential growth [8] according to

\[
A(t) = -\frac{\hbar}{2M} \frac{1}{2\omega_R + \dot{\gamma}(\omega_R) + \omega_R \dot{\gamma}'(\omega_R)} \exp(\omega_R t),
\]

and

\[
S(t) = -\frac{\hbar}{2M} \cot\left( \frac{\omega_R \hbar \beta}{2} \right) \frac{1}{2\omega_R + \dot{\gamma}(\omega_R) + \omega_R \dot{\gamma}'(\omega_R)} \exp(\omega_R t).
\]

Here, \( \dot{\gamma}'(z) \) denotes the derivative of \( \dot{\gamma}(z) \), and \( \omega_R \) is the Grote-Hynes frequency [1] given by the positive solution of \( \omega_R^2 + \omega_R \dot{\gamma}(\omega_R) = \omega_0^2 \). Eqs. (34) and (35) describe the unbounded motion at the parabolic barrier with corrections that are exponentially decaying in time (see [8] for details). Hence, the function \( u(x, r, t) \) in (26) becomes independent of time

\[
u_\infty = \sqrt{\frac{M}{2\hbar|\Lambda|}} (-r + i|\Lambda| \omega_R x),
\]

and the density matrix (23) reduces to the stationary nonequilibrium state derived in [2]. This time independent state describes a constant flux across the potential barrier and generalizes the well–known Kramers flux state to the temperature region where quantum effects are important. The width \( \Delta(t) \) from (33) saturates for large times at the finite value

\[
\Delta_\infty = \sqrt{\frac{2\hbar|\Lambda|}{M}}
\]

which coincides with the width of the diagonal part of the equilibrium distribution (24).

From the above discussion it is obvious that a lower bound of time where the stationary flux solution holds derives from \( \omega_R t \gg 1 \). For very long times depletion of states inside the potential well leads to a flux decreasing in time. Hence, for very long times anharmonicities
of the barrier potential become important. For a barrier potential with a quartic term as leading order anharmonicity the upper bound of time where the density matrix \( (23) \) is valid has been estimated in \([2]\). One obtains the condition \( \exp(\omega t) \ll q_a \sqrt{2M \omega_0 / \hbar|\Lambda|} \) where \( q_a \) denotes a characteristic length indicating a typical distance from the barrier top at which the anharmonic part of the potential becomes essential.

The density matrix \( (23) \) depends on local properties of the metastable potential near the barrier top only. On the other hand, the metastable state is assumed to be in thermal equilibrium near the well bottom. This means that the solution \( (23) \) must reduce to the thermal equilibrium state for coordinates \( q_f, q'_f \) on the left side of the barrier at distances small compared with \( q_a \). Now, for \( t = 0 \) the equilibrium state extends to the top of the barrier and the matching to the equilibrium state in the well is most critical for the stationary flux state where \( \Delta(t) \) is largest. However, this latter case was examined in \([2]\). One obtains the condition

\[
|\Lambda| \ll \frac{V_b}{\hbar \omega_0^2} \left( 1 - \frac{\omega_R^2 |\Lambda|}{\Omega} \right) \quad (38)
\]

where \( V_b \) is the barrier height with respect to the well bottom. From a physical point of view \( (38) \) defines the region where the influence of the heat bath on the escape dynamics is strong enough to equilibrate particles on a length scale smaller than the scale where anharmonicities becomes important. Only then nonequilibrium effects remain localized in coordinate space to the barrier region also for longer times. Especially in the classical region where \( k_B T \gg \hbar \omega_0 \) and for Ohmic damping \( \gamma(z) = \gamma \) Eq. \( (38) \) reduces to the well-known Kramers condition \([1]\) \( k_B T \omega_0 / V_b \ll \gamma \). Here, \( 1 - \omega_R^2 \approx \gamma \) for small damping has been used. When the temperature is lowered \( |\Lambda| \) decreases and the range of damping where the stationary solution \( (23) \) is valid becomes larger. This is investigated in detail in \([2]\).

