

# ADVANCES IN CHEMICAL PHYSICS

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## INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more and be broadly educated with respect to a large domain of science has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, a field that we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

I. PRIGOGINE  
STUART A. RICE

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# EVOLUTION TIMES OF PROBABILITY DISTRIBUTIONS AND AVERAGES—EXACT SOLUTIONS OF THE KRAMERS' PROBLEM

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## I. INTRODUCTION

The investigation of temporal scales (transition rates) of transition processes in various polystable systems driven by noise is a subject of great theoretical and practical importance in physics (semiconductor [1,2] and Josephson electronics [3], dynamics of magnetization of fine single-domain ferromagnetic particles [4–7]), chemistry and biology (transport of biomolecules in cell compartments and membranes [8], the motion of atoms and side groups in proteins [9], and the stochastic motion along the reaction coordinates of chemical and biochemical reactions [2,4,10–14]).

The first paper that was devoted to the escape problem in the context of the kinetics of chemical reactions and that presented approximate, but complete, analytic results was the paper by Kramers [11]. Kramers considered the mechanism of the transition process as noise-assisted reaction and used the Fokker–Planck equation for the probability density of Brownian particles to obtain several approximate expressions for the desired transition rates. The main approach of the Kramers’ method is the assumption that the probability current over a potential barrier is small and thus constant. This condition is valid only if a potential barrier is sufficiently high in comparison with the noise intensity. For obtaining exact timescales and probability densities, it is necessary to solve the Fokker–Planck equation, which is the main difficulty of the problem of investigating diffusion transition processes.

The Fokker–Planck equation is a partial differential equation. In most cases, its time-dependent solution is not known analytically. Also, if the Fokker–Planck equation has more than one state variable, exact stationary solutions are



very rare. That is why the most simple thing is to approximately obtain time characteristics when analyzing dynamics of diffusion transition processes.

Considering the one-dimensional Brownian diffusion (Brownian motion in the overdamped limit), we note that there are many different time characteristics, defined in different ways (see review [1] and books [2,15,16])—for example, decay time of metastable state or relaxation time to steady state. An often used method of eigenfunction analysis [2,15–18], when the timescale (the relaxation time) is supposed to be equal to an inverse minimal nonzero eigenvalue, is not applicable for the case of a large noise intensity because then higher eigenvalues should be also taken into account. In one-dimensional Fokker–Planck dynamics the moments of the first passage time (FPT) distribution can be calculated exactly, at least expressed by integrals [19]. But during the FPT approach, absorbing boundaries have additionally to be introduced. Both eigenfunction analysis and an FPT approach were widely used for describing different tasks in chemical physics [20–29].

However, most concrete tasks (see examples, listed above) are described by smooth potentials that do not have absorbing boundaries, and thus the moments of FPT may not give correct values of timescales in those cases.

The aim of this chapter is to describe approaches of obtaining exact time characteristics of diffusion stochastic processes (Markov processes) that are in fact a generalization of FPT approach and are based on the definition of characteristic timescale of evolution of an observable as integral relaxation time [5,6,30–41]. These approaches allow us to express the required timescales and to obtain almost exactly the evolution of probability and averages of stochastic processes in really wide range of parameters. We will not present the comparison of these methods because all of them lead to the same result due to the utilization of the same basic definition of the characteristic timescales, but we will describe these approaches in detail and outline their advantages in comparison with the FPT approach.

It should be noted that besides being widely used in the literature definition of characteristic timescale as integral relaxation time, recently “intra-well relaxation time” has been proposed [42] that represents some effective averaging of the MFPT over steady-state probability distribution and therefore gives the slowest timescale of a transition to a steady state, but a description of this approach is not within the scope of the present review.

## **II. INTRODUCTION INTO THE BASIC THEORY OF RANDOM PROCESSES**

### **A. Continuous Markov Processes**

This chapter describes methods of deriving the exact time characteristics of overdamped Brownian diffusion only, which in fact corresponds to continuous

Markov process. In the next few sections we will briefly introduce properties of Markov processes as well as equations describing Markov processes.

If we will consider arbitrary random process, then for this process the conditional probability density  $W(x_n, t_n | x_1, t_1; \dots; x_{n-1}, t_{n-1})$  depends on  $x_1, x_2, \dots, x_{n-1}$ . This leads to definite “temporal connexity” of the process, to existence of strong aftereffect, and, finally, to more precise reflection of peculiarities of real smooth processes. However, mathematical analysis of such processes becomes significantly sophisticated, up to complete impossibility of their deep and detailed analysis. Because of this reason, some “tradeoff” models of random processes are of interest, which are simple in analysis and at the same time correctly and satisfactory describe real processes. Such processes, having wide dissemination and recognition, are Markov processes. Markov process is a mathematical idealization. It utilizes the assumption that noise affecting the system is white (i.e., has constant spectrum for all frequencies). Real processes may be substituted by a Markov process when the spectrum of real noise is much wider than all characteristic frequencies of the system.

A continuous Markov process (also known as a diffusive process) is characterized by the fact that during any small period of time  $\Delta t$  some small (of the order of  $\sqrt{\Delta t}$ ) variation of state takes place. The process  $x(t)$  is called a Markov process if for any ordered  $n$  moments of time  $t_1 < \dots < t < \dots < t_n$ , the  $n$ -dimensional conditional probability density depends only on the last fixed value:

$$W(x_n, t_n | x_1, t_1; \dots; x_{n-1}, t_{n-1}) = W(x_n, t_n | x_{n-1}, t_{n-1}) \quad (2.1)$$

Markov processes are processes without aftereffect. Thus, the  $n$ -dimensional probability density of Markov process may be written as

$$W(x_1, t_1; \dots; x_n, t_n) = W(x_1, t_1) \prod_{i=2}^n W(x_i, t_i | x_{i-1}, t_{i-1}) \quad (2.2)$$

Formula (2.2) contains only one-dimensional probability density  $W(x_1, t_1)$  and the conditional probability density. The conditional probability density of Markov process is also called the “transition probability density” because the present state comprehensively determines the probabilities of next transitions. Characteristic property of Markov process is that the initial one-dimensional probability density and the transition probability density completely determine Markov random process. Therefore, in the following we will often call different temporal characteristics of Markov processes “the transition times,” implying that these characteristics primarily describe change of the evolution of the Markov process from one state to another one.

The transition probability density satisfies the following conditions:

1. The transition probability density is a nonnegative and normalized quantity:

$$W(x, t|x_0, t_0) \geq 0, \quad \int_{-\infty}^{+\infty} W(x, t|x_0, t_0) dx = 1$$

2. The transition probability density becomes Dirac delta function for coinciding moments of time (physically this means small variation of the state during small period of time):

$$\lim_{t \rightarrow t_0} W(x, t|x_0, t_0) = \delta(x - x_0)$$

3. The transition probability density fulfills the Chapman–Kolmogorov (or Smoluchowski) equation:

$$W(x_2, t_2|x_0, t_0) = \int_{-\infty}^{+\infty} W(x_2, t_2|x_1, t_1)W(x_1, t_1|x_0, t_0) dx_1 \quad (2.3)$$

If the initial probability density  $W(x_0, t_0)$  is known and the transition probability density  $W(x, t|x_0, t_0)$  has been obtained, then one can easily get the one-dimensional probability density at arbitrary instant of time:

$$W(x, t) = \int_{-\infty}^{+\infty} W(x_0, t_0)W(x, t|x_0, t_0) dx_0 \quad (2.4)$$

## B. The Langevin and the Fokker–Planck Equations

In the most general case the diffusive Markov process (which in physical interpretation corresponds to Brownian motion in a field of force) is described by simple dynamic equation with noise source:

$$\frac{dx(t)}{dt} = -\frac{d\Phi(x, t)}{h dx} + \xi(t) \quad (2.5)$$

where  $\xi(t)$  may be treated as white Gaussian noise (Langevin force),  $\langle \xi(t) \rangle = 0$ ,  $\langle \xi(t)\xi(t + \tau) \rangle = D(x, t)\delta(\tau)$ ,  $\Phi(x)$  is a potential profile, and  $h$  is viscosity. The equation that has in addition the second time derivative of coordinate multiplied by the mass of a particle is also called the Langevin equation, but that one describes not the Markov process itself, but instead a set of two Markov processes:  $x(t)$  and  $dx(t)/dt$ . Here we restrict our discussion by considering only Markov processes, and we will call Eq. (2.5) the Langevin equation, which in physical interpretation corresponds to overdamped Brownian motion. If the diffusion coefficient  $D(x, t)$  does not depend on  $x$ , then Eq. (2.5) is

called a Langevin equation with an additive noise source. For  $D(x, t)$  depending on  $x$ , one speaks of a Langevin equation with multiplicative noise source. This distinction between additive and multiplicative noise may not be considered very significant because for the one-variable case (2.5), for time-independent drift and diffusion coefficients, and for  $D(x, t) \neq 0$ , the multiplicative noise always becomes an additive noise by a simple transformation of variables [2].

