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Classical and Quantum Escape Rates of Particles from Potential Wells for All Values of the Dissipation

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Thesis submitted to the University of Dublin
for the degree of Doctor of Philosophy

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2014

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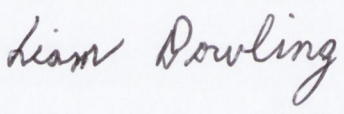

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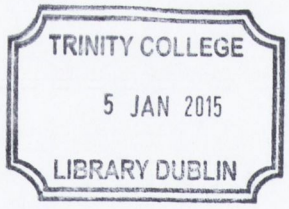

Summary

The thesis is concerned with the calculation of the escape rate of a Brownian particle out of a deep potential well. A new derivation of the Kramers energy controlled diffusion equation using only the concept of the Langevin equation with multiplicative noise is presented. This equation of motion for the distribution function of Brownian particles in a potential well is applicable when the dissipation to the thermal bath is very low. Hence, the various approaches to the calculation of the very low damping escape rate hitherto used may be reconciled, while simultaneously removing the obscurities associated with previous derivations. The method is then extended to the Kramers turnover problem, pertaining to the escape rate in the very low damping to the intermediate damping regime, in both the classical and semiclassical cases.

Acknowledgements

I would like to thank my supervisor Professor William Coffey for his guidance and encouragement. I also wish to thank Dr. Serguey Titov for helpful discussions. I am grateful to Professor Yuri Kalmykov for suggesting this research topic. Finally, I would like to thank Dr. Martin Burke for encouraging me to undertake this research.

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Chapter 1

Introduction

The thesis is concerned with the calculation of the escape rate of a Brownian particle out of a deep potential well. The objective is to explain in detail the very complicated steps involved in this problem which is of interest in a multitude of diverse physical systems involving the decay of a metastable state. Hitherto the subject has been presented in such a manner that it is virtually inaccessible to the reader even at doctoral student level. Two distinct mechanisms contribute to the escape rate, namely, *thermal activation overbarrier escapes* and *quantum–tunneling escapes*. Classical reaction rate theory as formulated by Arrhenius, Eyring, Wigner and others [1,2] ignores non-equilibrium effects due to the loss of particles from the well when they escape due to thermal agitation. The Maxwell-Boltzmann distribution is assumed to apply everywhere in the well. The resulting application to the escape rate problem is called transition state theory (TST). The effects of friction are ignored and the results are applicable in situations where the thermal noise is sufficiently strong to thermalize the escaping particles but the friction has a negligible effect on the motion of the particles at the top of the barrier. Kramers was the first to include the effect of friction in the calculation of the escape rate. He showed that for sufficiently weak friction the escape rate is reduced due to depletion of the well population. He also showed that the escape rate is reduced if the friction is strong due to the slowing down of the particle motion at the top of the barrier. Kramers started by writing the Langevin equation for a point particle. The effect of the bath on a single

particle is represented in the Newtonian equation of motion of the particle by a systematic force proportional to the velocity, which slows down the motion, on which is superimposed a rapidly fluctuating random white noise force, which sustains the motion. Kramers then obtained the Fokker-Planck equation for the distribution function in the phase space of position and momentum of the Brownian particles in the well. Next Kramers postulated a steady injection of particles into the well to replace those lost at the barrier. He then obtained expressions for the escape rate Γ over the barrier by the flux-over-population method, which is the ratio of the current of escaping particles divided by the well population, both in the limit of intermediate to high dissipation (IHD) to the bath and very low dissipation (VLD). The IHD rate in the limit of vanishing dissipation yields the above mentioned TST rate, which is the upper bound of the escape rate. In the case of VLD, Kramers considered the effect of the bath as a very small perturbation on the large amplitude motion of a particle librating in the well with energy equal to the critical energy at which a particle will just escape the well. He wrote the Fokker-Planck equation in energy-phase variables and averaged over the fast phase variable to obtain a one-dimensional energy diffusion equation. The escape rate Γ was again calculated by the flux over population method.

The Kramers method of obtaining the energy diffusion equation is rather opaque and it is not easy to compare it with later treatments of VLD escape by Stratonovich [3], Zwanzig [4], Nitzan [1], and Hänggi et al. [2]. The first task of my thesis is to codify the various energy diffusion equations. I succeeded in Chapter 2 in showing that all the VLD equations are equivalent by utilizing the easily visualized low damping treatment of Stratonovich who utilized the Langevin equation written in energy-position variables and averaged out the position variable. This was the first new result of my thesis, namely, the clarification of the various energy controlled diffusion equations and the concept of the energy loss per cycle of the lightly damped periodic motion at the barrier energy introduced by Kramers. The material of this chapter is scheduled to appear as part of a review of energy controlled diffusion equations in *Advances in Chemical Physics* (in the press [32]).

Now Kramers obtained expressions for the escape rate Γ that are valid in the IHD and VLD regimes. However, he was unable to give the escape rate in the low damping (LD) or underdamped regime lying between VLD and intermediate dissipation (ID). This so-called *Kramers Turnover Problem* was solved nearly 50 years later by Mel'nikov and Meshkov [5], and Mel'nikov [6]. However, the calculations which involve an energy-action diffusion equation are short in detail and are not easily accessible to the reader. Hence I have described in detail how the Green function of the energy-action diffusion equation may be obtained and how the determination of the escape rate may be reduced to solving a Wiener-Hopf equation. I have also criticized and compared the Mel'nikov calculation, which relies on an *ad hoc* extrapolation of the low damping result to IHD, with the method of Grabert, Pollak and Hänggi [2], which works on the premise that the escape rate depends on the slowest over barrier normal mode rather than on the particle coordinate. Thus Chapter 3 concludes the classical part of my work which has appeared as part of a very large chapter in *Advances in Chemical Physics* [7].

Chapter 4 of the thesis describes the principles of high temperature semiclassical calculation of the escape rate, where the physical mechanism at work is the escape of particles due to tunneling near the top of the barrier. The three regimes envisaged by Kramers, namely, VLD, LD and IHD, also occur in quantum dissipative tunneling. Now an expression for the quantum IHD escape rate was first obtained by Wolynes [8] using path integrals. However, his calculations are so short on detail as to be virtually incomprehensible. An alternative approach to calculating the quantum escape rate was given by Pollak [9] where he considered the quantum particle linearly coupled to a set of harmonic oscillators representing the bosonic bath. Again the calculations, although more transparent than those of Wolynes, are short on detail and inaccessible to the general reader. I have therefore described Pollak's method in a manner accessible to the reader and I have clearly shown each step in the procedure. My calculations on this form part of a chapter in *Advances in Chemical Physics* [7].

The second more involved calculation of Γ is that of Mel'nikov [6] concern-

ing the LD case whence the VLD result simply emerges as a well defined limit. Mel'nikov used a method proposed by Larkin and Ovchinnikov [10] to calculate the probability that a particle starting in state j will be in state f after a time interval of t seconds. The probability of this noise-induced transition from state j to state f is then averaged over the state of the thermal bath. The resulting Green function then forms the kernel of the integral equation for the semiclassical energy distribution function which is again a Wiener-Hopf equation like in the classical LD case. Thus the semiclassical LD escape rate may be determined. However, the problem is more complicated than in the classical case because the depopulation factor, interpolating between the ID and VLD rates, must be determined for each particular potential in terms of the semiclassical matrix elements of the system-bath operator specifying the evolution of the state vector from one (relatively high) energy level to another in the well. Unlike the classical case, this adds an extra degree of complexity to the problem. These very involved calculations have been published in *Advances in Chemical Physics* [7] and are now at a level easily accessible to the reader. They are described in detail in Chapters 5 and 6 of the thesis along with details of how the quantum VLD rate emerges from these.

Chapter 2

Escape Rate Theory

This chapter presents a summary of reaction rate theory for escape, due to thermal fluctuations, of a particle from a one-dimensional potential well and its generalization to multidimensional systems [1] comprising many degrees of freedom. The main results of the effects of *dissipative* coupling to the bath as obtained by Kramers [11], i.e. for very small (energy controlled diffusion) and relatively large damping (spatially controlled diffusion), are summarized while the extension of Kramers' intermediate to high damping (IHD) escape rate for the dissipative coupling to the heat bath (spatially controlled diffusion) to many dimensions is very briefly outlined. The chapter concludes with a description of the Kramers turnover problem which arises when one wishes to treat the situation where *neither* energy controlled nor spatially controlled diffusion entirely prevails. The semiclassical quantum generalization of these results is also summarized. This will serve as a pointer to the detailed calculations to be presented later. The calculation of the classical Kramers energy controlled diffusion escape rate pertaining to very low damping (VLD) is described in detail in several Appendices as this is one of the cornerstones of the thesis.

2.1 Transition state theory

Chemical reactions in condensed phases can be modeled as three-stage processes [1] which may be summarized as follows. Reactants are brought together in

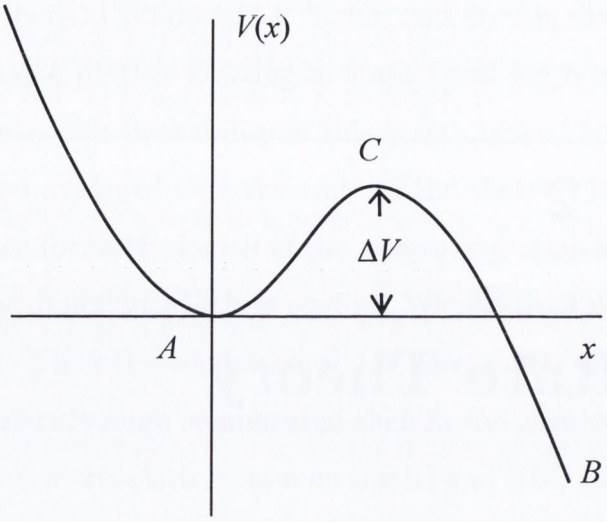

Figure 2.1: Single well potential function as the simplest example of escape over a barrier (from Coffey et al. [12]).

the first stage. The second stage involves the crossing of a potential barrier. When the barrier is high this barrier crossing or transition stage determines the rate of the chemical reaction. In the last stage the products are separated from each other. This conception of reaction rate theory began in the 1880s when Arrhenius [1, 2, 13–15] analysed experimental data and proposed an empirical equation for the rate coefficient of a chemical reaction which ultimately led to the idea of chemical reactions as arising in an assembly of particles situated at the bottom of a potential well subjected to thermal agitation. Thus a few particles out of the well population attain enough energy to escape over the potential barrier and never return [2]. The escape of a particle over the barrier represents a chemical reaction and x is called the reaction coordinate. A single well potential function (which we shall mostly be concerned with) is illustrated in Figure 2.1. The population of particles is initially trapped in the well near the point A by a high potential barrier at the point C and is thermalized very rapidly in the well. However, rare particles out of the population attain enough energy to escape over the barrier into region B, whence they never return. The barrier height ΔV is assumed to be large so that the rate of escape of particles is very small. In the

model for a chemical reaction the particles to the left of the barrier correspond to the *reactants* and particles that have crossed the barrier into region B correspond to the *products* of the chemical reaction. The Arrhenius law for the escape rate, Γ, (defined as the current of particles over the barrier divided by the total population in the well or flux–over–population) which can be justified in terms of transition state theory (TST), is [1, 2]

$$\Gamma = \Gamma^{\mathrm{TST}} = \frac{\omega_A}{2\pi} e^{-\Delta V/(k_B T)} \tag{2.1}$$

Here, ω_A is the angular frequency of a particle executing *small* oscillations about the bottom of the well. The frequency $\omega_A/2\pi$ is called the *attempt frequency* and it depends only on the shape of the potential. Using Taylor's theorem the potential near the bottom of the well may be approximated as [16] (the parabola)

$$V(x) \approx V(x_a) + (x - x_A)V'(x_A) + \frac{(x - x_A)^2}{2} V''(x_A) \tag{2.2}$$

and we obtain

$$\omega_A = \sqrt{\frac{V''(x_A)}{m}} \tag{2.3}$$

The escape rate given by Eq. (2.1) is the product of the attempt frequency and a Boltzmann factor $e^{-\Delta V/(k_B T)}$, weighing the escape from the well.
TST is based on two crucial assumptions [1]:

1. The thermal equilibrium (Maxwell–Boltzmann) distribution is maintained *throughout* the well *even* at the barrier C.

2. The rate coefficient is determined by the equilibrium flux across the boundary separating reactants and products.

Note that Γ^{TST} *does not depend on the coupling between the molecules and their environment* and so does not involve the dissipation to the bath. It depends only on the parameters that determine the equilibrium distribution. A simple derivation of Eq. (2.1) in terms of the forward flux at the transition state $x = x_C$ is given by Nitzan [1]. This equation yields the correct TST rate provided that $V(x)$ is taken as the *effective* potential of the reaction coordinate. In other words $V(x)$ is the potential of mean force along this coordinate when all other degrees

of freedom are in thermal equilibrium at any given point on it. A generalization of Eq. (2.1) to an $N+1$ dimensional system with a *separable* and *additive* Hamiltonian such as that pertaining to point particles has also been described by Nitzan [1] and is

$$\Gamma^{\mathrm{TST}} = \frac{1}{2\pi}\left(\prod_{i=0}^{N}\omega_{A,i}/\prod_{i=1}^{N}\omega_{C,i}\right)e^{-\Delta V/(k_BT)} \tag{2.4}$$

Here $\omega_{A,i}$ are the angular frequencies of the modes which diagonalize the Hessian of the potential in the vicinity of the well bottom x_A^{N+1}, where x^{N+1} designates the collection of coordinates $(x_0, x_1, \ldots, x_N)$ while $\omega_{C,i}$ are the angular frequencies of the modes which diagonalize the Hessian at the saddle point x_C^{N+1}. However, the product of angular frequencies in the denominator of Eq. (2.4) is only over the *stable* modes associated with the saddle point C. Thus the *imaginary* frequency $\omega_{C,0}$ or positive eigenvalue associated with the *unstable* barrier crossing mode along the reaction coordinate is excluded so that the TST rate is given [2] in terms of the product of all *stable* mode frequencies at the bottom of the well and the inverse of the product of the *stable* mode frequencies at the saddle point. Moreover, if the unstable mode associated with the reaction coordinate can also be identified in the vicinity of the well bottom and has frequency $\omega_{A,0}$ say then Eq. (2.4) can be rewritten as [1]

$$\Gamma^{\mathrm{TST}} = \frac{\omega_{A,0}}{2\pi}e^{-F_C/(k_BT)} \tag{2.5}$$

where the activation free energy F_C is given by

$$F_C = -k_BT\ln\int dx^N e^{-V(x^{N+1})} = W(x_{C,0}) = T(k_B\Delta V - S_C) \tag{2.6}$$

and

$$S_C = k_B\ln\left(\prod_{i=1}^{N}\frac{\omega_{A,i}}{\omega_{C,i}}\right) \tag{2.7}$$

S_C is the entropic component of the activation free energy. Since Eq. (2.4) can be written in the effective one dimensional form of Eq. (2.5) it is clear that we have a *free energy surface* associated with a *free energy barrier*. Equations (2.4)-(2.7) are important in the generalization (see below) of the IHD Kramers escape rate to many dimensions due to Langer [17]. In his treatment dissipative motion is

effectively modeled in the *entire* phase space of the system, whereby one treats explicitly the coupling to the bath degrees of freedom, as pointed out by Pollak et al. [18]. Eq. (2.4) can also be rewritten (details in [2]) as

$$\Gamma^{\mathrm{TST}} = \frac{k_B T}{h} \frac{Z^{\ddagger}}{Z_0} e^{-\Delta V/k_B T} \tag{2.8}$$

where

$$Z_0 = \prod_{i=0}^{N} \frac{k_B T}{\hbar \omega_{A,i}}, \qquad Z^{\ddagger} = \prod_{i=1}^{N} \frac{k_B T}{\hbar \omega_{C,i}} \tag{2.9}$$

are the harmonic approximations to the well and saddle partition functions respectively. In other words the potential in the well is represented by a paraboloid in hyperspace (in two degree of freedom systems an elliptical bowl) while the saddle is represented by an inverted paraboloid (in two degree of freedom systems a horse's saddle). An example is in the application of the theory to magnetic relaxation of classical spins [12].

Coffey et al [19] reviewed quantum effects in reaction rate theory and analysed in detail the quantum generalization of Eq. (2.1).

$$\Gamma \approx \frac{\omega_A}{2\pi} \Xi e^{-\Delta V/k_B T} \tag{2.10}$$

where

$$\Xi = \frac{\omega_C}{\omega_A} \frac{\sinh[\hbar\omega_A/(2k_B T)]}{\sin[\hbar\omega_C/(2k_B T)]} = \prod_{n=1}^{\infty} \frac{(2n\pi k_B T/\hbar)^2 + \omega_A^2}{(2n\pi k_B T/\hbar)^2 - \omega_C^2} \tag{2.11}$$

is the quantum correction to the classical TST result (essentially due to Wigner 1932 [20]). The angular frequencies $2\pi n k_B T/\hbar$ correspond to those of the bosonic bath (see Eq. (2.16) below). The physics of this is that the quantum correction factor Ξ represents an effective lowering of the potential barrier so enhancing the escape rate. The mechanism at work is high temperature quantum tunneling of particles near the top of the barrier. Note that the correction factor given by Eq. (2.11) diverges at a crossover temperature T_C given by $T_C = \hbar\omega_C/(2\pi k_B)$. The divergence occurs because the parabolic (or inverted oscillator) approximation for the potential is only valid near the top of the barrier. However, at very low temperatures $T << T_C$, the particle is near the bottom of the well, and the parabolic approximation to the barrier shape is not sufficient (see [21, Ch. 12]). In contrast, for $T > T_C$ the particle is near the top of the well and so transitions

due to tunneling near the top of the barrier dominate, and the parabolic approximation is accurate [19]. Eq. (2.11) was derived [19] using the Wigner function method which essentially allows one to calculate expectation values of quantum operators in the same way as classical ones by introducing a quasi–probability distribution (quasi– due to the Uncertainty Principle) in the phase space of positions and momenta of a particle. Wigner's idea in introducing the phase space quasi–distribution, which is the analogue of the classical joint distribution of positions and momenta, was to facilitate the calculation of high temperature quantum corrections (semiclassical) to thermodynamic equilibrium. The natural vehicle for this is the joint distribution of positions and momenta. Alternatively, the quantum correction, Ξ, may be derived without the use of the Wigner formalism because the escape rate may be written as [21] (the integration limits are $-\infty, \infty$ to take account of tunnelling)

$$\Gamma = Z_A^{-1} \int_{-\infty}^{\infty} t(E) e^{-E/(k_B T)} dE \tag{2.12}$$

where

$$t(E) = \left[1 + e^{2\pi(V_C - E)/(\hbar\omega_C)}\right]^{-1} \tag{2.13}$$

is the exact quantum transmission (penetration) coefficient (ignoring dissipation) of a parabolic barrier [22]. Hence

$$\Gamma = \frac{\hbar\omega_C}{2Z_A \sin[\hbar\omega_C/(2k_B T)]} e^{-V_C/(k_B T)} \tag{2.14}$$

Near the bottom of the well the partition function Z_A is approximated by that of a quantum harmonic oscillator so that [19]

$$Z_A \approx \frac{\pi\hbar}{\sinh[\hbar\omega_A/(2k_B T)]} e^{-V_A/(k_B T)} \tag{2.15}$$

Hence we have Eq. (2.10). It is helpful to recall that Eq. (2.15) may also be expressed as an infinite product, e.g.

$$\frac{1}{2\sinh(\hbar\omega_0/(2k_B T))} = \frac{k_B T}{\hbar\omega_0} \prod_{n=1}^{\infty} \frac{\nu_n^2}{\omega_0^2 + \nu_n^2} \tag{2.16}$$

where $\nu_n = 2\pi n k_B T/\hbar \quad n = 1, 2, \cdots$ are called the Bosonic Matsubara [23] frequencies. Eq. (2.16) follows from Eq. (4.5.68) of Abramowitz and Stegun [24]

which represents $\sinh z$ as an infinite product, namely,

$$\sinh z = z \prod_{k=1}^{\infty} \left(1 + \frac{z^2}{k^2 \pi^2} \right) \tag{2.17}$$

This relatively high (i.e. $T > T_C$) temperature quantum correction to the exponential factor in Eq. (2.10) was essentially obtained by Wigner [20]. The multidimensional generalization of Eq. (2.10) where at the transition state we have N real oscillators with frequencies $\omega_{C,j}$, $j = 1, \ldots, N$ and one imaginary frequency oscillator with frequency $\omega_{C,0}$ (effectively as in an inverted pendulum) is [2]

$$\Gamma = \frac{\omega_{C,0}}{2\pi} \frac{\sinh[\hbar\omega_{A,0}/(2k_BT)]}{\sin[\hbar\omega_{C,0}/(2k_BT)]} \left(\prod_{j=1}^{N} \frac{\sinh[\hbar\omega_{A,j}/(2k_BT)]}{\sinh[\hbar\omega_{C,j}/(2k_BT)]} \right) e^{-\Delta V/(k_BT)} \tag{2.18}$$

However, classical TST relies entirely on the concept of *equilibrium flux* (i.e. probability current) calculated for example [1] via the Maxwellian velocity distribution through a carefully chosen surface. This simplification often provides a good approximation to the observed nonequilibrium rate and for high energy barriers the dynamical effects sometimes lead to relatively small corrections. Nevertheless, in other cases notably superparamagnetism, where TST is used to calculate the reversal time of the magnetization of the single domain particle involved, nonequilibrium effects may yield corrections of several orders of magnitude [12, Chapter 9]. A very unsatisfactory feature of both classical and quantum TST is that they predict *escape in the absence of coupling to a heat bath* which contradicts the fluctuation-disspiation theorem [12]. For example, TST assumes that thermal equilibrium prevails everywhere so that the Maxwell-Boltzmann distribution holds throughout the well even near the barrier top at C. However, this is invalid as the loss of particles from the well at C will disturb that distribution. This defect was remedied for classical TST by the pioneering work of Kramers [11] which we have briefly alluded to.

2.2 Kramers' contribution to escape rate theory

Kramers' idea was to derive a formula for the escape rate, Γ, that accounted for the disturbance to the equilibrium distribution in a well due to the loss of

particles at the barrier. This was achieved by using the theory of Brownian motion to represent the interaction between the heat bath and a particular or tagged particle of the bath. In the Kramers model [2, 11, 13], the particle coordinate x represents, as usual, the *reaction coordinate*. The value of this coordinate, x_A, at the bottom of the well at A represents the *reaction state*, the value, x_B, in region B represents the *product state*, and the value, x_C, at the saddle point, represents the *transition state*. In his calculations of 1940, Kramers [11, 14] made the following assumptions:

1. The particles are initially trapped in the well near the minimum of the potential at the point A.

2. The barrier height is very large compared with $k_B T$.

3. The particles receive energy from the surrounding heat bath and a Maxwell-Boltzmann distribution distribution is attained rapidly in the well.

4. Quantum effects are negligible.

5. Since the barrier height is very large, the rate of escape of particles is very small so that the disturbance to the Maxwell–Boltzmann distribution in the depths of the well is very small (quasistationary). Effectively the disturbance is then confined to a *boundary layer* or *skin* in the barrier region.

6. A particle that escapes over the barrier never returns.

7. The dynamics of a particle of the reacting system may be modeled by the theory of the Brownian motion, including the inertia of the particle.

In order to incorporate non–equilibrium effects Kramers introduced a dissipation dependent prefactor, μ, so that

$$\Gamma = \mu \Gamma^{\mathrm{TST}} = \mu \frac{\omega_A}{2\pi} e^{-\Delta V/(k_B T)} \tag{2.19}$$

where μ removes the possibility that escape can occur in the absence of dissipation to the bath. His objective was to calculate the prefactor μ from a *microscopic*

model of the chemical reaction. The model incorporates dissipation by considering an assembly of *Brownian particles* in a potential well. Thus all the (c. 10^{24}) degrees of freedom of the system comprising a tagged particle and the bath are represented by the Newtonian equation of motion of the *single* tagged particle supplemented by a systematic frictional force slowing down the particle and a very rapidly fluctuating white noise driving force which stops it reverting to a completely dead state. If this were not so one cannot observe Brownian motion. The dissipation dependent prefactor μ is governed by the *stochastic differential equation* underlying the Brownian motion of a single particle, i.e. the Langevin equation for the evolution of the random (state) variables (position and momentum constituting the state vector in the state or phase space of positions and momenta of the single particle), and the associated *probability density diffusion equation* describing the evolution of the density of the realizations (phase points) of these random variables in phase space. This is the Fokker-Planck equation (FPE), which like the Boltzmann equation [12, 25], of which it is but a particular form, is a *closed* equation for the *single particle* or reduced probability density function (pdf) comprising a joint distribution function in phase space. In the Fokker–Planck equation, the hydrodynamical or convective derivative is no longer zero as in the Liouville equation because the streaming motion (governed by Hamilton's equations) along hitherto constant energy trajectories in phase space described by the Liouville equation is disturbed by the bath–particle interaction which leads to dissipation and fluctuations in the energy trajectories. Now Kramers was able to calculate the value of μ in two specific regions of damping: intermediate to high damping (IHD) and very low damping (VLD) for adiabatic collisions. We may summarize by saying that the basic idea is to mimic the effect of the heat bath on any given particle of the assembly of circa 10^{24} particles by postulating in the Langevin picture that the effect of the bath on a (tagged) particle is represented by a frictional term in the Newtonian equation of motion of the particle. This force acting alone would ultimately drive the particle towards a dead state (collapsing energy trajectories). However, thermal fluctuations due to the bath which maintain the observed Brownian motion are represented by a

rapidly fluctuating white noise driving force causing the equation of motion to have a particular integral.

2.2.1 IHD or spatially controlled diffusion escape rate

To obtain asymptotes of the escape process Kramers considered a tagged particle of one degree of freedom so he treated the barrier as an inverted parabola. Since the escape over the barrier is an exponentially slow process he set $\dot{\rho} = 0$ in the Fokker–Planck equation (2.20) below. The Fokker–Planck equation is the probability density diffusion equation governing the *reduced* or *single particle* distribution function (pdf), $\rho(x, p, t)$ of the positions and momenta in phase space of a particle, namely,

$$L_{FP}\rho = \frac{\partial \rho}{\partial t} = \frac{dV}{dx}\frac{\partial \rho}{\partial p} - \frac{p}{m}\frac{\partial \rho}{\partial x} + \beta\frac{\partial}{\partial p}\left(\rho p + mk_BT\frac{\partial \rho}{\partial p}\right) \tag{2.20}$$

and the quasi-stationary probability density diffusion equation is that equation with $\dot{\rho} = 0$. Notice that the Fokker–Planck equation may in general be written in terms of the convective derivative

$$\frac{D\rho}{Dt} = \beta\frac{\partial}{\partial p}\left(\rho p + mk_BT\frac{\partial \rho}{\partial p}\right) \tag{2.21}$$

where β is the friction coefficient per unit mass, x is the position and p is the momentum. (The particular Fokker–Planck equation for point particles with separable and additive Hamiltonians is known as the Klein–Kramers equation.) The terms in β comprising dissipation and fluctuations represent the effect of the bath on the single particle pdf. The conservative or Liouville terms (first two on right hand side) represent Hamilton's equations for the *single particle*, namely, $H = p^2/(2m) + V(x)$, $\dot{p} = -\partial H/\partial x$, and $\dot{x} = \partial H/\partial p$, and in the absence of dissipation and fluctuations describe the *streaming motion* along a trajectory of constant energy, $H = E$, in phase space governed by the Liouville equation $D\rho/Dt = 0$. The dissipative and fluctuation terms are contained in the Langevin equation

$$\dot{p} = -\frac{\partial V}{\partial x} - \beta p + F(t) \tag{2.22}$$

where the effect of the bath on the particle is represented by the *systematic* retarding force $-\beta p$ mentioned above which tends to destroy the streaming motion, superimposed on which is a *very rapidly fluctuating* white noise force $F(t)$ which in contrast tries to sustain it, the net effect being diffusion of the trajectories. Kramers linearized the Langevin equation, and so the quasistationary Fokker–Planck equation, about the barrier top allowing him to find the escape rate (frequency) as the flux over population i.e. J/N, where J is the current of particles over the barrier and N is the total number of particles in the well. The origin of J is the steady current needed to replenish those particles which escape across the barrier so that the quasistationary distribution will be maintained. For the IHD rate the region of non–equilibrium is in the immediate vicinity of the top of the barrier and so *lies well inside the range where the barrier shape may be approximated by an inverted parabola* which is crucial to the calculation of that rate. The Kramers formula for the IHD escape rate is

$$\Gamma^{\mathrm{IHD}} = \left[\sqrt{1+\beta^2/(4\omega_C^2)} - \beta/(2\omega_C)\right] \Gamma^{\mathrm{TST}} \tag{2.23}$$

where ω_C is the characteristic angular frequency of the inverted oscillator approximation to the potential $V(x)$ in the vicinity of the barrier. The correction to the TST result is essentially the positive eigenvalue (characterizing the unstable barrier crossing mode) of the Langevin equation associated with the Klein-Kramers equation (however omitting the noise) linearized (inverted parabola approximation) about the saddle point of the potential $V(x)$. The reader should recall that in a driven linear time-invariant system the response is determined by the eigenfunctions of the transition matrix. Equation (2.23) formally holds [14], see below, when the energy loss per cycle of the motion of a particle librating in the well with energy equal to the barrier energy E_C, is significantly greater than $k_B T$.

The energy loss per cycle of the motion of a barrier crossing particle is $\beta S(E_C)$ (see Appendix 2.D), where S is the action of a librating particle *without dissipation* evaluated at the barrier energy $E = E_C$.

The IHD asymptotic formula was derived by supposing [12]:

(i) that the barrier is so high and the dissipative coupling to the bath so strong

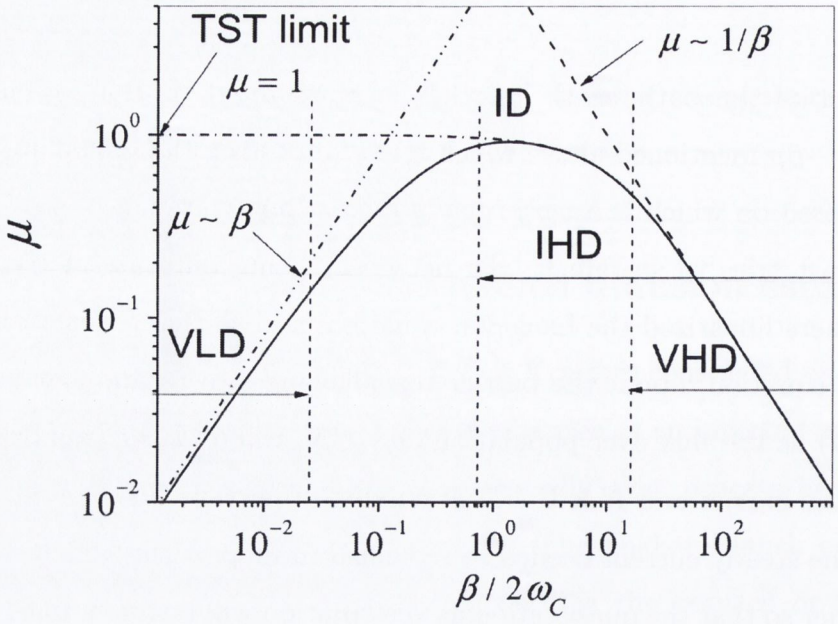

Figure 2.2: Prefactor μ vs. $\beta/2\omega_C$, showing the VLD, VHD and IHD regions and the TST limit. The underdamped region essentially extends from ID to zero damping. Overdamped from ID to VHD. The escape rate can never exceed the TST rate which serves as an upper bound for it (from Coffey et al. [12]).

that a Maxwell-Boltzmann distribution distribution always holds at the bottom of the well, and

(ii) that the Langevin equation may be linearized in the region very close to top of the barrier, so that all the coefficients in the corresponding Klein-Kramers equation are linear in the positions and velocities. Hence we speak of a linearized Klein-Kramers equation.

If this is so, then the quasi-stationary Klein-Kramers equation may be integrated by introducing an independent variable which is a linear combination of the two phase variables x and p so that it becomes an *ordinary* differential equation in a *single* variable. Notice from Eq. (2.23) that if $\beta >> \omega_C$ (overdamped system) we get the very high damping (VHD) result,

$$\Gamma^{\mathrm{VHD}} = \frac{\omega_C}{\beta}\Gamma^{\mathrm{TST}} = \frac{\omega_A \omega_C}{2\pi\beta} e^{-\Delta V/(k_B T)} \tag{2.24}$$

However, for small friction (such that $\beta S(E_C) << k_B T$) the IHD formula fails, predicting like the TST formula escape in the *absence of coupling to the bath* [14]. This failure can be attributed to the fact that for small friction the

region of significant departure from the Maxwell-Boltzmann distribution in the well extends far beyond the region where the potential may be approximated by an inverted parabola. Kramers treated the extremely underdamped case, when β is almost vanishingly small, using an *energy controlled diffusion* model, the gist of which is to consider closed librational trajectories of the deterministic (streaming) motion infinitesimally close to the barrier energy and then to assume that they become fuzzy due to dissipation and fluctuations. Then some of them will become *open* trajectories, traveling on which a particle may escape the well.

2.2.2 VLD or energy controlled diffusion escape rate

We mentioned that Kramers obtained a second formula for the escape rate which is valid in the very low damping (VLD) case, where the energy loss per cycle $\beta S(E_C)$ of a librating particle with energy equal to the barrier energy E_C is very much less than the mean thermal energy $k_B T$. He considered particles librating in the well at the critical barrier energy. In the *absence* of damping and fluctuations the particles stream, according to $D\rho/Dt = 0$, along the closed phase space trajectory corresponding to the critical energy. Thus they cannot on their own escape the well. However, the stochastic forces due to the bath will disturb the streaming motion in the vicinity of the barrier, so that the energy trajectories will diffuse (i.e. have millions of trajectories rather than the single trajectory of the deterministic motion) and some of them will open due to thermal fluctuations because the motion on the critical trajectory is *metastable*, so that the particles on those trajectories may escape. Kramers solved the VLD problem by transforming the Fokker–Planck equation into a new equation, using only the energy, E, and phase as variables. He postulated that the energy, E, diffuses very slowly while the phase is very fast. Kramers then averaged the transformed equation over the phase and got an evolution equation for the one–dimensional energy distribution function $w(E,t)$ namely

$$\dot{w}(E,t) = \beta \frac{\partial}{\partial E} \left\{ S(E) \left[1 + k_B T \frac{\partial}{\partial E} \right] \left[\frac{\omega(E)}{2\pi} w(E,t) \right] \right\} \tag{2.25}$$

The quasi–stationary solution, $\dot{w}(E,t) = 0$, of Eq. (2.25) with constant injected current (in order to replace the particles lost at the barrier so that $\dot{w}$ still remains

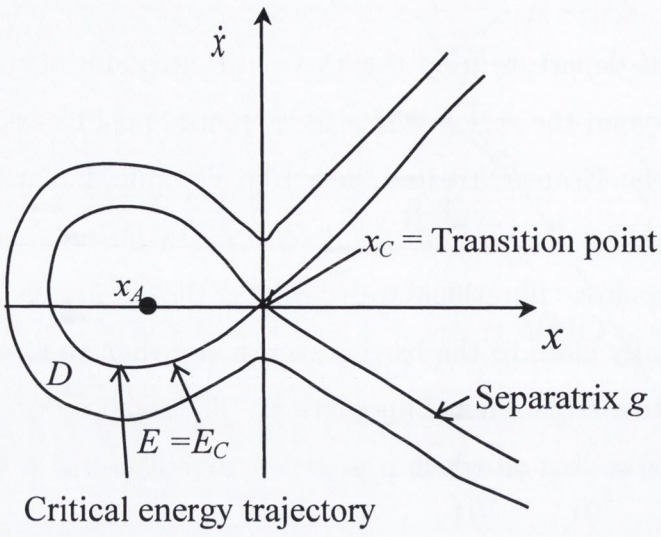

Figure 2.3: The critical energy curve in phase space (adapted from Coffey et al. [12]). The figure is greatly magnified. The separation between the (closed) critical energy trajectory and the open separatrix on which the particle escapes is infinitesmal.

zero) then yields in the high barrier limit the VLD formula (or energy controlled diffusion rate)

$$\Gamma^{\mathrm{VLD}} = \frac{\beta S(E_C)}{k_B T} \frac{\omega_A}{2\pi} e^{-\Delta V/(k_B T)} = \frac{\beta S(E_C)}{k_B T} \Gamma^{\mathrm{TST}} = \Delta \Gamma^{\mathrm{TST}} \tag{2.26}$$

where $S(E_C) = \oint_{E=E_C} p\, dx$ is the action over an entire oscillation in the well of a particle with energy equal to the barrier energy and the parameter

$$\Delta = \frac{\text{Energy loss per cycle of a librating particle with energy } E_C \text{ at onset}}{\text{Thermal energy}} \tag{2.27}$$

This formula holds when $\beta S(E_C) << k_B T$ and unlike the TST result vanishes when $\beta \to 0$, so that escape is impossible without coupling to the bath. The value of this calculation, which represents the single most important contribution of Kramers to reaction rate theory, is incomparable as through the parameter Δ it allows us to establish criteria for the range of validity of the VLD and IHD escape rates. All that is required to calculate the VLD rate is then a *knowledge of the classical undamped dynamics of the closed critical energy trajectory.*

Kramers made several estimates of the range of validity of both IHD and VLD formulas and the intermediate (or moderate) damping (ID) regime where the TST

Eq. (2.1) holds with a high degree of accuracy. However, as we saw, he was unable to give a formula in the underdamped regime lying between IHD and VLD, as there $\beta S(E_C) \approx k_B T$ so that no small perturbation parameter now exists. In other words the energy loss is balanced by the gain in thermal energy from the bath. This is known as the *Kramers turnover problem* essentially because the escape rate switches from being dominated by *energy controlled diffusion* where the escape rate is proportional to the friction, to being dominated by *spatially controlled diffusion* where the escape rate is inversely proportional to it. In this general underdamped region neither the *purely energy* nor the *purely spatially controlled* diffusion mechanism dominates. The Kramers turnover problem was solved nearly 50 years later by Mel'nikov [6], and Mel'nikov and Meshkov [5]. By means of a transformation of Eq. (2.20), with the energy E regarded as a parameter which specifies the momentum p for a given value of the position variable x (see Appendix 2.G), they constructed an energy–action diffusion equation (3.38 below) valid in the barrier region and determined its Green function which represents the conditional (transition) probability that a particle commencing in the barrier region with (initial) energy E' will return to it with energy E. This is a sharply peaked Gaussian distribution which resembles a delta function due to the small change in energy on a typical noisy trajectory infinitesimally close to the undamped deterministic librational trajectory where the conditional pdf is just the Dirac delta function $\delta(E - E')$ representing the fact that there is no alteration in energy in a single cycle in this loss free case. The Green function at a given action, namely $g(E, S|E', 0)) \equiv g(E - E', S)$, satisfies the energy–action diffusion equation

$$\frac{\partial g}{\partial S} = \beta \frac{\partial}{\partial E}\left(g + k_B T \frac{\partial g}{\partial E}\right) \tag{2.28}$$

and is given by the Gaussian distribution

$$g(E - E', S) = \frac{1}{\sqrt{4\pi k_B T \Delta}} e^{-\frac{(E-E'+\Delta)^2}{4k_B T \Delta}}, \quad -\infty < E - E' < \infty \tag{2.29}$$

where the mean $< E - E' >= -\Delta$, and the variance $\sigma^2 =< (E - E')^2 >= 2k_B T\Delta$. The characteristic function (Fourier transform over energy normalized by $k_B T$) is

$$\tilde{g}(\lambda) = e^{-\Delta(\lambda^2 + 1/4)} \tag{2.30}$$

where Δ is the Kramers dissipation parameter (see Chapter 3).