### IV. DECAY RATE AND RELATION TO OTHER APPROACHES

In this section the time dependent density matrix derived above is used to evaluate expectation values, in particular the average flux across the barrier. Further, the relation of
the theory to other approaches to rate constants is discussed.

A. Average flux and decay rate

Clearly, the solution (23) contains all relevant information about the nonequilibrium state. Now, we want to evaluate the total probability flux at the barrier top \( q = 0 \). One has

\[
J(t) = \frac{1}{2M} \langle \hat{p} \delta(\hat{q}) + \delta(\hat{q}) \hat{p} \rangle_t
\]

(39)

where the expectation value \( \langle \cdot \rangle_t \) is calculated with respect to the time dependent nonequilibrium state. From (39) one has in coordinate representation

\[
J(t) = \frac{\hbar}{iM} \frac{\partial}{\partial x_f} \rho(x_f, 0, t) \bigg|_{x_f=0}.
\]

(40)

Since the essential contribution to the population in the well comes from the region near the well bottom, the normalization constant \( Z \) in (40) can be approximated by the partition function of a damped harmonic oscillator with frequency \( \omega_w \) at the well bottom, i.e.

\[
Z = \frac{1}{\omega_w \hbar \beta} \left( \prod_{n=1}^{\infty} \frac{\nu_n^2}{\nu_n^2 + |\nu_n| \hat{\gamma}(|\nu_n|) + \omega_w^2} \right) \exp(\beta V_b). 
\]

(41)

Here, \( V_b \) denotes the barrier height with respect to the well bottom. Note that the potential was set to 0 at the barrier top. Inserting (23) for \( r_f = 0 \) and (41) into (40) one obtains

\[
J(t) = \Gamma \eta(t)
\]

(42)

where

\[
\Gamma = \lim_{t \to \infty} J(t) = \frac{\omega_w}{2\pi} \omega_R \left( \prod_{n=1}^{\infty} \frac{\nu_n^2 + |\nu_n| \hat{\gamma}(|\nu_n|) + \omega_w^2}{\nu_n^2 + |\nu_n| \hat{\gamma}(|\nu_n|) - \omega_0^2} \right) \exp(-\beta V_b)
\]

(43)

denotes the decay rate of the metastable system in the well. We recall that the Grote-Hynes frequency \( \omega_R \) is given by the positive solution of \( \omega_R^2 + \omega_R \hat{\gamma}(\omega_R) = \omega_0^2 \). The rate (43) describes thermally activated transitions across the barrier where the prefactor takes into account quantum corrections [2,10,11]. For the time dependent function \( \eta(t) \) one gets
\[
\eta(t) = \frac{\dot{S}(t)}{\omega_R S(t)} \left( 1 - \frac{\hbar^2 \Lambda^2}{M^2 S(t)^2} \right)^{-1/2}.
\] (44)

This way we have found an analytical result for the dynamic behavior of the average flux which is usually studied numerically, see e.g. [12]. For long times \(\omega_R t \gg 1\) the above function approaches 1. For very small times one obtains from (27)

\[
\eta(t) = \frac{1}{\omega_R} \sqrt{\frac{\Omega}{\omega_0^2 |\Lambda|}} + \mathcal{O}(t^2)
\] (45)

which gives a finite flux for \(t \to 0^+\) while, according to the initial preparation (19), the limit \(t \to 0^-\) leads to a vanishing flux [see also (31) and (32)]. Specifically, for finite damping

\[
\eta(0) = \frac{1}{\omega_R} \sqrt{\frac{\Omega}{\omega_0^2 |\Lambda|}}
\] (46)

is always larger than 1. As a consequence, the probability flux for \(t \to 0^+\) exceeds the rate (13). For very high temperatures where \(\hbar \beta \ll 1\), Eq. (46) reduces to \(\eta(0) = 1/\omega_R\). The corresponding probability flux \(J(0) = \Gamma/\omega_R\) coincides with the result of classical transition state theory [1]

\[
\Gamma_{cl} = \frac{\omega_w}{2\pi} \exp(-\beta V_b).
\] (47)

Here, we have used the fact that the term in brackets in the prefactor of (13) approaches 1 for \(\hbar \beta \ll 1\). For lower temperatures \(|\Lambda|\) decreases and \(\eta(0)\) becomes larger than \(1/\omega_R\).