Equation (2.5) is a stochastic differential equation. Some required characteristics of stochastic process may be obtained even from this equation either by cumulant analysis technique [43] or by other methods, presented in detail in Ref. 15. But the most powerful methods of obtaining the required characteristics of stochastic processes are associated with the use of the Fokker–Planck equation for the transition probability density.

The transition probability density of continuous Markov process satisfies to the following partial differential equations ( $W_{x_0}(x, t) \equiv W(x, t|x_0, t_0)$ ):

$$\frac{\partial W_{x_0}(x, t)}{\partial t} = -\frac{\partial}{\partial x} [a(x, t)W_{x_0}(x, t)] + \frac{\partial^2}{\partial x^2} \left[ \frac{D(x, t)}{2} W_{x_0}(x, t) \right] \quad (2.6)$$

$$\frac{\partial W_{x_0}(x, t)}{\partial t_0} = -a(x_0, t_0) \frac{\partial}{\partial x_0} W_{x_0}(x, t) - \frac{D(x_0, t_0)}{2} \frac{\partial^2}{\partial x_0^2} W_{x_0}(x, t) \quad (2.7)$$

Equation (2.6) is called the Fokker–Planck equation (FPE) or forward Kolmogorov equation, because it contains time derivative of final moment of time  $t > t_0$ . This equation is also known as Smoluchowski equation. The second equation (2.7) is called the backward Kolmogorov equation, because it contains the time derivative of the initial moment of time  $t_0 < t$ . These names are associated with the fact that the first equation used Fokker (1914) [44] and Planck (1917) [45] for the description of Brownian motion, but Kolmogorov [46] was the first to give rigorous mathematical argumentation for Eq. (2.6) and he was first to derive Eq. (2.7). The derivation of the FPE may be found, for example, in textbooks [2,15,17,18].

The function  $a(x, t)$  appearing in the FPE is called the drift coefficient, which, due to Stratonovich’s definition of stochastic integral, has the form [2]

$$a(x, t) = -\frac{d\Phi(x, t)}{h dx} - \frac{1}{2} \frac{dD(x, t)}{dx}$$

where the first term is due to deterministic drift, while the second term is called the spurious drift or the noise-induced drift. It stems from the fact that during a change of  $\xi(t)$ , also the coordinate of Markov process  $x(t)$  changes and therefore  $\langle D(x(t), t)\xi(t) \rangle$  is no longer zero. In the case where the diffusion coefficient does not depend on the coordinate, the only deterministic drift term is present in the drift coefficient.

Both partial differential equations (2.6) and (2.7) are linear and of the parabolic type. The solution of these equations should be nonnegative and normalized to unity. Besides, this solution should satisfy the initial condition:

$$W(x, t | x_0, t_0) = \delta(x - x_0) \quad (2.8)$$

For the solution of real tasks, depending on the concrete setup of the problem, either the forward or the backward Kolmogorov equation may be used. If the one-dimensional probability density with known initial distribution deserves needs to be determined, then it is natural to use the forward Kolmogorov equation. Contrariwise, if it is necessary to calculate the distribution of the mean first passage time as a function of initial state  $x_0$ , then one should use the backward Kolmogorov equation. Let us now focus at the time on Eq. (2.6) as much widely used than (2.7) and discuss boundary conditions and methods of solution of this equation.

The solution of Eq. (2.6) for infinite interval and delta-shaped initial distribution (2.8) is called the fundamental solution of Cauchy problem. If the initial value of the Markov process is not fixed, but distributed with the probability density  $W_0(x)$ , then this probability density should be taken as the initial condition:

$$W(x, t_0) = W_0(x) \quad (2.9)$$

In this case the one-dimensional probability density  $W(x, t)$  may be obtained in two different ways.

1. The first way is to obtain the transition probability density by the solution of Eq. (2.6) with the delta-shaped initial distribution and after that averaging it over the initial distribution  $W_0(x)$  [see formula (2.4)].
2. The second way is to obtain the solution of Eq. (2.6) for one-dimensional probability density with the initial distribution (2.9). Indeed, multiplying (2.6) by  $W(x_0, t_0)$  and integrating by  $x_0$  while taking into account (2.4), we get the same Fokker–Planck equation (2.6).

Thus, the one-dimensional probability density of the Markov process fulfills the FPE and, for delta-shaped initial distribution, coincides with the transition probability density.

For obtaining the solution of the Fokker–Planck equation, besides the initial condition one should know boundary conditions. Boundary conditions may be quite diverse and determined by the essence of the task. The reader may find enough complete representation of boundary conditions in Ref. 15.

Let us discuss the four main types of boundary conditions: reflecting, absorbing, periodic, and the so-called natural boundary conditions that are much more widely used than others, especially for computer simulations.

First of all we should mention that the Fokker–Planck equation may be represented as a continuity equation:

$$\frac{\partial W(x, t)}{\partial t} + \frac{\partial G(x, t)}{\partial x} = 0 \quad (2.10)$$

Here  $G(x, t)$  is the probability current:

$$G(x, t) = a(x, t)W(x, t) - \frac{1}{2} \frac{\partial}{\partial x} [D(x, t)W(x, t)] \quad (2.11)$$

*Reflecting Boundary.* The reflecting boundary may be represented as an infinitely high potential wall. Use of the reflecting boundary assumes that there is no probability current behind the boundary. Mathematically, the reflecting boundary condition is written as

$$G(d, t) = 0 \quad (2.12)$$

where  $d$  is the boundary point. Any trajectory of random process is reflected when it contacts the boundary.

*Absorbing Boundary.* The absorbing boundary may be represented as an infinitely deep potential well just behind the boundary. Mathematically, the absorbing boundary condition is written as

$$W(d, t) = 0 \quad (2.13)$$

where  $d$  is the boundary point. Any trajectory of random process is captured when it crosses the absorbing boundary and is not considered in the preboundary interval. If there are one reflecting boundary and one absorbing boundary, then eventually the whole probability will be captured by the absorbing boundary; and if we consider the probability density only in the interval between two boundaries, then the normalization condition is not fulfilled. If, however, we will think that the absorbing boundary is nothing else but an infinitely deep potential well and will take it into account, then total probability density (in preboundary region and behind it) will be normalized.

*Periodic Boundary Condition.* If one considers Markov process in periodic potential, then the condition of periodicity of the probability density may be treated as boundary condition:

$$W(x, t) = W(x + X, t) \quad (2.14)$$

where  $X$  is the period of the potential. The use of this boundary condition is especially useful for computer simulations.

*Natural Boundary Conditions.* If the Markov process is considered in infinite interval, then boundary conditions at  $\pm\infty$  are called natural. There are two possible situations. If the considered potential at  $+\infty$  or  $-\infty$  tends to  $-\infty$  (infinitely deep potential well), then the absorbing boundary should be supposed at  $+\infty$  or  $-\infty$ , respectively. If, however, the considered potential at  $+\infty$  or  $-\infty$  tends to  $+\infty$ , then it is natural to suppose the reflecting boundary at  $+\infty$  or  $-\infty$ , respectively.