Using the Green function Eq. (2.29) as kernel and the principle of superposition Mel'nikov and Meshkov [5] then wrote an integral equation for the evolution (spread) of the energy distribution function due to dissipation and fluctuations in the critical or barrier region which is as already mentioned a boundary layer.[1] The integral equation for an arbitrary initial distribution of energy $f(E', 0)$ for a trajectory near the barrier is then, by the principle of superposition

$$f(E, S) = \int_{-\infty}^{0} f(E', 0) g(E - E', S) dE' \tag{2.31}$$

Mel'nikov and Meshkov then converted Eq. (2.31) into a Wiener–Hopf equation by appropriate use of the boundary conditions (see Section 3.3 below) which they could then solve by standard methods [14, 26, 27]. The escape rate is then found by normalizing the population so that $\Gamma = \tau^{-1} = J = \int_0^\infty f(E) dE$ and τ is the lifetime of a particle in the well. The precise details of the calculation, which involves taking the Fourier transform of $f(E)$, $\phi^{\pm}(\lambda)$ given by Eq. (3.59) below, in both halves ($\pm$) of the complex (λ) plane and then using the Wiener–Hopf method, are given in Chapter 3. Hence we can find the prefactor $\mu = A(\Delta)$ as it is equal to $\phi^{+}(0)$ where the Fourier transform over energy is

$$\phi^{\pm}(\lambda) = \frac{\pi}{\omega_A} e^{\frac{\Delta V}{k_B T}} \int_{-\infty}^{\infty} U(\pm E) f(E) e^{\frac{i\lambda E}{k_B T}} dE \tag{2.32}$$

where $U(x)$ is the unit step function and λ is dimensionless. Thus Mel'nikov and Meshkov obtained an escape rate formula which is valid for all values of the friction β, namely,

$$\Gamma = A(\Delta) \Gamma^{\mathrm{IHD}} \tag{2.33}$$

where the Kramers dissipation parameter $\Delta = \beta S(E_C)/(k_B T)$ is, as we saw, the ratio of the energy loss per cycle of a particle librating with energy equal to the

[1]The energy action diffusion equation represents drift under a constant force and diffusion in energy space. The action plays the role of the time variable in conventional diffusion. An informative way of describing the process is also to write the corresponding Langevin equation with the energy as the dependent variable. This is discussed in the Appendices below and in Chapter 3.

barrier energy to the thermal energy, and

$$A(\Delta) = \exp\left(\frac{1}{2\pi}\int_{-\infty}^{\infty} \ln\left[1 - e^{-\Delta(\lambda^2+1/4)}\right] \frac{d\lambda}{\lambda^2 + 1/4}\right) \tag{2.34}$$

is called the depopulation factor [28] because in the underdamped case the flow across the barrier leads to a *depopulation* of the upper energy regions in the well. This depletion effect completely dominates the escape rate for very weakly damped systems [28]. In fact it leads to the boundary condition of zero density at the barrier used in VLD (cf Eq. (2.115) below) which is not in general true in the underdamped region as demonstrated by Mel'nikov [6]. Thus, it is clear how Mel'nikov solved the problem in the entire underdamped region lying between TST (ID) and zero damping. The final formula (2.33) is then obtained in heuristic fashion by simply multiplying the exact low damping escape rate by the IHD rate. (For a detailed discussion of this point see Chapter 3 where the "rigorous" calculation of Pollak, Grabert and Hänggi [18] (and revisited by Pollak and Ankerhold [29]) is summarized.) This assumption is prompted by the fact that both the underdamped rate and the IHD rate tend in the appropriate limits to the same upper bound, namely the TST rate. Finally $A(\Delta)$ [14] tends to Δ in the VLD limit while $A(\Delta)$ tends to 1 in the ID limit.

2.2.3 Summary of the Kramers results

We saw that:

(i) the Kramers IHD result fails for low damping because the region of departure from the equilibrium in the well is far greater in spatial extent than the region near the barrier top where the inverted parabola approximation is valid.

(ii) Kramers treated the VLD case by considering a particle librating in the well with energy equal to the saddle energy, E_C. Without any fluctuation/dissipation the motion of this large oscillation pendulum characterized by librational motion on the closed trajectory with energy E_C would persist forever. However, in the nearly upright position the pendulum is *metastable*,

and if it is coupled to a bath the thermal fluctuations may cause the bob to escape from the librational trajectory. In other words, the fluctuations may cause this *separatrix* trajectory, dividing the bounded motion in the well from the unbounded one outside, to become an escape trajectory (cf. the energy is now a random variable with a Gaussian distribution given by Eq. (2.29)). Kramers treated the VLD case by writing the Klein–Kramers equation in energy–phase variables and considering trajectories in the vicinity of the barrier in energy–angle (phase) space. Because the damping is very small he is able to average over the angle (or phase) variable. Now since the Liouville equation is simply the derivative of the distribution function w.r.t. the phase, he used that equation (conservation of density in phase), thereby postulating that the disturbance to the streaming motion at the critical energy is almost negligible, to eliminate the conservative term in the transformed Klein–Kramers equation, meaning that he assumed no coupling between dissipative and conservative terms. This procedure yielded an energy diffusion equation whence, by assuming that all particles that reach the separatrix cross the barrier, the escape rate is easily calculated by the flux–over–population method as detailed in the Appendices to this Chapter. The latter assumption is only true for VLD and has been justified rigorously by Mel'nikov [6] (see also Chapter 3).

However, this energy controlled diffusion result cannot apply in the entire underdamped region because of Kramers' assumption that the coupling between the Liouville and conservative terms in the transformed Klein–Kramers equation can be ignored so that he can use the Liouville equation to eliminate the phase. Instead the Klein–Kramers equation in the barrier region must be written in energy–action variables and the variation of the distribution function w.r.t. the action, which is ignored in the VLD case, is now included [6]. Thus the energy trajectories at a given action diffuse, c.f. his remark: "We consider a thin ring of thickness dI ...". This (partial) energy action diffusion equation may then be converted into an integral equation (details in Chapter 3) ultimately yielding in terms of the depopu-

lation factor a formula for the escape rate which is valid in the entire low damping region. According to [5] the escape rate in the entire range of damping may then be determined heuristically by simply multiplying the LD escape rate by the IHD rate (cf. Eq. (2.33)).

(iii) The precise definition of the escape rate, which was obtained asymptotically by Kramers and by Mel'nikov and Meshkov, is in fact the *high barrier limit* of $1/(2T_{\mathrm{MFPT}})$ where T_{MFPT} is the mean first passage time from the bottom to the summit of the well. If a multidimensional representation space is involved however, leading to a multidimensional PDE, e.g. as in the Klein–Kramers equation, T_{MFPT} is difficult to calculate because, although one can write a formal expression for it, one cannot use quadratures so that a Fourier expansion of the distribution function is always involved [30].

(iv) The IHD escape rate Γ^{IHD} in the limit of vanishing friction becomes the TST result. Eq. (2.1). This behaviour is inconsistent [14] with the assumptions made in the derivation of Γ^{IHD}. Instead this limit yielding Γ^{TST} should be termed *intermediate damping.* In contrast, the correct formula is Eq. (2.26) which can be written as

$$\Gamma^{\mathrm{VLD}} = \frac{\beta S(E_C)\omega_A}{2\pi k_B T} e^{-\Delta V/(k_B T)} \tag{2.35}$$

Using as an approximation the harmonic oscillator action [31] $S_C = 2\pi\Delta V/\omega_A$ Eq. (2.35) becomes

$$\Gamma = \Gamma^{\mathrm{VLD}} = \frac{\beta\Delta V}{k_B T} e^{-\Delta V/(k_B T)} \tag{2.36}$$

If we define a dimensionless friction parameter $\alpha = 2\pi\beta/\omega_A$ Eq. (2.36) becomes

$$\Gamma = \frac{\alpha\Delta V}{k_B T}\Gamma^{\mathrm{TST}} \tag{2.37}$$

$\alpha\Delta V$ is approximately the energy loss per cycle. Hence, the condition for the validity of the VLD Eq. (2.36) becomes $\alpha\Delta V << k_B T$, while one would expect the IHD formula to be valid if $\alpha\Delta V \geq k_B T$. The damping $\alpha\Delta V \approx k_B T$ defines a *crossover region*, where neither VLD nor IHD formulas are valid. This criterion serves to define the *Kramers turnover region.*

The Kramers theory may be verified numerically for high potential barriers by calculating the smallest nonvanishing eigenvalue of the Klein-Kramers equation [14]. Since the barrier is high ($\Delta V/(k_B T) > 5$) the escape rate is tiny. The smallest nonvanishing eigenvalue is then *exponentially smaller* than the higher order ones, which pertain to the fast motion inside the well.

As just alluded to, another way of treating the problem is to consider the escape rate as $1/(2T_{\mathrm{MFPT}})$ where T_{MFPT} is the mean first passage time from the well bottom to the summit of the well. This has the advantage that in one dimension an exact integral formula for T_{MFPT} exists. For details of the method see [14, 32]. The Kramers escape rate for VHD and VLD which are governed by 1-D diffusion equations may then be calculated via the asymptotic expansion of T_{MFPT} as comprehensively illustrated for VLD in Appendix 2.C. However, it seems impossible at present to extend the integral formula calculation to more than one dimension, which is necessary in order to treat the turnover region, as a simple method of solution of the multidimensional PDE which involves the adjoint Fokker–Planck operator does not exist in the form of quadratures. The extension of the Kramers IHD theory to many degrees of freedom is essential for the calculation of the quantum IHD rate. Thus we summarize it here.

2.3 Extension of Kramers' IHD result to many dimensions

The Kramers IHD rate which applies to a system governed by the Langevin equations (x, p are the state variables (2-dimensional phase space), 1 degree of freedom)

$$\dot{x} = \frac{p}{m} \tag{2.38}$$

$$\dot{p} = -\beta p - \frac{\partial V}{\partial x} + F(t) \tag{2.39}$$

where $F(t)$ is white noise, may be written in the form

$$\Gamma = \frac{\lambda_+ \omega_A}{2\pi\omega_C} e^{-\Delta V/(k_B T)} = \frac{\lambda_+}{\omega_C}\left(\frac{\omega_A}{2\pi} e^{-\Delta V/(k_B T)}\right) = \frac{\lambda_+}{\omega_C}\Gamma_{TST} \tag{2.40}$$

where

$$\lambda_+ = \sqrt{\omega_C^2 + \frac{\beta^2}{4}} - \beta/2 \tag{2.41}$$

is the positive eigenvalue of the set of noiseless Langevin equations for the motion of the random variables governing the evolution of the state variables, linearized in the barrier region (inverted parabola approximation) corresponding of course to the unstable barrier crossing mode ($e^{\lambda_+ t}$). Now

$$\frac{\omega_A}{\omega_C} = \sqrt{\frac{\det \mathbf{E}^A}{|\det \mathbf{E}^C|}} \tag{2.42}$$

where $\det \mathbf{E}^C = -\omega_C^2$ and $\det \mathbf{E}^A = \omega_A^2$ are the Hessians (determinants) of the Hessian matrices of the saddle and well energies, when the inverted parabola and parabola approximations to the saddle and well energies are taken. The multidimensional Kramers problem was first solved in the VHD limit by Brinkman [33] and Landauer and Swanson [34]. However, the most complete treatment is due to Langer in 1969 [17], who considered the IHD limit. He generalized the Kramers IHD result to a system of N degrees of freedom characterized by a $2N$ dimensional phase space yielding (details in [14])

$$\Gamma = \frac{\lambda_+}{2\pi} \sqrt{\frac{\det \mathbf{E}^A}{|\det \mathbf{E}^C|}} e^{-(E_C - E_A)/(k_B T)} \tag{2.43}$$

Here E_A and E_C are the Hessian matrices of the well and saddle energies in the paraboloid and inverted paraboloid approximation. λ_+ is the (positive) eigenvalue (associated with the barrier crossing mode) of the linearized set of Langevin equations for the state variables in the vicinity of the barrier. Eq. (2.43) may be written as

$$\Gamma = \lambda_+ \frac{\omega_{A,0}}{2\pi} \left(\prod_{i=1}^{N} \omega_{A,i} / \prod_{i=1}^{N} \omega_{C,i} \right) e^{-\Delta V/(k_B T)} \tag{2.44}$$

Eq. (2.44) is of the same form as Eq. (2.4). Moreover, it constitutes a generalization of Becker and Döring's famous 1935 calculation [12] of the rate of condensation of a supersaturated vapour. Now as well put by Hänggi et al. [2] the generalization of the Kramers rate due to Langer is then equivalent to a multidimensional TST rate where the dissipative motion is modeled in the entire phase space of the system, i.e. one treats explicitly the coupling to the bath

degrees of freedom as was accomplished by Pollak [18] who showed how to relate the products of quantum partition functions to memory friction. Thus Langer's expression is the TST rate *in the entire representation or phase space* i.e. with all the degrees of freedom included. Note that λ_+ the eigenvalue associated with the unstable barrier crossing mode effectively represents a renormalized barrier frequency known [2] as the Grote–Hynes frequency. Again Langer's formula only applies in the strong coupling limit where the *effects of nonequilibrium due to energy controlled diffusion are negligible.*

This identification with TST in the complete phase space is extremely important because as we shall see in Chapter 4 it allows one to generalize, without the use of path integrals, the IHD result to the (high temperature) quantum case as was originally done by Pollak [18] (see quantum IHD escape rate below).

As an example we mention for the purposes of illustration that Coffey et al. [14] used Langer's method to derive the IHD result of Kramers. The linearized Langevin equation (omitting the noise) in the barrier region is

$$\begin{aligned}\begin{pmatrix} \dot{x} \\ \dot{p} \end{pmatrix} &= \begin{pmatrix} 0 & 1 \\ -1 & -m\beta \end{pmatrix} \begin{pmatrix} -m\omega_C^2 x \\ p/m \end{pmatrix} \\ &= \begin{pmatrix} 0 & 1/m \\ m\omega_C^2 & -\beta \end{pmatrix} \begin{pmatrix} x \\ p \end{pmatrix} \end{aligned} \tag{2.45}$$

or

$$\dot{\mathbf{X}} = \mathbf{A}\mathbf{X}, \quad \mathbf{A} = \begin{pmatrix} 0 & 1/m \\ m\omega_C^2 & -\beta \end{pmatrix} \tag{2.46}$$

with secular equation

$$\det(\mathbf{A} - \lambda \mathbf{I}) = 0 \tag{2.47}$$

which has solution

$$\lambda_\pm = \pm\sqrt{\omega_C^2 + \beta^2/4} - \beta/2 \tag{2.48}$$

The positive eigenvalue corresponding to the *unstable barrier crossing mode*, is then

$$\lambda_+ = \sqrt{\omega_C^2 + \beta^2/4} - \beta/2 \tag{2.49}$$

The Hessian matrices of the saddle and well energies (in the parabolic approximation) are given by

$$\mathbf{E}^C = \begin{pmatrix} m\omega_C^2 & 0 \\ 0 & -1/m \end{pmatrix} \quad \text{and} \quad \mathbf{E}^A = \begin{pmatrix} m\omega_A^2 & 0 \\ 0 & -1/m \end{pmatrix} \tag{2.50}$$

Thus, the Hessians are given by $\det \mathbf{E}^C = -\omega_C^2$ and $\det \mathbf{E}^A = \omega_A^2$, and so

$$\sqrt{\frac{\det \mathbf{E}^A}{|\det \mathbf{E}^C|}} = \frac{\omega_A}{\omega_C} \tag{2.51}$$

The escape rate is then

$$\Gamma = \frac{\lambda_+ \omega_A}{2\pi\omega_C} e^{-\Delta V/(k_B T)} = \frac{\omega_A}{2\pi} \left[\sqrt{1 + \left(\frac{\beta}{2\omega_C}\right)^2} - \frac{\beta}{2\omega_C} \right] e^{-\Delta V/(k_B T)} \tag{2.52}$$

Equation (2.52) is Kramers' IHD Eq. (2.23). We should mention that the calculations leading to Langer's general IHD rate Eq. (2.43), which essentially rely on the Kramers method of forcing in the IHD limit the multidimensional Fokker–Planck equation into a one-dimensional Fokker–Planck equation for a linear combination of the state variables, are very long and involved. Thus we only quote the result here in so far as it is needed.

2.4 Quantum IHD Escape Rate

The quantum IHD rate was first obtained by Wolynes [8] using path integrals. This derivation is rather involved and the result was obtained in a far simpler way by Pollak [2, 9, 35] by recognizing that the IHD rate is simply the TST rate in the complete phase (representation) space of the system consisting of bath and particle. Thus Eq. (2.8) applies. The basic idea underlying the approach of Pollak lies in the reasoning of Grabert [28] that the escape dynamics is governed in both classical and quantum cases by the *unstable normal mode coordinate* and not the *particle configuration coordinate* [2]. We note that:

1. The multidimensional normal mode TST rate is the spatial diffusion controlled Kramers rate as anticipated by Langer.

2. The unstable normal mode dynamics decouples from the other modes very near to the barrier, so near in fact that the normal mode dynamics governed of course by the harmonic approximation are virtually exact. (Full details in Chapter 4). Furthermore the loss of energy in this unstable mode governs the escape rate process.

In more succinct terms Pollak [35] starts from a generalized Langevin equation which may be derived from the Hamiltonian of a particle bilinearly coupled to a harmonic bath. In order to calculate the escape rate he must then according to Eq. (2.8) evaluate the quantum partition functions at the barrier and the well via a normal mode analysis. This is so because the harmonic approximation implies that the Hamiltonian in the vicinity of the well and barrier may be written in separable form as the sum of $N+1$ harmonic oscillators, N of which are real and one is imaginary. Then after relatively long calculations, which are described in Chapter 4, Pollak found that at temperatures above the critical temperature, the quantum IHD rate is simply

$$\Gamma^{\mathrm{IHD}} = \Xi \frac{\omega_A}{2\pi} \left[\sqrt{1 + \left(\frac{\beta}{2\omega_C} \right)^2} - \frac{\beta}{2\omega_C} \right] e^{-\frac{\Delta V}{k_B T}} \tag{2.53}$$

where (details in Chapter 4)

$$\Xi = \frac{\Gamma(1 + \lambda_C^+/\nu)\Gamma(1 + \lambda_C^-/\nu)}{\Gamma(1 + \lambda_A^+/\nu)\Gamma(1 + \lambda_A^-/\nu)} \tag{2.54}$$

and the eigenvalues are

$$\lambda_C^{\pm} = \frac{\beta}{2} \pm \sqrt{\left(\frac{\beta^2}{4} + \omega_C^2 \right)}, \qquad \lambda_A^{\pm} = \frac{\beta}{2} \pm \sqrt{\left(\frac{\beta^2}{4} - \omega_A^2 \right)} \tag{2.55}$$

In practice the quantum correction Ξ only weakly depends on the dissipation and is well approximated by Eq. (2.11) which is repeated below

$$\Xi = \frac{\omega_C}{\omega_A} \frac{\sinh[\hbar\omega_A/(2k_BT)]}{\sin[\hbar\omega_C/(2k_BT)]} = \prod_{n=1}^{\infty} \frac{(2n\pi k_B T/\hbar)^2 + \omega_A^2}{(2n\pi k_B T/\hbar)^2 - \omega_C^2}$$

This is the original quantum TST result as obtained by Wigner [14, 19]. Another noteworthy result is that the equilibrium distribution for this model [18] of a particle bilinearly coupled to a bath of harmonic oscillators now depends on the damping.

2.5 Quantum Low Damping Escape Rate

Just as the classical case the quantum IHD rate fails in the underdamped region. The first attempt to tackle this problem appears to have been made by Mel'nikov [36] (and references therein). In the quantum case (to paraphrase Mel'nikov [6]) in contrast to the escape rate for the classical regime where one starts from the Fokker–Planck equation we must instead specify the Hamiltonian of the *entire system* consisting of the particle and its heat bath recalling that one is interested in the escape rate for a system exhibiting viscous friction in the classical regime. In itself this condition is insufficient to define the entire system in a unique way. However it is enough to determine the particle action which is obtained by integrating over the bath variables. This condition [6] is vital because then all models of the heat bath are equivalent as far as Γ is concerned provided they can reproduce the same Langevin equation in the classical limit.

Now Mel'nikov [6, 36] proceeds in the manner of Kramers by using two different models of the bath. We have already summarized the IHD rate as treated by Pollak [35]. In the underdamped regime Mel'nikov includes the interaction of a particle with a Boson bath by incorporating a term linear in the particle coordinate describing the effects of the (Johnson-Nyquist) noise (which is Gaussian) on the Hamiltonian (operator) of the particle so that

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(x) + x\hat{\eta}(t) = \hat{H}_0 + x\hat{\eta} \tag{2.56}$$

where $\hat{\eta}(t)$ denotes the Johnson–Nyquist noise operator. The spectral density of this bath is then given by the Planck distribution defined in terms of the Fourier transform of the autocorrelation function of the noise operator namely

$$\begin{aligned} D(\Omega) &= \int_{-\infty}^{\infty} < \hat{\eta}(t)\hat{\eta}(t+\tau) >_T e^{i\Omega\tau}\, d\tau \\ &= m\beta\hbar\Omega[\coth(\hbar\Omega/(2k_BT)) - 1] \end{aligned} \tag{2.57}$$

and $< \hat{\eta}(t) >_T = 0$ where the subscript T denotes averaging over the bath states. In the classical limit, $\hbar \to 0$, Eq. (2.57) yields the usual white noise spectral density $D = 2m\beta k_BT$. However, as just stated, each quantum particle by its very nature now presents *a range of possible quantum states as well as the thermal*

distribution of a huge assembly (bath) of such particles over a range of possible states. The classical transition probability in energy space or Green function, which forms the kernel of the original Eq. (2.31) for $f(E)$, must therefore be replaced by the statistical density matrix (stemming from the evolution operator for the state vector) which includes both thermal and quantum effects. Hence we can no longer calculate the Green function via the Fokker–Planck equation transformed to energy-action variables. Nevertheless, to determine the leading quantum corrections to the escape rate in the underdamped regime we may use the semiclassical approximation based on the Jeffreys-Wentzel-Kramers-Brillouin (JWKB) approximation [6, 14] whereby the energy levels (eigenvalues) in the vicinity of the barrier are distributed quasicontinuously. Thus the matrix elements of both the position $\hat{x}$ and evolution $\hat{\Phi}$ operators in the interaction representation may be represented in terms of the Fourier transform of the classical trajectory. This is in essence the method proposed by Larkin and Ovchinnikov [10]. Their calculations ultimately yield an integral equation for the population of escaping quantum particles $f(E)$, namely,

$$f(E) = \int_{-\infty}^{\infty} \frac{g(E - E')f(E')}{\left[1 + \exp\left(\frac{2\pi E}{\hbar\omega_C}\right)\right]} \, dE' \tag{2.58}$$

where the kernel contains the quantum reflection factor $r(E)$ for an inverted parabolic barrier as well as the Green function which is to be identified with the statistical density matrix calculated via the evolution operator $\hat{\Phi}$ for the state vector specifying, in the interaction representation, the noise induced energy transitions from E to E' in a cycle of the motion in the well infinitesimally close to the separatrix, in the appropriate semiclassical approximation. (Note the limits of integration are $-\infty$, ∞, unlike in the classical expression, in order to take account of tunneling.) The function $f(E)$ now represents the quantum probability distribution of the escaping particles and is valid of course only at temperatures above the critical temperature [19] at which the parabolic approximation to the barrier fails. The integral equation for $f(E)$ differs from the classical one in two vital respects because (a) it includes (cf. Eq. (2.58)) the reflection factor for the inverted parabolic barrier and (b) the Green function must be calculated in

a semiclassical manner. This was accomplished by Larkin and Ovchinnikov by essentially starting from the expression for the undamped classical trajectory of the librational motion in the well of a particle with energy equal to the barrier energy. The amplitude of the quantum transition from a state E' to E (recall that $E \approx E'$) in one cycle of the periodic motion under the influence of the noise may then be formally written down using the interaction picture in terms of the matrix elements of the time ordered system–bath operator $\hat{\Phi}$ specifying the evolution of the state vector from state E' to E in the interaction representation. Hence the Green function (or statistical density matrix) may also be formally written down semi–classically as, (the angular braces with subscript T denote averaging over the thermal states of the bath),

$$g(E, E') =< |A(E, E')|^2 >_T \tag{2.59}$$

and the amplitudes are given by

$$\begin{aligned} A(E, E') &= \langle E|\hat{T} \exp\left(-\tfrac{i}{\hbar}\int_{-\infty}^{\infty} \hat{\eta}(t)\hat{x}(t)dt\right)|E'\rangle \\ &= \langle E|\hat{\Phi}|E'\rangle \end{aligned} \tag{2.60}$$

where $\hat{\Phi} = \hat{T} \exp\left(-\frac{i}{\hbar}\int_{-\infty}^{\infty} \hat{\eta}(t)\hat{x}(t)dt\right)$.

Thus by using the semiclassical approximation for the matrix elements of $\hat{\Phi}$ in the presence of the noise and averaging over the thermal distribution using the centred Gaussian properties of the Johnson–Nyquist quantum noise we have a closed form for the Green function. This is rendered as the inverse Fourier transform of the characteristic function of the energy distribution

$$\tilde{g}(\lambda) = \exp[\tilde{w}(\lambda) - \tilde{w}(0)] \tag{2.61}$$

which should be compared with the classical result

$$\tilde{g}(\lambda) = e^{-\Delta(\lambda^2+1/4)} \tag{2.62}$$

Now the Green function $g(E - E')$ unlike the classical one always involves the quantum transition probability w determined by Fermi's Golden Rule [4] for the position operator $\hat{x}(t)$ in the presence of the noise in the first order of

perturbation theory. Thus unlike the classical case where the Green function is canonical in the sense that the sole (Kramers) parameter Δ is the ratio of the friction times the action of the undamped periodic motion at the saddle energy to the thermal energy, the parameters of the quantum Green function depend on integrals involving the precise nature of the potential. For any given potential the matrix elements must be calculated explicitly as we shall see later, e.g.

$$w(E-E') = \frac{2\pi}{\hbar} |< E|\hat{x}|E' >|^2 m\beta(E-E') \coth\left[\frac{E-E'}{2K_BT} - 1\right] \tag{2.63}$$

where recalling the JWKB approximation, we have

$$< E|\hat{x}|E' >= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} x(t) \exp[i(E-E')t/\hbar]dt \tag{2.64}$$

which are the semi–classical matrix elements.[2] $x(t)$ represents the classical critical energy trajectory [6] corresponding to the periodic librational motion in the well at this energy and the matrix elements are given by the Fourier transform over time. Hence the characteristic function $\hat{g}(\lambda)$ may be determined (Eq. (2.61)) .

In reality since the motion in the well is periodic the Fourier integral in Eq. (2.64) is a Fourier series. However, on the critical energy trajectory the period of the motion effectively tends to infinity so we can always replace Fourier series by Fourier integrals and vice versa. This replacement will be used extensively in Chapter 6 which deals with the detailed calculation of the quantum underdamped rate.

Using the above results the Wiener–Hopf method may be used to solve the integral equation as before and recalling that as far as quantum effects are concerned only those particles that penetrate the classically opaque potential barrier via tunneling contribute to the escape rate so that the rate is given by the following equation involving the penetration coefficient in the underdamped regime

[2]Compare the classical expression $\Phi_0(\omega) = |\chi(\omega)|^2\Phi_i(\omega)$ for the power spectral density of a random process that has been filtered by a linear time–invariant filter with frequency response $\chi(\omega)$. Clearly the quantum amplitudes play the role of the frequency response.

$$\Gamma = \frac{1}{\tau} = \int_{-\infty}^{\infty} \frac{f(E)dE}{1+\exp(-2\pi E/(\hbar\omega_C))}$$

$$= A(\Delta, y)\frac{\omega_C}{2\pi}\frac{\sinh[\hbar\omega_A/(2k_BT)]}{\sin[\hbar\omega_C/(2k_BT)]}e^{-\Delta V/(k_BT)} \tag{2.65}$$

The depopulation factor is then given by

$$A(\Delta, y) = \exp\left[\int_{-\infty}^{\infty} \frac{y\sin(\pi y)\ln\left[1-e^{-\Delta R(\lambda,y)}\right]}{\cosh(2\pi y\lambda)-\cos(\pi y)}d\lambda\right] \tag{2.66}$$

where

$$y = \frac{\hbar\omega_C}{2\pi k_BT} \tag{2.67}$$

and where we have written $\Delta R(\lambda, y) = \tilde{w}(0) - \tilde{w}(\lambda - i/2)$ where $\tilde{w}(\lambda)$ is the Fourier transform of the quantum transition probability in the presence of noise in the first order of perturbation theory given by Eq. (2.63) which replaces the classical arguement $\Delta(\lambda^2 + 1/4)$. Notice that in the quantum case the depopulation factor $A(\Delta, y)$ takes into account the interaction of the Brownian particle with the heat bath via the dissipation parameter Δ and *also includes* the high temperature quantum effects via the quantum parameter y. In many cases if absolute precision is not required we can replace $\Delta R(\lambda, y)$ by its classical value. We reiterate that unlike the classical case if this approximation is not made the depopulation factor has to be *calculated explicitly for each particular potential.*

2.6 Conclusion

The objective in writing the first part of this chapter was simply to provide a rough guide for the reader through the maze of subsequent rather involved calculations. At this stage it is advantageous to give, in the form of Appendices, a derivation of the VLD rate using the energy controlled diffusion equation as derived by Stratonovich's method [3].

Appendices

2.A Derivation of the Kramers energy controlled diffusion equation from the lightly damped Langevin equation

Stratonovich [3, (Eq. 4.223)] writes the Langevin equation as

$$\mu^2\ddot{x} + \dot{x} - f(x) = \xi(t) \tag{2.68}$$

where in the present context $\xi(t)$ is white noise defined in his notation via the statistical averages

$$\langle\xi\rangle = 0, \quad \langle\xi(t)\xi(t+\tau)\rangle = \kappa\,\delta(\tau)$$

where κ is the noise strength. Write $1/\mu = \epsilon$ so that the inertial term, i.e. the one involving $\ddot{x}$, is large and $t = t/\epsilon$, where $\epsilon << 1$. Thus the motion is very lightly damped. (The calculation has also been carried out by Coffey et al [32] in actual as opposed to normalized variables.)

Then Eq. (2.68) becomes

$$\ddot{x} + \epsilon\dot{x} - f(x) = \sqrt{\epsilon}\,\xi(t) \tag{2.69}$$

Now the usual Langevin equation we have written is

$$\ddot{x} + \beta\dot{x} + \frac{1}{m}\frac{dV}{dx} = \frac{\lambda(t)}{m} \tag{2.70}$$

and the autocorrelation function of the white noise force $\lambda(t)$ is

$$\langle\lambda(t)\lambda(t+\tau)\rangle = 2\,\zeta k_B T\,\delta(\tau)$$

Furthermore if $m = 1$ we have

$$\ddot{x} + \beta\dot{x} + \frac{dV}{dx} = \lambda(t) \tag{2.71}$$

Comparing Eqs. (2.69) and (2.71) we have $\epsilon = \beta$ and $\sqrt{\epsilon}\,\xi(t) = \lambda(t)$. If ϵ is small Eq. (2.69) describes the behaviour of a system performing nonlinear oscillations under the influence of *weak frictional* forces and *weak external* fluctuations. In

other words the system is only *very lightly* coupled to the bath. Now introduce the energy and the position x as slow and fast variables respectively

$$E = \frac{1}{2}\dot{x}^2 + V(x) \tag{2.72}$$

where

$$V(x) = -\int_{x_1}^{x} f(z)dz \tag{2.73}$$

is the potential function. Multiply Eq. (2.69) by $\dot{x}$ to obtain

$$\dot{x}\ddot{x} + \epsilon\dot{x}^2 - f(x)\dot{x} = \sqrt{\epsilon}\,\dot{x}\,\xi(t) \tag{2.74}$$

Differentiating Eq. (2.72) with respect to t we have

$$\begin{aligned} \dot{E} &= \dot{x}\ddot{x} + \frac{dV}{dx}\dot{x} \\ &= \dot{x}\ddot{x} - f(x)\dot{x} \end{aligned} \tag{2.75}$$

From Eqs. (2.74) and (2.75) we have the fluctuation equation for the energy

$$\dot{E} = -\epsilon\,\dot{x}^2 + \sqrt{\epsilon}\,\dot{x}\,\xi(t) \tag{2.76}$$

Now from Eq. (2.72) we have

$$\dot{x}(t) = \sqrt{2(E - V(x))} \tag{2.77}$$

(taking the positive sign which is all that will be needed for our purposes) yielding

$$\dot{E}(t) = -2\epsilon[E - V(x)] + \sqrt{2\epsilon[E - V(x)]}\,\xi(t) \tag{2.78}$$

The system is governed by the two fluctuation equations (2.77) and (2.78). However, the multiplicative noise appears explicitly in only one of them. Now from Stratonovich [3, (Eq. 4.33)] we have the probability density diffusion equation for the single space variable y

$$\dot{w}(y) = -\frac{\partial}{\partial y}[K_1(y)w(y)] + \frac{\kappa}{2}\frac{\partial^2}{\partial y^2}[K_2(y)w(y)] \tag{2.79}$$

which is called the Fokker-Planck equation. The probability current is

$$G(y) = K_1(y)w(y) - \frac{\kappa}{2}\frac{\partial}{\partial y}[K_2(y)w(y)] \tag{2.80}$$

Now the Fokker-Planck equation can also be written in the form of the continuity equation

$$\dot{w} + \frac{\partial G}{\partial y} = 0 \tag{2.81}$$

while the corresponding (unique) Langevin equation is (Stratonovich Eq. (4.178))

$$\dot{y} = K_1(y) - \frac{\kappa}{4}\frac{\partial K_2(y)}{\partial y} + \sqrt{K_2(y)}\,\xi(t) \tag{2.82}$$

where $K_1(y)$ is the *deterministic* drift and $-(\kappa/4)\partial K_2(y)/\partial y$ represents the *noise induced* drift arising from the multiplicative noise. Having written the Langevin equations (2.77) and (2.78) we now want the corresponding Fokker-Planck equation in position-energy space. We can do this via a heuristic argument which has been justified rigorously from first principles by Coffey et al [32] .

First Eq. (2.77) is a 1-dimensional Langevin equation in the state variable x without explicit noise and by inspection of Eq. (2.82) we see that the drift coefficient

$$\kappa_1(x) = \sqrt{2(E-V)} \tag{2.83}$$

say. Thus by inspection of Eq. (2.79) we see that the state variable x contributes only a (deterministic) drift term

$$-\frac{\partial}{\partial x}\sqrt{2(E-V)}w(x,E) \tag{2.84}$$

and *no diffusion* term to the Fokker-Planck equation for $w(x,E)$. Equation (2.78) on the other hand contains a *multiplicative noise* term giving rise to noise-induced drift

$$\sqrt{\kappa_2(E)} = \sqrt{2\epsilon(E-V)} \tag{2.85}$$

say. Now we have to evaluate $\kappa_1(E)$ in Eq (2.78). Using Eq. (2.82) we have

$$K_1(E) - \frac{\epsilon\kappa}{2} = -2\epsilon(E-V) \tag{2.86}$$

Hence the proper drift term comprising both the *deterministic* and the *noise-induced* drift is

$$K_1(E) = -2\epsilon\left[(E-V) - \frac{\kappa}{4}\right] \tag{2.87}$$

Thus the state variable E gives rise by inspection of Eq. (2.82) to an overall drift term

$$\frac{\partial}{\partial E}\left\{2\epsilon\left[(E-V) - \frac{\kappa}{4}\right]\right\}w(x,E) \tag{2.88}$$

in the Fokker-Planck equation for $w(x, E)$. Finally the diffusion term is (again by inspection of Eq. (2.82))

$$\frac{\kappa}{2}\frac{\partial^2}{\partial E^2}[2\epsilon(E - V)w(x, E)] \tag{2.89}$$

Hence we have the Fokker-Planck equation in the two state variables (x, E) for the evolution of the joint pdf $w(x, E)$ in position-energy space, namely,

$$\begin{aligned}\dot{w}(x, E) = &-\frac{\partial}{\partial x}\left[\sqrt{2(E - V(x))}\, w(x, E)\right] + 2\epsilon\frac{\partial}{\partial E}\left[E - V(x) - \frac{\kappa}{4}\right] w(x, E) \\ &+ \frac{\kappa}{2}\frac{\partial^2}{\partial E^2}\left\{2\epsilon[E - V(x)]\, w(x, E)\right\}\end{aligned} \tag{2.90}$$

where

$$\kappa = \int_{-\infty}^{\infty} \langle \xi \xi_\tau \rangle d\tau \tag{2.91}$$

Thus it is clear how the Langevin equations (2.77) and (2.78) give rise to a 2-D Fokker-Planck equation with x and E as variables. We require the quasi-stationary solution for the pdf in energy space, therefore we must now reduce Eq. (2.90) to a one-dimensional diffusion equation in the energy. (Notice that everywhere we shall differentiate the various pdfs by specifying the argument.)

This is accomplished as follows. First, if ϵ is small (small friction) E is sensibly preserved during a large number of oscillations and the time the particle spends in the interval between x and $x + \Delta x$ is then inversely proportional to the velocity $\dot{x}(t) = \sqrt{2(E - V(x)}$. Hence we have the conditional pdf

$$w(x|E) = \begin{cases} A[E - V(x)]^{-1/2} & \text{for } V(x) < E, \\ 0 & \text{for } V(x) > E. \end{cases} \tag{2.92}$$

where A is a constant. (The $\sqrt{2}$ has been absorbed into the constant.)
To determine A we have

$$1 = A\int_{R(E)} \frac{dx}{\sqrt{E - V(x)}} \tag{2.93}$$

The integration is over the region $R(E)$ (the domain of the well) defined by $V(x) < E$, in other words inside the well.
Next define

$$\varphi(E) = \int_{R(E)} \sqrt{E - V(x)} dx \tag{2.94}$$

Then on differentiation with respect to E

$$\varphi'(E) = \frac{1}{2}\int_{R(E)} \frac{dx}{\sqrt{E - V(x)}} \tag{2.95}$$

and $A = \dfrac{1}{2\varphi'(E)}$.