**B. Flux–flux correlation function**

The propagating function can also be used to determine correlation functions. Here we consider the right–left spatial correlation function

\[
C_{RL}(t) = \text{tr} \{ \Theta[q(t)] \Theta[-q] \rho_{\beta} \} = \langle \Theta[q(t)] \Theta[-q] \rangle_{\beta}
\] (48)

where \(\Theta(\cdot)\) denotes the step function. Time derivatives of \(C_{RL}(t)\) lead to further correlation functions, in particular the flux–flux correlation. Below we will see that these correlations are connected with other rate formulas.
Now, let us evaluate $C_{RL}(t)$ explicitly. Within the presented real time approach this correlation function may formally be looked upon as the expectation value of $\Theta(q)$ at time $t$ of a system with an initial “density matrix” $\Theta(-q)\rho_{\beta}$. The corresponding preparation function then takes the form

$$\lambda(x_i, r_i, \bar{x}, \bar{r}) = \Theta(-r_i - x_i/2) \delta(x_i - \bar{x}) \delta(r_i - \bar{r}).$$  \hspace{1cm} (49)

This way, using (7), the correlation function may be written as

$$C_{RL}(t) = \int dr_f dx_i dr_i \Theta(r_f) \Theta(-r_i - x_i/2) \tilde{J}(0, r_f, t, x_i, r_i)$$

$$= \int dr_f dx_i dr_i' \Theta(r_f) \Theta(-r_i') \tilde{J}(0, r_f, t, x_i, r_i' - x_i/2)$$  \hspace{1cm} (50)

where the propagating function $\tilde{J}(x_f, r_f, t, x_i, r_i)$ is given in (21). We proceed as in section III B and first evaluate the $x_i$ and afterwards the $r_i$ integration. Here, the maximum of the exponent in the propagating function with respect to $x_i$ and $r_i'$ lies at

$$x_i^0 = \frac{2M\omega_0}{\hbar} A(t) \frac{r_f}{\Lambda}$$

$$r_i'^0 = \frac{M}{\hbar} [S(t) + iA(t)] \frac{r_f}{\Lambda}.$$  \hspace{1cm} (51)

Introducing shifted coordinates $\hat{x}_i = x_i - x_i^0$ and $\hat{r}_i' = r_i' - r_i'^0$ a straightforward calculation shows that

$$\Sigma_{\beta}(x_i, r_i' - x_i/2) + \tilde{\Sigma}(0, r_f, t, x_i, r_i' - x_i/2) =$$

$$-iM\hat{x}_i^2 \frac{8\Lambda A(t)^2}{\hbar^2 \Lambda^2} \left\{ [S(t) + iA(t)]^2 - \frac{\hbar^2 \Lambda^2}{M^2} \right\} + \frac{iM(\hat{r}_i')^2}{2\Lambda} - \frac{M\hat{x}_i \hat{r}_i'}{2\Lambda A(t)} [S(t) + iA(t)].$$  \hspace{1cm} (52)

The Gaussian integrals with respect to $\hat{x}_i$ and $\hat{r}_i'$ are now readily performed. Finally, after some further manipulations, we end up with

$$C_{RL}(t) = \frac{1}{Z} \frac{1}{\pi \hbar \beta} \left( \prod_{n=1}^{\infty} \nu_n^2 u_n \right) \int_0^\infty dx \exp(x^2) \int_0^\infty dy \exp(-y^2)$$

$$= \frac{1}{Z} \frac{1}{4\pi \hbar \beta} \left( \prod_{n=1}^{\infty} \nu_n^2 u_n \right) \log \left( \frac{1 + z(t)}{1 - z(t)} \right)$$  \hspace{1cm} (53)

where
\[
z(t) = \left\{ 1 - \frac{\hbar^2 \Lambda^2}{M^2 [S(t) + iA(t)]^2} \right\}^{1/2}.
\]  