In conclusion, we can list several most widely used methods of solution of the FPE [1,2,15–18]:

1. Method of eigenfunction and eigenvalue analysis
2. Method of Laplace transformation
3. Method of characteristic function
4. Method of exchange of independent variables
5. Numerical methods

### III. APPROXIMATE APPROACHES FOR ESCAPE TIME CALCULATION

#### A. The Kramers' Approach and Temperature Dependence of the Prefactor of the Kramers' Time

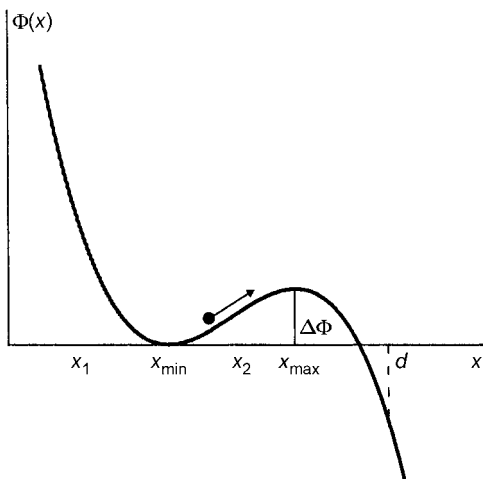
The original work of Kramers [11] stimulated research devoted to calculation of escape rates in different systems driven by noise. Now the problem of calculating escape rates is known as Kramers' problem [1,47].

Let us consider the potential  $\Phi(x)$  describing a metastable state, depicted in Fig. 1.

Initially, an overdamped Brownian particle is located in the potential minimum, say somewhere between  $x_1$  and  $x_2$ . Subjected to noise perturbations, the Brownian particle will, after some time, escape over the potential barrier of the height  $\Delta\Phi$ . It is necessary to obtain the mean decay time of metastable state [inverse of the mean decay time (escape time) is called the escape rate].

To calculate the mean escape time over a potential barrier, let us apply the Fokker–Planck equation, which, for a constant diffusion coefficient  $D = 2kT/h$ , may be also presented in the form

$$\frac{\partial W(x, t)}{\partial t} = \frac{\partial}{\partial x} \left\{ \frac{kT}{h} e^{-\Phi(x)/kT} \frac{\partial}{\partial x} \left[ e^{\Phi(x)/kT} W(x, t) \right] \right\} \quad (3.1)$$



**Figure 1.** Potential describing metastable state.

where we substituted  $a(x) = -\frac{d\Phi(x)}{h dx}$ , where  $k$  is the Boltzmann constant,  $T$  is the temperature, and  $h$  is viscosity.

Let us consider the case when the diffusion coefficient is small, or, more precisely, when the barrier height  $\Delta\Phi$  is much larger than  $kT$ . As it turns out, one can obtain an analytic expression for the mean escape time in this limiting case, since then the probability current  $G$  over the barrier top near  $x_{\max}$  is very small, so the probability density  $W(x, t)$  almost does not vary in time, representing quasi-stationary distribution. For this quasi-stationary state the small probability current  $G$  must be approximately independent of coordinate  $x$  and can be presented in the form

$$G = -\left\{ \frac{kT}{h} e^{-\Phi(x)/kT} \frac{\partial}{\partial x} \left[ e^{\Phi(x)/kT} W(x, t) \right] \right\} \quad (3.2)$$

Integrating (3.2) between  $x_{\min}$  and  $d$ , we obtain

$$G \int_{x_{\min}}^d e^{\Phi(x)/kT} dx = \frac{kT}{h} \left[ e^{\Phi(x_{\min})/kT} W(x_{\min}, t) - e^{\Phi(d)/kT} W(d, t) \right] \quad (3.3)$$

or if we assume that at  $x = d$  the probability density is nearly zero (particles may for instance be taken away that corresponds to absorbing boundary), we can express the probability current by the probability density at  $x = x_{\min}$ , that is,

$$G = \frac{kT}{h} e^{\Phi(x_{\min})/kT} W(x_{\min}, t) / \int_{x_{\min}}^d e^{\Phi(x)/kT} dx \quad (3.4)$$



If the barrier is high, the probability density near  $x_{\min}$  will be given approximately by the stationary distribution:

$$W(x, t) \approx W(x_{\min}, t)e^{-[\Phi(x) - \Phi(x_{\min})]/kT} \quad (3.5)$$

The probability  $P$  to find the particle near  $x_{\min}$  is

$$P = \int_{x_1}^{x_2} W(x, t) dx \approx W(x_{\min}, t)e^{\Phi(x_{\min})/kT} \int_{x_1}^{x_2} e^{-\Phi(x)/kT} dx \quad (3.6)$$

If  $kT$  is small, the probability density becomes very small for  $x$  values appreciably different from  $x_{\min}$ , which means that  $x_1$  and  $x_2$  values need not be specified in detail.

The escape time is introduced as the probability  $P$  divided by the probability current  $G$ . Then, using (3.4) and (3.6), we can obtain the following expression for the escape time:

$$\tau = \frac{h}{kT} \int_{x_1}^{x_2} e^{-\Phi(x)/kT} dx \int_{x_{\min}}^d e^{\Phi(x)/kT} dx \quad (3.7)$$

Whereas the main contribution to the first integral stems from the region around  $x_{\min}$ , the main contribution to the second integral stems from the region around  $x_{\max}$ . We therefore expand  $\Phi(x)$  for the first and the second integrals according to

$$\Phi(x) \approx \Phi(x_{\min}) + \frac{1}{2}\Phi''(x_{\min})(x - x_{\min})^2 \quad (3.8)$$

$$\Phi(x) \approx \Phi(x_{\max}) - \frac{1}{2}|\Phi''(x_{\max})|(x - x_{\max})^2 \quad (3.9)$$

We may then extend the integration boundaries in both integrals to  $\pm\infty$  and thus obtain the well-known Kramers' escape time:

$$\tau = \frac{2\pi h}{\sqrt{\Phi''(x_{\min})|\Phi''(x_{\max})|}} e^{\Delta\Phi/kT} \quad (3.10)$$

where  $\Delta\Phi = \Phi(x_{\max}) - \Phi(x_{\min})$ . As shown by Edholm and Leimar [48], one can improve (3.10) by calculating the integrals (3.7) more accurately—for example, by using the expansion of the potential in (3.8) and (3.9) up to the fourth-order term. One can ask the question: What if the considered potential is such that either  $\Phi''(x_{\max}) = 0$  or  $\Phi''(x_{\min}) = 0$ ? You may see that Kramers' formula (3.10) does not work in this case. This difficulty may be easily overcome because we know how Kramers' formula has been derived: We may substitute the required

TABLE I  
Temperature Dependence of the Prefactor of Escape Time

$\tau_0(kT) \sim$		$\Phi_t(x) \sim$					
		$ x ^{1/2}$	$ x ^{2/3}$	$ x $	$x^2$	$x^4$	$x^\infty$
$\Phi_b(x) \sim$	$ x ^{1/2}$	$(kT)^3$	$(kT)^{5/2}$	$(kT)^2$	$(kT)^{3/2}$	$(kT)^{5/4}$	$(kT)^1$
	$ x ^{2/3}$	$(kT)^{5/2}$	$(kT)^2$	$(kT)^{3/2}$	$(kT)^1$	$(kT)^{3/4}$	$(kT)^{1/2}$
	$ x $	$(kT)^2$	$(kT)^{3/2}$	$(kT)^1$	$(kT)^{1/2}$	$(kT)^{1/4}$	$(kT)^0$
	$x^2$	$(kT)^{3/2}$	$(kT)^1$	$(kT)^{1/2}$	$(kT)^0$	$(kT)^{-1/4}$	$(kT)^{-1/2}$
	$x^4$	$(kT)^{5/4}$	$(kT)^{3/4}$	$(kT)^{1/4}$	$(kT)^{-1/4}$	$(kT)^{-1/2}$	$(kT)^{-3/4}$
	$ x ^\infty$	$(kT)^1$	$(kT)^{1/2}$	$(kT)^0$	$(kT)^{-1/2}$	$(kT)^{-3/4}$	$(kT)^{-1}$

potential into integrals in (3.7) and derive another formula, similar to Kramers' formula:

$$\tau = \tau_0(kT)e^{\Delta\Phi/kT} \quad (3.11)$$

where the prefactor  $\tau_0(kT)$  is a function of temperature and reflects particular shape of the potential. For example, one may easily obtain this formula for a piecewise potential of the fourth order. Formula (3.11) for  $\tau_0(kT) = \text{const}$  is also known as the Arrhenius law.