Now by definition the two-dimensional or joint probability density function $w(x, E)$ can be written in the form

$$w(x, E) = w(E)w(x|E) = \frac{w(E)}{2\varphi'(E)\sqrt{E - V(x)}} \tag{2.96}$$

Then substituting Eq. (2.96) into Eq. (2.90) we ultimately obtain (details below) the following one-dimensional diffusion equation in the energy

$$\dot{w}(E) = \epsilon\frac{\partial}{\partial E}\left[\left(\frac{\varphi(E)}{\varphi'(E)} - \frac{\kappa}{2}\right)w(E)\right] + \frac{\epsilon\kappa}{2}\frac{\partial^2}{\partial E^2}\left[\frac{\varphi(E)}{\varphi'(E)}w(E)\right] \tag{2.97}$$

Aside: Consider the left hand side of Eq. (2.90). Integrating with respect to x we have by definition

$$\begin{aligned}\int_{R(E)} \dot{w}(x, E)\, dx &= \frac{d}{dt}\int_{R(E)} w(x, E)\, dx \\ &= \frac{dw(E)}{dt} \\ &= \dot{w}(E)\end{aligned}$$

Consider now the first term on the right hand side of Eq. (2.90). Using Eq. (2.96) we have

$$\begin{aligned}-\frac{\partial}{\partial x}\left[\sqrt{2(E - V(x))}\, w(x, E)\right] &= -\frac{\partial}{\partial x}\left[\frac{\sqrt{2(E - V(x))}\, w(E)}{2\varphi'(E)\sqrt{E - V(x)}}\right] \\ &= -\frac{\partial}{\partial x}\left[\frac{w(E)}{\sqrt{2}\varphi'(E)}\right] \\ &= 0\end{aligned}$$

because the expression in the square brackets is a function of E only and so the partial derivative with respect to x must be zero.

Next consider the second term on the right hand side of Eq. (2.90). Again using the joint pdf, Eq. (2.96), we have

$$2\epsilon\frac{\partial}{\partial E}\left[\left(E-V(x)-\frac{\kappa}{4}\right)w(x,E)\right]=2\epsilon\frac{\partial}{\partial E}\left[\left(E-V(x)-\frac{\kappa}{4}\right)\frac{w(E)}{2\varphi'(E)\sqrt{E-V(x)}}\right]$$

$$=\epsilon\frac{\partial}{\partial E}\left[\left(\sqrt{E-V(x)}-\frac{\kappa}{4\sqrt{E-V(x)}}\right)\frac{w(E)}{\varphi'(E)}\right]$$

Now integrate with respect to x over the domain of the well $R(E)$ and using Eqs. (2.94) and (2.95) we obtain

$$\epsilon\frac{\partial}{\partial E}\left[\int_{R(E)}\left(\sqrt{E-V(x)}-\frac{\kappa}{4\sqrt{E-V(x)}}\right)dx\frac{w(E)}{\varphi'(E)}\right]=\epsilon\frac{\partial}{\partial E}\left[\left(\frac{\varphi(E)}{\varphi'(E)}-\frac{\kappa}{2}\right)w(E)\right]$$

which is a function of the energy only.

Finally, consider the third term on the right hand side of Eq. (2.90). Using Eq. (2.96) we have

$$\frac{\kappa}{2}\frac{\partial^2}{\partial E^2}\left\{2\epsilon[E-V(x)]w(x,E)\right\}=\epsilon\kappa\frac{\partial^2}{\partial E^2}\left[\frac{(E-V(x))\,w(E)}{2\varphi'(E)\sqrt{E-V(x)}}\right]$$

$$=\epsilon\kappa\frac{\partial^2}{\partial E^2}\left[\frac{\sqrt{(E-V(x))}\,w(E)}{2\varphi'(E)}\right]$$

Integrating with respect to x over the domain of the well $R(E)$ and using Eq. (2.94) we have

$$\int_{R(E)}\epsilon\kappa\frac{\partial^2}{\partial E^2}\left[\frac{\sqrt{(E-V(x))}\,w(E)}{2\varphi'(E)}\right]dx=\frac{\epsilon\kappa}{2}\frac{\partial^2}{\partial E^2}\left[\frac{\varphi(E)}{\varphi'(E)}\,w(E)\right]$$

which is again a function of E only. Hence corresponding to the quasi-stationary Langevin equation we have for VLD the Fokker-Planck equation in energy space

$$\dot{w}(E)=\epsilon\frac{\partial}{\partial E}\left[\left(\frac{\varphi(E)}{\varphi'(E)}-\frac{\kappa}{2}\right)w(E)\right]+\frac{\epsilon\kappa}{2}\frac{\partial^2}{\partial E^2}\left[\frac{\varphi(E)}{\varphi'(E)}w(E)\right] \tag{2.98}$$

This appears to me to be the most transparent way of deriving the energy controlled diffusion equation as it follows automatically from Eq. (2.92). This equation is widely used in the quantum mechanics of the harmonic oscillator in order to compare the classical probability with the quantum one.

2.B Connection between Stratonovich, Kramers, and Praestgaard–van Kampen calculations

Stratonovich's Eq. (4.254), alias (2.99) below, is identical to that given by Praestgaard and van Kampen [38], and also to that originally given by Kramers, which is not immediately obvious. This may be demonstrated as follows. We have

$$\dot{w}(E,t) = \epsilon \frac{\partial}{\partial E}\left\{\left[\frac{\varphi(E)}{\varphi'(E)} - \frac{\kappa}{2}\right] w(E,t) + \frac{\epsilon\kappa}{2}\frac{\partial}{\partial E}\left[\frac{\varphi(E)}{\varphi'(E)} w(E,t)\right]\right\} \tag{2.99}$$

where

$$\varphi'(E) = \frac{d\varphi}{dE} = \frac{2\pi}{\omega(E)} \tag{2.100}$$

Substituting Eq. (2.100) in Eq. (2.99) we have

$$\begin{aligned}\dot{w}(E,t) &= \epsilon \frac{\partial}{\partial E}\left\{\left[\frac{\omega(E)}{2\pi}\varphi(E) - \frac{\kappa}{2}\right] w(E,t) + \frac{\kappa}{2}\frac{\partial}{\partial E}\left[\frac{\omega(E)}{2\pi}\varphi(E) w(E,t)\right]\right\} \\ &= \epsilon \frac{\partial}{\partial E}\left\{\left[\frac{\omega(E)}{2\pi}\varphi(E) - \frac{\kappa}{2}\right] w(E,t) + \frac{\kappa}{2}\frac{\partial}{\partial E}\left[\varphi(E)\left(\frac{\omega(E)}{2\pi} w(E,t)\right)\right]\right\}\end{aligned} \tag{2.101}$$

Now

$$\begin{aligned}\frac{\partial}{\partial E}\left[\varphi(E)\left(\frac{\omega(E)}{2\pi} w(E,t)\right)\right] &= \frac{\partial \varphi(E)}{\partial E}\left(\frac{\omega(E)}{2\pi} w(E,t)\right) + \varphi(E)\frac{\partial}{\partial E}\left(\frac{\omega(E)}{2\pi} w(E,t)\right) \\ &= w(E,t) + \varphi(E)\frac{\partial}{\partial E}\left(\frac{\omega(E)}{2\pi} w(E,t)\right)\end{aligned} \tag{2.102}$$

Substituting Eq. (2.102) in Eq. (2.101) we have

$$\begin{aligned}\dot{w}(E,t) &= \epsilon \frac{\partial}{\partial E}\left\{\left[\frac{\omega(E)}{2\pi}\varphi(E) w(E,t) - \frac{\kappa}{2} w(E,t)\right] + \frac{\kappa}{2} w(E,t)\right. \\ &\qquad \left. + \frac{\kappa}{2}\varphi(E)\frac{\partial}{\partial E}\left(\frac{\omega(E)}{2\pi} w(E,t)\right)\right\} \\ &= \epsilon \frac{\partial}{\partial E}\left\{\frac{\omega(E)}{2\pi}\varphi(E) w(E,t) + \frac{\kappa}{2}\varphi(E)\frac{\partial}{\partial E}\left(\frac{\omega(E)}{2\pi} w(E,t)\right)\right\} \\ &= \epsilon \frac{\partial}{\partial E}\left\{\varphi(E)\left[\frac{\omega(E)}{2\pi} w(E,t) + \frac{\kappa}{2}\frac{\partial}{\partial E}\left(\frac{\omega(E)}{2\pi} w(E,t)\right)\right]\right\}\end{aligned}$$

or

$$\dot{w}(E,t) = \epsilon \frac{\partial}{\partial E}\left\{\varphi(E)\left[1 + \frac{\kappa}{2}\frac{\partial}{\partial E}\right]\left(\frac{\omega(E)}{2\pi} w(E,t)\right)\right\} \tag{2.103}$$

Now with the replacements $\kappa/2 \to k_BT, \quad \epsilon \to \beta, \quad \varphi(E) \to S(E)$, we have the energy controlled diffusion equation as given by Kramers, namely,

$$\dot{w}(E,t) = \beta \frac{\partial}{\partial E} \left\{ S(E) \left[1 + k_B T \frac{\partial}{\partial E} \right] \left(\frac{\omega(E)}{2\pi} w(E,t) \right) \right\} \tag{2.104}$$

Notice that in action space we have

$$\rho(S,t) = \frac{\omega(E)}{2\pi} w(E,t) \tag{2.105}$$

Using Eq. (2.105) in Eq. (2.104) we have

$$\frac{2\pi}{\omega(E)} \dot{\rho}(S,t) = \beta \frac{2\pi}{\omega(E)} \frac{\partial}{\partial S} \left\{ S \left[1 + \frac{2\pi k_B T}{\omega(E)} \frac{\partial}{\partial S} \right] \rho(S,t) \right\}$$

$$\dot{\rho}(S,t) = \beta \frac{\partial}{\partial S} \left[S\rho(S,t) + \frac{2\pi k_B T S}{\omega(E)} \frac{\partial \rho(S,t)}{\partial S} \right] \tag{2.106}$$

which is the Kramers action diffusion equation. Note that either Eq. (2.106) or Eq. (2.104) leads directly to the quasi-stationary solution (see Appendix 2.C below)

$$-J = \beta S \left[\left(1 + k_B T \frac{\partial}{\partial E} \right) \frac{\omega(E)}{2\pi} w(E) \right] \tag{2.107}$$

which yields the Kramers VLD escape rate. We have therefore proved that Stratonovich's Eq. (4.254), alias Eq. (2.97), is entirely equivalent to the Kramers equation (2.104). The proper calculation of the multiplicative noise contribution to the drift is central to this result. However, it appears that the Stratonovich method starting from his Langevin Eq. (4.246), alias Eq. (2.69), for small β is superior to all others because the latter contain strong elements of 'hand waving'. The merit of the Stratonovich approach is that by starting from the energy Langevin equations involving multiplicative noise, namely,

$$\dot{x} = \sqrt{2[E - V(x)]}$$

$$\dot{E} = -2\epsilon[E - V(x)] + \sqrt{2\epsilon[E - V(x)]}\, \xi(t)$$

one can see clearly all the assumptions that are being made which is not at all obvious in the other approaches.

Finally, the equivalence of the energy-controlled diffusion Eq. (2.104) and the equation given by Praestgaard and van Kampen [38] is easily proved as follows.

We have, with the usual replacements $\kappa/2 \to k_B T$, $\epsilon \to \beta$, and $\varphi(E) \to S(E)$ in Eq. (2.99), the equation

$$\dot{w}(E) = \beta \frac{\partial}{\partial E} \left(\frac{\overline{p^2(E)}}{m} - k_B T \right) w + \beta k_B T \frac{\partial^2}{\partial E^2} \left(\frac{\overline{p^2(E)}}{m} w \right) \tag{2.108}$$

$$\frac{\overline{p^2(E)}}{m} = \frac{\omega(E) S(E)}{2\pi} = \frac{\omega(E)}{2\pi} \oint p \, dx \tag{2.109}$$

where the overbar denotes the mean value over one cycle of the undamped librational motion at energy E in the well (cf Appendix 2.D below). Equation (2.108) corresponds to that given by Praestgaard and van Kampen because it may be rewritten as

$$\dot{w}(E) = \beta \frac{\partial}{\partial E} \left\{ \left[\frac{\omega(E)}{2\pi} S(E) - kT \right] w(E) + \frac{\omega(E) S(E)}{2\pi} kT \frac{\partial w(E)}{\partial E} + w(E) kT + S(E) w(E) \frac{kT}{2\pi} \frac{\partial \omega(E)}{\partial E} \right\} \tag{2.110}$$

which transparently reduces to the Kramers equation (2.104).

2.C Kramers VLD rate for a particle with a separable and additive Hamiltonian moving in a potential $V(x)$

In order to calculate the VLD rate from Eq. (2.104) above we seek the steady state solution with injected current (constant), $\dot{w} = 0$. We then have from Eq (2.107)

$$-J = \beta S \left[1 + k_B T \frac{\partial}{\partial E} \right] \frac{w \omega}{2\pi} \tag{2.111}$$

Equation (2.111) can be rewritten as

$$\left[\frac{w \omega}{2\pi} + k_B T \frac{\partial}{\partial E} \left(\frac{w \omega}{2\pi} \right) \right] = -\frac{J}{\beta S(E)} \tag{2.112}$$

Now let

$$y = \frac{w \omega}{2\pi} \tag{2.113}$$

We then have

$$\frac{dy}{dE} + \frac{y}{k_B T} = -\frac{J}{\beta S k_B T} \tag{2.114}$$

This is a 1st order linear ordinary differential equation. The solution is

$$y(E) = Ce^{-\frac{E}{k_B T}} - \frac{J}{\beta k_B T} \int_{E_C}^{E} \frac{e^{-\frac{E-E'}{k_B T}}}{S(E')} dE' \tag{2.115}$$

We assume following Kramers that $w(E_C) = 0$. In other words all particles that reach the seperatrix disappear. We emphasize that this *Ansatz* is valid only in VLD (cf Mel'nikov [6]). From Eqs. (2.113) and (2.115) we have

$$y(E_C) = \frac{\omega(E_C) w(E_C)}{2\pi} = Ce^{-\frac{E_C}{kT}}$$

Now $\omega(E_C) \to 0$ $\because$ periodic time in well at this energy $\to \infty \implies C = 0$.
Hence, interchanging the limits

$$\begin{aligned} w(E) &= \frac{J\, 2\pi}{\beta k_B T \omega} \int_{E}^{E_C} \frac{e^{-\frac{E-E'}{k_B T}}}{S(E')} dE' \\ &= -\frac{J\, 2\pi e^{-\frac{E}{kT}}}{\beta k_B T \omega} \int_{E}^{E_C} \frac{e^{\frac{E'}{k_B T}}}{S(E')} dE' \end{aligned} \tag{2.116}$$

Let N denote the number of particles in the well and for convenience take $E_A = 0$, then

$$N = \int_0^{E_C} w(E) dE \tag{2.117}$$

Using Eq. (2.116) in (2.117) we have

$$N = \frac{J}{\beta k_B T} \int_0^{E_C} \frac{2\pi e^{-\frac{E}{k_B T}}}{\omega(E)} dE \int_E^{E_C} \frac{e^{\frac{E'}{k_B T}}}{S(E')} dE' \tag{2.118}$$

The escape rate is then $\Gamma = \dfrac{J}{N}$ by the flux-over-population method. Now as far as the outer integral is concerned it is dominated by the lower limit where $\omega(E) \approx \omega_A$, i.e. the angular frequency of small oscillations (independent of E) while the inner integral is dominated by the contribution of the action near E_C.

$$\therefore N \approx \frac{J\,2\pi}{\beta k_B T \omega_A} \int_0^{E_C} e^{-\frac{E}{k_B T}} dE \int_E^{E_C} \frac{e^{\frac{E'}{k_B T}}}{S(E_C)} dE' \tag{2.119}$$

$$= \frac{J\,2\pi}{\beta k_B T \omega_A} \left(-k_B T e^{-\frac{E}{k_B T}} \Big|_0^{E_C} \right) \left(\frac{k_B T e^{\frac{E'}{k_B T}}}{S(E_C)} \Big|_0^{E_C} \right)$$

$$\approx \frac{J\,2\pi}{\beta k_B T \omega_A} (k_B T) \left(\frac{k_B T e^{\frac{E_C}{k_B T}}}{S(E_C)} \right)$$

$$= \frac{J\,2\pi\,k_B T\,e^{\frac{E_C}{k_B T}}}{\beta\,\omega_A\,S(E_C)} \tag{2.120}$$

The escape rate $\Gamma = J/N$ is

$$\Gamma = \frac{\beta\,S(E_C)\,\omega_A\,e^{-\frac{E_C}{k_B T}}}{k_B T\,2\pi} \tag{2.121}$$

where $\beta S(E_C)$ is the energy loss per cycle of a particle librating in the well with energy equal to the critical energy E_C at which the particle just escapes the well and $E_C = \Delta V$ since we have taken the zero of potential to be at $E_A = 0$.

In general if we do not set $E_A = 0$ we have

$$\Gamma = \frac{\beta\,S(E_C)\,\omega_A\,e^{-\frac{\Delta V}{k_B T}}}{k_B T\,2\pi} \tag{2.122}$$

where $\Delta V = E_C - E_A$.

This is Kramers escape rate for low friction.

2.D Energy loss per cycle

We saw that $\beta S(E_C)$ is the mean energy loss per cycle of the periodic motion in the well at the saddle energy.

Let $E(t)$ denote the total energy at time t of a particle executing librational motion in the well (ignoring the noise). The instantaneous rate of change of the total energy of the particle with respect to time, $dE(t)/dt$, is equal to the frictional force acting on the particle times the velocity of the particle. We have

$$\frac{dE(t)}{dt} = -\beta\,m \left(\frac{p(t)}{m} \right) \times \left(\frac{p(t)}{m} \right)$$

$$= -\frac{\beta\,p^2(t)}{m} \tag{2.123}$$

where β is the damping coefficient. One should note that in Eq. (2.123) p may be understood (effectively as in the perturbation theory context) in the conservative (undamped) sense because we assume the VLD limit. Integrating both sides of Eq. (2.123) we obtain

$$E(t) - E(0) = -\beta \int_0^t \frac{p^2(\tau)}{m} d\tau \tag{2.124}$$

Consider the case where the initial energy of the particle $E(0)$ is equal to the barrier energy E_C. Let T denote the time required for a particle with initial energy E_C to complete one cycle of the librational motion in the well. The change in energy from time $t = 0$ to time $t = T$ is

$$\begin{aligned} \Delta E &= E(T) - E_C \\ &= -\beta \int_0^T \frac{p^2(\tau)}{m} d\tau \\ &= -\beta \int_0^T p(\tau) \frac{dx(\tau)}{d\tau} d\tau \\ &= -\beta \int_{C_1} p\, dx \end{aligned} \tag{2.125}$$

where C_1 is the trajectory in phase–space of the particle from time $t = 0$ to time $t = T$. Let C_2 denote the trajectory in phase–space of a particle oscillating in the well in the absence of friction ($\beta = 0$, $E(t) = E_C$). In the extremely underdamped regime the contour C_1 is approximately the closed contour C_2 and

$$\begin{aligned} \int_{C_1} p\, dx &\approx \oint_{C_2} p\, dx \\ &= S(E_C) \end{aligned} \tag{2.126}$$

where $S(E_C)$ is the increase in the action of the particle executing this trajectory. Substituting Eq. (2.126) in Eq. (2.125) we have for the change in energy in one cycle

$$\Delta E \approx -\beta S(E_C) \tag{2.127}$$

$\beta\, S(E_C)$ is the energy loss per cycle of a particle librating in the well with energy E_C. Thus the loss is entirely determined by the Newtonian dynamics in the well.

2.E Transformation of energy density function to action density function

For convenience we use the notation of Landau and Lifshitz [16]. The abbreviated action S_0 for a given energy E is defined as

$$S_0(q, E) = \int p(q, E)\, dq \tag{2.128}$$

The action variable I is defined as

$$I = \oint p\, dq/2\pi \tag{2.129}$$

the integral being taken over the path for one period of libration for given energy E. From Eqs. (2.128) and (2.129) we see that during each period of the oscillatory motion of the particle in the well the action on the archetypal closed trajectory in phase space (p, q) increases by $2\pi I$. For a closed system I is a function of the energy alone and so S_0 can be written as a function $S_0(q, I)$. Landau and Lifshitz use the formula for canonical transformations [16, Eq. (45.8)] to obtain

$$p = \frac{\partial S_0(q, I)}{\partial q} \tag{2.130}$$

and the angle variable w (not to be confused with the density used elsewhere)

$$w = \frac{\partial S_0(q, I)}{\partial I} \tag{2.131}$$

The action variable I and the angle variable w are called canonical variables. The new Hamiltonian H' is simply the original Hamiltonian H expressed in terms of the new variables. H' is the energy $E(I)$, expressed as a function of the action variable. Hamilton's equations in canonical variables are

$$\dot{I} = 0, \quad \dot{w} = \frac{dE(I)}{dI} = \omega(I) \tag{2.132}$$

Let $S(E)$ denote the increase in action during each period of the oscillatory motion of a particle with energy E in the well.

$$\begin{aligned} S(E) &= 2\pi I(E) \\ \frac{dS}{dI} &= 2\pi, \quad \frac{dI}{dS} = \frac{1}{2\pi} \\ \frac{dE}{dS} &= \frac{dE}{dI}\frac{dI}{dS} \\ &= \omega\left(\frac{1}{2\pi}\right) \\ dE &= \frac{\omega(E)}{2\pi} dS \end{aligned} \tag{2.133}$$

Let P_E denote the probability density function for a particle in the well as a function of the total energy of the particle E. Similarly let P_S denote the probability density as a function of the action S. The probability that the energy of the particle in the well lies between E and $E + dE$ is

$$P_E(E)\, dE \tag{2.134}$$

Similarly, the probability that the action for the particle lies between S and $S+dS$ is

$$P_S(S)\, dS \tag{2.135}$$

From Eqs. (2.133)-(2.135) we have

$$P_E(E)\left[\frac{\omega(E)}{2\pi}\right] dS = P_S(S) dS \tag{2.136}$$

$$P_S(S) = P_E(E)\left[\frac{\omega(E)}{2\pi}\right] \tag{2.137}$$

2.F Nonlinear pendulum dynamics

In this Appendix we show that the period of the motion of a pendulum increases with increasing amplitude of oscillation and we consider the motion of the pendulum in three distinct regimes of its total energy. A detailed discussion of nonlinear pendulum dynamics can be found in the book *The Pendulum, a case*

study in physics by G. L. Baker and J. A. Blackburn [39]. See also Article 44 in *A Treatise on Analytical Dynamics*, 2nd Ed., by E. T. Whittaker [40] where the complete solution of the pendulum problem is given in terms of the Jacobian elliptic functions.

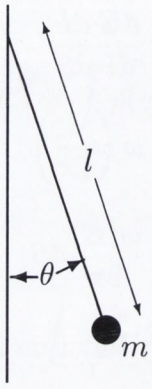

Figure 2.4: The simple pendulum with a point mass bob

The undamped, unforced equation of motion of the simple pendulum, obtained using Newton's second law, is

$$ml\frac{d^2\theta}{dt^2} = -mg\sin\theta$$

or

$$\frac{d^2\theta}{dt^2} + \frac{g}{l}\sin\theta = 0 \tag{2.138}$$

If the amplitude of oscillation is small Eq. (2.138) can be linearized by using the approximation $\sin\theta \approx \theta$. However, for large amplitudes the linearized approximation is no longer valid and we must solve the nonlinear equation of motion for the simple pendulum. The total energy E of the pendulum is the sum of its kinetic and potential energies

$$E = \frac{1}{2}ml^2\left(\frac{d\theta}{dt}\right)^2 + mgl(1-\cos\theta) \tag{2.139}$$

Case 1: $E < 2mgl$ (Oscillatory Motion)

In this case the angular velocity $\dot{\theta} = 0$ when $\theta = \pm\alpha$, where $|\alpha| < \pi$.

Eq (2.139) can then be written as

$$\left(\frac{d\theta}{dt}\right)^2 = \frac{2g}{l}(\cos\theta - \cos\alpha) \tag{2.140}$$

Using the identity $\cos\theta = 1 - 2\sin^2(\theta/2)$ in Eq. (2.140) we obtain

$$\frac{d\theta}{dt} = \pm 2\sqrt{\frac{g}{l}\left[\sin^2\left(\frac{\alpha}{2}\right) - \sin^2\left(\frac{\theta}{2}\right)\right]} \tag{2.141}$$

Following Baker and Blackburn [39] we introduce two new variables, φ and k, via the substitutions

$$\sin\frac{\theta}{2} = \sin\frac{\alpha}{2}\sin\varphi \tag{2.142}$$

and

$$k = \sin\left(\frac{\alpha}{2}\right) \tag{2.143}$$

Eq. (2.141) can now be written as

$$\begin{aligned}\frac{d\theta}{dt} &= \pm 2\sqrt{\frac{g}{l}\left(k^2 - k^2\sin^2\varphi\right)} \\ &= \pm 2k\sqrt{\frac{g}{l}}\cos\varphi\end{aligned} \tag{2.144}$$

Differentiating both sides of Eq. (2.142) with respect to t we have

$$\frac{1}{2}\cos\left(\frac{\theta}{2}\right)\frac{d\theta}{dt} = \sin\left(\frac{\alpha}{2}\right)\cos\varphi\frac{d\varphi}{dt} \tag{2.145}$$

Substituting Eqs. (2.143) and (2.144) in Eq. (2.145) we obtain

$$\frac{d\varphi}{dt} = \pm\sqrt{\frac{g}{l}}\sqrt{1 - k^2\sin^2\varphi} \tag{2.146}$$

Separating the variables in Eq. (2.146) and integrating we obtain

$$\int_0^{t_0} dt = \sqrt{\frac{l}{g}}\int_0^{\pi/2}\frac{d\varphi}{\sqrt{1 - k^2\sin^2\varphi}} \tag{2.147}$$

where we have set the time $t = 0$ when the pendulum is at the bottom of its arc ($\theta = 0$ and $\varphi = 0$), and time t_0 is when the pendulum reaches its maximum angular displacement $\theta = \alpha$ (corresponding to $\varphi = \pi/2$). The period T of the oscillation is therefore $T = 4\,t_0$, and is given by

$$T = 4\sqrt{\frac{l}{g}}\int_0^{\pi/2}\frac{d\varphi}{\sqrt{1 - k^2\sin^2\varphi}} \tag{2.148}$$

The integral in Eq. (2.148) is called an elliptic integral of the first kind. The integrand may be expanded using the binomial theorem and integrated term by

term to obtain [39]

$$T = 2\pi\sqrt{\frac{l}{g}}\left[1 + \left(\frac{1}{2}\right)^2 \sin^2\left(\frac{\alpha}{2}\right) + \left(\frac{1.3}{2.4}\right)^2 \sin^4\left(\frac{\alpha}{2}\right) + \cdots\right] \tag{2.149}$$

$$= 2\pi\sqrt{\frac{l}{g}} f(\alpha) \tag{2.150}$$

The graph of the normalized period (the function $f(\alpha)$ in Eq. (2.150)) versus the angular amplitude (α) is shown in Figure 2.5.

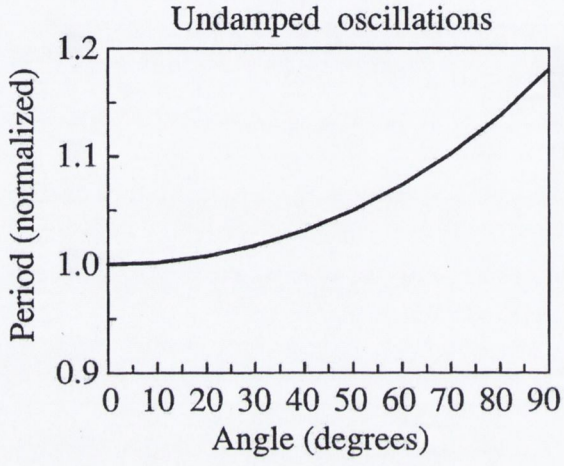

Figure 2.5: Normalized period of oscillation versus angular amplitude (from [39]).

Note that as $\alpha \to \pi$, the bob approaches verticality, the factor $\alpha/2 \to \pi/2$, the series $f(\alpha)$ diverges, and the period becomes infinitely large.

Case 2: $E = 2mgl$ (Inverted Pendulum, metastable with an imaginary period)

In this case the angular velocity $\dot{\theta} = 0$ when $\theta = \pm\pi$.

Substituting $\alpha = \pi$ in Eq. (2.141) we have

$$\frac{d\theta}{dt} = \pm 2\sqrt{\frac{g}{l}\left[1 - \sin^2\left(\frac{\theta}{2}\right)\right]}$$

$$= \pm 2\sqrt{\frac{g}{l}}\cos\left(\frac{\theta}{2}\right) \tag{2.151}$$

Again separating the variables in Eq. (2.151) and integrating, we obtain an expression for the time interval t between the pendulum being at the bottom of its

arc ($\theta = 0$) and being at the angular displacement θ

$$t = \frac{1}{2}\sqrt{\frac{l}{g}}\int_0^{\theta} \sec\frac{\theta}{2}\,d\theta = \sqrt{\frac{l}{g}}\ln\left[\tan\left(\frac{\theta}{4}+\frac{\pi}{4}\right)\right] \tag{2.152}$$

From Eq. (2.152) we see that as the pendulum approaches the vertical position, $\theta \to \pi$, and $t \to \infty$. The phase diagram for the pendulum with just enough energy to reach the upright vertical position is shown in Figure 2.6.

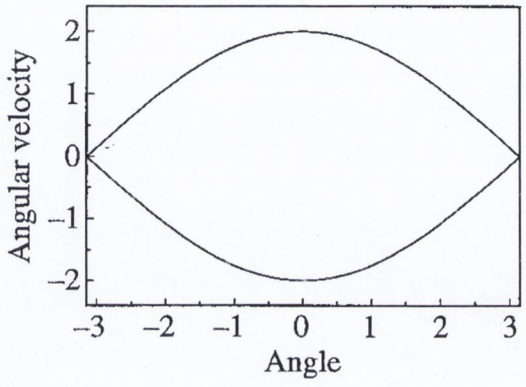

Figure 2.6: Phase diagram for a pendulum with just enough energy to reach the upright vertical position (from Baker and Blackburn [39]).

The phase space orbit corresponding to the critical energy $E = 2mgl$ is called the separatrix and marks the boundary between oscillatory and hindered rotary (or circulatory) motion of the pendulum.

Case 3: $E > 2mgl$ (Circulatory Motion)

In this case the motion of the pendulum is that of a hindered rotation. The angular velocity is a maximum when the bob is at the bottom and attains its minimum value when the bob is in the upright vertical position. The motion is again periodic in the sense of the Earth rotating about the sun. From the expression for the total energy, Eq (2.139), we have

$$\begin{aligned}\left(\frac{d\theta}{dt}\right)^2 &= \frac{2E}{ml^2} - \frac{2g}{l}(1-\cos\theta) \\ &= \frac{2E}{ml^2} - \frac{2g}{l}(1-1+2\sin^2\frac{\theta}{2}) \\ &= \frac{2E}{ml^2}\left[1 - \frac{2mgl}{E}\sin^2\frac{\theta}{2}\right]\end{aligned} \tag{2.153}$$

The angular velocity is

$$\frac{d\theta}{dt} = \sqrt{\frac{2E}{ml^2}}\sqrt{1 - k^2 \sin^2 \frac{\theta}{2}}, \tag{2.154}$$

where

$$k = \sqrt{\frac{2mgl}{E}} \tag{2.155}$$

Separating the variables and integrating with respect to θ from $\theta = 0$ to $\theta = \pi$, we obtain the time $T/2$ for one half rotation

$$\begin{aligned} \frac{T}{2} &= \sqrt{\frac{ml^2}{2E}} \int_0^{\pi} \frac{d\theta}{\sqrt{1 - k^2 \sin^2 \frac{\theta}{2}}} \\ &= \sqrt{\frac{2ml^2}{E}} \int_0^{\frac{\pi}{2}} \frac{d\left(\frac{\theta}{2}\right)}{\sqrt{1 - k^2 \sin^2 \frac{\theta}{2}}} \end{aligned} \tag{2.156}$$

Again the integrand may be expanded using the binomial theorem and integrated term by term to obtain the period of the circulatory motion [39]

$$T = \pi\sqrt{\frac{2ml^2}{E}} \left[1 + \left(\frac{1}{2}\right)^2 k^2 + \left(\frac{1.3}{2.4}\right)^2 k^4 + \cdots\right] \tag{2.157}$$

A graph of the period versus the energy of the pendulum is shown in Figure 2.7.

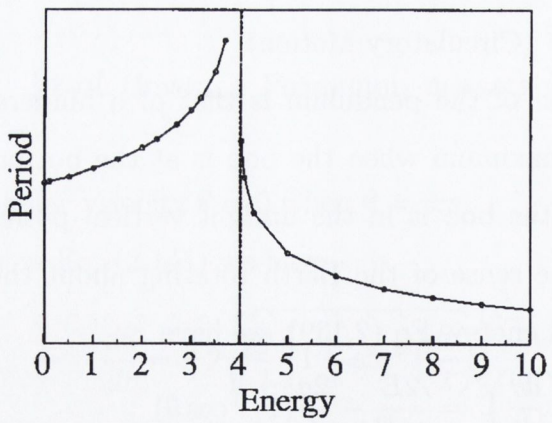

Figure 2.7: Graph of period versus the energy of the pendulum. The vertical line represents the critical energy (from Baker and Blackburn [39]).

2.G Form of position-energy diffusion equation (2.90) from the Langevin equation

The Langevin equation in normalized variables, namely,

$$\ddot{x} + \epsilon\,\dot{x} - f(x) = \sqrt{\epsilon}\,\xi(t) \tag{2.158}$$

forms the starting point of our derivation of Eq. (2.90). For the discussion of various transformations to position-energy variables it is useful to start from the Langevin equation in the direct physical variables, namely,

$$m\ddot{x} + \zeta\dot{x} + \frac{dV}{dx} = \lambda(t) \tag{2.159}$$

where $\lambda(t)$ is defined by the autocorrelation function

$$\langle\lambda(t)\lambda(t+\tau)\rangle = 2\zeta k_B T\delta(\tau) \tag{2.160}$$

Then as usual

$$\dot{x} = \sqrt{2[E - V(x)]/m} \tag{2.161}$$

$$\dot{E} = -\zeta\dot{x}^2 + \lambda(t)\dot{x} \tag{2.162}$$

This is the starting point of the derivation of Eq. (2.90) which is used by Coffey et al in the article "On the Kramers very low damping escape rate for point particles and classical spins" [32] which has been accepted for publication in *Advances in Chemical Physics.* Following from Eqs. (2.161) and (2.162) and using the properties of multiplicative noise we have

$$\begin{aligned}\dot{w}(x,E) = &-\frac{\partial}{\partial x}\left\{\sqrt{\frac{2}{m}[E - V(x)]}\right\}w(x,E) \\ &+\beta\frac{\partial}{\partial E}\left\{\frac{2[E-V(x)]}{k_BT}w(x,E) - w(x,E) + 2\frac{\partial}{\partial E}[E - V(x)]w(x,E)\right\}\end{aligned} \tag{2.163}$$

as is easily verified by appropriate replacements in Eq. (2.90). This is truly, as is Eq. (2.90) a diffusion equation in (x, E) space because both the drift and diffusuion coefficients have been calculated in the new variables (x, E), the evolution of which is governed by Eqs. (2.161) and(2.162) or equivalently (2.76) and

(2.77). The problem of the calculation of the drift and diffusion coefficients when a transformation to new variables is made in the Langevin equation is extensively discussed in Section (3.42) of Risken [41], while the transformation to new variables in the Fokker–Planck equation is also discussed in detail in his Section (4.9). Here the Jacobian of the transformation to the (x, E) joint pdf is involved. The Langevin method which is described by Coffey et al [32] with E and x as state variables from the onset, in conjunction with the general form of the Fokker–Planck equation, avoids these difficulties.

The foregoing paragraphs are particularly relevant to Section (3.2) of Chapter 3. Here we have $V(x)$ and considering only right going particles (see Section (3.2)) then

$$E = \frac{p^2}{2m} + V(x) \tag{2.164}$$

$$p = \sqrt{2m[E - V(x)]} \tag{2.165}$$

and let us define as in Section (3.2)

$$f(E, x) = \rho[p(E, x), x] \tag{2.166}$$

and

$$\rho(p, x) = F(E(p, x), x) \tag{2.167}$$

with ρ defined by Eq. (2.20). Then details in Eqs. (3.19) to (3.25) we end up with the quasi-stationary equation

$$\frac{\partial f}{\partial x} = \sqrt{-2mV(x)}\beta \frac{\partial}{\partial E}\left(f + k_B T \frac{\partial f}{\partial E}\right) \tag{2.168}$$

This equation does not have the same form as the evolution equation for $w(x, E)$. The difference arises because we have performed the transformation using the diffusion coefficients in (x, p) space. Thus Eq. (2.168) still remains a diffusion equation in (x, p) with E a parameter which specifies the momentum p for a given value of the position variable x. In order to get Eq. (2.163) from (2.168) we must write

$$w(x, E)\sqrt{\frac{2[E - V(x)]}{m}} = f(E, x) \tag{2.169}$$

Substituting this into Eq. (2.168) then immediately yields Eq. (2.163).

Chapter 3

Kramers Turnover Problem

3.1 Mel'nikov's solution of the Kramers turnover problem

We saw that in the Kramers model the motion of a particle librating in the well is governed by the Langevin equation

$$m\frac{d^2x}{dt^2} = -m\beta\frac{dx}{dt} - \frac{dV}{dx} + F(t) \tag{3.1}$$

where x is the position of a particle with mass m, β is the damping coefficient per unit mass, $V(x)$ is the potential and $F(t)$ is a zero–mean stationary white Gaussian noise driving force imposed by the bath which maintains the Brownian motion. The autocorrelation function of the driving force $F(t)$ is

$$\overline{F(t)F(t')} = 2k_BTm\beta\delta(t-t') \tag{3.2}$$

where k_B is the Boltzmann constant, T is the temperature, and the overbar denotes the statistical average over an ensemble of particles which have all started at time t with the same initial position $x(t) = x$ and momentum $p(t) = p$. The corresponding Fokker–Planck equation for the distribution $W(x,p,t)$ of an ensemble of noninteracting Brownian particles having momentum $p \equiv m\,dx/dt$ and position x is

$$\frac{\partial W}{\partial t} + \frac{p}{m}\frac{\partial W}{\partial x} - \frac{dV}{dx}\frac{\partial W}{\partial p} - \beta\frac{\partial}{\partial p}\left(Wp + mk_BT\frac{\partial W}{\partial p}\right) = 0 \tag{3.3}$$

Mel'nikov [6] began by considering the simplest example of a metastable state when a Brownian particle that escapes over the barrier has no chance of return. The corresponding single–well potential $V(x)$ is shown in Fig. 3.1 below.