(54)

For \( t \to 0 \) one has from (17)

\[
A(t) = -\frac{\hbar}{2M} t + O(t^3).
\]

(55)

Hence, \( z(t) \) tends to zero and \( C_{RL}(t) \) vanishes for \( t \to 0 \) as expected. Now, the time derivative of (53) yields

\[
\dot{C}_{RL}(t) = \langle \bar{F}(t) \Theta(-q) \rangle _\beta
= \frac{1}{Z} \frac{1}{2\pi \hbar^3} \left( \prod_{n=1}^{\infty} \nu_n^2 u_n \right) \frac{|\dot{S}(t)| + i|\dot{A}(t)|}{\left\{ |S(t) + iA(t)|^2 - \hbar^2 \Lambda^2 / M^2 \right\}^{1/2}}
\]

(56)

where

\[
\bar{F} = \frac{1}{2} [p\delta(q) + \delta(q)p]
\]

(57)

is the flux operator. Finally, a second time derivative gives the flux–flux correlation

\[
\ddot{C}_{RL}(t) = \langle \bar{F}(t) \bar{F} \rangle _\beta
= \frac{1}{Z} \frac{1}{2\pi \hbar^3} \left( \prod_{n=1}^{\infty} \nu_n^2 u_n \right) \times \left\{ \frac{|\dot{S}(t)| + i|\dot{A}(t)|}{\left\{ |S(t) + iA(t)|^2 - \hbar^2 \Lambda^2 / M^2 \right\}^{1/2}} - \frac{|\ddot{S}(t)| + i|\ddot{A}(t)|^2|S(t) + iA(t)|}{\left\{ |S(t) + iA(t)|^2 - \hbar^2 \Lambda^2 / M^2 \right\}^{3/2}} \right\}.
\]

(58)

The above three correlations are related to the escape rate out of the metastable well as will be seen in section [IV D].

C. An example: Drude damping

To illustrate the above results we now consider a Drude model with \( \gamma(t) = \gamma_0 \exp(-\omega_D t) \) by way of example. Clearly, in the limit \( \omega_D \gg \omega_0, \gamma \) the Drude model behaves like an Ohmic model except for very short times of order \( 1/\omega_D \). The Laplace-transform of \( \gamma(t) \) reads
\[ \hat{\gamma}(z) = \gamma \frac{\omega_D}{\omega_D + z}. \]  

Then, from (11) and (12) we obtain

\[ \Lambda = \frac{1}{\hbar \beta} \sum_{n=-\infty}^{\infty} \frac{1}{\nu_n^2 + |\nu_n|((\gamma \omega_D/\omega_D^2 + |\nu_n|) - \omega_0^2} \]  

and

\[ \Omega = \frac{1}{\hbar \beta} \sum_{n=-\infty}^{\infty} \frac{|\nu_n|((\gamma \omega_D/\omega_D^2 + |\nu_n|) - \omega_0^2}{\nu_n^2 + |\nu_n|((\gamma \omega_D/\omega_D^2 + |\nu_n|) - \omega_0^2}. \]

The time dependence of the nonequilibrium state is completely determined by the function \( S(t) \) in (18). Some of the algebra needed to evaluate \( S(t) \) for a Drude model explicitly is provided in recent work [13]. We obtain

\[ S(t) = \frac{\hbar}{M} \sum_{i=1}^{3} \left[ c_i \cot \left( \frac{\lambda_i \hbar \beta}{2} \right) \exp(\lambda_i t) \right] - \zeta(t). \]  