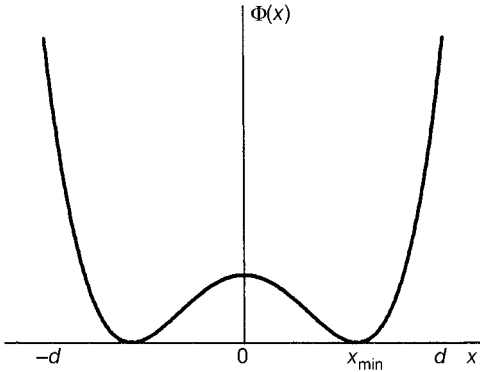
Influence of the shape of potential well and barrier on escape times was studied in detail in paper by Agudov and Malakhov [49].

In Table I, the temperature dependencies of prefactor  $\tau_0(kT)$  for potential barriers and wells of different shape are shown in the limiting case of small temperature (note, that  $|x|^\infty$  means a rectangular potential profile). For the considered functions  $\Phi_b(x)$  and  $\Phi_t(x)$  the dependence  $\tau_0(kT)$  vary from  $\tau_0 \sim (kT)^3$  to  $\tau_0 \sim (kT)^{-1}$ . The functions  $\Phi_b(x)$  and  $\Phi_t(x)$  are, respectively, potentials at the bottom of the well and the top of the barrier. As follows from Table I, the Arrhenius law (3.11) [i.e.  $\tau_0(kT) = \text{const}$ ] occurs only for such forms of potential barrier and well that  $1/p + 1/q = 1$ . This will be the case for a parabolic well and a barrier ( $p = 2, q = 2$ ), and also for a flat well ( $p = \infty$ ) and a triangle barrier ( $q = 1$ ), and, vice versa, for a triangle well ( $p = 1$ ) and a flat barrier ( $q = \infty$ ).

So, if one will compare the temperature dependence of the experimentally obtained escape times of some unknown system with the temperature dependence of Kramers' time presented in Table I, one can make conclusions about potential profile that describes the system.

## B. Eigenvalues as Transition Rates

Another widely used approximate approach for obtaining transition rates is the method of eigenfunction analysis. As an example, let us consider the symmetric bistable potential, depicted in Fig. 2.



**Figure 2.** Bistable symmetric potential.

Let us calculate the relaxation time of particles in this potential (escape time over a barrier) which agrees with inverse of the lowest nonvanishing eigenvalue  $\gamma_1$ . Using the method of eigenfunction analysis as presented in detail in Refs. 2, 15, 17, and 18 we search for the solution of the Fokker–Planck equation in the form

$$W(x, t) = X(x) \cdot T(t) \tag{3.12}$$

where  $X(x)$  and  $T(t)$  are functions of coordinate and time, and we obtain the system of two equations for functions  $X(x)$  and  $T(t)$ :

$$\frac{1}{T(t)} \frac{\partial T(t)}{\partial t} = -\gamma \tag{3.13}$$

$$\left\{ \frac{\partial}{\partial x} \left[ \frac{d\Phi(x)}{hd x} X(x) \right] + \frac{1}{2} \frac{\partial^2}{\partial x^2} [DX(x)] \right\} = -\gamma X(x) \tag{3.14}$$

where again for simplicity  $D = 2kT/h$ . Using the boundary conditions and a delta-shaped initial distribution, we can write the solution of the Fokker–Planck equation in the form

$$W(x, t) = \sum_{n=0}^{\infty} \frac{X_n(x)X_n(x_0)}{W_{st}(x_0)} e^{-\gamma_n(t-t_0)} \tag{3.15}$$

where  $X_0(x) = W_{st}(x)$  and  $\gamma_0 = 0$ . Here we consider only the case where the steady-state probability distribution does exist:  $W_{st}(x) \neq 0$ , and thus we should suppose reflecting boundary conditions  $G(\pm d) = 0$ . Analyzing expression (3.15) and taking into account that the eigenvalues  $\gamma_n$  represent a set such that  $\gamma_1 < \gamma_2 < \dots < \gamma_n$ , we can see that the exponent with minimal eigenvalue will

decay slower than the others and will thus reflect the largest timescale of decay which equals the inversed minimal nonzero eigenvalue.

So, Eq. (3.14) with boundary conditions is the equation for eigenfunction  $X_n(x)$  of the  $n$ th order. For  $X_0(x)$ , Eq. (3.14) will be an equation for stationary probability distribution with zero eigenvalue  $\gamma_0 = 0$ , and for  $X_1(x)$  the equation will have the following form:

$$\frac{\partial}{\partial x} \left\{ \frac{kT}{h} e^{-\Phi(x)/kT} \frac{\partial}{\partial x} \left[ e^{\Phi(x)/kT} X_1(x) \right] \right\} = -\gamma_1 X_1(x) \quad (3.16)$$

Integrating Eq. (3.16) and taking into account the reflecting boundary conditions (probability current is equal to zero at the points  $\pm d$ ), we get

$$\frac{kT}{h} \frac{\partial}{\partial x} e^{\Phi(x)/kT} X_1(x) = -\gamma_1 e^{\Phi(x)/kT} \int_x^d X_1(z) dz \quad (3.17)$$

Integrating this equation once again, the following integral equation for eigenfunction  $X_1(x)$  may be obtained:

$$X_1(x) = e^{-\Phi(x)/kT} \left[ e^{\Phi(d)/kT} X_1(d) - \frac{h\gamma_1}{kT} \int_x^d e^{\Phi(y)/kT} dy \int_y^d X_1(z) dz \right] \quad (3.18)$$

The eigenfunction  $X_1(x)$  belonging to the lowest nonvanishing eigenvalue must be an odd function for the bistable potential, that is,  $X_1(0) = 0$ . The integral equation (3.18) together with reflecting boundary conditions determine the eigenfunction  $X_1(x)$  and the eigenvalue  $\gamma_1$ . We may apply an iteration procedure that is based on the assumption that the noise intensity is small compared to the barrier height (this iteration procedure is described in the book by Risken [2]), and we obtain the following expression for the required eigenvalue in the first-order approximation:

$$\gamma_1 = (kT/h) \left/ \int_0^d e^{\Phi(y)/kT} dy \int_y^d e^{-\Phi(z)/kT} dz \right. \quad (3.19)$$

For a small noise intensity, the double integral may be evaluated analytically and finally we get the following expression for the escape time (inverse of the eigenvalue  $\gamma_1$ ) of the considered bistable potential:

$$\tau_b = \frac{\pi h}{\sqrt{|\Phi''(x_{\min})| |\Phi''(0)|}} e^{\Delta\Phi/kT} \quad (3.20)$$

The obtained escape time  $\tau_b$  for the bistable potential is two times smaller than the Kramers' time (3.10): Because we have considered transition over the barrier top  $x = 0$ , we have obtained only a half.

#### IV. THE FIRST PASSAGE TIME APPROACH

The first approach to obtain exact time characteristics of Markov processes with nonlinear drift coefficients was proposed in 1933 by Pontryagin, Andronov, and Vitt [19]. This approach allows one to obtain exact values of moments of the first passage time for arbitrary time constant potentials and arbitrary noise intensity; moreover, the diffusion coefficient may be nonlinear function of coordinate. The only disadvantage of this method is that it requires an artificial introducing of absorbing boundaries, which change the process of diffusion in real smooth potentials.