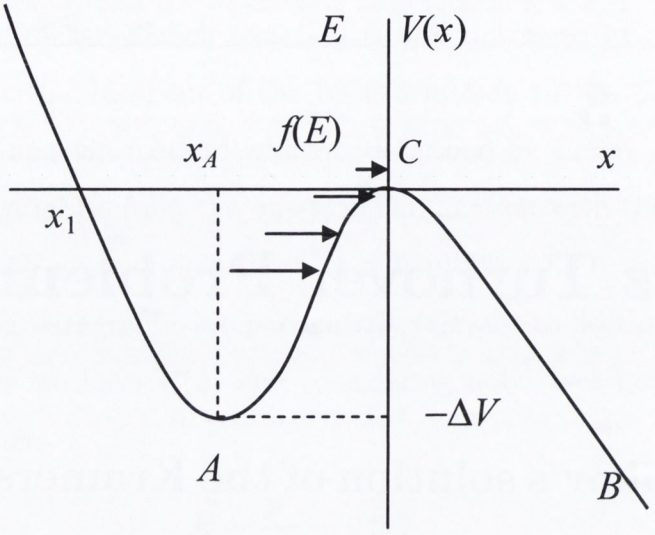

Figure 3.1: Escape from a single well.

The potential at the top of the barrier located at $x = 0$ is chosen to be zero. As before the depth of the well is $\Delta V \gg k_B T$, while the boundary condition

$$W(p, x, t) \to 0 \quad \text{as } x \to \infty \tag{3.4}$$

follows from the assumption that initially there are no particles at the far side of the barrier ($x > 0$). A Brownian particle trapped in a deep potential well resides there for a very long time, exceeding all relaxation times. The lifetime of a particle in a deep potential well can then be formulated rigorously in mathematical terms.

The relaxation of the initial distribution of particles is a two–stage process. The distribution of particles inside the potential well and in the vicinity of the barrier approaches its steady–state form in a comparatively short time. Then the escape of particles over the barrier results in an exponential decay of the distribution,

$$W(p, x, t) = W(p, x)e^{-(t/\tau)} \tag{3.5}$$

Inserting Eq. (3.5) in (3.3) we obtain

$$\frac{W}{\tau} - \frac{p}{m}\frac{\partial W}{\partial x} + \frac{dV}{dx}\frac{\partial W}{\partial p} + \beta\frac{\partial}{\partial p}\left(Wp + mk_B T\frac{\partial W}{\partial p}\right) = 0 \tag{3.6}$$

where $W(p,x)$ is the steady–state distribution. Mel'nikov points out that the solution of Eq. (3.6) is non–normalizable; $\iint W(p,x)dpdx = \infty$, as $W(p,x)$ diverges as $x \to \infty$, because the region outside the well is included. However, below we consider $W(p,x)$ only inside the well and moreover very close to the barrier.

Now, in the vicinity of the bottom of the potential well at $x = A$, the potential $V(x)$ can be represented by a harmonic oscillator of frequency $\omega_A = [V''(x_A)/m]^{1/2}$

$$V(x) \approx -\Delta V + \frac{1}{2}m\omega_A^2(x - x_A)^2 \tag{3.7}$$

where the zero of potential is taken at the barrier top located at $x = 0$.
Furthermore, near the bottom of the well the *normalized* distribution function, denoted by $\rho(p,x)$, is only slightly perturbed by escapes over the barrier and retains the Boltzmann form

$$\rho(p,x) \approx \rho_0(p,x) \equiv \frac{\omega_A}{2\pi T}\exp[-(E+\Delta V)/(k_BT)], \quad -E \gg k_BT \tag{3.8}$$

$$E \equiv \frac{p^2}{2m} + V(x) \tag{3.9}$$

where E is the total energy and $\rho_0(p,x)$ is the equilibrium distribution. Taking into account the rare escape of particles over the barrier Mel'nikov wrote

$$W(p,x,t) = N(t)\rho(p,x), \quad N(t) \propto \exp(-t/\tau) \tag{3.10}$$

where $N(t)$ is the number of particles in the well. Now the main contribution to the normalization condition,

$$\int_{-\infty}^{0} dx \int_{-\infty}^{\infty} W(p,x,t)dp = N(t) \tag{3.11}$$

like in the calculation of the VLD rate, comes from a narrow region near the bottom of the well, such that (cf Eq. (3.7)) $|x - x_A| \sim \omega_A^{-1}(k_BT/m)^{1/2}$. Moreover, in the separatrix region the flux of escaping particles, namely,

$$J = \int_{-\infty}^{\infty} \frac{p}{m} W(p,x,t)dp \tag{3.12}$$

calculated *near* the barrier top does not depend on x as long as $|V(x)| \ll \Delta V$. As before the conservation of the total number of particles of the ensemble (continuity

equation) $dN/dt = -J$ yields the connection between the lifetime $\tau = \Gamma^{-1}$ of a particle in the well and the current J,

$$1/\tau = J/N \tag{3.13}$$

Mel'nikov uses Eq. (3.13) to calculate $1/\tau$. He proceeds by noting that the first term in Eq. (3.6) is exponentially small and therefore the steady–state distribution obeys the equation

$$\frac{p}{m}\frac{\partial \rho}{\partial x} - \frac{dV}{dx}\frac{\partial \rho}{\partial p} - \beta \frac{\partial}{\partial p}\left(\rho p + m k_B T \frac{\partial \rho}{\partial p}\right) = 0 \tag{3.14}$$

with the boundary condition (3.8) and asymptotics (3.4). Mel'nikov notes that the quasi-stationary Eq. (3.14) cannot be solved analytically. However, for sufficiently deep potential wells ($k_B T \ll \Delta V$), we saw that one can apply different approaches, namely, Kramers VLD and IHD cases, in the regimes of weak and strong friction. Essentially by proceeding in this way he obtains an expression for τ applicable for arbitrary values of β.

3.2 The Green function of the Energy–Action Diffusion equation

Mel'nikov has shown that the underdamped Brownian motion near the barrier in a deep potential well can be described in terms of the Green function of the Fokker–Planck equation. He assumes that the flux over the barrier is due only to those particles in the vicinity of the barrier top with energy E that satisfies $|E| \leq k_B T$. He also assumes that the potential energy of these particles exceeds both the thermal energy $k_B T$ and the friction–induced energy loss per oscillation δ, so that $\Delta V \gg k_B T,\ \delta$. The total energy $E = p^2/2m + V(x)$ is the most slowly varying quantity, so Mel'nikov used it as a new variable instead of the momentum p in the Klein–Kramers equation. However, unlike in VLD (cf Eq. (2.97)) where only ratios of momentum dependent quantities are involved, the right– and left–going particles must now be treated separately. In the equations given below the indices + and − are associated with the right–going and left–going particles

respectively.

$$E = \frac{p^2}{2m} + V(x) \tag{3.15}$$

$$p = \pm\sqrt{2m[E - V(x)]} \equiv p_{\pm}(E, x) \tag{3.16}$$

$$f_{R,L}(E, x) = \rho[p_{\pm}(E, x), x] \tag{3.17}$$

$$\rho(p_{\pm}, x) = f_{R,L}[E(p_{\pm}, x), x] \tag{3.18}$$

Note that the function $f_{R,L}(E, x)$ defined in Eq. (3.17) is not the joint probability density function in energy E and position x. The value of the energy argument, E, in this function merely determines the value of the momentum argument in the function $f_{R,L}[E(p_{\pm}, x), x]$, for a given value of the position x (cf Appendix 2.G). Differentiating Eq. (3.18) with respect to $p_{\pm}$ and x, using the chain rule, we obtain,

$$\left.\frac{\partial\rho(p_{\pm}, x)}{\partial p_{\pm}}\right|_x = \left.\frac{\partial f_{R,L}[E(p_{\pm}, x), x]}{\partial E}\right|_x \left.\frac{\partial E(p_{\pm}, x)}{\partial p_{\pm}}\right|_x \tag{3.19}$$

and

$$\left.\frac{\partial\rho(p_{\pm}, x)}{\partial x}\right|_{p_{\pm}} = \left.\frac{\partial f_{R,L}[E(p_{\pm}, x), x]}{\partial E}\right|_x \left.\frac{\partial E(p_{\pm}, x)}{\partial x}\right|_{p_{\pm}} + \left.\frac{\partial f_{R,L}[E(p_{\pm}, x), x]}{\partial x}\right|_E \tag{3.20}$$

Differentiating Eq. (3.15) with respect to $p_{\pm}$ and x, we have

$$\left.\frac{\partial E(p_{\pm}, x)}{\partial p_{\pm}}\right|_x = \frac{p_{\pm}(E, x)}{m} \tag{3.21}$$

and

$$\left.\frac{\partial E(p_{\pm}, x)}{\partial x}\right|_{p_{\pm}} = \frac{dV(x)}{dx} \tag{3.22}$$

Using Eq. (3.21) we may rewrite Eq. (3.19) as

$$\left.\frac{\partial\rho(p_{\pm}, x)}{\partial p_{\pm}}\right|_x = \frac{p_{\pm}(E, x)}{m} \left.\frac{\partial f_{R,L}(E, x)}{\partial E}\right|_x \tag{3.23}$$

and using Eq. (3.22) we may rewrite Eq. (3.20) as

$$\left.\frac{\partial\rho(p_{\pm}, x)}{\partial x}\right|_{p_{\pm}} = \left.\frac{\partial f_{R,L}(E, x)}{\partial E}\right|_x \left(\frac{dV(x)}{dx}\right) + \left.\frac{\partial f_{R,L}(E, x)}{\partial x}\right|_E \tag{3.24}$$

Mel'nikov is then able to set $E = 0$ in the relationship for $p_{\pm}(E, x)$,

$$p(E, x) = \pm\sqrt{2m[E - V(x)]} \approx p(0, x) = \pm\sqrt{-2mV(x)} \tag{3.25}$$

because he has chosen the separatrix trajectory to effectively concide with $E = 0$ (see Fig. 3.1) and he supposes that the leading contributions to the escape stem from particles on (boundary layer) trajectories very close to that trajectory in a narrow range of energy $|E| \sim k_B T$, that differs but little from the zero energy associated with the barrier top. Furthermore, Mel'nikov notes that the main part of the trajectory lies inside the well where $|V(x)| \gg |E|$. Using Eqs. (3.23) and (3.24) the quasi-stationary Fokker–Planck equation (3.14) then takes on the form

$$\frac{\partial f_{R,L}}{\partial x} = \pm\sqrt{-2mV(x)}\beta\frac{\partial}{\partial E}\left(f_{R,L} + k_B T\frac{\partial f_{R,L}}{\partial E}\right) \tag{3.26}$$

with coefficients independent of E. In the vicinity of the left–hand turning point, where all the particles are reflected, we have

$$f_R(E, x) = f_L(E, x), \quad |x - x_1| \ll |x_1| \tag{3.27}$$

whereas near the barrier top $f_R = f_L$ only for $E < 0$. Since there are no particles going over the barrier into the well, the function f_L then vanishes for $E > 0$.

Mel'nikov then introduces the action s along the separatrix trajectory corresponding to $E = 0$. Let $s_L(x)$ denote the action of a particle that was reflected at the barrier top ($x = 0$) and is traveling to the left in position x. We denote the action of a particle that was reflected at the left–side turning point and so is travelling to the right at position x by $s_R(x)$.

$$s_L(x) = \int_0^x -\sqrt{-2mV(x')}dx' \tag{3.28}$$

$$s_R(x) = s_L(x_1) + \int_{x_1}^x \sqrt{-2mV(x')}dx' \tag{3.29}$$

Differentiating Eqs. (3.28) and (3.29) with respect to x, we have

$$\frac{ds_{R,L}}{dx} = \pm\sqrt{-2mV(x)} \tag{3.30}$$

We define

$$f(E, s_L(x)) \equiv f_L(E, x) \tag{3.31}$$

$$f(E, s_R(x)) \equiv f_R(E, x) \tag{3.32}$$

or in more compact notation

$$f(E, s_{R,L}(x)) \equiv f_{R,L}(E, x) \tag{3.33}$$

Differentiating $f_L(E,x)$ and $f_R(E,x)$ with respect to x, we have

$$\left.\frac{\partial f_L(E,x)}{\partial x}\right|_E = \left.\frac{\partial f(E,s_L(x))}{\partial s_L}\right|_E \frac{ds_L(x)}{dx}$$
$$= \left.\frac{\partial f(E,s_L(x))}{\partial s_L}\right|_E \left(-\sqrt{-2mV(x)}\right) \tag{3.34}$$

and

$$\left.\frac{\partial f_R(E,x)}{\partial x}\right|_E = \left.\frac{\partial f(E,s_R(x))}{\partial s_R}\right|_E \frac{ds_R(x)}{dx}$$
$$= \left.\frac{\partial f(E,s_R(x))}{\partial s_R}\right|_E \left(\sqrt{-2mV(x)}\right) \tag{3.35}$$

In more compact notation we have

$$\left.\frac{\partial f_{R,L}(E,x)}{\partial x}\right|_E = \left.\frac{\partial f(E,s_{R,L}(x))}{\partial s_{R,L}}\right|_E \left(\pm\sqrt{-2mV(x)}\right) \tag{3.36}$$

Using Eq. (3.36) the partial differential equation (3.26) can then be written as

$$\frac{\partial f(E,s_{R,L}(x))}{\partial s_{R,L}} = \beta\frac{\partial}{\partial E}\left[f(E,s_{R,L}(x)) + k_BT\frac{\partial f(E,s_{R,L}(x))}{\partial E}\right] \tag{3.37}$$

Since the action of a particle oscillating in the well (being a closed line integral) is *monotonically increasing* we can write Eq. (3.37) as

$$\frac{\partial f(E,s)}{\partial s} = \beta\frac{\partial}{\partial E}\left[f(E,s) + k_BT\frac{\partial f(E,s)}{\partial E}\right] \tag{3.38}$$

This equation describes diffusion and uniform drift in the energy space, like a Brownian particle being acted upon by gravity. Propagation along the separatrix trajectory is now parameterized by the action s. The initial condition (with $s = 0$) is

$$f(E,0) = \phi(E) \tag{3.39}$$

The solution to the energy–action diffusion equation may be obtained as follows. Taking the Fourier transform of the P.D.E. (3.38) and noting the initial condition (3.39) written in terms of the energy variable E, we have

$$\mathcal{F}\left\{\frac{\partial f(E,s)}{\partial s}\right\} = \beta k_BT\mathcal{F}\left\{\frac{\partial^2 f(E,s)}{\partial E^2}\right\} + \beta\mathcal{F}\left\{\frac{\partial f(E,s)}{\partial E}\right\} \tag{3.40}$$

and

$$\mathcal{F}\{f(E,0)\} = \mathcal{F}\{\phi(E)\} \tag{3.41}$$

Let $F(\xi, s)$ denote the Fourier transform of $f(E, s)$ with respect to the variable E. Using the well–known properties of the Fourier transform we have

$$\frac{dF(\xi, s)}{ds} = \left(-\xi^2 \beta k_B T + i\xi\beta\right) F(\xi, s) \tag{3.42}$$

and

$$F(\xi, 0) = \Phi(\xi) \tag{3.43}$$

where $\Phi(\xi)$ is the Fourier transform of $\phi(E)$. The solution of the transformed problem (Eqs. (3.42) and (3.43)) is

$$F(\xi, s) = \Phi(\xi) e^{-(\xi^2 \beta k_B T - i\xi\beta)s} \tag{3.44}$$

Taking the inverse Fourier transform of Eq. (3.44), we have

$$\begin{aligned} f(E, s) &= \phi(E) * \mathcal{F}^{-1}\{e^{-(\xi^2 \beta k_B T - i\xi\beta)s}\} \\ &= \phi(E) * \frac{1}{\sqrt{4\pi\beta k_B T s}} e^{-(E+\beta s)^2/(4\beta k_B T s)} \\ &= \int_{-\infty}^{\infty} \phi(E') \frac{1}{\sqrt{4\pi\beta k_B T s}} e^{-(E-E'+\beta s)^2/(4\beta k_B T s)} dE' \end{aligned} \tag{3.45}$$

where the asterisk denotes mathematical convolution. From Eq. (3.39) we have $\phi(E') = f(E', 0)$, and so Eq. (3.45) can be written as

$$f(E, s) = \int_{-\infty}^{\infty} f(E', 0) \frac{1}{\sqrt{4\pi\beta k_B T s}} e^{-(E-E'+\beta s)^2/(4\beta k_B T s)} dE' \tag{3.46}$$

Define the function $g(E - E', s)$ as

$$g(E - E', s) = \frac{1}{\sqrt{4\pi\beta k_B T s}} e^{-(E-E'+\beta s)^2/(4\beta k_B T s)} \tag{3.47}$$

Then Eq. (3.46) can be written as

$$f(E, s) = \int_{-\infty}^{\infty} f(E', 0) g(E - E', s) dE' \tag{3.48}$$

Note that if the initial distribution $f(E, 0) = \delta(E)$, then $f(E, s) = g(E, s)$. The function $g(E, s)$ is the impulse response of the system[1] and is called the Green function of Eq. (3.38).

[1]The function $g(E - E', s')$ is the response of the system to $f(E, 0) = \delta(E - E')$.

3.3 Integral Equation for the Distribution Function

In the case of the single potential well, which is the most elementary situation, we assume that after surmounting the barrier, the particles never return to the well.

$$f_L(E, 0) = 0, \quad \text{for } E > 0 \tag{3.49}$$

Near the top of the barrier the *flux of the left-going particles arises only due to reflections from the barrier of the right-going particles with* $E < 0$. The relationship between f_R and f_L is:

$$f_L[E, x(E)] = f_R[E, x(E)], \quad \text{for } E < 0 \tag{3.50}$$

where $x(E)$ is the root of the equation

$$V(x) = E, \quad x_A < x < 0 \tag{3.51}$$

corresponding to the right-side turning point at a given energy E. Equations (3.49) and (3.50) constitute boundary conditions for the integral equation because (a) they relate f_L to f_R for $E < 0$, and (b) no left-going particles exist at the barrier top. Particles with different values of energy E are reflected at different values of position $x(E)$. However, for $E \approx kT$ (the order of magnitude of a fluctuation), *the variation in the values of* $x(E)$ *is small in size compared to the overall extent of the well.* Hence, one may assume that all such particles propagate along trajectories very close to the trajectory for $E = E_C = 0$ (separatrix). The action $S(E)$ per oscillation is given by

$$S(E) = \oint \sqrt{2m[E - V(x)]}dx, \quad E < 0 \tag{3.52}$$

However, for very small energies characteristic of the seperatrix region we can neglect the difference between $S(0)$, the action at the barrier, and $S(E)$. Thus the basic parameter of the problem $S(0)$, namely, the action in the seperatrix region is now

$$S \equiv S(0) = \oint \sqrt{2m[-V(x)]}dx = 2\int_{x_1}^{0} \sqrt{2m[-V(x)]}dx \tag{3.53}$$

The integral equation (3.48) with the particular value $s = S$, corresponding to $E = 0$, can now be used to describe the evolution of $f(E, S)$ provided $|E| \sim k_B T$. Mel'nikov proceeded with his derivation of an integral equation by introducing a new function $f(E)$ such that

$$f(E) = f_R(E, 0), \quad \text{for } E > 0; \qquad f(E) = f_L[E, x(E)], \quad \text{for } E < 0 \tag{3.54}$$

where $x(E)$ is defined in Eq. (3.51). The significance of this is that the function $f(E)$ simultaneously gives the rate of escape of particles at the barrier top for energy $E > 0$ and the rate of reflection at the barrier for $E < 0$. Now the reflected particles proceed to the left-hand turning point whereupon they are reflected again. Having traversed the well these particles should then reach the barrier thereby reproducing the initial distribution $f(E)$. This boundary condition now transforms Eq. (3.48) into a *closed* integral equation for the function $f(E)$. Now in the vicinity of the separatrix trajectory ($E \approx 0$) the evolution of the particle distribution is governed by Green's function

$$g(E - E') \equiv g(E - E', S) = \frac{1}{\sqrt{4\pi k_B T \delta}} \exp\left[-\frac{(E - E' + \beta S)^2}{4 k_B T \delta}\right] \tag{3.55}$$

where $\delta \equiv \beta S$ is the energy loss per oscillation. Therefore by superposition Melnikov's integral equation for the energy distribution function for particles in the *vicinity* of the barrier top takes on the form of the Wiener–Hopf equation

$$f(E) = \int_{-\infty}^{0} f(E') g(E - E') dE' \tag{3.56}$$

Note that the upper limit of integration can now be taken as 0 since *there are no left-going particles at the barrier top with energy* $E > 0$. Furthermore because the exponential factor in the Green function $g(E - E')$ decays so rapidly we suffer no great error in extending the lower limit to $-\infty$. This is important as otherwise the problem cannot be posed as a Wiener-Hopf equation [27]. Moreover, we have the additional boundary condition that deep in the well $f(E)$ must become the Boltzmann distribution (cf Eq (3.8)), i.e.,

$$f(E) \approx f_0(E) = \frac{\omega_A}{2\pi k_B T} e^{-\frac{E - \Delta V}{k_B T}}, \quad -E \gg k_B T \tag{3.57}$$

Solving the integral equation (3.56) for $f(E)$ yields from Eqs. (3.12) and (3.13) the escape rate Γ in terms of $f(E)$

$$\Gamma = \frac{1}{\tau} = J = \int_0^\infty f(E)dE \tag{3.58}$$

In writing Eq (3.58) Mel'nikov has used the identity $m^{-1}p\,dp \equiv dE$ and has taken into account that in the underdamped regime only *positive* momenta contribute to the integral in Eq. (3.12).

3.4 Solving the Integral Equation for $f(E)$ by the Wiener–Hopf Method

Equation (3.56) for the energy distribution function represents the convolution of $g(E)$ and the one–sided function $f(E)\theta(-E)$ where $\theta(E)$ is Heaviside's theta or unit step function. Accordingly to solve this integral equation by the Wiener–Hopf method Mel'nikov introduced the one–sided Fourier transformations

$$\varphi^{\pm}(\lambda) = \frac{2\pi}{\omega_A} e^{\frac{\Delta V}{k_B T}} \int_{-\infty}^{\infty} f(E)\theta(\pm E) e^{\frac{i\lambda E}{k_B T}} dE \tag{3.59}$$

On comparing Eqs. (2.1), (3.58) and (3.59) we have

$$\Gamma = A\,\Gamma^{\mathrm{TST}} \tag{3.60}$$

where the prefactor A is given by

$$A = \varphi^{+}(0) \tag{3.61}$$

Using the boundary condition of a Maxwell–Boltzmann distribution deep in the well, i.e. Eq. (3.57), one may approximate $\varphi^{-}(\lambda)$ as

$$\varphi^{-}(\lambda) \approx -\frac{i}{\lambda + i}, \qquad |\lambda + i| \ll 1, \text{ and } \operatorname{Im}\lambda < -1 \tag{3.62}$$

Now, with Eqs. (3.55), (3.56), and (3.59) we have

$$\varphi^{-}(\lambda) + \varphi^{+}(\lambda) = \frac{2\pi}{\omega_A} e^{\frac{\Delta V}{k_B T}} \int_{-\infty}^{\infty} \left\{ \int_{-\infty}^{0} \frac{f(E')}{\sqrt{4k_B T \beta S}} e^{-\frac{(E-E'+\beta S)^2}{4k_B T \beta S}} e^{\frac{i\lambda E}{k_B T}} dE' \right\} dE \tag{3.63}$$

Using properties of Gaussian integrals Eq. (3.63) can be rewritten as

$$\varphi^-(\lambda) + \varphi^+(\lambda) = \tilde{g}(\lambda)\varphi^-(\lambda) \tag{3.64}$$

where

$$\tilde{g}(\lambda) = \int_{-\infty}^{\infty} g(E) e^{\frac{i\lambda E}{k_B T}} dE = e^{\frac{-\delta\lambda(\lambda+i)}{k_B T}} \tag{3.65}$$

To illustrate how the Wiener–Hopf method [27] may be used to determine $A = \varphi^+(0)$, Mel'nikov rewrote Eq. (3.64) as

$$\varphi^+(\lambda) + G(\lambda)\varphi^-(\lambda) = 0 \tag{3.66}$$

where

$$G(\lambda) = 1 - \tilde{g}(\lambda) = 1 - e^{\frac{-\delta\lambda(\lambda+i)}{k_B T}} \tag{3.67}$$

The functions $\varphi^+(\lambda)$ and $\varphi^-(\lambda)$ are analytic in the upper and lower complex half–planes of λ, the only exception being the pole of $\varphi^-(\lambda)$ at $\lambda = -i$. The solution of Eq. (3.64) may now be determined in terms of $G(\lambda)$ as follows. We have from Eq. (3.64)

$$\ln\left[-\varphi^+(\lambda)\right] = \ln\varphi^-(\lambda) + \ln G(\lambda) \tag{3.68}$$

We now use Cauchy's integral formula (see Appendix 3.1) to decompose $\ln G(\lambda)$ into two terms $\ln G^+(\lambda)$ and $\ln G^-(\lambda)$, analytic in the corresponding half–planes of λ

$$\ln G(\lambda) = \ln G^+(\lambda) + \ln G^-(\lambda) \tag{3.69}$$

where

$$\ln G^{\pm}(\lambda) = \pm\frac{1}{2\pi i}\lim_{\epsilon\to 0}\int_{-\infty}^{\infty}\frac{\ln G(\lambda')}{\lambda' - \lambda \mp i\epsilon}d\lambda' \tag{3.70}$$

Both $G^+(\lambda)$ and $G^-(\lambda)$ are entire functions which have no zeros in the half–planes $\mathrm{Im}\,\lambda > 0$ and $\mathrm{Im}\,\lambda < 0$ respectively. Moreover, both $G^+(\lambda)$ and $G^-(\lambda) \to 1$ as $\lambda \to \infty$. Clearly

$$G^+(\lambda)G^-(\lambda) \equiv G(\lambda) \tag{3.71}$$

We can now rewrite Eq. (3.68) as

$$\ln\left[-\varphi^+(\lambda)\right] - \ln G^+(\lambda) = \ln\varphi^-(\lambda) + \ln G^-(\lambda) \tag{3.72}$$

As the functions on both sides of Eq. (3.72) are analytic in different half–planes of λ, both sides must be equal to an *entire* function which is chosen so as to satisfy the boundary condition Eq. (3.62), and which may be taken as $\ln h(\lambda)$, so that

$$\ln\left[-\varphi^+(\lambda)\right] - \ln^+ G(\lambda) = \ln\varphi^-(\lambda) + \ln^- G(\lambda) = \ln h(\lambda) \tag{3.73}$$

or equivalently

$$\varphi^+(\lambda) = -h(\lambda)G^+(\lambda) \tag{3.74}$$

and

$$\varphi^-(\lambda) = h(\lambda)/G^-(\lambda) \tag{3.75}$$

From Eqs. (3.62) and (3.75) we have

$$\begin{aligned}\varphi^-(\lambda) &= h(\lambda)/G^-(\lambda) \\ &= -\frac{i}{\lambda+i}, \qquad \text{for } |\lambda+i| \ll 1, \text{ and } \operatorname{Im}\lambda < -1\end{aligned} \tag{3.76}$$

Thus,

$$h(\lambda) = -\frac{iG^-(\lambda)}{\lambda+i}, \qquad \text{for } |\lambda+i| \ll 1, \text{ and } \operatorname{Im}\lambda < -1 \tag{3.77}$$

Let

$$h(\lambda) = -\frac{iG^-(-i)}{\lambda+i} \tag{3.78}$$

Inserting Eq. (3.78) into Eqs. (3.74) and (3.75) yields the solution of the Wiener–Hopf Eq. (3.72), namely,

$$\varphi^+(\lambda) = \frac{iG^+(\lambda)G^-(-i)}{\lambda+i} \quad \text{and} \quad \varphi^-(\lambda) = -\frac{iG^-(-i)}{G^-(\lambda)(\lambda+i)} \tag{3.79}$$

Thus the prefactor $A = \varphi^+(0)$ is given by

$$A = G^+(0)G^-(-i) \tag{3.80}$$

Now $G^-(-i) = [G^+(0)]^*$ where the asterisk denotes complex conjugation. This can be verified [14] by displacement of the contour of integration in Eq. (3.70) to the line Im $\lambda = -i/2$

$$\begin{aligned}\ln G^\pm(\lambda) &= \pm\frac{1}{2\pi i}\lim_{\epsilon\to 0}\int_{-\infty-\frac{i}{2}}^{\infty-\frac{i}{2}} \frac{\ln G(\lambda')}{\lambda'-\lambda\mp i\epsilon}d\lambda' \\ &= \pm\frac{1}{2\pi i}\lim_{\epsilon\to 0}\int_{-\infty}^{\infty} \frac{\ln G(\lambda'-\frac{i}{2})}{\lambda'-\lambda-\frac{i}{2}\mp i\epsilon}d\lambda'\end{aligned} \tag{3.81}$$

where the shifted function

$$G(\lambda - i/2) = 1 - \tilde{g}(\lambda - i/2) = 1 - e^{-\Delta(\lambda^2+1/4)} \tag{3.82}$$

is real [cf. Eq. (6.9)].

Using Eq. (3.81) we have

$$\ln G^-(-i) = -\frac{1}{2\pi i} \lim_{\epsilon \to 0} \int_{-\infty}^{\infty} \frac{\ln G(\lambda' - \frac{i}{2})}{\lambda' + \frac{i}{2} + i\epsilon} d\lambda' \tag{3.83}$$

and

$$\ln G^+(0) = \frac{1}{2\pi i} \lim_{\epsilon \to 0} \int_{-\infty}^{\infty} \frac{\ln G(\lambda' - \frac{i}{2})}{\lambda' - \frac{i}{2} - i\epsilon} d\lambda' \tag{3.84}$$

Taking the complex conjugate of $\ln G^+(0)$ we have

$$\begin{aligned} \left[\ln G^+(0)\right]^* &= -\frac{1}{2\pi i} \lim_{\epsilon \to 0} \int_{-\infty}^{\infty} \frac{\left[\ln G(\lambda' - \frac{i}{2})\right]^*}{\lambda' + \frac{i}{2} + i\epsilon} d\lambda' \\ &= -\frac{1}{2\pi i} \lim_{\epsilon \to 0} \int_{-\infty}^{\infty} \frac{\ln G(\lambda' - \frac{i}{2})}{\lambda' + \frac{i}{2} + i\epsilon} d\lambda' \\ &= \ln G^-(-i) \end{aligned} \tag{3.85}$$

Using Eq. (3.85) we can write

$$G^-(-i) = \left[G^+(0)\right]^* \tag{3.86}$$

and therefore

$$A = G^+(0)G^-(-i) = |G^+(0)|^2 \tag{3.87}$$

Using Eq. (3.84) we obtain the depopulation factor Eq. (2.34), namely,

$$A(\Delta) = |G^+(0)|^2 = \exp\left(\frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{\ln\left\{1 - \exp\left[-\Delta(\lambda^2 + 1/4)\right]\right\}}{\lambda^2 + 1/4} d\lambda\right) \tag{3.88}$$

One can show (details in [14]) that

$$A(\Delta) \sim \Delta \text{ for } \Delta \ll 1 \text{ and } A(\Delta) \to 1 \text{ for } \Delta \gg 1 \tag{3.89}$$

so regaining the VLD and IHD results, respectively.

3.5 Kramers VLD result

In the VLD limit, the integral equation (3.56) reduces to the differential equation

$$\delta \frac{d}{dE}\left(f + k_B T \frac{df}{dE}\right) = 0, \quad \delta \ll k_B T \tag{3.90}$$

subject to the boundary conditions (3.57) and

$$f(0) = 0 \tag{3.91}$$

We now determine $f(E)$ from Eq. (3.90) and then use it to calculate the VLD escape rate. We have

$$\frac{df}{dE} + \frac{1}{k_B T} f = C_1 \tag{3.92}$$

where C_1 is a constant to be determined. Now, the general solution of the differential equation

$$\frac{dy}{dx} = p(x)y = r(x) \tag{3.93}$$

is [42]

$$y(x) = e^{-h}\left[\int e^{h} r dx + c\right], \quad h = \int p(x)dx \tag{3.94}$$

where c is an arbitrary constant. The solution of Eq. (3.92) is therefore

$$\begin{aligned} f(E) &= e^{-\left(\frac{E}{k_B T}\right)}\left[C_1 \int e^{\left(\frac{E}{k_B T}\right)} dE + C_2\right] \\ &= C_1 k_B T + C_2 e^{-\left(\frac{E}{k_B T}\right)} \end{aligned} \tag{3.95}$$

We now use the boundary conditions (3.57) and (3.91) to determine the constants C_1 and C_2, yielding $C_1 = -[\omega_A/2\pi(k_B T)^2]\exp[-\Delta V/(k_B T)]$, $C_2 = -C_1 k_B T$, and

$$f(E) = \frac{\omega_A}{2\pi k_B T}\left[e^{-\frac{E}{k_B T}} - 1\right] e^{-\frac{\Delta V}{k_B T}} \tag{3.96}$$

Mel'nikov [6] justified the boundary condition $f(0) = 0$ by calculating the average energy of the escaping particles and deduced that $f(0) \sim \omega_A \delta (k_B T)^{-2} \exp(-\Delta V/(k_B T))$ which is negligible only in the VLD case. To obtain the VLD escape rate we must evaluate the current J at the barrier, which is defined as

$$J = -\delta\left(f + k_B T \frac{df}{dE}\right)\Big|_{E=0} \tag{3.97}$$

Now $f(0) = 0$, and $\Gamma = -J$ since we have normalized to one particle in the well. The escape rate is therefore given by

$$\Gamma = -\delta k_B T \frac{df}{dE}\Big|_{E=0} \tag{3.98}$$

Using Eq. (3.96) in Eq. (3.98) we have

$$\Gamma = \frac{\omega_A \delta}{2\pi k_B T} e^{-\left(\frac{\Delta V}{k_B T}\right)} \tag{3.99}$$

which is the Kramers VLD result.

3.6 Criticisms of the ad hoc approach of Mel'nikov and Meshkov

A disadvantage of the original calculations of Kramers is that the prefactor (transmission factor) of the escape rate is determined by essentially two separate approaches that are valid for very weak and high damping respectively [28]. The results are then combined in an *ad hoc* fashion to yield an interpolation formula valid in the entire range of damping cf Eqs. (2.33) and (2.34).

However, Grabert [28] and Pollak et al. [18] proposed a unified theory based on a normal mode approach to the dissipative dynamics that has its origin in the generalized Langevin equation for the coordinate q, namely,

$$M\ddot{q} + \int_0^t \eta(t-t')\dot{q}(t') + \frac{\partial V}{\partial q} = F(t) \tag{3.100}$$

Here, the system coordinate q of effective mass M moves in a potential $V(q)$, experiences a friction kernel $\eta(t)$ and a random force $F(t)$, that originates from the thermal motion of the liquid. The force $F(t)$ is Gaussian and satisfies the second fluctuation dissipation theorem

$$\langle F(t)F(0)\rangle = k_B T\eta(t) \tag{3.101}$$

Kramers treated the problem in the Markovian limit, that is, $\eta(t) = 2M\beta\delta(t)$, where β is the static friction parameter usually taken to be proportional to the viscosity of the fluid. The unified theory proposed by Grabert [28] and Pollak et al. [18] may be described in two steps. The first of these, as shown by Zwanzig [1, 43], is to transform the generalized Langevin equation into a Hamiltonian where the system is linearly coupled to a bath of harmonic oscillators. The second step [35, 44, 45] is a transformation of the coordinates of the Hamiltonian to normal modes. At the barrier one may then immediately identify the unstable normal mode associated with the barrier crossing [17]. At energies close to the barrier energy the normal mode dynamics are virtually exact [9, 35]. Hence, a multidimensional TST in the normal mode coordinates can be used and is equivalent to the spatial diffusion limited or IHD rate. The essence of the approach of Pollak [9, 35] and Pollak et al. [18] is that the unstable normal mode decouples

from the other modes very near the barrier allowing one to describe the problem by a single degree of freedom stochastic process for the energy loss in the unstable normal mode. This immediately yields the escape rate that is very similar to that obtained by Mel'nikov and Meshkov [5, 6]. However, two vital differences must be emphasised. The theory of Grabert [28] and Pollak [18] et al. *deals with the unstable normal mode energy along the reaction and not the physical configuration coordinate.* Second, the theory is formulated for arbitrary (non–Ohmic) friction, so that it is identical to that of Mel'nikov and Meshkov [5, 6] only in the weak coupling limit. However, it goes smoothly without any *ad hoc* assumptions to the correct spatial diffusion IHD limit that is synonymous with the multidimensional TST limit, and of course with Ohmic damping being assumed.

For $E \lesseqgtr 0$ let $f(E)dE$ be the probability of finding, in one unit of time, the system in the barrier region at a turning point of the unstable normal mode with a mode energy lying between E and $E + dE$. The escape rate is then given by

$$\Gamma = \int_0^\infty f(E)\, dE \tag{3.102}$$

since all particles with $E > 0$ escape. If $E < 0$ the particle returns to the well where all modes are coupled and exchange energy [28]. The loss of energy ΔE in the *unstable normal mode* now determines the conditional probability $g(E|E')$dE (assuming high barriers) that a system leaving the barrier region with normal-mode energy E' will return to the barrier with an energy lying between E and $E+dE$ in the unstable normal mode. The steady-state distribution $f(E)$ is given by the integral equation

$$f(E) = \int_{-\Delta V}^0 g(E|E')f(E')\, dE' \tag{3.103}$$

Deep in the well $f(E)$ approaches the equilibrium distribution [28] $f_{eq}(E)$ given by

$$f_{eq}(E) = \frac{1}{2\pi k_B T}\frac{\omega_A \lambda^+}{\omega_C} \exp\left[-\frac{E + \Delta V}{k_B T}\right] \tag{3.104}$$

where λ^+ denotes the unstable normal mode angular frequency (the Grote–Hynes frequency). In the case of frequency-independent damping λ^+ is given by

$$\lambda^+ = \left(\omega_C^2 + \eta^2/4\right)^{1/2} - \eta/2 \tag{3.105}$$

Since the distribution $f(E)$ approaches $f_{eq}(E)$ for $E \ll 0$, the lower limit of integration in Eq. (3.103) can be shifted to $-\infty$, and the integral equation for $f(E)$ can then be written as

$$f(E) = \int_{-\infty}^{0} g(E|E')f(E')\,dE' \tag{3.106}$$

Grabert [28] made the *Ansatz* $f(E) = f_{eq}(E)\exp\left(\frac{1}{2}\beta E\right)\phi(\beta E)$ which transforms Eq. (3.106) into a Wiener-Hopf equation with a symmetric kernel that can be solved by standard methods.