Here, \( \lambda_i, i = 1, 2, 3 \) denote the poles of \( \hat{A}(z) \) given by the three solutions of

\[ z^3 + \omega_D z^2 + z(\gamma \omega_D^2 - \omega_0^2) - \omega_D = 0. \]

For the coefficients \( c_i \) one has

\[ c_1 = (\lambda_2^2 - \lambda_3^2)/\phi \]
\[ c_2 = (\lambda_3^2 - \lambda_1^2)/\phi \]
\[ c_3 = (\lambda_1^2 - \lambda_2^2)/\phi \]

where

\[ \phi = (\lambda_1 - \lambda_2)\lambda_1\lambda_2 + (\lambda_2 - \lambda_3)\lambda_2\lambda_3 + (\lambda_3 - \lambda_1)\lambda_1\lambda_3. \]

Further, we have introduced the time dependent function

\[ \zeta(t) = \frac{\gamma \omega_D^2}{\hbar \beta} \sum_{n=-\infty}^{\infty} \frac{|\nu_n| \exp(-|\nu_n|t)}{(\lambda_1^2 - \nu_n^2)(\lambda_2^2 - \nu_n^2)(\lambda_3^2 - \nu_n^2)}. \]

which can also be written in terms of hypergeometric functions as
\[ \zeta(t) = -\frac{1}{\hbar \beta} \sum_{i=1}^{3} \frac{c_i}{\lambda_i} \left[ F(1, \frac{\lambda_i}{\nu}; 1 + \frac{\lambda_i}{\nu}; e^{-\nu t}) - F(1, -\frac{\lambda_i}{\nu}; 1 - \frac{\lambda_i}{\nu}; e^{-\nu t}) \right]. \] (67)

With these results for \( \Lambda, \Omega, \) and \( S(t) \) and a Drude frequency \( \omega_D = 100 \omega_0 \) we have investigated the time evolution of the nonequilibrium state numerically. In Fig. 1 the width \( \Delta(t) \) of the nonequilibrium state in position space, given in \((33)\), is depicted as a function of \( t \) for various temperatures. For high temperatures damping effects are relevant for intermediate times only while for lower temperatures they are essential for all times. For small times \( \Delta(t) \) grows faster for stronger damping and reaches a larger asymptotic value for large times. This is due to the quantum mechanical effect that stronger damping suppresses the fluctuations of the coordinate and therefore enhances fluctuations of the momentum.

The relaxation of the time dependent flux \((42)\) across the potential barrier to the time independent decay rate \((43)\) is determined by the function \( \eta(t) \) in \((44)\). In Fig. 2 the time dependence of \( \eta(t) \) is depicted for various temperatures. One sees that in the region of moderate damping the simple TST result \( \Gamma_{\text{TST}} = \Gamma \eta(0) \) for the rate constant gives a satisfactory estimate of the true rate only for high temperatures. When the temperature is decreased \( \eta(0) \) grows and depends strongly on the damping strength. Furthermore, for lower temperatures the average flux across the barrier becomes stationary faster for stronger damping.

D. Relation to other rate formulas

In the previous section we have calculated the probability flux across the potential barrier using the time dependent density matrix \((7)\) with the initial preparation \((19)\). In particular, we have shown that the flux becomes time independent for times \( \omega_R t \gg 1 \) leading to the escape rate. Here, we want to regain the escape rate using rate formulas first introduced by Yamamoto \([14]\) and Miller \([15]\). First, let us consider Yamamoto’s rate formula

\[ \Gamma = \lim_{t \to \infty} \frac{1}{\hbar \beta} \int_{0}^{h \beta} d\lambda \langle \Theta[-q(-i\lambda)] \dot{\Theta}[-q(t)] \rangle_{\beta} \] (68)
where the limit is understood as \( t \gg 1/\omega_R \). Here, the right hand side can be transformed to read

\[
\frac{1}{\hbar \beta} \int_0^{\hbar \beta} d\lambda (\Theta[-q(-i\lambda)]\Theta[-q(t)])_\beta = \frac{i}{\hbar \beta} ([\Theta[-q(t)], \Theta[-q]])_\beta.
\] (69)