##### A. Probability to Reach a Boundary by One-Dimensional Markov Processes

Let continuous one-dimensional Markov process  $x(t)$  at initial instant of time  $t = 0$  have a fixed value  $x(0) = x_0$  within the interval  $(c, d)$ ; that is, the initial probability density is the delta function:

$$W(x, 0) = \delta(x - x_0), \quad x_0 \in (c, d)$$

It is necessary to find the probability  $Q(t, x_0)$  that a random process, having initial value  $x_0$ , will reach during the time  $t > 0$  the boundaries of the interval  $(c, d)$ ; that is, it will reach either boundary  $c$  or  $d$ :  $Q(t, x_0) = \int_{-\infty}^c W(x, t) dx + \int_d^{+\infty} W(x, t) dx$ .

Instead of the probability to reach boundaries, one can be interested in the probability

$$P(t, x_0) = 1 - Q(t, x_0)$$

of nonreaching the boundaries  $c$  and  $d$  by Markov process, having initial value  $x_0$ . In other words,

$$P(t, x_0) = P\{c < x(t) < d, 0 < t < T\}, \quad x_0 \in (c, d)$$

where  $T = T(c, x_0, d)$  is a random instant of the first passage time of boundaries  $c$  or  $d$ .

We will not present here how to derive the first Pontryagin's equation for the probability  $Q(t, x_0)$  or  $P(t, x_0)$ . The interested reader can see it in Ref. 19 or in Refs. 15 and 18. We only mention that the first Pontryagin's equation may be obtained either via transformation of the backward Kolmogorov equation (2.7) or by simple decomposition of the probability  $P(t, x_0)$  into Taylor expansion in the vicinity of  $x_0$  at different moments  $\tau$  and  $t + \tau$ , some transformations and limiting transition to  $\tau \rightarrow 0$  [18].

The first Pontryagin's equation looks like

$$\frac{\partial Q(t, x_0)}{\partial t} = a(x_0) \frac{\partial Q(t, x_0)}{\partial x_0} + \frac{D(x_0)}{2} \frac{\partial^2 Q(t, x_0)}{\partial x_0^2} \quad (4.1)$$

Let us point out the initial and boundary conditions of Eq. (4.1). It is obvious that for all  $x_0 \in (c, d)$  the probability to reach boundary at  $t = 0$  is equal to zero:

$$Q(0, x_0) = 0, \quad c < x_0 < d \quad (4.2)$$

At the boundaries of the interval (i.e., for  $x_0 = c$  and  $x_0 = d$ ) the probability to reach boundaries for any instant of time  $t$  is equal to unity:

$$Q(t, c) = Q(t, d) = 1 \quad (4.3)$$

This means that for  $x_0 = c, x_0 = d$  the boundary will be surely reached already at  $t = 0$ . Besides these conditions, usually one more condition must be fulfilled:

$$\lim_{t \rightarrow \infty} Q(t, x_0) = 1, \quad c \leq x_0 \leq d$$

expressing the fact that the probability to pass boundaries somewhere for a long enough time is equal to unity.

The compulsory fulfillment of conditions (4.2) and (4.3) physically follows from the fact that a one-dimensional Markov process is nondifferentiable; that is, the derivative of Markov process has an infinite variance (instantaneous speed is an infinitely high). However, the particle with the probability equals unity drifts for the finite time to the finite distance. That is why the particle velocity changes its sign during the time, and the motion occurs in an opposite directions. If the particle is located at some finite distance from the boundary, it cannot reach the boundary in a trice—the condition (4.2). On the contrary, if the particle is located near a boundary, then it necessarily crosses the boundary—the condition (4.3).

Let us mention that we may analogically solve the tasks regarding the probability to cross either only the left boundary  $c$  or the right one  $d$  or regarding the probability to not leave the considered interval  $[c, d]$ . In this case, Eq. (4.1) is valid, and only boundary conditions should be changed.

Also, one can be interested in the probability of reaching the boundary by a Markov process, having random initial distribution. In this case, one should first solve the task with the fixed initial value  $x_0$ ; and after that, averaging for all possible values of  $x_0$  should be performed. If an initial value  $x_0$  is distributed in the interval  $(c_1, d_1) \supset (c, d)$  with the probability  $W_0(x_0)$ , then, following the theorem about the sum of probabilities, the complete probability to reach

boundaries  $c$  and  $d$  is defined by the expression

$$Q(t) = \int_c^d Q(t, x_0) W_0(x_0) dx_0 + P\{c_1 < x_0 < c, t = 0\} + P\{d < x_0 < d_1, t = 0\} \tag{4.4}$$

**B. Moments of the First Passage Time**

One can obtain an exact analytic solution to the first Pontryagin equation only in a few simple cases. That is why in practice one is restricted by the calculation of moments of the first passage time of absorbing boundaries, and, in particular, by the mean and the variance of the first passage time.

If the probability density  $w_T(t, x_0)$  of the first passage time of boundaries  $c$  and  $d$  exists, then by the definition [18] we obtain

$$w_T(t, x_0) = \frac{\partial}{\partial t} Q(t, x_0) = -\frac{\partial}{\partial t} P(t, x_0) \tag{4.5}$$

Taking a derivative from Eq. (4.1), we note that  $w_T(t, x_0)$  fulfills the following equation:

$$\frac{\partial w_T(t, x_0)}{\partial t} = a(x_0) \frac{\partial w_T(t, x_0)}{\partial x_0} + \frac{D(x_0)}{2} \frac{\partial^2 w_T(t, x_0)}{\partial x_0^2} \tag{4.6}$$

with initial and boundary conditions

$$\begin{aligned} w_T(0, x_0) &= 0, & c < x_0 < d \\ w_T(t, c) &= w_T(t, d) = \delta(t) \end{aligned} \tag{4.7}$$

for the case of both absorbing boundaries and

$$w_T(t, d) = \delta(t), \quad \left. \frac{\partial w_T(t, x_0)}{\partial x_0} \right|_{x_0=c} = 0 \tag{4.8}$$

for the case of one absorbing (at the point  $d$ ) and one reflecting (at the point  $c$ ) boundaries.

The task to obtain the solution to Eq. (4.6) with the above-mentioned initial and boundary conditions is mathematically quite difficult even for simplest potentials  $\Phi(x_0)$ .

Moments of the first passage time may be expressed from the probability density  $w_T(t, x_0)$  as

$$T_n = T_n(c, x_0, d) = \int_0^\infty t^n w_T(t, x_0) dt, \quad n = 1, 2, 3, \dots \tag{4.9}$$

Multiplying both sides of Eq. (4.6) by  $e^{i\Omega t}$  and integrating it for  $t$  going from 0 to  $\infty$ , we obtain the following differential equation for the characteristic function  $\Theta(i\Omega, x_0)$ :

$$-i\Omega\Theta(i\Omega, x_0) = a(x_0)\frac{\partial\Theta(i\Omega, x_0)}{\partial x_0} + \frac{D(x_0)}{2}\frac{\partial^2\Theta(i\Omega, x_0)}{\partial x_0^2} \quad (4.10)$$

where  $\Theta(i\Omega, x_0) = \int_0^\infty e^{i\Omega t} w_T(t, x_0) dt$ .

Equation (4.10) allows to find one-dimensional moments of the first passage time. For this purpose let us use the well-known representation of the characteristic function as the set of moments:

$$\Theta(i\Omega, x_0) = 1 + \sum_{n=1}^{\infty} \frac{(i\Omega)^n}{n!} T_n(c, x_0, d) \quad (4.11)$$

Substituting (4.11) and its derivatives into (4.10) and equating terms of the same order of  $i\Omega$ , we obtain the chain of linear differential equations of the second order with variable coefficients:

$$\frac{D(x_0)}{2} \frac{d^2 T_n(c, x_0, d)}{dx_0^2} + a(x_0) \frac{dT_n(c, x_0, d)}{dx_0} = -n \cdot T_{n-1}(c, x_0, d) \quad (4.12)$$

Equations (4.11) allow us to sequentially find moments of the first passage time for  $n = 1, 2, 3, \dots$  ( $T_0 = 1$ ). These equations should be solved at the corresponding boundary conditions, and by physical implication all moments  $T_n(c, x_0, d)$  must have nonnegative values,  $T_n(c, x_0, d) \geq 0$ .