Their unified theory, based on the energy in the unstable normal mode at the barrier, then yields in the notation of [18]

$$\Gamma = \frac{\omega_A}{2\pi} e^{-\Delta V/(k_B T)} \frac{\lambda^+}{\omega_C} \exp\left(\frac{1}{\pi}\int_{-\infty}^{\infty} \frac{dy}{1+y^2} \ln\left[1 - e^{-\Delta(1+y^2)/4}\right]\right) \tag{3.107}$$

where $\Delta = \Delta E/(k_B T)$, and ΔE is the average energy loss of the unstable normal mode, evaluated for the $E = 0$ trajectory. This energy loss does not in general coincide with the energy loss along the physical particle coordinate. For $\Delta \gg 1$, Γ reduces to the multidimensional TST value as incorporated in the boundary condition for $f(E)$, namely,

$$\Gamma = \frac{\omega_A}{2\pi}\frac{\lambda^+}{\omega_C} e^{-\Delta V/(k_B T)} \tag{3.108}$$

On the other hand, for Δ of the order of unity or smaller [1] the distribution $f(E)$ now contains nonequilibrium effects giving rise to a transmission factor < 1 that is below that of the multidimensional TST value. Moreover, for very low damping

$$\Gamma = \Gamma^{\mathrm{VLD}} = \Gamma^{\mathrm{TST}} \frac{\Delta}{k_B T} \tag{3.109}$$

which reduces for the original Kramers model (Ohmic friction) to $\Delta = \beta S(0)$, that is, the energy controlled diffusion result.

Appendices

3.A Separations in the Wiener–Hopf method

The Cauchy integral formula can be used to obtain the separations $\ln G^+(\lambda)$ and $\ln G^-(\lambda)$ needed in the Wiener–Hopf method [27, 46]. Suppose that $\ln G(\lambda) = \ln G(\sigma + i\omega)$ is analytic in the strip $a < \omega < b$ and that $\ln G(\sigma + i\omega) \to 0$ as $\sigma \to \pm\infty$, uniformly in the strip $a < \omega < b$. Choose ω_+ and ω_- so that $a < \omega_+ < \omega < \omega_- < b$.

Using Cauchy's integral formula we can write

$$\ln G(\lambda) = \frac{1}{2\pi i} \oint_C \frac{\ln G(\lambda')}{\lambda' - \lambda} d\lambda' \tag{3.110}$$

where C is a counterclockwise rectangular contour formed by the segments $\mathrm{Re}(\lambda) = \pm L$ and the segments $\mathrm{Im}(\lambda) = \omega_\pm$. The integrals over the first segments go to zero when $L \to \infty$. We then have

$$\ln G(\lambda) = \ln G^+(\lambda) + \ln G^-(\lambda) \tag{3.111}$$

where

$$\ln G^\pm(\lambda) = \pm \frac{1}{2\pi i} \int_{-\infty + i\omega_\pm}^{\infty + i\omega_\pm} \frac{G(\lambda')}{\lambda' - \lambda} d\lambda' \tag{3.112}$$

The functions $\ln G^+(\lambda)$ and $\ln G^-(\lambda)$ are analytic in the half–planes $\mathrm{Im}(\lambda) > \omega_+$ and $\mathrm{Im}(\lambda) < \omega_-$ respectively. If $\omega_+ = -\epsilon$ and $\omega_- = \epsilon$, we have

$$\begin{aligned} \ln G^\pm(\lambda) &= \pm \frac{1}{2\pi i} \int_{-\infty \mp i\epsilon}^{\infty \mp i\epsilon} \frac{G(\lambda')}{\lambda' - \lambda} d\lambda' \\ &= \pm \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{\ln G(\lambda' \mp i\epsilon)}{\lambda' - \lambda \mp i\epsilon} d\lambda' \end{aligned} \tag{3.113}$$

Taking the limit $\epsilon \to 0$ we obtain Eq. (3.70).

3.B Mean and Variance of the Energy Loss per oscillation

We can determine the mean and variance of the energy loss per oscillation in energy controlled diffusion from an energy Langevin equation. Our energy–action diffusion equation is

$$\frac{\partial f(E,s)}{\partial s} = \beta \frac{\partial}{\partial E}\left[f(E,s) + k_B T \frac{\partial f(E,s)}{\partial E}\right] \tag{3.114}$$

Consider the stochastic differential equation

$$\zeta \dot{x} + \frac{\partial V}{\partial x} = \lambda(t) \tag{3.115}$$

$$\langle \lambda(t) \rangle = 0, \qquad \langle \lambda(t_1)\lambda(t_2) \rangle = 2k_B T \zeta \delta(t_1 - t_2) \tag{3.116}$$

The corresponding Smoluchowski equation is

$$\frac{\partial g(x,t)}{\partial t} = \frac{kT_B}{\zeta}\frac{\partial}{\partial x}\left(\frac{\partial g}{\partial x} + \frac{g}{k_B T}\frac{\partial V}{\partial x}\right) \tag{3.117}$$

Eq. (3.114) can be rewritten as

$$\frac{\partial f(E,s)}{\partial s} = k_B T \beta \frac{\partial}{\partial E}\left[\frac{f(E,s)}{k_B T} + \frac{\partial f(E,s)}{\partial E}\right] \tag{3.118}$$

Eq. (3.118) is in the form of Eq. (3.117) with $\partial V/\partial x = 1$ and $\zeta = 1/\beta$ The Langevin equation associated with Eq. (3.118) is

$$\frac{1}{\beta}\frac{\partial E}{\partial s} + 1 = N(s) \tag{3.119}$$

where $N(s)$ is zero–mean white noise

$$\langle N(s) \rangle = 0, \qquad \langle N(s_1)N(s_2) \rangle = \frac{2k_B T}{\beta}\delta(s_1 - s_2) \tag{3.120}$$

Taking the average on both sides of Eq. (3.119) we have

$$\frac{1}{\beta}\frac{\partial \langle E \rangle}{\partial s} + 1 = 0 \tag{3.121}$$

The solution of Eq. (3.121) is

$$\langle E \rangle = -\beta s + c \tag{3.122}$$

where c is a constant. At $s = 0$, $\langle E \rangle = E'$ and so the constant $c = E'$. Let S denote the action after one oscillation of the particle in the well. We have

$$\langle E - E' \rangle = -\beta S \tag{3.123}$$

We now wish to determine the variance of the energy loss per oscillation from the Langevin equation.

$$\langle [E - E']^2 - \langle E - E' \rangle^2 \rangle = 2\beta k_B T S \tag{3.124}$$

Using Eq. (3.123) in Eq. (3.124) we have

$$\langle [E - E']^2 \rangle - (-\beta S)^2 = 2\beta k_B T S \tag{3.125}$$

$$\langle [E - E']^2 \rangle = 2\beta k_B T S + \beta^2 S^2 \tag{3.126}$$

Now,

$$\begin{aligned} \langle (E - E')^2 \rangle &= \langle E^2 \rangle - 2E' \langle E \rangle + (E')^2 \\ &= 2k_B T S + \beta^2 S^2 \end{aligned} \tag{3.127}$$

Using Eq. (3.123) in Eq. (3.127) we have

$$\langle E^2 \rangle = (E')^2 - 2E'\beta S + 2k_B T \beta S + \beta^2 S^2 \tag{3.128}$$

Chapter 4

IHD Escape Rate for Quantum Brownian Motion

4.1 Escape Rate in the IHD Region

Following Mel'nikov [6], we recall that in the classical regime one starts with the Langevin equation or the corresponding Fokker–Planck equation. In the quantum regime, however, one must start by specifying the Hamiltonian of the problem. Now we wish to study the decay rate for particles that experience viscous friction in the classical regime. This condition is insufficient to define the system consisting of particle and heat bath in a unique way. Nevertheless it is still enough to uniquely determine the effective action of the particle obtained by integration over the variables describing the bath. According to Mel'nikov [6] this conclusion is very important because all models of the heat bath are then equivalent as far as the results for the escape rate are concerned *provided they reproduce the same Langevin equation in the classical limit.* Mel'nikov [6] considered two different models of the heat bath. In the underdamped regime he accounted for the interaction of a particle with the bath by adding a term describing the effects of the (Johnston-Nyquist) noise on the Hamiltonian (operator) of the particle. In contrast in the overdamped regime he assumed that the effect of the bath is mimicked by a string coupled to the particle and tightened in a direction perpendicular to the direction of motion of the particle. Ultimately these procedures lead via a

quantum depopulation factor to a high temperature quantum escape rate valid for all values of the dissipation in the same *ad hoc* manner as the classical case.

We reiterate that in considering the classical case Kramers [11] effectively proceeded using what are essentially two separate theories. In purely *energy controlled diffusion* it is assumed that the dynamics of the particle are almost Newtonian because of the very weak coupling to the bath and the noisy motion is then treated simply as a small perturbation of the noiseless undamped librational motion at the barrier energy governed by Newton's equations. Thus the VLD case always reduces to the solution of a problem in the classical dynamics. On the other hand, in the IHD or *spatially controlled diffusion* limit the problem is treated by approximating the potential in the vicinity of the well and saddle by a (hyper) paraboloid and inverted (hyper) paraboloid respectively. The corresponding linearized multidimensional Fokker–Planck equation is then solved in the vicinity of the barrier in the manner described above. The two approaches are then combined as in the classical Meshkov-Mel'nikov approach via a depopulation factor to yield a formula for the escape rate valid for all values of the dissipative coupling to the bath.

However, as we have mentioned, the first systematic (i.e., without *ad hoc* assumptions) solution of the classical Kramers turnover problem was given by Grabert [28], and Pollak et al. [18]. This solution was based on two observations. The first being that escape does not occur along the original system coordinate but along the unstable normal mode of the combined system and bath [2]. The second was a systematic perturbative treatment [28] of the nonlinear part of the potential which couples the unstable mode with the bath of stable modes. This treatment was extended by Rips and Pollak [47] to provide a consistent solution of the quantum Kramers turnover problem. Their method represents a synthesis of the treatment of the well and barrier dynamics of Mel'nikov [6], and Larkin and Ovchinnikov [10], and the normal mode approach to the classical Kramers turnover problem of Pollak *et al.* In reviewing and simplifying the work of Mel'nikov we shall first give the derivation of the IHD quantum rate in the relatively straightforward manner proposed by Pollak [35], as this constitutes the

most transparent method of attack on the problem which was originally solved by Wolynes [8] in 1981 using path integrals. Pollak [35] started from the equivalence of the generalised Langevin equation for a Brownian particle to the equation of motion of a particle moving in a potential and bilinearly coupled to a bath of harmonic oscillators. This procedure (which demonstrates using normal mode analysis that classically the IHD Kramers rate is equivalent to a harmonic multi-dimensional TST rate) may be extended to the quantum case by quantizing the system plus bath Hamiltonian consisting at the transition state of an assembly of real oscillators and one with imaginary frequency of oscillation representing the unstable barrier crossing mode. It leads to the result of Wolynes without using path integrals. Alternative calculations [14] based on extensions of Langers imaginary part of the free energy method to include quantum effects also yield that result. The string-particle model in its essentials goes back to Lamb's (1900) attempt to explain radiation damping in classical electrodynamics [19].

In this section, we use the notation of Pollak's paper [35], namely, q is a coordinate, $V(q)$ is the potential, $V^{\#}$ is barrier height, and $\eta(t)$ is a time-dependent friction related to the zero-mean Gaussian random force $F(t)$ by the fluctuation-dissipation relation, that is,

$$\langle F(0)F(t)\rangle = k_B T\eta(t) \tag{4.1}$$

The generalized Langevin equation (for the classical particle) is [9, 35]

$$M\ddot{q} + \int_0^t \eta(t-t')\dot{q}(t')\,dt' + \frac{\partial V}{\partial q} = F(t) \tag{4.2}$$

This equation may be derived from a Hamiltonian with a harmonic oscillator bath [48], that is,

$$H = \frac{p_q^2}{2M} + V(q) + \sum_{j=1}^{N}\left[\frac{p_j^2}{2m_j} + \frac{1}{2}m_j\left(\omega_j x_j + \frac{C_j}{m_j\omega_j}q\right)^2\right] \tag{4.3}$$

(See also [49].) Here, (p_j, x_j) are the momenta and coordinates of the jth bath oscillator whose mass and frequency are m_j and ω_j, respectively. C_j couples the jth bath oscillator to the system. By assuming that at time $t = 0$, the bath is in thermal equilibrium, it can be shown [48] that $q(t)$ is governed by Eq. (4.2) [and

Eq. (4.1)], where the time-dependent friction $\eta(t)$ is

$$\eta(t) = \sum_{j=1}^{N} \frac{C_j^2}{m_j \omega_j^2} \cos \omega_j t \tag{4.4}$$

The spectral density of the bath $J(\omega)$ is defined as [49]

$$J(\omega) \equiv \frac{\pi}{2} \sum_{j=1}^{N} \frac{C_j^2}{m_j \omega_j} \delta(\omega - \omega_j) \tag{4.5}$$

Hence using Eq. (4.4), the time-dependent friction $\eta(t)$ can be expressed in terms of the inverse Fourier cosine transform of the spectral density $J(\omega)$ as

$$\eta(t) = \frac{2}{\pi} \int_{-\infty}^{\infty} \frac{J(\omega)}{\omega} \cos \omega t \, d\omega \tag{4.6}$$

Now it is possible to obtain the continuum limit for the dynamics by defining $J(\omega)$ as a continuous function instead of defining each amplitude C_j separately [21]. We now take the Laplace transform of $\eta(t)$, that is,

$$\tilde{\eta}(s) = \int_0^{\infty} e^{-st} \eta(t) \, dt \tag{4.7}$$

so that with Eq. (4.6)

$$\tilde{\eta}(s) = \frac{2}{\pi} \int_0^{\infty} e^{-st} \int_{-\infty}^{\infty} \frac{J(\omega)}{\omega} \cos \omega t \, d\omega \, dt = \frac{2}{\pi} \int_{-\infty}^{\infty} \frac{s}{\omega(s^2 + \omega^2)} J(\omega) \, d\omega \tag{4.8}$$

By using Eq. (4.4) the Laplace transform $\tilde{\eta}(s)$ may also be written as

$$\tilde{\eta}(s) = \sum_{j=1}^{N} \frac{C_j^2}{m_j \omega_j^2} \left(\frac{s}{s^2 + \omega_j^2} \right) \tag{4.9}$$

We wish to calculate the quantum escape rate and do so as follows. First, the Hamiltonian given in Eq. (4.3) may be regarded as a quantum Hamiltonian. For a *finite* discrete set of oscillators one may then evaluate the thermal decay rate using harmonic quantum transition state theory (TST) as mentioned in the Introduction. Having obtained the TST expression one may take the continuum limit, so yielding an estimate for the quantum IHD escape rate of particles governed by the generalized Langevin equation.

To implement this, we must according to harmonic TST Eqs. (2.4) and (2.18), and the generalized Kramers-Langer-Grote-Hynes expression (2.44), evaluate the

quantum partition functions at the well, taken as $q = 0$, and the barrier ($q = q_{\#}$). The partition functions may then be evaluated via a normal mode analysis at the barrier and the well. To derive the rate expression essentially using Eq. (2.44), we first undertake the normal mode analysis. We assume that the potential may be approximated as

$$V(q) \approx \frac{1}{2} M \omega_0^2 q^2 \tag{4.10}$$

in the vicinity of the well and as

$$V(q) \approx V^{\#} - \frac{1}{2} M \omega_{\#}^2 (q - q_{\#})^2 \tag{4.11}$$

at the barrier. Here, ω_0 is the angular frequency of small oscillations about the well bottom and $\omega_{\#}$ is the imaginary frequency at the barrier. The harmonic approximations embodied in Eqs. (4.10) and (4.11) imply that the Hamiltonian in the vicinity of the well and barrier may be written in *separable form* like in Eq. (2.4) as that of a sum of $N + 1$ harmonic oscillators. This is achieved [50] by first transforming to mass-weighted coordinates

$$q' = M^{1/2} q, \quad x'_j = m_j^{1/2} x_j \tag{4.12}$$

and then diagonalizing the $(N + 1) \times (N + 1)$ force constant (Hessian) matrix defined by the second derivatives of the potential at the well and the barrier.

The Hamiltonian, that is equation (4.3), with the small oscillation approximation Eq. (4.10) and with the transformation Eq. (4.12) becomes

$$H = \frac{p_q^2}{2M} + \frac{M \omega_0^2 q^2}{2} + \sum_{j=1}^{N} \left[\frac{p_j^2}{2m_j} + \frac{1}{2} \left(m_j^{1/2} \omega_j x_j + \frac{C_j}{m_j^{1/2} \omega_j} q \right)^2 \right] \tag{4.13}$$

and with Eq. (4.12) it is now

$$H = \frac{p_q^2}{2M} + \frac{1}{2} \omega_0^2 q'^2 + \sum_{j=1}^{N} \left[\frac{p_j^2}{2m_j} + \frac{1}{2} \left(x'_j \omega_j + \frac{C_j}{m_j^{1/2} M^{1/2} \omega_j} q' \right)^2 \right] \tag{4.14}$$

From this equation and Eq. (4.10) it is clear that the well is located at $q' = x'_j = 0$, $j = 1 \ldots, N$.

The second-derivative (Hessian) matrix of the potential (with respect to the mass-weighted coordinates) at the well is denoted by $\mathbf{K}$ and has the following structure

$$\mathbf{K} = \begin{pmatrix} H''_{q',q'} & H''_{q',x'_1} & H''_{q',x'_2} & \cdots & H''_{q',x'_N} \\ H''_{x'_1,q'} & H_{x'_1,x'_1} & H_{x'_1,x'_2} & \cdots & H''_{x'_1,x'_N} \\ H''_{x'_2,q'} & H_{x'_2,x'_1} & H_{x'_2,x'_2} & \cdots & H''_{x'_2,x'_N} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ H''_{x'_N,q'} & H_{x'_N,x'_1} & H_{x'_N,x'_2} & \cdots & H''_{x'_N,x'_N} \end{pmatrix} \tag{4.15}$$

where the derivatives of H are

$$H''_{q',q} = \omega_0^2 + \sum_{j=1}^{N} \frac{C_j^2}{M m_j \omega_j^2} \tag{4.16}$$

$$H''_{x'_j,q'} = H''_{q',x'_j} = \frac{C_j}{M^{1/2} m_j^{1/2}}, \quad j = 1, 2, \ldots, N \tag{4.17}$$

and

$$H''_{x'_i,x'_j} = \omega_j^2 \delta_{ij}, \quad i, j = 1, 2, \ldots, N \tag{4.18}$$

Thus we have the Hessian matrix for the well dynamics

$$\mathbf{K} = \begin{pmatrix} \omega_0^2 + \sum_{j=1}^{N} \frac{C_j^2}{M m_j \omega_j^2} & \frac{C_1}{(M m_1)^{1/2}} & \frac{C_2}{(M m_2)^{1/2}} & \cdots & \frac{C_N}{(M m_N)^{1/2}} \\ \frac{C_1}{(M m_1)^{1/2}} & \omega_1^2 & 0 & \cdots & 0 \\ \frac{C_2}{(M m_2)^{1/2}} & 0 & \omega_2^2 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \frac{C_N}{(M m_N)^{1/2}} & \omega_1^2 & 0 & \cdots & \omega_N^2 \end{pmatrix} \tag{4.19}$$

We have $N+1$ equations and the $N+1$ eigenvalues of $\mathbf{K}$ are denoted by λ_i^2, $i = 0, 1, \ldots, N$. The λ_i are the normal mode frequencies in the well. The matrix $\mathbf{K}$ reads in the diagonal basis

$$\mathbf{K}' = \begin{pmatrix} \lambda_0^2 & 0 & \cdots & 0 \\ 0 & \lambda_1^2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \lambda_N^2 \end{pmatrix} \tag{4.20}$$

Now prompted by the form of the harmonic TST escape rate Eq. (2.44), consider the determinants of the matrices $\mathbf{K}' + s^2\mathbf{I}$ and $\mathbf{K} + s^2\mathbf{I}$ ($\mathbf{I}$ is the $(N+1) \times (N+1)$ identity matrix). These are respectively

$$\det[\mathbf{K}' + s^2\mathbf{I}] = \left(\lambda_0^2 + s^2\right) \prod_{j=1}^{N} \left(\lambda_j^2 + s^2\right) \tag{4.21}$$

$$\det[\mathbf{K} + s^2\mathbf{I}] = \left(\omega_0^2 + s^2 + \sum_{j=1}^{N} \frac{C_j^2}{M m_j \omega_j^2} - \sum_{j=1}^{N} \frac{C_j^2}{M m_j \left(\omega_j^2 + s^2\right)}\right) \prod_{j=1}^{N} \left(\omega_j^2 + s^2\right) \tag{4.22}$$

Using Eq. (4.9), we then have

$$\begin{aligned} \det[\mathbf{K} + s^2\mathbf{I}] &= \left(\omega_0^2 + s^2 + \frac{s}{M} \sum_{j=1}^{N} \frac{C_j^2 s}{m_j \omega_j^2 \left(\omega_j^2 + s^2\right)}\right) \prod_{j=1}^{N} \left(\omega_j^2 + s^2\right) \\ &= \left(\omega_0^2 + s^2 + s\tilde{\eta}(s)/M\right) \prod_{j=1}^{N} \left(\omega_j^2 + s^2\right) \end{aligned} \tag{4.23}$$

Noting that $\det[\mathbf{K}' + s^2\mathbf{I}] = \det[\mathbf{K} + s^2\mathbf{I}]$ (the matrix $\mathbf{K}'$ is the matrix $\mathbf{K}$ in the diagonal basis) we have from Eqs. (4.21) and (4.23)

$$\begin{aligned} \det[\mathbf{K} + s^2\mathbf{I}] &= \left(\lambda_0^2 + s^2\right) \prod_{j=1}^{N} \left(\lambda_j^2 + s^2\right) \\ &= \left(\omega_0^2 + s^2 + s\tilde{\eta}(s)/M\right) \prod_{j=1}^{N} \left(\omega_j^2 + s^2\right) \end{aligned} \tag{4.24}$$

This is Pollak's equation (13) [35, a].

Now the saddle point is located at $q' = q'_{\#}$ and $x'_j = -[C_j/(m_j M)^{1/2}\omega_j^2]q'_{\#}$, $j = 1, \ldots, N$. The second-derivative matrix at the saddle point, denoted by $\mathbf{K}^{\#}$, is of the same structure as $\mathbf{K}$, the only difference is that ω_0^2 is replaced by $-\omega_0^2$. The eigenvalues of $\mathbf{K}^{\#}$ are denoted by $-\lambda_0^{\#2}, \lambda_j^{\#2}$; $j = 1, 2, \ldots, N$. The lowest eigenvalue is as usual (Section 2.4) associated with the unstable mode and is negative [35, a]. Using reasoning similar to that used to obtain Eq. (4.24), we have

$$\begin{aligned} \det[\mathbf{K}^{\#} + s^2\mathbf{I}] &= \left(-\lambda_0^{\#2} + s^2\right) \prod_{j=1}^{N} \left(\lambda_j^{\#2} + s^2\right) \\ &= \left(-\omega_{\#}^2 + s^2 + s\tilde{\eta}(s)/M\right) \prod_{j=1}^{N} \left(\omega_j^2 + s^2\right) \end{aligned} \tag{4.25}$$

Dividing Eq. (4.24) by Eq. (4.25) as required by Eq. (2.44), we get

$$\frac{\lambda_0^2+s^2}{-\lambda_0^{\#2}+s^2}\prod_{j=1}^{N}\frac{\lambda_j^2+s^2}{\lambda_j^{\#2}+s^2}=\frac{\omega_0^2+s^2+s\tilde{\eta}(s)/M}{-\omega_\#^2+s^2+s\tilde{\eta}(s)/M}$$

Rearranging we have

$$\prod_{j=1}^{N}\frac{\lambda_j^2+s^2}{\lambda_j^{\#2}+s^2}=\left(\frac{-\lambda_0^{\#2}+s^2}{\lambda_0^2+s^2}\right)\frac{\omega_0^2+s^2+s\tilde{\eta}(s)/M}{-\omega_\#^2+s^2+s\tilde{\eta}(s)/M} \tag{4.26}$$

This is Pollak's equation (15) [35, b]. This expression will enable us to evaluate the escape rate as detailed below.

So far the calculation is entirely classical. Now recalling that in the classical case, the IHD rate is simply the TST rate in the complete phase space of the system we may (cf. Eq. (2.44)) use a similar argument to calculate the IHD quantum rate from quantum TST.

4.2 Quantum Transition State Theory

The harmonic transition state theory expression for the rate of decay Γ as mentioned in Chapter 2 (cf. Eqs. (2.8) and (2.18)) (for a detailed proof see [1,51]) is well-known:

$$\Gamma=\left(\frac{k_BT}{2\pi\hbar}\right)\frac{Z^{\#}}{Z^0} \tag{4.27}$$

Here, $Z^{\#}$ and Z^0 are the partition functions at the transition state and at reactants. At the transition state we have N real oscillators with frequencies $\lambda_j^{\#}$, $j=1,\ldots,N$ and one imaginary frequency oscillator with imaginary frequency $\lambda_0^{\#}$. Therefore, the quantum partition function is at the saddle

$$Z^{\#}=\frac{\hbar\lambda_0^{\#}/(2k_BT)}{\sin\left(\hbar\lambda_0^{\#}/(2k_BT)\right)}e^{-V^{\#}/(k_BT)}\prod_{j=1}^{N}\frac{1}{2\sinh\left(\hbar\lambda_j^{\#}/(2k_BT)\right)} \tag{4.28}$$

Note the well-known divergence of $Z^{\#}$ at low temperatures [35]. The quantum partition function at the well is

$$Z^0=\frac{1}{2\sinh(\hbar\lambda_0/(2k_BT))}e^{-V^0/(k_BT)}\prod_{j=1}^{N}\frac{1}{2\sinh\left(\hbar\lambda_j/(2k_BT)\right)} \tag{4.29}$$

Therefore, the thermal decay rate, that is, Eq. (4.27), becomes

$$\Gamma = \frac{\lambda_0^{\#}}{2\pi} \frac{\sinh(\hbar\lambda_0/(2k_BT))}{\sin(\hbar\lambda_0^{\#}/(2k_BT))} e^{-(V^{\#}-V^0)/(k_BT)} \prod_{j=1}^{N} \frac{\sinh\left(\hbar\lambda_j/(2k_BT)\right)}{\sinh\left(\hbar\lambda_j^{\#}/(2k_BT)\right)} \tag{4.30}$$

We can write this as the *classical* TST rate times a *quantum* correction factor Ξ, namely,

$$\Gamma = \frac{\omega_0}{2\pi} \left(\frac{\lambda_0^{\#}}{\omega_{\#}}\right) e^{-(V^{\#}-V^0)/(k_BT)}\, \Xi \tag{4.31}$$

where

$$\Xi = \left(\frac{\omega_{\#}}{\omega_0}\right) \frac{\sinh(\hbar\lambda_0/(2k_BT))}{\sin(\hbar\lambda_0^{\#}/(2k_BT))} \prod_{j=1}^{N} \frac{\sinh\left(\hbar\lambda_j/(2k_BT)\right)}{\sinh\left(\hbar\lambda_j^{\#}/(2k_BT)\right)} \tag{4.32}$$

Now at very high temperatures we can use the following approximations: $\sinh x \approx x$ and $\sin x \approx x$ for small values of x. Therefore in this limit

$$\Xi \approx \frac{\omega_{\#}\lambda_0}{\omega_0\lambda_0^{\#}} \prod_{j=1}^{N} \frac{\lambda_j}{\lambda_j^{\#}} \tag{4.33}$$

However, from Eq. (4.26) with $s = 0$ we have

$$\prod_{j=1}^{N} \left(\frac{\lambda_j}{\lambda_j^{\#}}\right)^2 = \left(\frac{\omega_0\lambda_0^{\#}}{\omega_{\#}\lambda_0}\right)^2$$

Rearranging we then have

$$\frac{\omega_{\#}\lambda_0}{\omega_0\lambda_0^{\#}} \prod_{j=1}^{N} \frac{\lambda_j}{\lambda_j^{\#}} = 1 \tag{4.34}$$

Thus in the very high-temperature limit, we recover the classical IHD rate ($\Xi = 1$) in the complete phase space of the particle-bath system, that is, the Kramers–Grote–Hynes rate expression [2] for general memory friction. To evaluate Ξ in the general case, Pollak used the following identities [52]

$$\sinh x = x \prod_{k=1}^{\infty} \left(1 + \frac{x^2}{k^2\pi^2}\right), \quad \sin x = x \prod_{k=1}^{\infty} \left(1 - \frac{x^2}{k^2\pi^2}\right)$$

Using these, we then have

$$\frac{\sinh\left(\hbar\lambda_j/(2k_BT)\right)}{\sinh\left(\hbar\lambda_j^{\#}/(2k_BT)\right)} = \frac{\lambda_j}{\lambda_j^{\#}} \prod_{k=1}^{\infty} \frac{k^2\nu^2 + \lambda_j^2}{k^2\nu^2 + \lambda_j^{\#2}}$$

where $\nu = 2\pi k_B T/\hbar$. Equation (4.32) may now be written as

$$\Xi = \frac{\omega_\#}{\omega_0}\left(\frac{\lambda_0}{\lambda_0^\#}\prod_{k=1}^{\infty}\frac{k^2\nu^2+\lambda_0^2}{k^2\nu^2-\lambda_0^{\#2}}\right)\prod_{j=1}^{N}\left(\frac{\lambda_j}{\lambda_j^\#}\prod_{k=1}^{\infty}\frac{k^2\nu^2+\lambda_j^2}{k^2\nu^2+\lambda_j^{\#2}}\right)$$

$$= \frac{\omega_\#\lambda_0}{\omega_0\lambda_0^\#}\left(\prod_{j=1}^{N}\frac{\lambda_j}{\lambda_j^\#}\right)\left(\prod_{k=1}^{\infty}\frac{k^2\nu^2+\lambda_0^2}{k^2\nu^2-\lambda_0^{\#2}}\right)\prod_{j=1}^{N}\left(\prod_{k=1}^{\infty}\frac{k^2\nu^2+\lambda_j^2}{k^2\nu^2+\lambda_j^{\#2}}\right) \tag{4.35}$$

Insertion of Eq. (4.34) in Eq. (4.35) yields

$$\Xi = \prod_{k=1}^{\infty}\left[\frac{k^2\nu^2+\lambda_0^2}{k^2\nu^2-\lambda_0^{\#2}}\prod_{j=1}^{N}\left(\frac{k^2\nu^2+\lambda_j^2}{k^2\nu^2+\lambda_j^{\#2}}\right)\right] \tag{4.36}$$

Using Eq. (4.26) with $s = k\nu$, where the $k\nu$ are called the Matsubara (Bosonic) frequencies (which are a manifestation of the quantum fluctuations), we have

$$\prod_{j=1}^{N}\left(\frac{k^2\nu^2+\lambda_j^2}{k^2\nu^2+\lambda_j^{\#2}}\right) = \frac{\omega_0^2+k^2\nu^2+(k\nu/M)\tilde{\eta}(k\nu)}{-\omega_\#^2+k^2\nu^2+(k\nu/M)\tilde{\eta}(k\nu)}\left(\frac{-\lambda_0^{\#2}+k^2\nu^2}{\lambda_0^2+k^2\nu^2}\right) \tag{4.37}$$

Substituting the right-hand side of Eq. (4.37) in Eq. (4.36), we finally have the quantum correction factor

$$\Xi = \prod_{k=1}^{\infty}\frac{\omega_0^2+k^2\nu^2+(k\nu/M)\tilde{\eta}(k\nu)}{-\omega_\#^2+k^2\nu^2+(k\nu/M)\tilde{\eta}(k\nu)} \tag{4.38}$$

We saw in detail in Chapter 3 how Mel'nikov solved the classical Kramers problem of escape from a single well by deriving a universal formula that is valid for all values of the damping. In the same way the quantum rate $\Gamma_{\rm M}$ for escape from a single well above the crossover temperature between tunneling and thermal activation may be written heuristically as

$$\Gamma_{\rm M} = \Upsilon\Gamma^{\rm IHD} \tag{4.39}$$

Here, Υ is the quantum depopulation factor and $\Gamma^{\rm IHD}$ is the quantum escape rate for the single well potential in the IHD region, given by

$$\Gamma^{\rm IHD} = \Xi\,\Gamma_{\rm cl}^{\rm IHD} \tag{4.40}$$

where $\Gamma_{\rm cl}^{\rm IHD}$ is the classical IHD escape rate for a single well potential (cf. Eq. (2.23)). The determination of Υ will be the subject of Chapters 5 and 6.

Chapter 5

Semiclassical Green Function in the Underdamped Quantum Regime

We are again concerned with the underdamped case. However, we can no longer use the Fokker–Planck equation to determine the escape rate. The calculation requires instead the semiclassical density matrix which in turn requires the determination of the semiclassical Green function. Hence we proceed in the systematic way proposed by Larkin and Ovchinnikov [10]. They commence with the Hamiltonian of a quantum particle, interacting with a thermal bath, which is represented as

$$\hat{H}(t) = \hat{H}_0(x) + \hat{x}\hat{\eta}(t) \tag{5.1}$$

where $\hat{H}(x) = \hat{p}^2/2m + V(x)$ is the *unperturbed* Hamiltonian of the particle with coordinate x, executing classically a librational trajectory with energy equal to the barrier energy in the well potential $V(x)$, where $\hat{x}\hat{\eta}(t)$ describes the interaction with the heat bath which is supposed linear in the particle coordinate x. Furthermore, the noise operator $\hat{\eta}(t)$ is assumed to be zero-mean Gaussian with spectral density given by (we are dealing with Johnson–Nyquist noise so that we have a Boson bath)

$$D(\Omega) = \int_{-\infty}^{\infty} \langle \hat{\eta}(t)\hat{\eta}(t+\tau)\rangle_T \, e^{i\Omega\tau} d\tau = m\beta\hbar\Omega \left[\coth(\hbar\Omega/(2k_BT)) - 1\right] \tag{5.2}$$

where the subscript T denotes averaging over the heat bath states. In the classical limit $\hbar \to 0$, this becomes the usual white noise spectral density $D(\Omega) = 2m\beta k_B T$.

The first step in the calculation of the density matrix is to determine the solution $\psi(t)$ of the time–dependent Schrödinger equation pertaining to the noise –perturbed librational motion in the well, namely

$$i\hbar \frac{\partial \psi}{\partial t} = \left(\hat{H}_0(x) + \hat{x}\hat{\eta}(t) \right) \psi \tag{5.3}$$

using time–dependent perturbation theory. Consider the Hamiltonian $\hat{H}$ given by

$$\hat{H} = \hat{H}_0 + \xi \hat{x}\hat{\eta}'(t) \tag{5.4}$$

where $\hat{\eta}'(t) = \hat{\eta}(t)/\xi$, and $\xi \ll 1$. Here $\hat{H}$ is the sum of the unperturbed Hamiltonian $\hat{H}_0$ and the (weak) noise perturbation $\xi \hat{x}\hat{\eta}'(t)$. When the particle interacts with the noise perturbation $\xi \hat{x}\hat{\eta}'(t)$, it either absorbs or emits energy, corresponding to transitions from one unperturbed eigenstate to another. Suppose that the system (particle) is initially in an *unperturbed* eigenstate $|\psi_i\rangle$ of $\hat{H}_0$. Time–dependent perturbation [53, 54] theory then enables us, via the calculation of the evolution operator, to determine the probability that the system will be found at a later time in another *unperturbed* eigenstate $|\psi_f\rangle$.

5.1 Solution of the Schrödinger equation

The time–dependent Schrödinger equation (5.3) may be rewritten as

$$i\hbar \frac{\partial \psi}{\partial t} = \left(\hat{H}_0(x) + \xi \hat{x}\hat{\eta}'(t) \right) \psi \tag{5.5}$$

We assume that we can expand the perturbed wave function $\psi(t)$ as a power series in ξ

$$\psi(t) = \psi_0(t) + \xi\psi_1(t) + \xi^2\psi_2(t) + \cdots \tag{5.6}$$

Using the perturbation expansion Eq. (5.6) in Eq. (5.5)we have

$$i\hbar \frac{\partial}{\partial t} \left(\psi_0(t) + \xi\psi_1(t) + \xi^2\psi_2(t) + \cdots \right) = \left(\hat{H}_0 + \xi \hat{x}\hat{\eta}'(t) \right) \left(\psi_0(t) + \xi\psi_1(t) + \xi^2\psi_2(t) + \cdots \right) \tag{5.7}$$

We now equate terms with like powers of ξ in Eq. (5.7). This leads to a series of equations for the terms in the expansion, shown here up to second order:

$$i\hbar\frac{\partial\psi_0}{\partial t} = \hat{H}_0\psi_0 \tag{5.8}$$

$$i\hbar\frac{\partial\psi_1}{\partial t} = \hat{H}_0\psi_1 + \hat{x}\hat{\eta}'(t)\psi_0 \tag{5.9}$$

$$i\hbar\frac{\partial\psi_2}{\partial t} = \hat{H}_0\psi_2 + \hat{x}\hat{\eta}'(t)\psi_1 \tag{5.10}$$

Now, the solution of the linear inhomogeneous first–order differential equation

$$\frac{dx(t)}{dt} = ax(t) + b(t) \tag{5.11}$$

is [4, pages 198-200]

$$x(t) = e^{at}x(0) + \int_0^t dt_1 e^{a(t-t_1)}b(t_1) \tag{5.12}$$

whence the solutions of Eqs. (5.8–5.10) are

$$\psi_0(t) = e^{-\frac{i}{\hbar}\hat{H}_0 t}\psi_0(0) \tag{5.13}$$

$$\psi_1(t) = e^{-\frac{i}{\hbar}\hat{H}_0 t}\psi_1(0) - \frac{i}{\hbar}e^{-\frac{i}{\hbar}\hat{H}_0 t}\int_0^t dt_1 e^{\frac{i}{\hbar}\hat{H}_0 t_1}\hat{x}\hat{\eta}'(t_1)\psi_0(t_1) \tag{5.14}$$

and

$$\psi_2(t) = e^{-\frac{i}{\hbar}\hat{H}_0 t}\psi_2(0) - \frac{i}{\hbar}e^{-\frac{i}{\hbar}\hat{H}_0 t}\int_0^t dt_1 e^{\frac{i}{\hbar}\hat{H}_0 t_1}\hat{x}\hat{\eta}'(t_1)\psi_1(t_1) \tag{5.15}$$

Using Eq. (5.13) in Eq. (5.14) we have the first order perturbation

$$\begin{aligned}\psi_1(t) =& e^{-\frac{i}{\hbar}\hat{H}_0 t}\psi_1(0) - \frac{i}{\hbar}e^{-\frac{i}{\hbar}\hat{H}_0 t}\int_0^t dt_1 e^{\frac{i}{\hbar}\hat{H}_0 t_1}\hat{x}e^{-\frac{i}{\hbar}\hat{H}_0 t_1}e^{\frac{i}{\hbar}\hat{H}_0 t_1}\hat{\eta}'(t_1)e^{-\frac{i}{\hbar}\hat{H}_0 t_1}\psi_0(0)\\ =& e^{-\frac{i}{\hbar}\hat{H}_0 t}\psi_1(0) - \frac{i}{\hbar}e^{-\frac{i}{\hbar}\hat{H}_0 t}\int_0^t dt_1\hat{x}_I(t_1)\hat{\eta}'_I(t_1)\psi_0(0)\end{aligned} \tag{5.16}$$

where $\hat{x}_I(t) = e^{i\hat{H}_0 t/\hbar}\hat{x}e^{-i\hat{H}_0 t/\hbar}$ and $\hat{\eta}'_I(t) = e^{i\hat{H}_0 t/\hbar}\hat{\eta}'(t)e^{-i\hat{H}_0 t/\hbar}$ are operators in the interaction representation. Using Eq. (5.16) in Eq. (5.15) we obtain the second order perturbation

$$\begin{aligned}\psi_2(t) = & e^{-\frac{i}{\hbar}\hat{H}_0 t}\psi_2(0) - \frac{i}{\hbar}e^{-\frac{i}{\hbar}\hat{H}_0 t}\int_0^t dt_1\hat{x}_I(t_1)\hat{\eta}'_I(t_1)\psi_1(0)\\ & - \frac{1}{\hbar^2}e^{-\frac{i}{\hbar}\hat{H}_0 t}\int_0^t dt_1\hat{x}_I(t_1)\hat{\eta}'_I(t_1)\int_0^{t_1} dt_2\hat{x}_I(t_2)\hat{\eta}'_I(t_2)\psi_0(0)\end{aligned} \tag{5.17}$$

Thus, the general solution of Eq. (5.5) is the series

$$\begin{aligned}\psi(t) =& e^{-\frac{i}{\hbar}\hat{H}_0 t}\left[\psi_0(0)+\xi\psi_1(0)+\xi^2\psi_2(0)+\cdots\right] \\ &- \xi\frac{i}{\hbar}e^{-\frac{i}{\hbar}\hat{H}_0 t}\int_0^t dt_1\hat{x}_I(t_1)\hat{\eta}'_I(t_1)\left[\psi_0(0)+\xi\psi_1(0)+\cdots\right] \\ &- \xi^2\frac{1}{\hbar^2}e^{-\frac{i}{\hbar}\hat{H}_0 t}\int_0^t dt_1\hat{x}_I(t_1)\hat{\eta}'_I(t_1)\int_0^{t_1} dt_2\hat{x}_I(t_2)\hat{\eta}'_I(t_2)\left[\psi_0(0)+\cdots\right]+\cdots\end{aligned} \tag{5.18}$$

or, equivalently,

$$\begin{aligned}\psi(t) =& e^{-\frac{i}{\hbar}\hat{H}_0 t}\Bigg[1-\frac{i}{\hbar}\int_0^t dt_1\hat{x}_I(t_1)\hat{\eta}_I(t_1)-\frac{1}{\hbar^2}\int_0^t dt_1\hat{x}_I(t_1)\hat{\eta}_I(t_1)\int_0^{t_1} dt_2\hat{x}_I(t_2)\hat{\eta}_I(t_2) \\ &+\frac{i}{\hbar^3}\int_0^t dt_1\hat{x}_I(t_1)\hat{\eta}_I(t_1)\int_0^{t_1} dt_2\hat{x}_I(t_2)\hat{\eta}_I(t_2)\int_0^{t_2} dt_3\,\hat{x}_I(t_3)\hat{\eta}_I(t_3)+\cdots\Bigg]\psi(0)\end{aligned} \tag{5.19}$$

where $\hat{\eta}_I(t) = e^{i\hat{H}_0 t/\hbar}\hat{\eta}(t)e^{-i\hat{H}_0 t/\hbar}$.