On the other hand, taking into account that \( \Theta(q) = 1 - \Theta(-q) \) one has from (48)

\[
\text{Im} \{ C_{RL}(t) \} = -\text{Im} \{ C_{LL}(t) \} = \frac{i}{2} (\Theta[-q(t)] \Theta[-q])_\beta.
\] (70)

Hence, we get from (69)

\[
\Gamma = \frac{2}{\hbar \beta} \lim_{t \to \infty} \text{Im} \{ C_{RL}(t) \}.
\] (71)

The result (53) can now be inserted into the above rate formula. First, from (34) and (35) one obtains for times \( \omega_R t \gg 1 \)

\[
\text{Im} \left\{ \log \left( \frac{1 + z(t)}{1 - z(t)} \right) \right\} = 2 \text{arctan} \left[ A(t)/S(t) \right].
\] (72)

Thus, we obtain from (53)

\[
\lim_{t \to \infty} \text{Im} \{ C_{RL}(t) \} = \frac{\omega_R \hbar \beta}{2} \frac{1}{Z} \frac{1}{2\pi \hbar \beta} \left( \prod_{n=1}^{\infty} \nu_n^2 u_n \right)
\] (73)

which combines with (71) and the normalization (41) to yield the escape rate (13).

On the other hand, the time derivative \( \dot{C}_{RL}(t) \) given in (56) determines Miller’s rate formula (13)

\[
\Gamma = \lim_{t \to \infty} \dot{C}_{RL}(t).
\] (74)

In the long time limit the imaginary part of \( \dot{C}_{RL}(t) \) becomes exponentially small and

\[
\lim_{t \to \infty} \dot{C}_{RL}(t) = \frac{1}{Z} \frac{1}{2\pi \hbar \beta} \left( \prod_{n=1}^{\infty} \nu_n^2 u_n \right) \omega_R
\] (75)

yields with (74) again the rate (13).

We note that for long times the flux-flux autocorrelation function (58) becomes exponentially small. This indicates a constant flux across the barrier independent of the initial preparation of the nonequilibrium state in the metastable well.
V. CONCLUSIONS

Within the path integral approach we have evaluated the time dependent density matrix of a metastable system in the vicinity of a barrier top when preparing the system at $t = 0$ in thermal equilibrium on the left side of the barrier only (19). The explicit solution (23) is valid over a wide range of time excluding very long times and for high as well as for lower temperatures where quantum effects become important. The nonequilibrium state approaches an equilibrium state as one moves away from the barrier top. Condition (38) on the damping strength ensures that equilibrium is reached within the range of validity of the harmonic approximation for the barrier potential.

In particular, we have studied the relaxation of the time dependent nonequilibrium state to the stationary flux state. We found that the corresponding time dependent normalized flux across the barrier is decaying in time. For very high temperatures the initial flux coincides with the transition state theory rate. For long times the flux coincides with the stationary decay rate of the metastable state which was shown to be identical with the well-known rate formula for thermally activated decay in the presence of quantum corrections. Furthermore, we have shown that the real time approach can also be used to evaluate correlation functions which are encountered in other rate formulas.

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FIGURES

FIG. 1. Width $\Delta(t)$ in position space of the nonequilibrium state for high temperatures $\hbar\beta\omega_0 = 0.05$ (thick lines) and lower temperatures $\hbar\beta\omega_0 = 2.0$ (thin lines) for a Drude model with $\omega_D/\omega_0 = 100$. Solid lines indicate small damping with $\gamma = 0.1$, dashed lines stronger damping with $\gamma = 3.0$.

FIG. 2. Time dependence of the average flux across the barrier $\eta(t)$ for two temperatures and a Drude model with $\omega_D/\omega_0 = 100$ and with various damping strengths.