Boundary conditions for Eq. (4.12) may be obtained from the corresponding boundary conditions (4.7) and (4.8) of Eqs. (4.1) and (4.6). If boundaries  $c$  and  $d$  are absorbing, we obtain the following from Eq. (4.7):

$$T(c, c, d) = T(c, d, d) = 0 \quad (4.13)$$

If one boundary, say  $c$ , is reflecting, then one can obtain the following from Eq. (4.8):

$$T(c, d, d) = 0, \quad \left. \frac{\partial T(c, x_0, d)}{\partial x_0} \right|_{x_0=c} = 0 \quad (4.14)$$

If we start solving Eq. (4.12) from  $n = 1$ , then further moments  $T_n(c, x_0, d)$  will be expressed from previous moments  $T_m(c, x_0, d)$ . In particular, for  $n = 1, 2$  we obtain

$$\frac{D(x_0)}{2} \frac{d^2 T_1(c, x_0, d)}{dx_0^2} + a(x_0) \frac{dT_1(c, x_0, d)}{dx_0} + 1 = 0 \quad (4.15)$$

$$\frac{D(x_0)}{2} \frac{d^2 T_2(c, x_0, d)}{dx_0^2} + a(x_0) \frac{dT_2(c, x_0, d)}{dx_0} + 2T_1(c, x_0, d) = 0 \quad (4.16)$$



Equation (4.15) was first obtained by Pontryagin and is called the second Pontryagin equation.

The system of equations (4.12) may be easily solved. Indeed, making substitution  $Z = dT_n(c, x_0, d)/dx_0$  each equation may be transformed in the first-order differential equation:

$$\frac{D(x_0)}{2} \frac{dZ}{dx_0} + a(x_0)Z = -n \cdot T_{n-1}(c, x_0, d) \tag{4.17}$$

The solution of (4.17) may be written by quadratures:

$$Z(x_0) = \frac{dT_n(c, x_0, d)}{dx_0} = e^{\varphi(x_0)} \left[ A - \int_c^{x_0} \frac{2nT_{n-1}(c, y, d)}{D(y)} e^{-\varphi(y)} dy \right] \tag{4.18}$$

where  $\varphi(y) = \int \frac{2a(y)}{D(y)} dy$  and  $A$  is an arbitrary constant, determined from boundary conditions.

When one boundary is reflecting (e.g.,  $c$ ) and another one is absorbing (e.g.,  $d$ ), then from (4.18) and boundary conditions (4.14) we obtain

$$T_n(c, x_0, d) = 2n \int_{x_0}^d e^{\varphi(x)} \int_c^x \frac{T_{n-1}(c, y, d)}{D(y)} e^{-\varphi(y)} dy dx \tag{4.19}$$

Because  $dT_n(c, x_0, d)/dx_0 < 0$  for any  $c < x_0 < d$  and  $dT_n(c, x_0, d)/dx_0 = 0$  for  $x_0 = c$ , and, as follows from (4.12),  $d^2T_n(c, x_0, d)/dx_0^2 < 0$  for  $x_0 = c$ , the maximal value of the function  $T_n(c, x_0, d)$  is reached at  $x_0 = c$ .

For the case when both boundaries are absorbing, the required moments of the first passage time have more complicated form [18].

When the initial probability distribution is not a delta function, but some arbitrary function  $W_0(x_0)$  where  $x_0 \in (c, d)$ , then it is possible to calculate moments of the first passage time, averaged over initial probability distribution:

$$T_n(c, d) = \int_c^d T_n(c, x_0, d) W_0(x_0) dx_0 \tag{4.20}$$

We note that recently the equivalence between the MFPT and Kramers' time was demonstrated in Ref. 50.

## V. GENERALIZATIONS OF THE FIRST PASSAGE TIME APPROACH

### A. Moments of Transition Time

As discussed in the previous section, the first passage time approach requires an artificial introduction of absorbing boundaries; therefore, the steady-state

probability distribution in such systems does not exist, because eventually all particles will be absorbed by boundaries. But in the large number of real systems the steady-state distributions do exist, and in experiments there are usually measured stationary processes; thus, different steady-state characteristics, such as correlation functions, spectra, and different averages, are of interest.

The idea of calculating the characteristic timescale of the observable evolution as an integral under its curve (when the characteristic timescale is taken as the length of the rectangle with the equal square) was adopted a long time ago for calculation of correlation times and width of spectral densities (see, e.g., Ref. 51). This allowed to obtain analytic expressions of linewidths [51] of different types of oscillators that were in general not described by the Fokker–Planck equation. Later, this definition of timescales of different observables was widely used in the literature [5,6,14,24,30–41,52,53]. In the following we will refer to any such defined characteristic timescale as “integral relaxation time” [see Refs. 5 and 6], but considering concrete examples we will also specify the relation to the concrete observable (e.g., the correlation time).

However, mathematical evidence of such a definition of characteristic timescale has been understood only recently in connection with optimal estimates [54]. As an example we will consider evolution of the probability, but the consideration may be performed for any observable. We will speak about the transition time implying that it describes change of the evolution of the transition probability from one state to another one.

*The Transition Probability.* Suppose we have a Brownian particle located at an initial instant of time at the point  $x_0$ , which corresponds to initial delta-shaped probability distribution. It is necessary to find the probability  $Q_{c,d}(t, x_0) = Q(t, x_0)$  of transition of the Brownian particle from the point  $c \leq x_0 \leq d$  outside of the considered interval  $(c, d)$  during the time  $t > 0$ :  $Q(t, x_0) = \int_{-\infty}^c W(x, t) dx + \int_d^{+\infty} W(x, t) dx$ . The considered transition probability  $Q(t, x_0)$  is different from the well-known probability to pass an absorbing boundary. Here we suppose that  $c$  and  $d$  are arbitrary chosen points of an arbitrary potential profile  $\Phi(x)$ , and boundary conditions at these points may be arbitrary:  $W(c, t) \geq 0$ ,  $W(d, t) \geq 0$ .

The main distinction between the transition probability and the probability to pass the absorbing boundary is the possibility for a Brownian particle to come back in the considered interval  $(c, d)$  after crossing boundary points (see, e.g., Ref. 55). This possibility may lead to a situation where despite the fact that a Brownian particle has already crossed points  $c$  or  $d$ , at the time  $t \rightarrow \infty$  this particle may be located within the interval  $(c, d)$ . Thus, the set of transition events may be not complete; that is, at the time  $t \rightarrow \infty$  the probability  $Q(t, x_0)$  may tend to the constant, smaller than unity:  $\lim_{t \rightarrow \infty} Q(t, x_0) < 1$ , as in the case

where there is a steady-state distribution for the probability density  $\lim_{t \rightarrow \infty} W(x, t) = W_{st}(x) \neq 0$ . Alternatively, one can be interested in the probability of a Brownian particle to be found at the moment  $t$  in the considered interval  $(c, d)$   $P(t, x_0) = 1 - Q(t, x_0)$ . In the following, for simplicity we will refer to  $Q(t, x_0)$  as decay probability and will refer to  $P(t, x_0)$  as survival probability.