5.2 Time-ordering operator

The perturbed wavefunction Eq. (5.19) can be written in a more compact repeated integral form, leading to a closed exponential representation, by using the time-ordering operator $\hat{T}$, which places operators with later time arguments to the left of operators with earlier time arguments, for example,

$$\hat{T}\left[\hat{x}_I(t_1)\hat{\eta}_I(t_1)\hat{x}_I(t_2)\hat{\eta}_I(t_2)\right] = \begin{cases}\hat{x}_I(t_1)\hat{\eta}_I(t_1)\hat{x}_I(t_2)\hat{\eta}_I(t_2), & t_2 \le t_1 \\ \hat{x}_I(t_2)\hat{\eta}_I(t_2)\hat{x}_I(t_1)\hat{\eta}_I(t_1), & t_2 > t_1\end{cases} \tag{5.20}$$

Now,

$$\int_0^t dt_1\int_0^{t_1} dt_2\,\hat{x}_I(t_1)\hat{\eta}_I(t_1)\hat{x}_I(t_2)\hat{\eta}_I(t_2) = \int_0^t dt_2\int_0^{t_2} dt_1\,\hat{x}_I(t_2)\hat{\eta}_I(t_2)\hat{x}_I(t_1)\hat{\eta}_I(t_1) \tag{5.21}$$

$$\int_0^t dt_1\int_0^{t_1} dt_2\,\hat{x}_I(t_1)\hat{\eta}_I(t_1)\hat{x}_I(t_2)\hat{\eta}_I(t_2) = \int_0^t dt_1\int_0^{t_1} dt_2\,\hat{T}\left[\hat{x}_I(t_1)\hat{\eta}_I(t_1)\hat{x}_I(t_2)\hat{\eta}_I(t_2)\right] \tag{5.22}$$

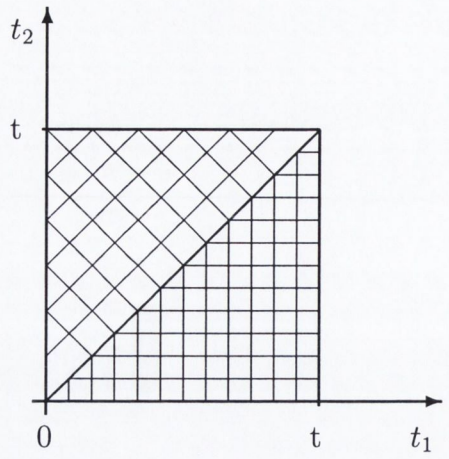

Figure 5.1: Areas of integration for the integrals $\int_0^t dt_1 \int_0^{t_1} dt_2\, \hat{x}(t_1)\hat{\eta}(t_1)\hat{x}(t_2)\hat{\eta}(t_2)$ and $\int_0^t dt_2 \int_0^{t_2} dt_1\, \hat{x}(t_2)\hat{\eta}(t_2)\hat{x}(t_1)\hat{\eta}(t_1)$.

and

$$\begin{aligned}\int_0^t dt_2 \int_0^{t_2} dt_1\, \hat{x}_I(t_2)\hat{\eta}_I(t_2)\hat{x}_I(t_1)\hat{\eta}_I(t_1) &= \int_0^t dt_2 \int_0^{t_2} dt_1\, \hat{T}\left[\hat{x}_I(t_1)\hat{\eta}_I(t_1)\hat{x}_I(t_2)\hat{\eta}_I(t_2)\right] \\ &= \int_0^t dt_1 \int_{t_1}^t dt_2\, \hat{T}\left[\hat{x}_I(t_1)\hat{\eta}_I(t_1)\hat{x}_I(t_2)\hat{\eta}_I(t_2)\right]\end{aligned} \tag{5.23}$$

From Eqs. (5.21), (5.22) and (5.23) we have

$$\begin{aligned}\int_0^t dt_1 \int_0^{t_1} dt_2\, \hat{x}_I(t_1)\hat{\eta}_I(t_1)\hat{x}_I(t_2)\hat{\eta}_I(t_2) &= \frac{1}{2}\left[\int_0^t dt_1 \int_0^{t_1} dt_2\, \hat{T}\left[\hat{x}_I(t_1)\hat{\eta}_I(t_1)\hat{x}_I(t_2)\hat{\eta}_I(t_2)\right]\right. \\ &\quad \left. + \int_0^t dt_1 \int_{t_1}^t dt_2\, \hat{T}\left[\hat{x}_I(t_1)\hat{\eta}_I(t_1)\hat{x}_I(t_2)\hat{\eta}_I(t_2)\right]\right] \\ &= \frac{1}{2}\int_0^t dt_1 \int_0^t dt_2\, \hat{T}\left[\hat{x}_I(t_1)\hat{\eta}_I(t_1)\hat{x}_I(t_2)\hat{\eta}_I(t_2)\right]\end{aligned} \tag{5.24}$$

In general we have the repeated integral form

$$\begin{aligned}&\int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_N} dt_N\, \hat{x}_I(t_1)\hat{\eta}_I(t_1)\hat{x}_I(t_2)\hat{\eta}_I(t_2)\cdots\hat{x}_I(t_N)\hat{\eta}_I(t_N) = \\ &\qquad \frac{1}{N!}\int_0^t dt_1 \int_0^t dt_2 \cdots \int_0^t dt_N\, \hat{T}\left[\hat{x}_I(t_1)\hat{\eta}_I(t_1)\hat{x}_I(t_2)\hat{\eta}_I(t_2)\cdots\hat{x}_I(t_N)\hat{\eta}_I(t_N)\right]\end{aligned} \tag{5.25}$$

5.3 Time-evolution operator

Using the time-ordering operator $\hat{T}$ we can now rewrite the perturbation series Eq. (5.19) in closed form as

$$\begin{aligned}\psi(t) = e^{-\frac{i}{\hbar}\hat{H}_0 t}\Bigg[1 - \frac{i}{\hbar}\int_0^t dt_1\, \hat{T}[\hat{x}_I(t_1)\hat{\eta}_I(t_1)] \\ + \frac{1}{2!}\left(-\frac{i}{\hbar}\right)^2 \int_0^t dt_1 \int_0^t dt_2\, \hat{T}[\hat{x}_I(t_1)\hat{\eta}_I(t_1)\hat{x}_I(t_2)\hat{\eta}_I(t_2)] \\ + \frac{1}{3!}\left(-\frac{i}{\hbar}\right)^3 \int_0^t dt_1 \int_0^t dt_2 \int_0^t dt_3\, \hat{T}[\hat{x}_I(t_1)\hat{\eta}_I(t_1)\hat{x}_I(t_2)\hat{\eta}_I(t_2)\hat{x}_I(t_3)\hat{\eta}_I(t_3)] + \cdots\Bigg]\psi(0) \\ = e^{-\frac{i}{\hbar}\hat{H}_0 t}\left[\hat{T}e^{-\frac{i}{\hbar}\int_0^t dt_1 \hat{x}_I(t_1)\hat{\eta}_I(t_1)}\right]\psi(0)\end{aligned} \tag{5.26}$$

where the evolution operator in Eq. (5.26) is given by

$$\begin{aligned}\hat{T}e^{-\frac{i}{\hbar}\int_0^t dt_1 \hat{x}_I(t_1)\hat{\eta}_I(t_1)} &= 1 - \frac{i}{\hbar}\int_0^t dt_1\, \hat{T}[\hat{x}_I(t_1)\hat{\eta}_I(t_1)] \\ &\quad + \frac{1}{2!}\left(-\frac{i}{\hbar}\right)^2 \int_0^t dt_1 \int_0^t dt_2\, \hat{T}[\hat{x}_I(t_1)\hat{\eta}_I(t_1)\hat{x}_I(t_2)\hat{\eta}_I(t_2)] \\ &\quad + \frac{1}{3!}\left(-\frac{i}{\hbar}\right)^3 \int_0^t dt_1 \int_0^t dt_2 \int_0^t dt_3\, \hat{T}[\hat{x}_I(t_1)\hat{\eta}_I(t_1)\hat{x}_I(t_2)\hat{\eta}_I(t_2)\hat{x}_I(t_3)\hat{\eta}_I(t_3)] + \cdots \\ &= 1 - \frac{i}{\hbar}\int_0^t dt_1 \hat{x}_I(t_1)\hat{\eta}_I(t_1) - \frac{1}{\hbar^2}\int_0^t dt_1 \hat{x}_I(t_1)\hat{\eta}_I(t_1)\int_0^{t_1} dt_2 \hat{x}_I(t_2)\hat{\eta}_I(t_2) \\ &\quad + \frac{i}{\hbar^3}\int_0^t dt_1 \hat{x}_I(t_1)\hat{\eta}_I(t_1)\int_0^{t_1} dt_2 \hat{x}_I(t_2)\hat{\eta}_I(t_2)\int_0^{t_2} dt_3\, \hat{x}_I(t_3)\hat{\eta}_I(t_3) + \cdots\end{aligned} \tag{5.27}$$

Now the time evolution of the state vector $|\psi(t_i)\rangle$ is given by

$$|\psi(t)\rangle = \hat{U}(t, t_i)|\psi(t_i)\rangle \tag{5.28}$$

where $\hat{U}(t, t_i)$ is the time evolution operator, or propagator, in the Schrödinger representation. In the interaction representation we have

$$|\psi(t)\rangle_I = \hat{U}_I(t, t_i)|\psi(t_i)\rangle_I \tag{5.29}$$

where the state vector $|\psi(t)\rangle_I$ is defined in terms of the Schrödinger state vector $|\psi(t)\rangle$ by

$$|\psi(t)\rangle_I = e^{\frac{i}{\hbar}\hat{H}_0 t}|\psi(t)\rangle \tag{5.30}$$

and

$$\hat{U}_I(t,t_i) = e^{\frac{i}{\hbar}\hat{H}_0 t}\hat{U}(t,t_i)e^{-\frac{i}{\hbar}\hat{H}_0 t_i} \tag{5.31}$$

Note that if $t = 0$ in Eq. (5.30) we have

$$|\psi(0)\rangle_I = |\psi(0)\rangle \tag{5.32}$$

From Eqs (5.28 – 5.30) we have

$$\begin{aligned} |\psi(t)\rangle &= e^{-\frac{i}{\hbar}\hat{H}_0 t}|\psi(t)\rangle_I \\ &= e^{-\frac{i}{\hbar}\hat{H}_0 t}\hat{U}_I(t,0)|\psi(0)\rangle_I \\ &= e^{-\frac{i}{\hbar}\hat{H}_0 t}\hat{U}_I(t,0)|\psi(0)\rangle \end{aligned} \tag{5.33}$$

Eq. (5.33) gives the time evolution of the state vector $|\psi(0)\rangle$. Comparing Eqs. (5.33) and (5.26) we obtain the following expression for the time evolution operator in the interaction representation

$$\hat{U}_I(t,0) = \hat{T}e^{-\frac{i}{\hbar}\int_0^t dt_1 \hat{x}_I(t_1)\hat{\eta}_I(t_1)} \tag{5.34}$$

5.4 Transition probability

Let $|j\rangle$ denote the jth eigenstate of the unperturbed Hamiltonian at time $t = 0$. The time evolution, $|\psi(t)\rangle_I$, of $|j\rangle$ in the interaction representation is

$$|\psi(t)\rangle_I = \hat{U}_I(t,0)|j\rangle \tag{5.35}$$

Let $A_{jf}(t)$ denote the projection of $|\psi(t)\rangle_I$ onto the basis $|f\rangle$, then

$$\begin{aligned} A_{jf}(t) &= \langle f|\psi(t)\rangle_I \\ &= \langle f|\hat{U}_I(t,0)|j\rangle \\ &= \langle f|\hat{T}e^{-\frac{i}{\hbar}\int_0^t dt_1 \hat{x}_I(t_1)\hat{\eta}_I(t_1)}|j\rangle \end{aligned} \tag{5.36}$$

so that $A_{jf}(t)$ is the component of $|\psi(t)\rangle_I$ along the vector $|f\rangle$. The probability that at time t the system will be in the eigenstate $|f\rangle$ of the unperturbed Hamiltonian is by definition $|A_{jf}|^2$. Using Eq. (5.27) in Eq. (5.36) we have

$$\begin{aligned} A_{jf}(t) = \langle f| \Bigg[1 &- \frac{i}{\hbar}\int_0^t dt_1 \hat{x}_I(t_1)\hat{\eta}_I(t_1) \\ &- \frac{1}{\hbar^2}\int_0^t dt_1 \hat{x}_I(t_1)\hat{\eta}_I(t_1)\int_0^{t_1} dt_2 \hat{x}_I(t_2)\hat{\eta}_I(t_2) + \cdots \Bigg] |j\rangle \end{aligned}$$

$$= \delta_{jf} - \frac{i}{\hbar}\int_0^t dt_1 \langle f|\hat{x}_I(t_1)|j\rangle \hat{\eta}(t_1)$$
$$- \frac{1}{\hbar^2}\sum_n \int_0^t dt_1 \langle f|\hat{x}_I(t_1)|n\rangle \hat{\eta}(t_1) \int_0^{t_1} dt_2 \langle n|\hat{x}_I(t_2)|j\rangle \hat{\eta}(t_2) + \cdots \quad (5.37)$$

where we have used $\sum_n |n\rangle\langle n| = \hat{I}$, the identity operator, to write

$$\langle f|\hat{x}_I(t_1)\hat{x}_I(t_2)|j\rangle = \sum_n \langle f|\hat{x}_I(t_1)|n\rangle\langle n|\hat{x}_I(t_2)|j\rangle \quad (5.38)$$

In order to simplify Eq. (5.37) we first recall that since the (upper) energy levels in the well in the vicinity of the barrier top are densely spaced and so are *quasi-continuous*, the matrix elements of the position operator $\hat{x}_I(t)$ in the interaction representation are given by the semiclassical formula [9, 10]

$$\langle f|\hat{x}_I(t)|j\rangle = \frac{\omega}{2\pi}\oint x_j(\tau) e^{-\frac{i}{\hbar}(E_f - E_j)(\tau - t)} d\tau \quad (5.39)$$

Here $x_j(\tau)$ denotes the position at time τ of a particle, with energy E_j, librating on the classical trajectory with angular frequency ω, and the integration is over a complete cycle of the classical librational motion of the particle. With $t = 0$ in Eq. (5.39) we have $\hat{x}_I(0)=\hat{x}$, and

$$\langle f|\hat{x}|j\rangle = \frac{\omega}{2\pi}\oint x_j(\tau) e^{-\frac{i}{\hbar}(E_f - E_j)\tau} d\tau \quad (5.40)$$

Clearly Eq. (5.40) gives the Fourier coefficient for the complex exponential of frequency $(E_f - E_j)/\hbar$ in the Fourier series representation of the periodic function $x_j(t)$. The Fourier series for $x_j(t)$ is then by definition

$$x_j(t) = \sum_f \langle f|\hat{x}|j\rangle e^{\frac{i}{\hbar}(E_f - E_j)t} \quad (5.41)$$

Now on account of the densely spaced energy levels, the semiclassical matrix elements must decrease quickly with the energy difference $|E_f - E_j|$, and thus are smooth functions of the energy E_j [10]. Furthermore, as the large amplitude motion of the particle in the well is still periodic we can therefore regard the amplitudes $A_{jf}(t) = \langle f|\hat{U}(t,0))|j\rangle$ of the noise induced transitions (or matrix elements of the time evolution operator $\hat{U}(t,0)$) which are given by Eq. (5.37) as the Fourier coefficients in the Fourier series representation of a periodic function $A(u)$, such that

$$A(u) = \sum_f A_{jf}(t)\, e^{\frac{i}{\hbar}(E_f - E_j)u} \quad (5.42)$$

with

$$A_{jf}(t) = \frac{\omega}{2\pi} \oint A(u) e^{-\frac{i}{\hbar}(E_f - E_j)u} du \tag{5.43}$$

We note that the classical librational motion of a particle with energy equal to the barrier energy represents the slowest librational motion in the well (period–amplitude dependence of an anharmonic oscillator (cf. Appendix 2.F)). A particle executing this slow cycle may be regarded [6] (see Fig. 3.1) as starting from the point $x = 0$ at $t = -\infty$ and returning to that point as $t \to \infty$. The importance of this observation is that the Fourier series Eq. (5.42) then goes over into a Fourier integral.

Now our immediate objective is to derive in semiclassical fashion a closed form expression for the sum of the series $A(u)$ which will then be used to calculate the Green function using the properties of the Gaussian noise operator $\hat{\eta}(t)$. First we substitute expansion (5.37) into Eq. (5.42). Our Fourier series then becomes

$$\begin{aligned} A(u) = \sum_f e^{\frac{i}{\hbar}(E_f - E_j)u} \Bigg\{ \delta_{jf} - \frac{i}{\hbar} \int_0^t dt_1 \langle f|\hat{x}_I(t_1)|j\rangle \hat{\eta}_I(t_1) \\ - \frac{1}{\hbar^2} \sum_n \int_0^t dt_1 \langle f|\hat{x}_I(t_1)|n\rangle \hat{\eta}_I(t_1) \int_0^{t_1} dt_2 \langle n|\hat{x}_I(t_2)|j\rangle \hat{\eta}_I(t_2) + \cdots \Bigg\} \end{aligned} \tag{5.44}$$

Our objective will be accomplished if we can find (in the semiclassical sense) the sum of this series. This is done as follows using the semiclassical representation of the matrix elements $\langle f|\hat{x}_I(t)|j\rangle$ of the position operator $\hat{x}_I(t)$ given by Eq. (5.39). First we rewrite Eq. (5.44) as

$$\begin{aligned} A(u) = \sum_f e^{\frac{i}{\hbar}(E_f - E_j)u} \Bigg\{ \delta_{jf} - \frac{i}{\hbar} \frac{\omega}{2\pi} \int_0^t dt_1 \hat{\eta}_I(t_1) \oint d\tau x_j(\tau) e^{-\frac{i}{\hbar}(E_f - E_j)(\tau - t_1)} \\ - \frac{1}{\hbar^2} \left(\frac{\omega}{2\pi}\right)^2 \sum_n \int_0^t dt_1 \hat{\eta}_I(t_1) \oint d\tau_1 x_n(\tau_1) e^{-\frac{i}{\hbar}(E_f - E_n)(\tau_1 - t_1)} \\ \times \int_0^{t_1} dt_2 \hat{\eta}_I(t_2) \oint d\tau_2 x_j(\tau_2) e^{-\frac{i}{\hbar}(E_n - E_j)(\tau_2 - t_2)} + \cdots \Bigg\} \end{aligned} \tag{5.45}$$

Because of the identities

$$e^{\frac{i}{\hbar}(E_f-E_j)u}\delta_{jf} = \delta_{jf} \tag{5.46}$$

$$e^{\frac{i}{\hbar}(E_f-E_j)u}e^{-\frac{i}{\hbar}(E_f-E_j)(\tau-t_1)} = e^{-\frac{i}{\hbar}(E_f-E_j)(\tau-t_1-u)}, \quad \text{and} \tag{5.47}$$

$$e^{\frac{i}{\hbar}(E_f-E_j)u}e^{-\frac{i}{\hbar}(E_f-E_n)(\tau_1-t_1)}e^{-\frac{i}{\hbar}(E_n-E_j)(\tau_2-t_2)} = e^{-\frac{i}{\hbar}(E_f-E_n)(\tau_1-t_1-u)}e^{-\frac{i}{\hbar}(E_n-E_j)(\tau_2-t_2-u)} \tag{5.48}$$

we can rewrite Eq. (5.45) as

$$\begin{aligned} A(u) = \sum_f \Bigg[& \delta_{jf} - \frac{i}{\hbar}\frac{\omega}{2\pi}\int_0^t dt_1\hat{\eta}_I(t_1)\oint d\tau x_j(\tau)e^{-\frac{i}{\hbar}(E_f-E_j)(\tau-t_1-u)} \\ & - \frac{1}{\hbar^2}\left(\frac{\omega}{2\pi}\right)^2\sum_n\int_0^t dt_1\hat{\eta}_I(t_1)\oint d\tau_1 x_n(\tau_1)e^{-\frac{i}{\hbar}(E_f-E_n)(\tau_1-t_1-u)} \\ & \times\int_0^{t_1} dt_2\hat{\eta}_I(t_2)\oint d\tau_2 x_j(\tau_2)e^{-\frac{i}{\hbar}(E_n-E_j)(\tau_2-t_2-u)} + \cdots \Bigg] \end{aligned} \tag{5.49}$$

Now the densely spaced energies E_n in Eq. (5.49) are all close to E_j [10] so that we are free to substitute x_j for x_n in that equation. Using Eq. (5.39) we can rewrite Eq. (5.49) as

$$\begin{aligned} A(u) &= \sum_f \Bigg[\delta_{jf} - \frac{i}{\hbar}\int_0^t dt_1\langle f|\hat{x}_I(t_1+u)|j\rangle\hat{\eta}_I(t_1) \\ &\quad - \frac{1}{\hbar^2}\sum_n\int_0^t dt_1\langle f|\hat{x}_I(t_1+u)|n\rangle\hat{\eta}_I(t_1)\int_0^{t_1} dt_2\langle n|\hat{x}_I(t_2+u)|j\rangle\hat{\eta}_I(t_2) + \cdots \Bigg] \\ &= 1 - \frac{i}{\hbar}\int_0^t dt_1\sum_f\langle f|\hat{x}_I(t_1+u)|j\rangle\hat{\eta}_I(t_1) \\ &\quad - \frac{1}{\hbar^2}\sum_n\int_0^t dt_1\sum_f\langle f|\hat{x}_I(t_1+u)|n\rangle\hat{\eta}_I(t_1)\int_0^{t_1} dt_2\langle n|\hat{x}_I(t_2+u)|j\rangle\hat{\eta}_I(t_2) + \cdots \\ &= 1 - \frac{i}{\hbar}\int_0^t dt_1 x_j(t_1+u)\hat{\eta}_I(t_1) \\ &\quad - \frac{1}{\hbar^2}\sum_n\int_0^t dt_1 x_n(t_1+u)\hat{\eta}_I(t_1)\int_0^{t_1} dt_2\langle n|\hat{x}(t_2+u)|j\rangle\hat{\eta}_I(t_2) + \cdots \end{aligned} \tag{5.50}$$

Substituting x_j for x_n in the third term on the right–hand side of Eq. (5.50) we

have

$$
\begin{aligned}
A(u) &= 1 - \frac{i}{\hbar}\int_0^t dt_1 x_j(t_1+u)\hat{\eta}_I(t_1) \\
&\quad - \frac{1}{\hbar^2}\int_0^t dt_1 x_j(t_1+u)\hat{\eta}_I(t_1)\int_0^{t_1} dt_2 \sum_n \langle n|\hat{x}(t_2+u)|j\rangle \hat{\eta}_I(t_2) + \cdots \\
&= 1 - \frac{i}{\hbar}\int_0^t dt_1 x_j(t_1+u)\hat{\eta}_I(t_1) \\
&\quad - \frac{1}{\hbar^2}\int_0^t dt_1 x_j(t_1+u)\hat{\eta}_I(t_1)\int_0^{t_1} dt_2 x_j(t_2+u)\hat{\eta}_I(t_2) + \cdots
\end{aligned} \tag{5.51}
$$

that is, the sum becomes

$$
A(u) = \hat{T} e^{-\frac{i}{\hbar}\int_0^t x_j(u+t_1)\hat{\eta}_I(t_1)dt_1} \tag{5.52}
$$

which is the desired closed integral form expression for the Fourier expansion of the periodic function $A(u)$. Now recall that the Fourier coefficients $A_{jf}(t)$ in Eq. (5.42) are the matrix elements of the evolution operator $\hat{U}_I(t,0)$ (see Eq. (5.37)) for the state vector in the interaction representation. Therefore consider the case where the system is in state j at time $t = 0$. The probability of observing the perturbed system in another state f at time t, averaged over the state of the thermal bath, is then given by the density matrix

$$
W_{jf}(t) = \left\langle |A_{jf}(t)|^2 \right\rangle_T = \langle A_{jf} A_{jf}^* \rangle_T \tag{5.53}
$$

where $A_{jf}(t)$ is given by Eq. (5.43) and $\langle\rangle_T$ denotes thermal averaging. However, using Eq. (5.43) we may also rewrite Eq. (5.53) in terms of $A(u)$ as follows

$$
\begin{aligned}
W_{jf}(t) &= \left\langle \left(\frac{\omega}{2\pi}\right)^2 \oint A(u_1) e^{-\frac{i}{\hbar}(E_f - E_j)(u_1)} du_1 \oint A^*(u_2) e^{\frac{i}{\hbar}(E_f - E_j)(u_2)} du_2 \right\rangle_T \\
&= \left\langle \left(\frac{\omega}{2\pi}\right)^2 \oint du_1 \oint du_2\, e^{-\frac{i}{\hbar}(E_f - E_j)(u_1 - u_2)} A(u_1) A^*(u_2) \right\rangle_T \\
&= \left(\frac{\omega}{2\pi}\right)^2 \oint du_1 \oint du_2\, e^{-\frac{i}{\hbar}(E_f - E_j)(u_1 - u_2)} \langle A(u_1) A^*(u_2) \rangle_T
\end{aligned} \tag{5.54}
$$

Furthermore, using Eqs. (5.51) and (5.52) the correlation function $\langle A(u_1)A^*(u_2)\rangle_T$

can be written as

$$\begin{aligned}
\langle A(u_1)A^*(u_2)\rangle_T &= \left\langle \hat{T}\exp\left[-\frac{i}{\hbar}\int_0^t x_j(u_1+t')\hat{\eta}_I(t')dt'\right]\hat{T}\exp\left[\frac{i}{\hbar}\int_0^t x_j(u_2+t'')\hat{\eta}_I(t'')dt''\right]\right\rangle_T \\
&= \left\langle\left[1-\frac{i}{\hbar}\int_0^t dt_1 x_j(t_1+u_1)\hat{\eta}_I(t_1) - \frac{1}{2\hbar^2}\int_0^t dt_1 x_j(t_1+u_1)\hat{\eta}_I(t_1)\int_0^{t_1} dt_2 x_j(t_2+u_1)\hat{\eta}_I(t_2)+\cdots\right]\right. \\
&\times\left.\left[1+\frac{i}{\hbar}\int_0^t dt_1 x_j(t_1+u_2)\hat{\eta}_I(t_1) - \frac{1}{2\hbar^2}\int_0^t dt_1 x_j(t_1+u_2)\hat{\eta}_I(t_1)\int_0^{t_1} dt_2 x_j(t_2+u_2)\hat{\eta}_I(t_2)+\cdots\right]\right\rangle_T \\
&= 1-\frac{i}{\hbar}\int_0^t dt_1 x_j(t_1+u_1)\langle\hat{\eta}_I(t_1)\rangle_T + \frac{i}{\hbar}\int_0^t dt_1 x_j(t_1+u_2)\langle\hat{\eta}_I(t_1)\rangle_T \\
&\quad -\frac{1}{2\hbar^2}\int_0^t dt_1\int_0^{t_1} dt_2 x_j(t_1+u_1)x_j(t_2+u_1)\langle\hat{\eta}_I(t_1)\hat{\eta}_I(t_2)\rangle_T \\
&\quad -\frac{1}{2\hbar^2}\int_0^t dt_1\int_0^{t_1} dt_2 x_j(t_1+u_2)x_j(t_2+u_2)\langle\hat{\eta}_I(t_1)\hat{\eta}_I(t_2)\rangle_T \\
&\quad +\frac{1}{\hbar^2}\int_0^t dt_1\int_0^t dt_2 x_j(t_1+u_1)x_j(t_2+u_2)\langle\hat{\eta}_I(t_1)\hat{\eta}_I(t_2)\rangle_T+\cdots
\end{aligned} \tag{5.55}$$

Now

$$\begin{aligned}
&\int_0^t dt_1\int_0^t dt_2 x_j(t_1+u_1)x_j(t_2+u_2)\langle\hat{\eta}(t_1)\hat{\eta}(t_2)\rangle_T \\
&\qquad = \frac{1}{2}\left[\int_0^t dt_1\int_0^t dt_2 x_j(t_1+u_1)x_j(t_2+u_2)\langle\hat{\eta}(t_1)\hat{\eta}(t_2)\rangle_T\right. \\
&\qquad\quad \left.+\int_0^t dt_2\int_0^t dt_1 x_j(t_1+u_2)x_j(t_2+u_1)\langle\hat{\eta}(t_2)\hat{\eta}(t_1)\rangle_T\right]
\end{aligned} \tag{5.56}$$

Noting that $\langle\hat{\eta}(t)\rangle_T = 0$ and using Eq. (5.56) we can rewrite the correlation function Eq. (5.55) as

$$\begin{aligned}
\langle A(u_1)A^*(u_2)\rangle_T = 1 &- \frac{1}{2\hbar^2}\int_0^t dt_1\int_0^t dt_2 x_j(t_1+u_1)x_j(t_2+u_1)h_{11}(t_1,t_2) \\
&- \frac{1}{2\hbar^2}\int_0^t dt_1\int_0^t dt_2 x_j(t_1+u_2)x_j(t_2+u_2)h_{22}(t_1,t_2) \\
&+ \frac{1}{2\hbar^2}\int_0^t dt_1\int_0^t dt_2 x_j(t_1+u_1)x_j(t_2+u_2)h_{12}(t_1,t_2) \\
&+ \frac{1}{2\hbar^2}\int_0^t dt_1\int_0^t dt_2 x_j(t_1+u_2)x_j(t_2+u_1)h_{21}(t_1,t_2)+\cdots
\end{aligned} \tag{5.57}$$

where the noise correlation functions $h_{kl}(t_1, t_2)$ are given by

$$h_{11}(t_1,t_2) = \left\langle \hat{T}\hat{\eta}(t_1)\hat{\eta}(t_2)\right\rangle_T, \qquad h_{22}(t_1,t_2) = \left\langle \hat{T}^{-1}\hat{\eta}(t_2)\hat{\eta}(t_1)\right\rangle_T \tag{5.58}$$

$$h_{12}(t_1,t_2) = \langle\hat{\eta}(t_1)\hat{\eta}(t_2)\rangle_T, \qquad h_{21}(t_1,t_2) = \langle\hat{\eta}(t_2)\hat{\eta}(t_1)\rangle_T \tag{5.59}$$

and $\hat{T}^{-1}$ denotes the inverse time-ordering operator which places operators with later time arguments to the right of operators with earlier time arguments. Using Eq. (5.57) in Eq. (5.54) we then have the density matrix in the closed form

$$\begin{aligned} W_{jf} = \left(\frac{\omega}{2\pi}\right)^2 \oint\oint du_1 du_2\, e^{-\frac{i}{\hbar}(u_1-u_2)(E_f-E_j)} \\ \times \exp\Bigg[-\frac{1}{2\hbar^2}\int_0^t\int_0^t \Big\{x_j(u_1+t_1)x_j(u_1+t_2)h_{11}(t_1,t_2) \\ + x_j(u_2+t_1)x_j(u_2+t_2)h_{22}(t_1,t_2) - x_j(u_1+t_1)x_j(u_2+t_2)h_{12}(t_1,t_2) \\ - x_j(u_2+t_1)x_j(u_1+t_2)h_{21}(t_1,t_2)\Big\}dt_1dt_2\Bigg] \end{aligned} \tag{5.60}$$

Eq. (5.60) may also be deduced from Eq. (5.54) because for centred Gaussian random variables $\langle e^{iX}\rangle = e^{-\langle X^2/2\rangle}$ and linear transformations of Gaussian random variables are themselves Gaussian [7].

Now, the Fourier series for $x_j(t)$ is given by Eq. (5.41). Moreover, since $x_j(t)$ is real, $x_j(t) = x_j^*(t)$, and we have in terms of the semiclassical matrix elements

$$x_j(t) = \sum_f \langle f|\hat{x}|j\rangle e^{\frac{i}{\hbar}(E_f-E_j)t} = \sum_m \langle m|\hat{x}|j\rangle^* e^{-\frac{i}{\hbar}(E_m-E_f)t} \tag{5.61}$$

Using Eq. (5.61) we can write

$$\begin{aligned} x_j(u_1+t_1)x_j(u_1+t_2) &= \sum_{fm}\langle f|\hat{x}|j\rangle e^{\frac{i}{\hbar}(E_f-E_j)(u_1+t_1)}\langle m|\hat{x}|j\rangle^* e^{-\frac{i}{\hbar}(E_m-E_j)(u_1+t_2)} \\ &= \sum_{fm}\langle f|\hat{x}|j\rangle\langle m|\hat{x}|j\rangle^* e^{\frac{i}{\hbar}(E_f-E_j)(t_1-t_2)}e^{\frac{i}{\hbar}(E_f-E_m)(u_1+t_2)} \end{aligned} \tag{5.62}$$

$$x_j(u_2+t_1)x_j(u_2+t_2) = \sum_{fm}\langle f|\hat{x}|j\rangle\langle m|\hat{x}|j\rangle^* e^{\frac{i}{\hbar}(E_f-E_j)(t_1-t_2)}e^{\frac{i}{\hbar}(E_f-E_m)(u_2+t_2)} \tag{5.63}$$

$$x_j(u_1+t_1)x_j(u_2+t_2) = \sum_{fm}\langle f|\hat{x}|j\rangle e^{\frac{i}{\hbar}(E_f-E_j)(u_1+t_1)}\langle m|\hat{x}|j\rangle^* e^{-\frac{i}{\hbar}(E_m-E_j)(u_2+t_2)}$$
$$= \sum_{fm}\langle f|\hat{x}|j\rangle\langle m|\hat{x}|j\rangle^* e^{\frac{i}{\hbar}(E_f-E_j)(u_1-u_2+t_1-t_2)}e^{\frac{i}{\hbar}(E_f-E_m)(u_2+t_2)} \tag{5.64}$$

and

$$x_j(u_2+t_1)x_j(u_1+t_2) = \sum_{fm}\langle f|\hat{x}|j\rangle\langle m|\hat{x}|j\rangle^* e^{\frac{i}{\hbar}(E_f-E_j)(u_2-u_1+t_1-t_2)}e^{\frac{i}{\hbar}(E_f-E_m)(u_1+t_2)}$$
$$= \sum_{fm}\langle f|\hat{x}|j\rangle^*\langle m|\hat{x}|j\rangle e^{\frac{i}{\hbar}(E_f-E_j)(u_1-u_2+t_2-t_1)}e^{-\frac{i}{\hbar}(E_f-E_m)(u_1+t_2)} \tag{5.65}$$

The random process is assumed to be wide–sense stationary and so the autocorrelation function $\langle\eta(t_i)\eta(t_j)\rangle_T$ depends only on the time difference $t_i - t_j$. We have for the various autocorrelation functions

$$h_{12}(t_1,t_2) = \langle\eta(t_1)\eta(t_2)\rangle_T = h_{12}(t_1-t_2) \tag{5.66}$$

and

$$h_{21}(t_1,t_2) = \langle\eta(t_2)\eta(t_1)\rangle_T = h_{21}(t_2-t_1) \tag{5.67}$$

Now

$$h_{11}(t_1,t_2)+h_{22}(t_1,t_2) = h_{12}(t_1,t_2)+h_{21}(t_1,t_2)$$
$$= h_{12}(t_1-t_2)+h_{21}(t_2-t_1) \tag{5.68}$$

Next we substitute Eqs. (5.62)–(5.65) in Eq. (5.60) and note that by orthogonality

$$\oint e^{\frac{i}{\hbar}(E_f-E_m)t}dt = \frac{2\pi}{\omega}\delta_{fm} \tag{5.69}$$

Eq. (5.60) for the Green function can then be rewritten as

$$W_{jf} = \frac{\omega}{2\pi}\oint du\, e^{\frac{i}{\hbar}(E_f-E_j)u}\exp\left[\frac{2\pi}{\omega}\sum_f|\langle f|\hat{x}|j\rangle|^2\right.$$
$$\times\left\{\int_{-\infty}^{\infty}e^{\frac{i}{\hbar}(E_f-E_j)(-u+t_1-t_2)}\frac{h_{12}(t_1-t_2)+h_{21}(t_1-t_2)}{2\hbar^2}d(t_1-t_2)\right.$$
$$\left.\left.-\int_{-\infty}^{\infty}e^{\frac{i}{\hbar}(E_f-E_j)(t_1-t_2)}\frac{h_{12}(t_1-t_2)+h_{21}(t_1-t_2)}{2\hbar^2}d(t_1-t_2)\right\}\right] \tag{5.70}$$

where we have again exploited the rapid decrease of h to extend the limits to infinity in the integration with respect to $t_1 - t_2$. By introducing the (time-frequency domain) Fourier transform of the noise correlation functions $h_{k,l}(t)$

$$\tilde{h}_{kl}\left(\frac{E_f - E_j}{\hbar}\right) = \int_{-\infty}^{\infty} e^{\frac{i}{\hbar}(E_f - E_j)t} h_{kl}(t) dt \tag{5.71}$$

we can write

$$\int_{-\infty}^{\infty} e^{\frac{i}{\hbar}(E_f - E_j)t} \frac{h_{21}(t) + h_{12}(t)}{2\hbar^2} dt = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} e^{\frac{i}{\hbar}(E_f - E_j)t} h_{12}(t)\, dt$$

$$= \frac{1}{\hbar^2} D\left(\frac{E_f - E_j}{\hbar}\right) \tag{5.72}$$

where $D((E_f - E_j)/\hbar)$ is given by Eq. (5.2), leading to the following closed expression for W_{jf}

$$W_{jf} = \frac{\omega}{2\pi} \oint e^{\frac{i}{\hbar}(E_f - E_j)u} \exp\{\mathcal{W}(u) - \mathcal{W}(0)\} du \tag{5.73}$$

where

$$\mathcal{W}(u) = \sum_f w_{jf}\, e^{\frac{i}{\hbar}(E_f - E_j)u} \tag{5.74}$$

and w_{jf} is given by

$$w_{jf} = \frac{2\pi}{\hbar^2 \omega} |\langle f|\hat{x}|j\rangle|^2 D\left(\frac{E_f - E_j}{\hbar}\right) \tag{5.75}$$

Substituting Eqs. (5.40) and (5.2) in Eq. (5.75) we have

$$w_{jf} = \frac{\omega}{2\pi\hbar^2} \left| \oint x_j(\tau) e^{-\frac{i}{\hbar}(E)\tau} d\tau \right|^2 m\beta E \left[\coth\left(\frac{E}{2k_B T}\right) - 1\right] \tag{5.76}$$

Now the first order contribution to W_{jf} is

$$[W_{jf}]_1 = \frac{\omega}{2\pi} \oint e^{\frac{i}{\hbar}(E_f - E_j)u} \left[1 + \mathcal{W}(u) - \mathcal{W}(0)\right] du$$

$$= \frac{\omega}{2\pi} \oint e^{\frac{i}{\hbar}(E_f - E_j)u} \left[1 + \sum_{f'} w_{jf'}\, e^{\frac{i}{\hbar}(E_f - E_j)u} - \sum_{f'} w_{jf'}\right] du$$

$$= \delta_{fj} + w_{jf} - \delta_{fj} \sum_{f'} w_{jf'} \tag{5.77}$$

Because the energy levels near the top of the barrier are very closely spaced ($\hbar\omega \to 0$) we can write the sum $\sum_f w_{jf}$ as an integral (see Section 5.3 of Ref. 55)

$$\sum_f w_{jf} = \int_{-\infty}^{\infty} w(E)\, dE \tag{5.78}$$

where

$$w(E) = \rho(E)\frac{\omega}{2\pi\hbar^2}\left|\oint x_j(\tau)e^{-\frac{i}{\hbar}(E)\tau}d\tau\right|^2 m\beta E\left[\coth\left(\frac{E}{2k_BT}\right)-1\right] \tag{5.79}$$

and $\rho(E)$ is the density of states near the top of the barrier.

Substituting $\rho(E) = 1/\hbar\omega$ in Eq. (5.79) we have

$$\begin{aligned} w(E) &= \frac{1}{2\pi\hbar^3}\left|\oint x_j(\tau)e^{-\frac{i}{\hbar}(E)\tau}d\tau\right|^2 m\beta E\left[\coth\left(\frac{E}{2k_BT}\right)-1\right] \\ &= \frac{2\pi}{\hbar}\left|\frac{1}{2\pi\hbar}\oint x_j(\tau)e^{-\frac{i}{\hbar}(E)\tau}d\tau\right|^2 m\beta E\left[\coth\left(\frac{E}{2k_BT}\right)-1\right] \end{aligned} \tag{5.80}$$

Using Mel'nikov's notation in Eqs. (5.77) and (5.80), we make the replacements $E_f \to \epsilon$ and $E_j \to \epsilon'$, to obtain the first order contribution to the semiclassical Green function $g(\epsilon - \epsilon')$

$$g_1(\epsilon-\epsilon') = \delta(\epsilon-\epsilon') - \delta(\epsilon-\epsilon')\int_{-\infty}^{\infty} w(\epsilon'')\,d\epsilon'' + w(\epsilon-\epsilon') \tag{5.81}$$

where

$$w(\epsilon) = \frac{2\pi}{\hbar}\left|\langle\epsilon|\hat{x}|\epsilon'\rangle\right|^2 m\beta\epsilon\left[\coth\left(\frac{\epsilon}{2k_BT}\right)-1\right] \tag{5.82}$$

and

$$\langle\epsilon|\hat{x}|\epsilon'\rangle = \frac{1}{2\pi\hbar}\oint x_j(\tau)e^{-\frac{i}{\hbar}(\epsilon)\tau}d\tau \tag{5.83}$$

Equation (5.81) is Mel'nikov's Eq. (3.6). Note that the expression for $\langle\epsilon|\hat{x}|\epsilon'\rangle$ given by Mel'nikov [6] (Eq. (5.83) above) (see Appendix 5.A) is different from the expression for $\langle f|\hat{x}|j\rangle$ given by Larkin and Ovchinnikov [10] (Eq. (5.40)) because the wavefunctions $|f\rangle$ and $|j\rangle$ are normalized to a Kroneker delta, δ_{fj}, whereas the wavefunctions $|\epsilon\rangle$ and $|\epsilon'\rangle$ are normalized to a Dirac delta function, $\delta(\epsilon-\epsilon')$. The expression for the semiclassical Green function $g(\epsilon-\epsilon')$ then becomes [6,36]

$$\begin{aligned} g(\epsilon-\epsilon') =& e^{-\int_{-\infty}^{\infty} w(\epsilon)d\epsilon}\left[\delta(\epsilon-\epsilon') + w(\epsilon-\epsilon') + \frac{1}{2}\int_{-\infty}^{\infty} w(\epsilon-\epsilon'')w(\epsilon''-\epsilon')d\epsilon''\right. \\ &\left. + \frac{1}{6}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} w(\epsilon-\epsilon'')w(\epsilon''-\epsilon''')w(\epsilon'''-\epsilon')d\epsilon''d\epsilon''' + \cdots\right] \end{aligned} \tag{5.84}$$

which is Mel'nikov's Eq. (3.9). Next following Mel'nikov [6] we define the Fourier transform via

$$\check{f}(\lambda) = \int_{-\infty}^{\infty} f(\epsilon)e^{i\lambda\epsilon/(k_BT)}d\epsilon \tag{5.85}$$

With $\epsilon' = 0$ in Eq. (5.84) we have

$$g(\epsilon) = e^{-\int_{-\infty}^{\infty} w(\epsilon)d\epsilon} \left[\delta(\epsilon) + w(\epsilon) + \frac{1}{2}w(\epsilon) * w(\epsilon) + \frac{1}{6}w(\epsilon) * w(\epsilon) * w(\epsilon) + \cdots\right] \tag{5.86}$$

where the asterisk denotes convolution. Now the Fourier transform of the convolution of functions is the product of the Fourier transforms of the functions. Furthermore,

$$\int_{-\infty}^{\infty} w(\epsilon)d\epsilon = \check{w}(0) \tag{5.87}$$

Therefore the Fourier transform of the Green function $g(\epsilon)$ can be written in closed form as

$$\begin{aligned}\check{g}(\lambda) &= \exp\{-\check{w}(0)\}\left[1 + \check{w}(\lambda) + \frac{1}{2}\check{w}(\lambda)^2 + \frac{1}{6}\check{w}(\lambda)^3 + \cdots\right] \\ &= \exp\{-\check{w}(0)\}\exp\{\check{w}(\lambda)\} \\ &= \exp\{\check{w}(\lambda) - \check{w}(0)\}\end{aligned} \tag{5.88}$$

where $\hat{w}(\lambda)$ is the Fourier transform of $w(\epsilon)$ given by Eq. (5.82)

Appendix

5.A Expression for the matrix elements $\langle\epsilon|x|\epsilon'\rangle$

The Fourier integral over time expression for the matrix elements $\langle\epsilon|x|\epsilon'\rangle$ of the position operator $\hat{x}$, namely,

$$\langle\epsilon|x|\epsilon'\rangle = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} x(t)e^{(i/\hbar)(\epsilon-\epsilon')t}\,dt \tag{5.89}$$

where $x(t)$ is the position, at time t, of a particle with energy ϵ', traveling on the classical librational trajectory, may be briefly justified as follows.

We have, referring to closed librational trajectories in the well,

$$\epsilon = \frac{p^2}{2m} + V(x) \tag{5.90}$$

$$d\epsilon = \frac{p\,dp}{m} = v\,dp \tag{5.91}$$

Therefore for very small changes in energy, corresponding to densely spaced levels, we have

$$\epsilon - \epsilon' \approx v(\epsilon, x)[p(\epsilon, x) - p(\epsilon', x)]$$

or

$$p(\epsilon, x) - p(\epsilon', x) \approx \frac{\epsilon - \epsilon'}{v(\epsilon, x)} \tag{5.92}$$

The normalized semiclassical wave function [6, 22] is given by

$$|\epsilon, x\rangle = \left(\frac{1}{2\pi\hbar v(\epsilon, x)}\right)^{1/2} \exp\left(-\frac{i}{\hbar}\int_0^x p(\epsilon, x')\,dx'\right) \tag{5.93}$$

so that

$$\langle\epsilon|x|\epsilon'\rangle = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} \frac{x\,dx}{\sqrt{v(\epsilon, x)v(\epsilon', x)}} \exp\left(-\frac{i}{\hbar}\int_0^x [p(\epsilon', x') - p(\epsilon, x')]\,dx'\right) \tag{5.94}$$

Assuming that $v(\epsilon', x) \approx v(\epsilon, x)$ for very small changes in energy, as will be so in the semiclassical case, and using Eq. (5.92) we have

$$\langle\epsilon|x|\epsilon'\rangle \approx \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} \frac{x\,dx}{v(\epsilon, x)} \exp\left(\frac{i(\epsilon - \epsilon')}{\hbar}\int_0^x \frac{dx'}{v(\epsilon, x')}\right) \tag{5.95}$$

Now since $dt = dx/v$, Eq. (5.95) may be rewritten yielding Eq. (5.89).

For further details of semiclassical methods see [56].

Chapter 6

Escape Rate in the Underdamped Quantum Regime

6.1 Integral equation and its solution

In order to write down an integral equation similar to the classical Eq. (3.56) for the population of escaping particles we recall that in the quantum situation the penetration of the potential barrier becomes a random process specified by the penetration coefficient [22]. As before the energies of the escaping particles are distributed in a narrow range, $|\epsilon/(k_BT)| \approx 1 \ll \Delta V$, near the barrier top so that the potential can be approximated by the inverted parabola $V(x) \approx V_C - m\omega_C^2(x-x_C)^2/2$. The penetration coefficient through the parabolic potential barrier is given by Eq. (2.13) with $V_C = 0$, namely, $(1+\exp[-2\pi\epsilon/(\hbar\omega_C)])^{-1}$ [22]. The reflected particles on executing a cycle of the motion in the potential well will reproduce the distribution function $f(\epsilon)$. By using the Green function (5.84) and the reflection coefficient $(1+\exp[2\pi\epsilon/(\hbar\omega_C)])^{-1}$, we obtain, using Mel'nikov's notation [6], the integral equation for $f(\epsilon)$

$$f(\epsilon) = \int_{-\infty}^{\infty} \frac{g(\epsilon-\epsilon')f(\epsilon')}{1+\exp(2\pi\epsilon'/\hbar\omega_C)}\, d\epsilon' \tag{6.1}$$

The function $f(\epsilon)$ can be written as the convolution of $g(\epsilon)$ and $\varphi(\epsilon)$

$$f(\epsilon) = \int_{-\infty}^{\infty} g(\epsilon-\epsilon')\varphi(\epsilon')\, d\epsilon' \tag{6.2}$$

where

$$\varphi(\epsilon) = \frac{f(\epsilon)}{1 + \exp(2\pi\epsilon/\hbar\omega_C)} \tag{6.3}$$

The Fourier transformation (5.85) of $f(\epsilon)$ can therefore be written as

$$\check{f}(\lambda) = \check{g}(\lambda)\check{\varphi}(\lambda) \tag{6.4}$$

where $\check{g}(\lambda)$ and $\check{\varphi}(\lambda)$ are the Fourier transforms of $g(\epsilon)$ and $\varphi(\epsilon)$ respectively. Rewriting Eq. (6.3) as

$$f(\epsilon) = \varphi(\epsilon)[1 + \exp(2\pi\epsilon/\hbar\omega_C)] \tag{6.5}$$

and taking Fourier transforms in accordance with (5.85) we obtain

$$\check{f}(\lambda) = \check{\varphi}(\lambda) + \check{\varphi}(\lambda - i/y) \tag{6.6}$$

From Eqs. (6.4) and (6.6) we have in the λ domain

$$\check{\varphi}(\lambda) + \check{\varphi}(\lambda - i/y) = \check{g}(\lambda)\check{\varphi}(\lambda) \tag{6.7}$$

or

$$\check{\varphi}(\lambda - i/y) = -G(\lambda)\check{\varphi}(\lambda) \tag{6.8}$$

where

$$G(\lambda) = 1 - \check{g}(\lambda) \tag{6.9}$$

and the quantum parameter is

$$y = \hbar\omega_C/(2\pi k_B T) \tag{6.10}$$

Now just as the classical case we use the parabolic approximation for the potential near the bottom of the well. Furthermore, the probability density function of the energy of a particle moving in the harmonic oscillator potential in the vicinity of the well bottom is [19]

$$f(\epsilon) \approx \frac{e^{-(\Delta V+\epsilon)/(k_B T)}}{2\pi\hbar \sum_{n=0}^{\infty} e^{-\hbar\omega_A(n+1/2)/(k_B T)}}, \quad \epsilon \geq -\Delta V \tag{6.11}$$

Using the identity [52, 1.232-3]

$$\frac{1}{\sinh x} = 2\sum_{k=0}^{\infty} e^{-(2k+1)x}, \quad x > 0 \tag{6.12}$$

we have

$$2\sum_{n=0}^{\infty} e^{-(2n+1)\left[\frac{\hbar\omega_A}{2k_BT}\right]} = \frac{1}{\sinh\left(\frac{\hbar\omega_A}{2k_BT}\right)} \tag{6.13}$$

and

$$f(\epsilon) \approx \frac{\sinh[\hbar\omega_A/(2k_BT)]}{\pi\hbar} e^{-(\Delta V+\epsilon)/(k_BT)}, \quad \epsilon \geq -\Delta V \tag{6.14}$$

The Fourier transformation, as defined in Eq. (5.85), of Eq. (6.14) is

$$\check{f}(\lambda) \approx \int_{-\Delta V}^{\infty} \frac{\sinh[\hbar\omega_A/(2k_BT)]}{\pi\hbar} e^{-\left(\frac{\Delta V+\epsilon}{k_BT}\right)} e^{i\lambda\left(\frac{\epsilon}{k_BT}\right)} d\epsilon \tag{6.15}$$

Introducing the new variable $\epsilon' = \epsilon + \Delta V$, we can write Eq. (6.15) as

$$\begin{aligned}
\check{f}(\lambda) &\approx \frac{\sinh[\hbar\omega_A/(2k_BT)]}{\pi\hbar} \int_0^{\infty} e^{-\left(\frac{\epsilon'}{k_BT}\right)} e^{i\lambda\left(\frac{\epsilon'-\Delta V}{k_BT}\right)} d\epsilon' \\
&= \frac{\sinh[\hbar\omega_A/(2k_BT)]}{\pi\hbar} e^{-\left(\frac{i\lambda\Delta V}{k_BT}\right)} \int_0^{\infty} e^{\left[\frac{\epsilon'(i\lambda-1)}{k_BT}\right]} d\epsilon' \\
&= \frac{ik_BT}{\pi\hbar(\lambda+i)} \sinh\left(\frac{\hbar\omega_A}{2k_BT}\right) e^{-\left(\frac{i\lambda\Delta V}{k_BT}\right)}
\end{aligned} \tag{6.16}$$

and noting that $i\lambda \approx 1$ for $|\lambda + i| \ll 1$, we have

$$\check{f}(\lambda) \approx \frac{ik_BT}{\pi\hbar(\lambda+i)} \sinh\left(\frac{\hbar\omega_A}{2k_BT}\right) e^{-\left(\frac{\Delta V}{k_BT}\right)}, \qquad |\lambda + i| \ll 1 \tag{6.17}$$

Now, using Eq. (6.4) and with $\tilde{g}(\lambda)$ defined by Eq. (3.65) we have

$$\begin{aligned}
\check{f}(\lambda) &= \check{g}(\lambda)\check{\varphi}(\lambda) \\
&= \frac{\check{\varphi}(\lambda)}{e^{\frac{\delta\lambda(\lambda+i)}{k_BT}}}
\end{aligned} \tag{6.18}$$

Moreover,

$$\check{f}(\lambda) \approx \check{\varphi}(\lambda), \qquad |\lambda + i| \ll 1 \tag{6.19}$$

Comparing Eqs. (6.17) and (6.19) we then have the boundary condition

$$\check{\varphi}(\lambda) \approx \frac{ik_BT}{\pi\hbar(\lambda+i)} \sinh\left(\frac{\hbar\omega_A}{2k_BT}\right) e^{-\left(\frac{\Delta V}{k_BT}\right)}, \qquad |\lambda + i| \ll 1 \tag{6.20}$$

We must now solve Eq. (6.8) subject to the boundary condition (6.20). First, we write $G(\lambda) = G^+(\lambda)G^-(\lambda)$ where the functions $G^{\pm}(\lambda)$ are given by Eq. (3.70) which is rewritten below for convenience

$$\ln G^{\pm}(\lambda) = \pm\frac{1}{2\pi i} \lim_{\epsilon\to 0} \int_{-\infty}^{\infty} \frac{\ln G(\lambda')}{\lambda' - \lambda \mp i\epsilon} d\lambda' \tag{6.21}$$

Next, we introduce the auxiliary function

$$\psi(\lambda) = \frac{1}{G^-(\lambda)} \prod_{n=1}^{\infty} \frac{G^+(\lambda + in/y)}{G^-(\lambda - in/y)} \tag{6.22}$$

Then we see by direct substitution that

$$\begin{aligned}
\psi\left(\lambda - i/y\right) &= \frac{1}{G^-\left(\lambda - i/y\right)} \prod_{n=1}^{\infty} \frac{G^+\left(\lambda + i(n-1)/y\right)}{G^-\left(\lambda - i(n+1)/y\right)} \\
&= G^+(\lambda) \prod_{n=1}^{\infty} \frac{G^+(\lambda + in/y)}{G^-(\lambda - in/y)} \\
&= \frac{G^+(\lambda)G^-(\lambda)}{G^-(\lambda)} \prod_{n=1}^{\infty} \frac{G^+(\lambda + in/y)}{G^-(\lambda - in/y)} \\
&= G(\lambda)\psi(\lambda)
\end{aligned} \tag{6.23}$$

Taking the natural logarithm of Eq. (6.22) we have

$$\ln \psi(\lambda) = -\ln G^-(\lambda) + \sum_{n=1}^{\infty} \Big\{ \ln G^+(\lambda + in/y) - \ln G^-(\lambda - in/y) \Big\} \tag{6.24}$$

Using Eq. (6.21) we have the integral representations

$$-\ln G^-(\lambda) = \frac{1}{2\pi i} \lim_{\epsilon \to 0} \int_{-\infty}^{\infty} \frac{\ln G(\lambda')}{\lambda' - \lambda + i\epsilon} d\lambda' \tag{6.25}$$

$$\ln G^+(\lambda + in/y) = \frac{1}{2\pi i} \lim_{\epsilon \to 0} \int_{-\infty}^{\infty} \frac{\ln G(\lambda')}{\lambda' - (\lambda + in/y) - i\epsilon} d\lambda'$$

$$\ln G^-(\lambda - in/y) = -\frac{1}{2\pi i} \lim_{\epsilon \to 0} \int_{-\infty}^{\infty} \frac{\ln G(\lambda')}{\lambda' - (\lambda - in/y) + i\epsilon} d\lambda'$$

and

$$\ln G^+(\lambda + in/y) - \ln G^-(\lambda - in/y) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{2(\lambda' - \lambda) \ln G(\lambda')}{(\lambda' - \lambda)^2 + (n/y)^2} d\lambda' \tag{6.26}$$

Substituting Eqs. (6.25) and (6.26) in Eq. (6.24) and taking the inverse logarithm we finally obtain for the auxiliary function

$$\psi(\lambda) = \exp\left[\frac{1}{2\pi i} \int_{-\infty}^{\infty} \left\{ \frac{1}{\lambda' - \lambda} + 2 \sum_{n=1}^{\infty} \left(\frac{\lambda' - \lambda}{(\lambda' - \lambda)^2 + (n/y)^2} \right) \right\} \ln G(\lambda')\, d\lambda' \right] \tag{6.27}$$

Now the term in curly brackets sums to

$$\frac{1}{\lambda'-\lambda}+2\sum_{n=1}^{\infty}\left(\frac{\lambda'-\lambda}{(\lambda'-\lambda)^2+(n/y)^2}\right)=y\left[\frac{1}{(\lambda'-\lambda)y}+2\sum_{n=1}^{\infty}\left(\frac{(\lambda'-\lambda)y}{[(\lambda'-\lambda)y]^2+n^2}\right)\right]$$

$$=\frac{\pi y}{\tanh[\pi(\lambda'-\lambda)y]} \tag{6.28}$$

where we have used the identity [52, 1.421-4]

$$\pi\coth(\pi x)=\frac{1}{x}+2\sum_{k=1}^{\infty}\frac{x}{x^2+k^2}$$

Substituting Eq. (6.28) in Eq. (6.27) we obtain the closed form integral representation

$$\psi(\lambda)=\exp\left[\frac{y}{2i}\int_{-\infty}^{\infty}\frac{\ln G(\lambda')}{\tanh[\pi y(\lambda'-\lambda)]}\,d\lambda'\right] \tag{6.29}$$

It is clear from Eq. (6.20) that $\breve{\varphi}(\lambda)$ has a pole at $\lambda=-i$. Comparing Eqs. (6.8) and (6.23) we see that the original function $\breve{\varphi}(\lambda)$ differs from the auxiliary function $\psi(\lambda)$ only by a function that changes its sign upon shifting its argument by i/y. The function $1/\sinh[\pi y(\lambda+i)]$ has a pole at $\lambda=-i$, and has the desired translation property. Thus, the solution of Eq. (6.8) with boundary condition (6.20) is given in terms of the auxiliary function by

$$\breve{\varphi}(\lambda)=\frac{i\omega_C}{2\pi}\frac{\psi(\lambda)}{\psi(-i)}\frac{\sinh[\hbar\omega_A/(2k_BT)]}{\sinh[\hbar\omega_C(\lambda+i)/(2k_BT)]}e^{-\frac{\Delta V}{k_BT}} \tag{6.30}$$

6.2 Escape rate in the underdamped quantum regime

We saw in Chapter 2 that the lifetime τ of a Brownian particle in a deep potential well can be expressed via Eq. (2.10) [6]. However, like the classical case, the TST Eq. (2.10) in the quantum case applies only in the intermediate damping regime and so does not explicitly contain any dependence on the friction. Thus, in the underdamped regime, Eq. (2.10) must again be modified by introducing the depopulation factor $A(\Delta,y)$ so that

$$\tau^{-1}=A(\Delta,y)\frac{\omega_C}{2\pi}\frac{\sinh[\hbar\omega_A/(2k_BT)]}{\sin[\hbar\omega_C/(2k_BT)]}e^{-\frac{\Delta V}{k_BT}} \tag{6.31}$$

In the quantum case the depopulation factor $A(\Delta, y)$ takes into account the interaction of the Brownian particle with the heat bath via the dissipation parameter Δ, and also includes the high-temperature quantum tunneling effects near the top of the barrier via the quantum parameter y.

Now we know that as far as quantum effects are concerned only those particles that penetrate the classically opaque potential barrier via tunneling contribute to the escape rate, so that the rate is given by the following equation involving the penetration coefficient

$$\begin{aligned}
\tau^{-1} &= \int_{-\infty}^{\infty} \frac{f(\epsilon)\, d\epsilon}{1 + \exp(-2\pi\epsilon/\hbar\omega_C)} \\
&= \int_{-\infty}^{\infty} \frac{f(\epsilon) e^{2\pi\epsilon/\hbar\omega_C}\, d\epsilon}{1 + \exp(2\pi\epsilon/\hbar\omega_C)} \\
&= \int_{-\infty}^{\infty} \varphi(\epsilon) e^{2\pi\epsilon/\hbar\omega_C}\, d\epsilon \\
&= \check{\varphi}(-i/y)
\end{aligned} \tag{6.32}$$

With $\lambda = -i/y$ in Eq. (6.30) we have

$$\check{\varphi}(-i/y) = \frac{i\omega_C}{2\pi} \frac{\psi(-i/y)}{\psi(-i)} \frac{\sinh[\hbar\omega_A/(2k_BT)]}{\sinh[\hbar\omega_C(i - i/y)/(2k_BT)]} e^{-\frac{\Delta V}{k_BT}} \tag{6.33}$$

Using the identity

$$\sinh(ix) = i \sin x$$

we have

$$\begin{aligned}
\sinh\left[i\frac{\hbar\omega_C}{2k_BT}\left(1 - \frac{1}{y}\right)\right] &= i \sin\left[\frac{\hbar\omega_C}{2k_BT} - \pi\right] \\
&= -i \sin\left[\frac{\hbar\omega_C}{2k_BT}\right]
\end{aligned} \tag{6.34}$$

Substituting Eq. (6.34) in Eq. (6.33) we have

$$\check{\varphi}(-i/y) = -\frac{\omega_C}{2\pi} \frac{\psi(-i/y)}{\psi(-i)} \frac{\sinh[\hbar\omega_A/(2k_BT)]}{\sin[\hbar\omega_C/(2k_BT)]} e^{-\frac{\Delta V}{k_BT}} \tag{6.35}$$

Comparing Eqs. (6.31), (6.32) and (6.35) we see that the depopulation factor becomes

$$A(\Delta, y) = -\frac{\psi(-i/y)}{\psi(-i)} \tag{6.36}$$

By using Eq. (6.29) in (6.36) we then obtain

$$A(\Delta, y) = \exp\left[\frac{y}{2i}\int_{-\infty}^{\infty} \ln G(\lambda')\left\{\frac{1}{\tanh[\pi(y\lambda'+i)]} - \frac{1}{\tanh[\pi y(\lambda'+i)]}\right\} d\lambda'\right] \tag{6.37}$$

Next in order to simplify the integrand we use the identity [24, 4.5.46]

$$\coth A + \coth B = \frac{\sinh(A+B)}{\sinh A \sinh B}$$

which can be written as

$$\coth A - \coth B = -\frac{\sinh(A-B)}{\sinh A \sinh B} \tag{6.38}$$

since both $\sinh x$ and $\coth x$ are odd hyperbolic functions. Using Eq. (6.38) we then have

$$\frac{1}{\tanh[\pi(y\lambda'+i)]} - \frac{1}{\tanh[\pi y(\lambda'+i)]} = -\frac{\sinh[i\pi(1-y)]}{\sinh[\pi(y\lambda'+i)]\sinh[\pi y(\lambda'+i)]} \tag{6.39}$$

Now

$$\begin{aligned}\sinh[i\pi(1-y)] &= i\sin(\pi - \pi y) \\ &= -i\cos\pi \sin(\pi y) \\ &= i\sin(\pi y)\end{aligned} \tag{6.40}$$

Substituting Eq. (6.40) in Eq. (6.39) we have

$$\frac{1}{\tanh[\pi(y\lambda'+i)]} - \frac{1}{\tanh[\pi y(\lambda'+i)]} = -\frac{i\sin(\pi y)}{\sinh[\pi(y\lambda'+i)]\sinh[\pi y(\lambda'+i)]} \tag{6.41}$$

Next using the identity [24, 4.5.38]

$$\sinh A \sinh B = 1/2\left[\cosh(A+B) - \cosh(A-B)\right] \tag{6.42}$$

we have

$$\begin{aligned}\sinh[\pi(y\lambda'+i)]\sinh[\pi y(\lambda'+i)] &= 1/2\{\cosh[2\pi y\lambda' + i\pi(1+y)] - \cosh[i\pi(1-y)]\} \\ &= 1/2\{\cosh[2\pi y(\lambda'+i/2)+i\pi] - \cos[\pi(1-y)]\} \\ &= 1/2\{\cosh[2\pi y(\lambda'+i/2)]\cos\pi - \cos\pi\cos(\pi y)\} \\ &= -1/2\{\cosh[2\pi y(\lambda'+i/2)] - \cos(\pi y)\}\end{aligned} \tag{6.43}$$

where we have used the identities [24, 4.5.25] $\cosh(A+B) = \cosh A \cosh B + \sinh A \sinh B$, $\cosh(ix) = \cos x$, and $\sinh(ix) = i \sin x$. Substituting Eq. (6.43) in Eq. (6.41) we finally have

$$\frac{1}{\tanh[\pi(y\lambda' + i)]} - \frac{1}{\tanh[\pi y(\lambda' + i)]} = \frac{2i \sin(\pi y)}{\cosh[2\pi y(\lambda' + i/2)] - \cos(\pi y)} \tag{6.44}$$

Now from Eqs. (6.9) and (5.88) we also have

$$G(\lambda) = 1 - \exp\{\check{w}(\lambda) - \check{w}(0)\} \tag{6.45}$$

Substituting Eqs. (6.44) and (6.45) in Eq. (6.37) we then obtain the compact expression

$$\begin{aligned} A(\Delta, y) &= \exp\left[\int_{-\infty}^{\infty} \frac{y \sin(\pi y) \ln[1 - \exp\{\check{w}(\lambda') - \check{w}(0)\}]}{\cosh[2\pi y(\lambda' + i/2)] - \cos(\pi y)} \, d\lambda'\right] \\ &= \exp\left[\int_{-\infty+i/2}^{\infty+i/2} \frac{y \sin(\pi y) \ln\left[1 - e^{-\Delta R(\lambda, y)}\right]}{\cosh(2\pi y\lambda) - \cos(\pi y)} \, d\lambda\right] \\ &= \exp\left[\int_{-\infty}^{\infty} \frac{y \sin(\pi y) \ln\left[1 - e^{-\Delta R(\lambda, y)}\right]}{\cosh(2\pi y\lambda) - \cos(\pi y)} \, d\lambda\right] \end{aligned} \tag{6.46}$$

Here, we have written

$$\Delta R(\lambda, y) = \check{w}(0) - \check{w}(\lambda - i/2) \tag{6.47}$$

where $\check{w}(\lambda)$ is the Fourier transform of the quantum transition probability in the first order of perturbation theory $w(\epsilon)$ given by Eq. (5.82). In the extremely underdamped regime ($\Delta \ll 1$) we can use the identity

$$e^x = \sum_{n=0}^{\infty} \frac{1}{n!} x^n$$

to write

$$1 - e^{-\Delta R(\lambda, y)} \approx \Delta R(\lambda, y) \tag{6.48}$$

Using the approximation (6.48) in Eq. (6.46) we obtain

$$\begin{aligned} A(\Delta, y) &\approx \exp\left[\int_{-\infty}^{\infty} \frac{y \sin(\pi y)[\ln R(\lambda, y) + \ln \Delta]}{\cosh(2\pi y\lambda) - \cos(\pi y)} \, d\lambda\right] \\ &= a(y) \Delta^{\int_{-\infty}^{\infty} \frac{y \sin \pi y}{\cosh(2\pi y\lambda) - \cos \pi y} \, d\lambda} \end{aligned} \tag{6.49}$$

where

$$a(y) = \exp\left[\int_{-\infty}^{\infty} \frac{y\sin(\pi y)\ln R(\lambda, y)}{\cosh(2\pi y\lambda) - \cos(\pi y)}\, d\lambda\right] \tag{6.50}$$

Noting that $\cosh(2\pi y\lambda)$ is an even function of the variable λ, that $-\cos(\pi y) = \cos[\pi(1-y)]$, and using the identity [52, 3.514-1]

$$\int_0^{\infty} \frac{dx}{\cosh(ax) + \cos t} = \frac{t}{a\sin t} \qquad (0 < t < \pi, \quad a > 0) \tag{6.51}$$

we can write

$$\begin{aligned}
\int_{-\infty}^{\infty} \frac{y\sin(\pi y)d\lambda}{\cosh(2\pi y\lambda) - \cos(\pi y)} &= 2y\sin(\pi y)\int_0^{\infty} \frac{d\lambda}{\cosh(2\pi y\lambda) - \cos(\pi y)} \\
&= 2y\sin(\pi y)\int_0^{\infty} \frac{d\lambda}{\cosh(2\pi\lambda y) + \cos[\pi(1-y)]} \\
&= \frac{2y\sin(\pi y)[\pi(1-y)]}{2\pi y\sin[\pi(1-y)]} \\
&= \frac{2y\sin(\pi y)[\pi(1-y)]}{2\pi y\sin(\pi y)} \\
&= 1 - y, \qquad \text{for } 0 < y < 1
\end{aligned} \tag{6.52}$$

Substituting Eq. (6.52) in Eq. (6.49) we obtain the quantum depopulation factor as a product of a purely quantum and a classical factor with quantum modifications, namely,

$$A(\Delta, y) \approx a(y)\Delta^{1-y}, \qquad \Delta \ll 1, \quad 0 < y < 1 \tag{6.53}$$

where $y = \hbar\omega_C/(2\pi k_B T)$. The expressions (6.53) and (6.50) shows that with decreasing temperature T, since $y \to 1$ and $\Delta^{1-y} \to 1$, the contribution of quantum tunneling predominates over the effect of depletion of the distribution function. Therefore, the escape rate extrapolated to the low temperature $T = T_0 = \hbar\omega_C/(2\pi k_B)$ becomes *independent of dissipation.* For high temperatures ($k_B T \gg \hbar\omega_C$), $y \approx 0$ and since $a(0) = 1$, Eq. (6.53) yields the classical VLD result $A \approx \Delta$.

We saw [Eq. (5.40)] that in the semiclassical approximation the matrix elements $\langle\epsilon|\hat{x}(t)|\epsilon'\rangle$ of a quantum transition from state ϵ' to the state ϵ can be expressed, via the Fourier components of the classical trajectory $x(t)$, in Mel'nikov's

notation

$$\langle \epsilon | \hat{x}(t) | \epsilon' \rangle = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} x(t) e^{i(\epsilon - \epsilon')t/\hbar} \tag{6.54}$$

To obtain the matrix elements corresponding to the separatrix energy $\epsilon' = 0$ we must first determine the classical trajectory $x(t)$ for $\epsilon' = 0$.

Now the energy ϵ' is given by

$$\epsilon' = \frac{p^2}{2m} + V(x) \tag{6.55}$$

With $\epsilon' = 0$, we have

$$p = \sqrt{-2mV(x)},$$

and

$$\frac{dx}{dt} = \sqrt{-\frac{2V(x)}{m}}$$

Separating the variables and integrating we have

$$\int_0^t dt' = \int_{x_0}^{x} \sqrt{-\frac{m}{2V(x')}} dx'$$

where x_0 is the position of the particle at time $t = 0$. The classical trajectory $x(t)$ corresponding to energy $\epsilon' = 0$ is defined by the implicit relation

$$t(x) = \int_{x_0}^{x} \frac{dx'}{\sqrt{-2V(x')/m}} \tag{6.56}$$

Further progress and derivation of the expression for the quantum argument $R(\lambda, y)$ is only possible for *explicit* potentials $V(x)$. Here, we give examples of the calculation of the matrix elements $\langle \epsilon | \hat{x}(t) | \epsilon' \rangle$ for cubic, double-well, and periodic potentials. Before doing this however, we remark that having determined the quantum depopulation factor $A(\Delta, y)$ Mel'nikov extends his solution to all values of the damping via the *ad hoc* expression, taking a single well as an example, $\Gamma_{\mathrm{M}} = A(\Delta, y)\Gamma^{\mathrm{IHD}}$, where Γ^{IHD} is the quantum escape rate for the single well potential in question. For example, $\Gamma^{\mathrm{IHD}} = \Xi\, \Gamma_{\mathrm{cl}}^{\mathrm{IHD}}$ as calculated in Chapter 4. This *ad hoc* approach is of course subject to the same criticisms as pertain to the classical case.

6.2.1 $R(\lambda, y)$ for the cubic potential

We commence with the cubic potential, that is

$$V(x) = -\frac{1}{2}m\omega^2 x^2\left(1 - \frac{x}{x_1}\right) \tag{6.57}$$

We have for this potential

$$t(x) = \frac{1}{\omega}\int_{x_1}^{x} \frac{dx'}{x'\sqrt{1 - x'/x_1}} \tag{6.58}$$

Next we use the identity [52, 2.266]

$$\begin{aligned}\int \frac{dx}{x\sqrt{1 - x/x_1}} &= \operatorname{arccosh}\left(\frac{2 - x/x_1}{x/x_1}\right) \\ &= \operatorname{arccosh}\left(\frac{2x_1}{x} - 1\right)\end{aligned} \tag{6.59}$$

to rewrite Eq. (6.58) as

$$\begin{aligned}t(x) &= \frac{1}{\omega}\left[\operatorname{arccosh}\left(\frac{2x_1}{x'} - 1\right)\Big|_{x_1}^{x}\right] \\ &= \frac{1}{\omega}\left[\operatorname{arccosh}\left(\frac{2x_1}{x} - 1\right) - \operatorname{arccosh}(1)\right] \\ &= \frac{1}{\omega}\operatorname{arccosh}\left(\frac{2x_1}{x} - 1\right)\end{aligned} \tag{6.60}$$

Eq. (6.60) can be written as

$$\cosh(\omega t) + 1 = \frac{2x_1}{x}$$

so that the classical trajectory is given by

$$\begin{aligned}x(t) &= \frac{2x_1}{\cosh(\omega t) + 1} \\ &= \frac{x_1}{\frac{1}{2}[\cosh(\omega t) + 1]} \\ &= \frac{x_1}{\cosh^2(\omega t/2)}\end{aligned} \tag{6.61}$$

The particle starts from the barrier top, $x = 0$, at $t = -\infty$, is reflected from the left-hand turning point, $x = x_1$, and returns to the barrier top for $t \to \infty$.