*Moments of Transition Time.* Consider the probability  $Q(t, x_0)$  of a Brownian particle, located at the point  $x_0$  within the interval  $(c, d)$ , to be at the time  $t > 0$  outside of the considered interval. We can decompose this probability to the set of moments. On the other hand, if we know all moments, we can in some cases construct a probability as the set of moments. Thus, analogically to moments of the first passage time we can introduce moments of transition time  $\vartheta_n(c, x_0, d)$  taking into account that the set of transition events may be not complete, that is,  $\lim_{t \rightarrow \infty} Q(t, x_0) < 1$ :

$$\vartheta_n(c, x_0, d) = \langle t^n \rangle = \frac{\int_0^\infty t^n \frac{\partial Q(t, x_0)}{\partial t} dt}{\int_0^\infty \frac{\partial Q(t, x_0)}{\partial t} dt} = \frac{\int_0^\infty t^n \frac{\partial Q(t, x_0)}{\partial t} dt}{Q(\infty, x_0) - Q(0, x_0)} \quad (5.1)$$

Here we can formally denote the derivative of the probability divided by the factor of normalization as  $w_\tau(t, x_0)$  and thus introduce the probability density of transition time  $w_{c,d}(t, x_0) = w_\tau(t, x_0)$  in the following way:

$$w_\tau(t, x_0) = \frac{\partial Q(t, x_0)}{\partial t} \frac{1}{[Q(\infty, x_0) - Q(0, x_0)]} \quad (5.2)$$

It is easy to check that the normalization condition is satisfied at such a definition,  $\int_0^\infty w_\tau(t, x_0) dt = 1$ . The condition of nonnegativity of the probability density  $w_\tau(t, x_0) \geq 0$  is, actually, the monotonic condition of the probability  $Q(t, x_0)$ . In the case where  $c$  and  $d$  are absorbing boundaries the probability density of transition time coincides with the probability density of the first passage time  $w_T(t, x_0)$ :

$$w_T(t, x_0) = \frac{\partial Q(t, x_0)}{\partial t} \quad (5.3)$$

Here we distinguish  $w_\tau(t, x_0)$  and  $w_T(t, x_0)$  by different indexes  $\tau$  and  $T$  to note again that there are two different functions and  $w_\tau(t, x_0) = w_T(t, x_0)$  in the case of absorbing boundaries only. In this context, the moments of the FPT are

$$T_n(c, x_0, d) = \langle t^n \rangle = \int_0^\infty t^n \frac{\partial Q(t, x_0)}{\partial t} dt = \int_0^\infty t^n w_T(t, x_0) dt$$

Integrating (5.1) by parts, one can obtain the expression for the mean transition time (MTT)  $\vartheta_1(c, x_0, d) = \langle t \rangle$ :

$$\vartheta_1(c, x_0, d) = \frac{\int_0^\infty [Q(\infty, x_0) - Q(t, x_0)] dt}{Q(\infty, x_0) - Q(0, x_0)} \quad (5.4)$$

This definition completely coincides with the characteristic time of the probability evolution introduced in Ref. 32 from the geometrical consideration, when the characteristic scale of the evolution time was defined as the length of rectangle with the equal square, and the same definition was later used in Refs. 33–35. Similar ideology for the definition of the mean transition time was used in Ref. 30. Analogically to the MTT (5.4), the mean square  $\vartheta_2(c, x_0, d) = \langle t^2 \rangle$  of the transition time may also be defined as

$$\vartheta_2(c, x_0, d) = 2 \frac{\int_0^\infty \left( \int_t^\infty [Q(\infty, x_0) - Q(\tau, x_0)] d\tau \right) dt}{Q(\infty, x_0) - Q(0, x_0)} \quad (5.5)$$

Note that previously known time characteristics, such as moments of FPT, decay time of metastable state, or relaxation time to steady state, follow from moments of transition time if the concrete potential is assumed: a potential with an absorbing boundary, a potential describing a metastable state or a potential within which a nonzero steady-state distribution may exist, respectively. Besides, such a general representation of moments  $\vartheta_n(c, x_0, d)$  (5.1) gives us an opportunity to apply the approach proposed by Malakhov [34,35] for obtaining the mean transition time and easily extend it to obtain any moments of transition time in arbitrary potentials, so  $\vartheta_n(c, x_0, d)$  may be expressed by quadratures as it is known for moments of FPT.

Alternatively, the definition of the mean transition time (5.4) may be obtained on the basis of consideration of optimal estimates [54]. Let us define the transition time  $\vartheta$  as the interval between moments of initial state of the system and abrupt change of the function, approximating the evolution of its probability  $Q(t, x_0)$  with minimal error. As an approximation consider the following function:  $\psi(t, x_0, \vartheta) = a_0(x_0) + a_1(x_0)[1(t) - 1(t - \vartheta(x_0))]$ . In the following we will drop an argument of  $a_0$ ,  $a_1$ , and the relaxation time  $\vartheta$ , assuming their dependence on coordinates of the considered interval  $c$  and  $d$  and on initial coordinate  $x_0$ . Optimal values of parameters of such approximating function satisfy the condition of minimum of functional:

$$U = \int_0^{t_N} [Q(t, x_0) - \psi(t, x_0, \vartheta)]^2 dt \quad (5.6)$$

where  $t_N$  is the observation time of the process. As it is known, a necessary condition of extremum of parameters  $a_0$ ,  $a_1$ , and  $\vartheta$  has the form

$$\frac{\partial U}{\partial a_0} = 0, \quad \frac{\partial U}{\partial a_1} = 0, \quad \frac{\partial U}{\partial \vartheta} = 0 \quad (5.7)$$

It follows from the first condition that

$$\int_0^{t_N} \{Q(t, x_0) - a_0 - a_1[1(t) - 1(t - \vartheta)]\} dt = 0$$

Transform this condition to the form

$$\int_0^{t_N} Q(t, x_0) dt = a_0 t_N + a_1 \vartheta \quad (5.8)$$

The condition of minimum of functional  $U$  on  $\vartheta$  may be written as

$$Q(\vartheta, x_0) = a_0 + a_1/2 \quad (5.9)$$

Analogically, the condition of minimum of functional  $U$  on  $a_1$  is

$$\int_0^{\vartheta} Q(t, x_0) dt = (a_0 + a_1)\vartheta \quad (5.10)$$

The presented estimate is nonlinear, but this does not lead to significant troubles in processing the results of experiments. An increase of the observation time  $t_N$  allows us to adjust values of estimates, and slight changes of amplitudes  $a_0$  and  $a_1$  and a shift of the moment of abrupt change  $\vartheta$  of the approximating function are observed.

When considering analytic description, asymptotically optimal estimates are of importance. Asymptotically optimal estimates assume infinite duration of the observation process for  $t_N \rightarrow \infty$ . For these estimates an additional condition for amplitude of a leap is superimposed: The amplitude is assumed to be equal to the difference between asymptotic and initial values of approximating function  $a_1 = Q(0, x_0) - Q(\infty, x_0)$ . The only moment of abrupt change of the function should be determined. In such an approach the required quantity may be obtained by the solution of a system of linear equations and represents a linear estimate of a parameter of the evolution of the process.

To get an analytical solution of the system of equations (5.8), (5.9), and (5.10), let us consider them in the asymptotic case  $t_N \rightarrow \infty$ . Here we should take into account that the limit of  $a_0$  for  $t_N \rightarrow \infty$  is  $Q(\infty, x_0)$ . In asymptotic form for  $t_N \rightarrow \infty$ , Eq. (5.8) is

$$\vartheta = \frac{\int_0^{\infty} [Q(\infty, x_0) - Q(t, x_0)] dt}{Q(\infty, x_0) - Q(0, x_0)} \quad (5.11)$$

Therefore, we have again arrived at (5.4), which, as follows from the above, is an asymptotically optimal estimate. From the expression (5.9), another well-known

asymptotically optimal estimate immediately follows:

$$Q(\vartheta, x_0) = (Q(0, x_0) + Q(\infty, x_0))/2 \quad (5.12)$$

but this estimate gives much less analytic expressions than the previous one. It should be noted, that asymptotically optimal estimates are correct only for monotonic evolutions of observables.