The matrix elements $\langle\epsilon|\hat{x}(t)|\epsilon'\rangle$ for the cubic potential are then given, recalling Eq. (6.54), by the Fourier transform over the time variable in the classical trajectory

$$\langle\epsilon|x(t)|\epsilon'\rangle = \frac{x_1}{2\pi\hbar}\int_{-\infty}^{\infty}\frac{e^{i(\epsilon-\epsilon')t/\hbar}\,dt}{\cosh^2(\omega t/2)} \tag{6.62}$$

Using the Euler formula and noting that $\sin[(\epsilon-\epsilon')t/\hbar]$ is an odd function, whereas both $\cos[(\epsilon-\epsilon')t/\hbar]$ and $\cosh^2(\omega t/2)$ are even functions of the variable t, we can write Eq. (6.62) as

$$\begin{aligned}\langle\epsilon|x(t)|\epsilon'\rangle &= \frac{x_1}{2\pi\hbar}\left[\int_{-\infty}^{\infty}\frac{\cos[(\epsilon-\epsilon')t/\hbar]\,dt}{\cosh^2(\omega t/2)} + i\int_{-\infty}^{\infty}\frac{\sin[(\epsilon-\epsilon')t/\hbar]\,dt}{\cosh^2(\omega t/2)}\right]\\ &= \frac{x_1}{\pi\hbar}\int_{0}^{\infty}\frac{\cos[(\epsilon-\epsilon')t/\hbar]\,dt}{\cosh^2(\omega t/2)}\end{aligned} \tag{6.63}$$

Next we use the identity [52, 3.982-1]

$$\int_0^\infty \frac{\cos(ax)}{\cosh^2(\beta x)}\,dx = \frac{a\pi}{2\beta^2\sinh\left(\dfrac{a\pi}{2\beta}\right)}, \qquad (\mathrm{Re}\,\beta > 0, \quad a > 0) \tag{6.64}$$

to write Eq.(6.63) as

$$\begin{aligned}\langle\epsilon|x(t)|\epsilon'\rangle &= \frac{x_1}{\pi\hbar}\,\frac{\pi|\epsilon-\epsilon'|/\hbar}{2\left(\dfrac{\omega}{2}\right)^2\sinh\left(\dfrac{\pi|\epsilon-\epsilon'|/\hbar}{\omega}\right)}\\ &= \frac{2x_1|\epsilon-\epsilon'|}{\hbar^2\omega^2\sinh[\pi|\epsilon-\epsilon'|/(\hbar\omega)]}\end{aligned} \tag{6.65}$$

The quantum transition (Golden Rule) probability is then recalling Eq. (5.82)

$$\begin{aligned}w(\epsilon) &= \frac{2\pi}{\hbar}\left[\frac{2x_1|\epsilon|}{\hbar^2\omega^2\sinh[\pi|\epsilon|/(\hbar\omega)]}\right]^2 m\beta\epsilon\Big[\coth[\epsilon/(2k_BT)]-1\Big]\\ &= \frac{8\pi m\beta x_1^2\epsilon^3}{\hbar^5\omega^4\sinh^2[\pi\epsilon/(\hbar\omega)]}\left(\coth[\epsilon/(2k_BT)]-1\right)\end{aligned} \tag{6.66}$$

The Fourier transform $\breve{w}(\lambda)$ of the quantum transition probability $w(\epsilon)$ is given by

$$\breve{w}(\lambda) = \int_{-\infty}^{\infty}\frac{8\pi m\beta x_1^2\epsilon^3\left(\coth[\epsilon/(2k_BT)]-1\right)}{\hbar^5\omega^4\sinh^2[\pi\epsilon/(\hbar\omega)]}e^{i\lambda\epsilon/(k_BT)}\,d\epsilon \tag{6.67}$$

Using Eqs. (6.47) and (6.67) we have

$$\begin{aligned}\check{w}(0) - \check{w}(\lambda - i/2) &= \int_{-\infty}^{\infty} \frac{8\pi m\beta x_1^2 \epsilon^3 \left(\coth[\epsilon/(2k_BT)] - 1\right)}{\hbar^5\omega^4 \sinh^2[\pi\epsilon/(\hbar\omega)]} \left(1 - e^{i(\lambda - i/2)\epsilon/(k_BT)}\right) d\epsilon \\ &= \frac{8\beta\omega m x_1^2}{2k_BT\pi^4 y^5} \int_{-\infty}^{\infty} \frac{x^3 \left(\coth(x) - 1\right)}{\sinh^2[x/y]} \left(1 - e^{i(2\lambda - i)x}\right) dx \\ &= \Delta R(\lambda, y) \end{aligned} \tag{6.68}$$

where $x = \epsilon/(2k_BT)$ and $y = \hbar\omega/(2\pi k_BT)$.
Now $[\coth(x) - 1][1 - e^{i(2\lambda - i)x}]$ can be written as

$$[\coth(x) - 1][1 - e^{i(2\lambda - i)x}] = f_e(x) + f_o(x) \tag{6.69}$$

where $f_e(x)$ and $f_o(x)$ are even and odd functions respectively. Substituting Eq. (6.69) in Eq. (6.95) and noting that $x^3/\sinh^2(x/y)$ is an odd function of the variable x we have

$$\begin{aligned}\Delta R(\lambda, y) &= \frac{8\beta\omega m x_1^2}{2k_BT\pi^4 y^5} \int_{-\infty}^{\infty} \frac{x^3}{\sinh^2(x/y)} \Big(f_e(x) + f_o(x)\Big) dx \\ &= \frac{8\beta\omega m x_1^2}{2k_BT\pi^4 y^5} \int_{-\infty}^{\infty} \frac{x^3 f_o(x)}{\sinh^2(x/y)} dx \end{aligned} \tag{6.70}$$

Now

$$\begin{aligned}[\coth(x) - 1][1 - e^{i(2\lambda - i)x}] =& [\coth(x) - 1][(1 - \cos[(2\lambda - i)x]) - i\sin[(2\lambda - i)x]] \\ =& \Big\{ \coth(x)\left[1 - \cos[(2\lambda - i)x]\right] + i\sin[(2\lambda - i)x] \Big\} \\ &+ \Big\{ \left(\cos\left[(2\lambda - i)x\right] - 1\right) - i\coth(x)\sin\left[(2\lambda - i)x\right] \Big\} \\ =& f_o(x) + f_e(x) \end{aligned}$$

where

$$f_e(x) = \left(\cos\left[(2\lambda - i)x\right] - 1\right) - i\coth(x)\sin\left[(2\lambda - i)x\right] \tag{6.71}$$

and

$$
\begin{aligned}
f_o(x) &= \coth(x)\big[1-\cos[(2\lambda-i)x]\big] + i\sin[(2\lambda-i)x] \\
&= \frac{\cosh(x) - \big\{\cosh(x)\cos[(2\lambda-i)x] - i\sinh(x)\sin[(2\lambda-i)x]\big\}}{\sinh(x)} \\
&= \frac{\cosh(x) - \big\{\cosh(x)\cos[-i(2i\lambda+1)x] - i\sinh(x)\sin[-i(2i\lambda+1)x]\big\}}{\sinh(x)}
\end{aligned}
\tag{6.72}
$$

Now using the identities $\cosh(x)\cosh(y) - \sinh(x)\sinh(y) = \cosh(x-y)$, $\sin(-ix) = -i\sinh(x)$, $\cos(-ix) = \cosh(x)$, and $\cosh(ix) = \cos(x)$we have

$$
\begin{aligned}
\cosh(x)\cos[-i(2i\lambda+1)x] - i\sinh(x)\sin[-i(2i\lambda-1)x] &= \cosh(x)\cosh[(2i\lambda+1)x] \\
&\quad - \sinh(x)\sinh[(2i\lambda+1)] \\
&= \cosh(-2i\lambda x) \\
&= \cos(2\lambda x)
\end{aligned}
\tag{6.73}
$$

Substituting Eq. (6.73) in Eq. (6.72) we have

$$
f_o(x) = \frac{\cosh(x) - \cos(2\lambda x)}{\sinh(x)} \tag{6.74}
$$

Finally, substituting Eq. (6.74) in Eq. (6.70) we have

$$
\begin{aligned}
\Delta R(\lambda, y) &= \frac{8\beta\omega m x_1^2}{2k_B T\pi^4 y^5}\int_{-\infty}^{\infty} \frac{x^3\cosh(x) - \cos(2\lambda x)}{\sinh(x)\sinh^2(x/y)}dx \\
&= \frac{8\beta\omega m x_1^2}{15k_B T}\int_{-\infty}^{\infty} \frac{15x^3}{2\pi^4 y^5}\frac{\big[\cosh(x) - \cos(2\lambda x)\big]}{\sinh(x)\sinh^2(x/y)}dx
\end{aligned}
\tag{6.75}
$$

The dissipation parameter Δ is

$$
\Delta = \frac{\beta S}{k_B T} \tag{6.76}
$$

where the action per cycle at the barrier energy $\epsilon = 0$ is given by

$$
\begin{aligned}
S &= 2\int_{x_1}^{0} p\,dx \\
&= 2\left|\int_{x_1}^{0}\sqrt{-2mV(x)}dx\right|
\end{aligned}
\tag{6.77}
$$

Now from Eq. (6.57) we have

$$\sqrt{-2mV(x)} = m\omega x\sqrt{1-\frac{x}{x_1}} \tag{6.78}$$

Writing $z = 1 - x/x_1$, $x = x_1(1-z)$, and $dx = -x_1 dz$, we have

$$\begin{aligned}\int_{x_1}^{0} m\omega x\sqrt{1-\frac{x}{x_1}}dx &= -m\omega x_1^2\int_0^1 (1-z)z^{\frac{1}{2}}dz \\ &= -m\omega x_1^2\left[\left(\frac{2}{3}z^{\frac{3}{2}} - \frac{2}{5}z^{\frac{5}{2}}\right)\Big|_0^1\right] \\ &= -\frac{4m\omega x_1^2}{15}\end{aligned} \tag{6.79}$$

From Eqs. (6.76) to (6.79) we have

$$\Delta = \frac{8\beta\omega m x_1^2}{15k_BT} \tag{6.80}$$

Comparing Eqs. (6.75) and (6.80) we see that

$$\Delta R(\lambda, y) = \frac{15}{2\pi^4 y^5}\int_{-\infty}^{\infty}\frac{x^3\big[\cosh(x) - \cos(2\lambda x)\big]}{\sinh(x)\sinh^2(x/y)}dx \tag{6.81}$$

6.2.2 $R(\lambda, y)$ for the double–well potential

In like manner, we evaluate $R(\lambda, y)$ for a double-well potential that can be represented as

$$V(x) = -\frac{1}{2}m\omega^2x^2\left(1-\frac{x^2}{x_1^2}\right) \tag{6.82}$$

Substituting Eq. (6.82) in (6.56) we have

$$t(x) = \frac{1}{\omega}\int_{x_1}^{x}\frac{dx'}{x'\sqrt{1-(x')^2/x_1^2}} \tag{6.83}$$

Next we use the identity [52, 2.266]

$$\begin{aligned}\int\frac{dx}{x\sqrt{1-x^2/x_1^2}} &= \operatorname{arccosh}\left(\frac{2}{x(2/x_1)}\right) \\ &= \operatorname{arccosh}(x_1/x)\end{aligned} \tag{6.84}$$

to write Eq. (6.83) as

$$t(x) = \frac{1}{\omega}\left[\operatorname{arccosh}\left(\frac{x_1}{x'}\right)\Bigg|_{x'=x_1}^{x'=x}\right]$$

$$= \frac{1}{\omega}\left[\operatorname{arccosh}\left(\frac{x_1}{x}\right) - \operatorname{arccosh}\left(1\right)\right]$$

$$= \frac{1}{\omega}\operatorname{arccosh}\left(\frac{x_1}{x}\right) \tag{6.85}$$

The trajectory $x(t)$ is

$$x(t) = \frac{x_1}{\cosh(\omega t)} \tag{6.86}$$

The particle starts from $x = 0$ at $t = -\infty$ and returns to this point for $t \to \infty$. The matrix elements $\langle \epsilon | x(t) | \epsilon' \rangle$ for the double well potential are then given by

$$\langle \epsilon | x(t) | \epsilon' \rangle = \frac{x_1}{2\pi\hbar}\int_{-\infty}^{\infty} \frac{e^{i(\epsilon-\epsilon')t/\hbar}}{\cosh(\omega t)}\, dt$$

$$= \frac{x_1}{2\pi\hbar}\left[\int_{-\infty}^{\infty} \frac{\cos\left[(\epsilon-\epsilon')t/\hbar\right]}{\cosh(\omega t)} + i\int_{-\infty}^{\infty} \frac{\sin\left[(\epsilon-\epsilon')t/\hbar\right]}{\cosh(\omega t)}\right]$$

$$= \frac{x_1}{\pi\hbar}\int_{0}^{\infty} \frac{\cos\left[(\epsilon-\epsilon')t/\hbar\right]}{\cosh(\omega t)} \tag{6.87}$$

since both $\cos[(\epsilon - \epsilon')t/\hbar]$ and $\cosh(\omega t)$ are even functions, whereas $\sin[(\epsilon - \epsilon')t/\hbar]$ is an odd function of the variable t.

Next we use the identity [52, 3.981-3]

$$\int_0^{\infty} \frac{\cos(ax)}{\cosh(\beta x)}\, dx = \frac{\pi}{2\beta}\frac{1}{\cosh(a\pi/(2\beta))}, \qquad (\operatorname{Re}\beta > 0, \quad \text{all real } a) \tag{6.88}$$

to write Eq. (6.87) as

$$\langle \epsilon | x(t) | \epsilon' \rangle = \frac{x_1}{2\hbar\omega\cosh[\pi(\epsilon-\epsilon')/2\hbar\omega]} \tag{6.89}$$

Thus, the quantum transition probability in this case is

$$w(\epsilon) = \frac{\pi m\beta x_1^2\epsilon}{2\hbar^3\omega^2\cosh^2[\pi\epsilon/(2\hbar\omega)]}\left(\coth[\epsilon/(2k_BT)] - 1\right) \tag{6.90}$$

so that

$$\breve{w}(0) - \breve{w}(\lambda - i/2) = \int_{-\infty}^{\infty} w(\epsilon)\big(1 - e^{i(\lambda - i/2)\epsilon/(k_B T)}\big)\, d\epsilon$$

$$= \frac{\pi m \beta x_1^2}{2\hbar^3 \omega^2} \int_{-\infty}^{\infty} \frac{\epsilon\big[\coth[\epsilon/(2k_B T)] - 1\big]\big[1 - e^{i(2\lambda - i)\epsilon/(2k_B T)}\big]}{\cosh^2[\pi\epsilon/(2\hbar\omega)]}\, d\epsilon$$

$$= \frac{\omega m \beta x_1^2}{4\pi^2 k_B T y} \int_{-\infty}^{\infty} \frac{x\big[\coth(xy) - 1\big]\big[1 - e^{i(2\lambda - i)xy}\big]}{\cosh^2(x/2)}\, dx \qquad (6.91)$$

where $x = \pi\epsilon/(\hbar\omega)$ and $y = \hbar\omega/(2\pi k_B T)$.

Recalling Eq. (6.69) we have

$$[\coth(xy) - 1][1 - e^{i(2\lambda - i)xy}] = f_e(xy) + f_o(xy) \qquad (6.92)$$

Substituting Eq. (6.92) in Eq. (6.91) and noting that $x/\cosh^2(x/2)$ is an odd function of the variable x, we have

$$\breve{w}(0) - \breve{w}(\lambda - i/2) = \frac{\omega m \beta x_1^2}{4\pi^2 k_B T y} \int_{-\infty}^{\infty} \frac{x}{\cosh^2(x/2)} [f_e(xy) + f_o(xy)]\, dx$$

$$= \frac{\omega m \beta x_1^2}{4\pi^2 k_B T y} \int_{-\infty}^{\infty} \frac{x f_o(xy)}{\cosh^2(x/2)}\, dx \qquad (6.93)$$

Replacing x by xy in Eq.(6.74) we have

$$f_o(xy) = \frac{\cosh(xy) - \cos(2\lambda xy)}{\sinh(xy)} \qquad (6.94)$$

Substituting Eq. (6.94) in Eq. (6.93) we obtain

$$\breve{w}(0) - \breve{w}(\lambda - i/2) = \frac{2\omega m \beta x_1^2}{3k_B T} \frac{3}{8\pi^2 y} \int_{-\infty}^{\infty} \frac{x\big[\cosh(xy) - \cos(2\lambda xy)\big]}{\sinh(xy)\cosh^2(x/2)}\, dx$$

$$= \Delta R(\lambda, y) \qquad (6.95)$$

The dissipation parameter Δ is given by

$$\Delta = \frac{2\beta}{k_B T} \int_0^{x_1} \sqrt{-2V(x)m}\, dx$$

$$= \frac{2\beta}{k_B T} \int_0^{x_1} m\omega x \sqrt{1 - \frac{x^2}{x_1^2}}$$

$$= \frac{2\beta m \omega x_1^2}{3k_B T} \left[\left(1 - \frac{x^2}{x_1^2}\right)^{3/2} \Bigg|_0^{x_1} \right]$$

$$= \frac{2\beta m \omega x_1^2}{3k_B T} \qquad (6.96)$$

Comparing Eqs. (6.95) and (6.96) we see that

$$R(\lambda, y) = \frac{3}{8\pi^2 y} \int_{-\infty}^{\infty} \frac{x\big[\cosh(xy) - \cos(2\lambda xy)\big]}{\sinh(xy)\cosh^2(x/2)}\, dx \tag{6.97}$$

We will now evaluate $R(\lambda, y)$ in the classical limit $\hbar\omega/(2\pi k_B T) = y \to 0$.

$$\lim_{y\to 0} R(\lambda, y) = \lim_{y\to 0} \frac{3}{8\pi^2 y} \int_{-\infty}^{\infty} \frac{x\big[\cosh(xy) - \cos(2\lambda xy)\big]}{\sinh(xy)\cosh^2(x/2)}\, dx$$

$$= \frac{3}{8\pi^2} \int_{-\infty}^{\infty} \left[\lim_{y\to 0} \frac{\big[\cosh(xy) - \cos(2\lambda xy)\big]}{y\sinh(xy)}\right] \left[\frac{x}{\cosh^2(x/2)}\right] dx \tag{6.98}$$

Applying L'Hôpital's rule twice we have

$$\lim_{y\to 0} \frac{\big[\cosh(xy) - \cos(2\lambda xy)\big]}{y\sinh(xy)} = \lim_{y\to 0} \frac{x\sinh(yx) + 2\lambda x \sin(2\lambda yx)}{\sinh(yx) + xy\cosh(yx)}$$

$$= \lim_{y\to 0} \frac{x^2\cosh(yx) + 4\lambda^2 x^2 \cos(2\lambda yx)}{2x\cosh(yx) + x^2 y\sinh(yx)}$$

$$+ \frac{x}{2}\left(1 + 4\lambda^2\right) \tag{6.99}$$

Substituting Eq. (6.99) in Eq. (6.98) we have

$$\lim_{y\to 0} R(\lambda, y) = \frac{3}{4\pi^2}\left(\lambda^2 + \frac{1}{4}\right) \int_{-\infty}^{\infty} \frac{x^2}{\cosh^2(x/2)}\, dx$$

$$= \frac{3}{2\pi^2}\left(\lambda^2 + \frac{1}{4}\right) \int_{0}^{\infty} \frac{x^2}{\cosh^2(x/2)}\, dx \tag{6.100}$$

since the integrand is an even function of x. To evaluate the integral in Eq. (6.100) we use the identity [52, 3.536-1]

$$\int_0^{\infty} \frac{z^2}{\cosh^2(z)}\, dz = \frac{\pi^2}{12} \tag{6.101}$$

Writing $z = x/2$ this identity can be written as

$$\int_0^{\infty} \frac{z^2}{\cosh^2(z)}\, dz = \frac{1}{8}\int_0^{\infty} \frac{x^2}{\cosh^2(x/2)}\, dx = \frac{\pi^2}{12} \tag{6.102}$$

or

$$\int_0^{\infty} \frac{x^2}{\cosh^2(x/2)}\, dx = \frac{2\pi^2}{3} \tag{6.103}$$

Substituting Eq. (6.103) in Eq. (6.100) we have

$$\lim_{y\to 0} R(\lambda, y) = \lambda^2 + \frac{1}{4} \tag{6.104}$$

which is the (canonical) classical form. The foregoing classical expression has been used by Hänggi et al. [2] to simplify calculation of quantum escape rates.

6.2.3 $R(\lambda, y)$ for the periodic potential

Finally, we evaluate $R(\lambda, y)$ for the periodic potential

$$V(x) = -\frac{m\omega^2 x_1^2}{2\pi^2}\cos^2(\pi x/x_1) \tag{6.105}$$

Substituting Eq. (6.105) in (6.56) we obtain

$$t(x) = \frac{\pi}{\omega x_1}\int_0^x \frac{dx'}{\cos(\pi x'/x_1)} \tag{6.106}$$

Introducing the new variable $\theta = \pi x'/x_1$ and using the identity [52, 2.01-14]

$$\int \frac{d\theta}{\cos\theta} = \ln\left[\tan\left(\frac{\pi}{4}+\frac{\theta}{2}\right)\right] \tag{6.107}$$

we have

$$\begin{aligned}
\frac{\pi}{x_1}\int_0^x \frac{dx'}{\cos(\pi x'/x_1)} &= \int_0^{\pi x/x_1}\frac{d\theta}{\cos\theta} \\
&= \ln\left[\tan\left(\frac{\pi}{4}+\frac{\theta}{2}\right)\right]\Bigg|_0^{\pi x/x_1} \\
&= \ln\left[\tan\left(\frac{\pi}{4}+\frac{\pi x}{2x_1}\right)\right] - \ln\left[\tan\left(\frac{\pi}{4}\right)\right] \\
&= \ln\left[\tan\left(\frac{\pi}{4}+\frac{\pi x}{2x_1}\right)\right]
\end{aligned} \tag{6.108}$$

Substituting Eq. (6.108) in Eq. (6.106) we obtain

$$t(x) = \frac{1}{\omega}\ln\left[\tan\left(\frac{\pi}{4}+\frac{\pi x}{2x_1}\right)\right]$$

$$e^{\omega t} = \tan\left(\frac{\pi}{4}+\frac{\pi x}{2x_1}\right)$$

and

$$\begin{aligned}
x(t) &= \frac{2x_1}{\pi}\left[\arctan(e^{\omega t}) - \frac{\pi}{4}\right] \\
&= \frac{2x_1}{\pi}\arctan(e^{\omega t}) - \frac{x_1}{2}
\end{aligned} \tag{6.109}$$

The particle travels from $x = -x_1/2$ at $t = -\infty$ to $x = x_1/2$ at $t = \infty$.

The matrix elements for the periodic potential are given by

$$\begin{aligned}
\langle\epsilon|x(t)|\epsilon'\rangle &= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} x(t)e^{i(\epsilon-\epsilon')t/\hbar}\,dt \\
&= \frac{x_1}{\pi^2\hbar}\int_{-\infty}^{\infty}\left[\arctan\left(e^{\omega t}\right) - \frac{\pi}{4}\right]e^{i(\epsilon-\epsilon')t/\hbar}\,dt
\end{aligned} \tag{6.110}$$

Now

$$\int_{-\infty}^{\infty}\left[\arctan\left(e^{\omega t}\right)-\frac{\pi}{4}\right]e^{i(\epsilon-\epsilon')t/\hbar}\,dt=\left[\arctan(e^{\omega t})-\frac{\pi}{4}\right]\left[\frac{\hbar}{i(\epsilon-\epsilon')}e^{i(\epsilon-\epsilon')t/\hbar}\right]\Bigg|_{-\infty}^{\infty}$$

$$+\left(\frac{i\hbar\omega}{\epsilon-\epsilon'}\right)\int_{-\infty}^{\infty}\frac{e^{i(\epsilon-\epsilon')t/\hbar}\,e^{\omega t}}{1+e^{2\omega t}}\,dt \qquad (6.111)$$

The integral on the right hand side of Eq. (6.111) can be written as

$$\begin{aligned}\int_{-\infty}^{\infty}\frac{e^{i(\epsilon-\epsilon')t/\hbar}\,e^{\omega t}}{1+e^{2\omega t}}\,dt&=\int_{-\infty}^{\infty}\frac{e^{i(\epsilon-\epsilon')t/\hbar}}{2\cosh(\omega t)}\,dt\\&=\int_{-\infty}^{\infty}\frac{\cos[(\epsilon-\epsilon')t/\hbar]}{2\cosh(\omega t)}\,dt+i\int_{-\infty}^{\infty}\frac{\sin[(\epsilon-\epsilon')t/\hbar]}{2\cosh(\omega t)}\,dt\\&=\int_{0}^{\infty}\frac{\cos[(\epsilon-\epsilon')t/\hbar]}{\cosh(\omega t)}\,dt \qquad (6.112)\end{aligned}$$

Next we use the identity [52, 3.981-3]

$$\int_0^{\infty}\frac{\cos(ax)}{\cosh(\beta x)}\,dx=\frac{\pi}{2\beta}\frac{1}{\cosh\left[a\pi/(2\beta)\right]},\qquad(\mathrm{Re}\,\beta>0,\quad\text{all real } a)$$

to write

$$\int_0^{\infty}\frac{\cos[(\epsilon-\epsilon')t/\hbar]}{\cosh(\omega t)}\,dt=\frac{\pi}{2\omega\cosh\left[\pi(\epsilon-\epsilon')/(2\hbar\omega)\right]} \qquad (6.113)$$

We have

$$\begin{aligned}\left[\arctan(e^{\omega t})-\frac{\pi}{4}\right]\left[\frac{\hbar}{i(\epsilon-\epsilon')}e^{i(\epsilon-\epsilon')t/\hbar}\right]\Bigg|_{-\infty}^{\infty}&=\lim_{t\to\infty}-\frac{i\pi\hbar}{4(\epsilon-\epsilon')}\left[e^{i(\epsilon-\epsilon')t/\hbar}+e^{-i(\epsilon-\epsilon')t/\hbar}\right]\\&=\lim_{t\to\infty}-\frac{i\pi}{2}\,\frac{\cos[(\epsilon-\epsilon')t/\hbar]}{(\epsilon-\epsilon')/\hbar}\\&=0,\quad\text{if }(\epsilon-\epsilon')\neq 0 \qquad (6.114)\end{aligned}$$

From Eqs. (6.110) to (6.114) we obtain

$$\langle\epsilon|x(t)|\epsilon'\rangle=\begin{cases}\dfrac{ix_1}{2\pi(\epsilon-\epsilon')\cosh\left[\pi(\epsilon-\epsilon')/(2\hbar\omega)\right]}, & \text{if } (\epsilon-\epsilon')\neq 0\\ 0, & \text{if } (\epsilon-\epsilon')=0\end{cases} \qquad (6.115)$$

The quantum transition probability, $w(\epsilon)$, is then given by

$$w(\epsilon)=\begin{cases}\dfrac{m\beta x_1^2}{2\pi\hbar}\dfrac{\left[\coth[\epsilon/(2k_BT)]-1\right]}{\epsilon\cosh^2\left[\pi\epsilon/(2\hbar\omega)\right]}, & \text{if } \epsilon\neq 0\\ 0, & \text{if } \epsilon=0\end{cases} \qquad (6.116)$$

so that

$$\check{w}(0) - \check{w}(\lambda - i/2) = \frac{m\beta x_1^2}{2\pi\hbar} \int_{-\infty}^{\infty} \frac{\left[\coth[\epsilon/(2k_BT)] - 1\right]\left[1 - e^{-i(2\lambda - i)\epsilon/(2k_BT)}\right]}{\epsilon \cosh^2\left[\pi\epsilon/(2\hbar\omega)\right]} d\epsilon$$

$$= \frac{m\beta\omega x_1^2}{4\pi^2 k_B T y} \int_{-\infty}^{\infty} \frac{\left[\coth(x) - 1\right]\left[1 - e^{-i(2\lambda - i)x}\right]}{x \cosh^2\left[x/(2y)\right]} dx$$

$$= \Delta R(\lambda, y) \tag{6.117}$$

where $x = \epsilon/(2k_BT)$ and $y = \hbar\omega/(2\pi k_BT)$.

Substituting Eq. (6.69) in Eq. (6.117), noting that $1/[x\cosh^2(x/2y)]$ is an odd function of the variable x, and substituting for $f_o(x)$ using Eq. (6.74) we have

$$\Delta R(\lambda, y) = \frac{m\beta\omega x_1^2}{4\pi^2 k_B T y} \int_{-\infty}^{\infty} \frac{1}{x\cosh^2} \left[f_e(x) + f_o(x)\right] dx$$

$$= \frac{m\beta\omega x_1^2}{4\pi^2 k_B T y} \int_{-\infty}^{\infty} \frac{f_o(x)}{x\cosh^2\left[x/(2y)\right]} dx$$

$$= \frac{2m\beta\omega x_1^2}{\pi^2 k_B T} \frac{1}{8y} \int_{-\infty}^{\infty} \frac{\cosh(x) - \cos(2\lambda x)}{x\sinh(x)\cosh^2\left[x/(2y)\right]} dx \tag{6.118}$$

The dissipation parameter Δ is given by

$$\Delta = \frac{\beta}{k_BT} \int_{-\frac{x_1}{2}}^{\frac{x_1}{2}} p\, dx$$

$$= \frac{\beta}{k_BT} \int_{-\frac{x_1}{2}}^{\frac{x_1}{2}} \sqrt{-2mV(x)}\, dx \tag{6.119}$$

Substituting Eq. (6.105) in Eq. (6.119) we have

$$\Delta = \frac{\beta}{k_BT} \int_{-\frac{x_1}{2}}^{\frac{x_1}{2}} \frac{m\omega x_1}{\pi} \cos\left(\frac{\pi x}{x_1}\right) dx$$

$$= \frac{2m\beta\omega x_1^2}{\pi^2 k_B T} \tag{6.120}$$

Comparing Eqs. (6.118) and (6.120) we see that

$$R(\lambda, y) = \frac{1}{8y} \int_{-\infty}^{\infty} \frac{\cosh(x) - \cos(2\lambda x)}{x\sinh(x)\cosh^2\left[x/(2y)\right]} dx \tag{6.121}$$

Chapter 7

Conclusions

I have attempted to present a clear and detailed exposition of the very abstruse derivations and calculations involved in determining the Kramers escape rate for all values of the damping, in both the classical and semiclassical cases.

Despite its fundamental importance, the original derivation of the VLD escape rate for point particles by Kramers [11] is to some extent imperfectly understood. Indeed Hänggi et al. [2] have remarked that Kramers achieved his result by use of "some subtle almost acrobatic mathematics". Moreover, the difficulties are compounded by the variety of methods of derivation of the energy controlled diffusion equation. In order to overcome this confusion I have given a clear derivation of that equation in Chapter 2. This derivation is based simply on the transformation of the Langevin equation to slow energy and fast configuration variables, and using the concept of multiplicative noise, and the elimination of the fast variable in order to get the energy controlled diffusion equation for VLD. I have also shown how to derive the expression for the mean energy loss per cycle. The advantage of the Langevin equation method is that *inter alia* it shows how the VLD calculation based on multiplicative noise may be generalized to classical spins [62].

In Appendix (2.F) I have compared the motion of a particle, with energy equal to the barrier energy, to the motion of a pendulum which has just enough energy to reach the (inverted) vertical position, so that the slightest fluctuating force may drive the pendulum into the running state which corresponds to the

particle escaping over the barrier of a periodic potential.

To obtain an analytical expression for the VLD escape rate from an isolated well, we start by considering the undamped librational motion of a particle in the well with energy equal to the barrier energy. We then determine the Green's function that governs the diffusion of energy of the particle due to thermal agitation in one cycle of the librational motion in the well. If, due to a thermal fluctuation, the particle returns to the top of the barrier with energy greater than the barrier energy it will escape from the well. The energy distribution of the escaping particles may then be written down as the solution of an integral equation of the Wiener–Hopf type. This equation may be solved subject to appropriate boundary conditions, yielding the classical escape rate in the entire underdamped region in terms of a depopulation factor. A formula for the escape rate valid for all values of the dissipation to the bath is then written down using Mel'nikov's [5, 6, 36] *ad hoc* assumption that the prefactor of this rate is simply the underdamped prefactor multiplied by the Kramers IHD prefactor. I have extensively reviewed the criticism of this assumption by Pollak et al. [18] based on treating the Brownian particle as an entity bilinearly coupled to a string (infinite chain of harmonic oscillators) that plays the role of friction, with the motion of the particle being determined by a generalized Langevin equation.

Turning now to the quantum case, where we confine ourselves to relatively high temperatures, we first treat the IHD quantum rate by recognizing that the multidimensional Kramers rate is simply the TST rate in the complete phase space of the particle plus bath system as described by Langer [17] , Grote and Hynes [2], and Pollak [18, 35]. Thus given an appropriate model for the bath–particle coupling and a suitable generalized Langevin equation, one may simply calculate the IHD rate from harmonic quantum TST. This calculation is accomplished using Pollak's model of a particle governed by a generalized Langevin equation and bilinearly coupled to a bath of harmonic oscillators. In doing this, we have eschewed the path integral methods of Wolynes [8] and Mel'nikov [6], as in general the calculations involving these are less transparent than those of Pollak [35]. Since Pollak's calculations are short on detail, I have described his

method in a manner accessible to the general reader and I have clearly shown each step in the procedure.

As we have seen Mel'nikov [6] developed a scheme to calculate the classical escape rate that is valid in the entire underdamped regime. He extended this approach, based on the solution of a Wiener–Hopf equation, to the calculation of the escape rate in the quantum case. This extension was achieved by incorporating changes due to the energy level quantization near the bottom of the well, the penetration of the potential barrier due to quantum tunneling, and the modification of the kernel of the Wiener–Hopf equation due to the presence of quantum fluctuations, into the scheme he had developed for calculating the classical escape rate. A notable difference between his expression for the quantum escape rate and that in the classical case is that the depopulation factor for the quantum rate, unlike the classical $A(\Delta) = |G^{+}(0)|^2 = \exp\left[\frac{1}{2\pi}\int_{-\infty}^{\infty} \frac{\ln\{1-\exp[-\Delta(\lambda^2+1/4)]\}}{\lambda^2+1/4}\, d\lambda\right]$, does not have a canonical form, so that the matrix elements must be calculated expilcitly for each particular potential.

Again, the derivation of the Mel'nikov expression for the quantum escape rate lacks detail and is almost incomprehensible to the general reader. I have therefore given a step-by-step account of how to obtain Mel'nikov's expression for the escape rate in the underdamped quantum regime. We start by writing the Hamiltonian of a particle interacting with the Boson bath and show how perturbation theory can be used to solve the time-dependent Schrödinger equation pertaining to the noise–perturbed librational motion in the well. We obtain an expression for the time evolution operator in the interaction representation, $\hat{U}_I(t,0)$. $|\psi(t)\rangle_I$, the time evolution of $|j\rangle$, the jth eigenstate of the unperturbed Hamiltonian at time $t = 0$, is then $|\psi(t)\rangle_I = \hat{U}_I(t,0)|j\rangle$. $A_{jf}(t)$, the projection of $|\psi(t)\rangle_I$ onto the eigenstate $|f\rangle$, is given by $A_{jf}(t) = \langle f|\hat{U}_I(t,0)|j\rangle$. The probability that at time t the system will be in the eigenstate $|f\rangle$ of the unperturbed Hamiltonian is $|A_{jf}(t)|^2$. We obtain an expression for $A_{jf}(t)$ which can then be simplified by recalling that since the quantized energy levels in the vicinity of the barrier top are quasi-continuous, the matrix elements of the position operator in the interaction representation are given by the semi-classical formula, Eq. (5.39).

Following Larkin and Ovchinnikov [10] we define the periodic function $A(u)$ given by Eq. (5.42) and derive a closed form expression for $A(u)$ which is used to calculate the Green function. The probability of observing the perturbed system in state $|f\rangle$ at time t averaged over the state of the thermal bath is then given by $W_{jf}(t) = \langle |A_{jf}(t)|^2 \rangle_T$ where $\langle \rangle_T$ denotes thermal averaging. We eventually obtain a closed form expression for W_{jf} which is a function of w_{jf}, the probability of transition from state j to state$f$ calculated in the first-order perturbation approximation (Fermi's Golden Rule). Having obtained the expression for the Green's function we proceed using Mel'nikov's notation and assume that the potential in the vicinity of the barrier top may be represented, as in the classical case, by an inverted parabola. To include the effect of quantum tunneling near the top of the barrier we divide the Green function by the reflection coefficient for the parabolic barrier. Finally, we use the principle of superposition to write an integral equation for the population of escaping particles. This equation is of the Wiener–Hopf type and may be solved to yield the escape rate in the entire underdamped region at temperatures above the critical temperature at which the parabolic approximation to the barrier potential fails. We reiterate that unlike the classical case, where the dynamical prefactor is a function only of the Kramers dissipation parameter Δ, and so has a canonical form, the prefactor is now also a function of the quantum parameter $\hbar\omega_C/(2\pi k_B T)$, where ω_C is the frequency associated with the barrier. The escape rate in the entire range of damping is then determined using the same *ad hoc* assumption as before, namely, the quantum rate is determined by the product of the IHD and underdamped rates.

Finally, I have given a detailed account of the calculations required to determine the escape rate in the underdamped quantum regime for three specific potentials: the cubic potential, the double–well potential, and the periodic potential, which requires in each case the semi-classical matrix elements.

In all cases the escape rate formulae, both classical and quantum, which we have described must be tested against the escape rate rendered by exact numerical solution of the master equation for the given problem. In the classical case this has been accomplished for a variety of potentials [12, Chapter 10]. Thus it may

be inferred that the Mel'nikov approach provides a good approximation to the inverse of the smallest non-vanishing eigenvalue of the governing master equation, which is the Fokker–Planck equation in phase-space for high barriers and for all values of the damping. Regarding the quantum rate, Cleary et al. [57–59] have shown that the escape rate for a periodic cosine potential, calculated by means of a master equation for the Wigner distribution in phase-space, is in good agreement with that calculated using the Mel'nikov formalism.

This concludes our discussion of the classical and quantum treatment of the Kramers turnover problem and its application to the calculation of the lifetime of a particle in a potential well. The work reported in Chapters 3, 4, 5 and 6 of the thesis forms part of a lengthy review article [7] entitled "Longest relaxation time of relaxation processes for classical and quantum Brownian motion in a potential: escape rate theory approach", which has been published in *Advances in Chemical Physics*, Vol. 153, pp. 111–309, 2013. The material in Chapter 2 of the thesis has been reported as part of a second review article [32] entitled "On the Kramers very low damping escape rate for point particles and classical spins", which is to appear in a forthcoming volume of the *Advances in Chemical Physics*.

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