In many practical cases the MTT is a more adequate characteristic than the MFPT. As an example (for details see the end of Section V.E.5), if we consider the decay of a metastable state as a transition over a barrier top and we compare mean decay time obtained using the notion of integral relaxation time (case of a smooth potential without absorbing boundary) and the MFPT of the absorbing boundary located at the barrier top, we obtain a twofold difference between these time characteristics even in the case of a high potential barrier in comparison with the noise intensity (5.120). This is due to the fact that the MFPT does not take into account the backward probability current and therefore is sensitive to the location of an absorbing boundary. For the considered situation, if we will move the boundary point down from the barrier top, the MFPT will increase up to two times and tend to reach a value of the corresponding mean decay time which is less sensitive to the location of the boundary point over a barrier top. Such weak dependence of the mean decay time from the location of the boundary point at the barrier top or further is intuitively obvious: Much more time should be spent to reach the barrier top (activated escape) than to move down from the barrier top (dynamic motion). Another important example is noise delayed decay (NDD) of unstable states (see below Fig. 4, case  $N$  without potential barrier). It was assumed before that the fluctuations can only accelerate the decay of unstable states [56]. However, in Refs. 57–69 it was found that there are systems that may drop out of these rules. In particular, in the systems considered in Refs. 57–69 the fluctuations can considerably increase the decay time of unstable and metastable states. This effect may be studied via MFPT (see, e.g., Ref. 64), but this characteristic significantly underestimates it [69]. As demonstrated in Ref. 69, the NDD phenomenon appears due to the action of two mechanisms. One of them is caused by the nonlinearity of the potential profile describing the unstable state within the considered interval. This mechanism is responsible for the resonant dependence of MFPT on the noise intensity. Another mechanism is caused by inverse probability current directed into the considered interval. The latter cannot be accounted for by the MFPT method. In Refs. 34 and 69, asymptotic expressions of the decay time of unstable states were obtained for small noise intensities, and it has been demonstrated that if the first derivative of the potential is negative (for the potential oriented as depicted in Fig. 4), the fluctuations acting in dynamic systems always increase the decay time of the unstable state in the limit of a small noise intensity.

Finally, for additional support of the correctness and practical usefulness of the above-presented definition of moments of transition time, we would like to mention the duality of MTT and MFPT. If one considers the symmetric potential, such that  $\Phi(-\infty) = \Phi(+\infty) = +\infty$ , and obtains moments of transition time over the point of symmetry, one will see that they absolutely coincide with the corresponding moments of the first passage time if the absorbing boundary is located at the point of symmetry as well (this is what we call “the principle of conformity” [70]). Therefore, it follows that the probability density (5.2) coincides with the probability density of the first passage time:  $w_\tau(t, x_0) = w_T(t, x_0)$ , but one can easily ensure that it is so, solving the FPE numerically. The proof of the principle of conformity is given in the appendix.

In the forthcoming sections we will consider several methods that have been used to derive different integral relaxation times for cases where both drift and diffusion coefficients do not depend on time, ranging from the considered mean transition time and to correlation times and time scales of evolution of different averages.

## B. The Effective Eigenvalue and Correlation Time

In this section we consider the notion of an effective eigenvalue and the approach for calculation of correlation time by Risken and Jung [2,31]. A similar approach has been used for the calculation of integral relaxation time of magnetization by Garanin et al. [5,6].

Following Ref. 2 the correlation function of a stationary process  $K(t)$  may be presented in the following form:

$$K(t) = K(0) \sum_{n=1}^{\infty} V_n \exp(-\lambda_n |t|) \quad (5.13)$$

where matrix elements  $V_n$  are positive and their sum is one (for details see Ref. 2, Section 12.3):

$$\sum_{n=1}^{\infty} V_n = 1$$

The required correlation function (5.13) may be approximated by the single exponential function

$$K_{\text{eff}}(t) = K_2 \exp(-\lambda_{\text{eff}} |t|), \quad \frac{1}{\lambda_{\text{eff}}} = \sum_{n=1}^{\infty} \frac{V_n}{\lambda_n} \quad (5.14)$$

which has the same area and the same value at  $t = 0$  as the exact expression. The same basic idea was used in Refs. 5 and 6 for the calculation of integral relaxation times of magnetization. The behavior of  $\lambda_{\text{eff}}$  was studied in Refs. 71 and 72.

The correlation time, given by  $1/\lambda_{\text{eff}}$ , may be calculated exactly in the following way. Let us define the normalized correlation function of a stationary process by

$$\begin{aligned}\Psi(t) &= K(t)/K(0) \\ K(t) &= \langle \Delta r(x(t')) \Delta r(x(t' + t)) \rangle \\ \Delta r(x(t')) &= r(x(t')) - \langle r \rangle\end{aligned}\tag{5.15}$$

The subtraction of the average  $\langle r \rangle$  guarantees that the normalized correlation function  $\Psi(t)$  vanishes for large times. Obviously,  $\Psi(t)$  is normalized according to  $\Psi(0) = 1$ . A correlation time may be defined by

$$\tau_c = \int_0^\infty \Psi(t) dt\tag{5.16}$$

For an exponential dependence we then have  $\Psi(t) = \exp(-t/\tau_c)$ . For the considered one-dimensional Markov process the correlation time may be found in the following way. Alternatively to (5.15) the correlation function may be written in the form

$$K(t) = \int \Delta r(x) \tilde{W}(x, t) dx\tag{5.17}$$

where  $\tilde{W}(x, t)$  obeys the FPE (2.6) with the initial condition

$$\tilde{W}(x, 0) = \Delta r(x) W_{st}(x)\tag{5.18}$$

where  $W_{st}(x) = \frac{N}{D(x)} \exp\left\{\int \frac{2a(x)}{D(x)} dx\right\}$  is the stationary probability distribution. Introducing

$$\rho(x) = \int_0^\infty \tilde{W}(x, t) dt\tag{5.19}$$

Eq. (5.16) takes the form

$$\tau_c = \frac{1}{K(0)} \int_{-\infty}^\infty \Delta r(x) \rho(x) dx\tag{5.20}$$



Due to initial condition (5.18),  $\rho(x)$  must obey

$$-\Delta r(x)W_{st}(x) = \left\{ -\frac{d}{dx}a(x) + \frac{d^2}{dx^2}\frac{D(x)}{2} \right\} \rho(x) \tag{5.21}$$

This equation may be integrated leading to

$$\rho(x) = W_{st}(x) \int_{-\infty}^x \frac{2f(x')}{D(x')W_{st}(x')} dx' \tag{5.22}$$

with  $f(x)$  given by

$$f(x) = - \int_{-\infty}^x \Delta r(x)W_{st}(x) dx \tag{5.23}$$

Inserting (5.22) into (5.20) we find, after integration by parts, the following analytical expression for the correlation time:

$$\tau_c = \frac{1}{K(0)} \int_{-\infty}^{\infty} \frac{2f^2(x)}{D(x)W_{st}(x)} dx \tag{5.24}$$

### C. Generalized Moment Expansion for Relaxation Processes

To our knowledge, the first paper devoted to obtaining characteristic time scales of different observables governed by the Fokker–Planck equation in systems having steady states was written by Nadler and Schulten [30]. Their approach is based on the generalized moment expansion of observables and, thus, called the “generalized moment approximation” (GMA).

The observables considered are of the type

$$M(t) = \int_c^d \int_c^d f(x)W(x, t | x_0)g(x_0) dx_0 dx \tag{5.25}$$

where  $W(x, t | x_0)$  is the transition probability density governed by the Fokker–Planck equation

$$\frac{\partial W(x, t)}{\partial t} = \frac{\partial}{\partial x} \left\{ W_{st}(x) \frac{\partial}{\partial x} \left[ \frac{D(x)}{2W_{st}(x)} \right] \right\} \tag{5.26}$$

$g(x_0)$  is initial probability distribution and  $f(x)$  is some test function that monitors the distribution at the time  $t$ . The reflecting boundary conditions at points  $c$  and  $d$  are supposed, which leads to the existence of steady-state probability distribution  $W_{st}(x)$ :

$$W_{st}(x) = \frac{C}{D(x)} \exp \left[ \int_{x'}^x \frac{2a(x)}{D(x)} dx \right] \tag{5.27}$$

where  $C$  is the normalization constant.

The observable has initial value  $M(0) = \langle f(x)g_0(x) \rangle$  and relaxes asymptotically to  $M(\infty) = \langle f(x) \rangle \langle g_0(x) \rangle$ . Here  $g_0(x) = g(x)/W_{st}(x)$ . Because the time development of  $M(t)$  is solely due to the relaxation process, one needs to consider only  $\Delta M(t) = M(t) - M(\infty)$ .

The starting point of the generalized moment approximation (GMA) is the Laplace transformation of an observable:

$$\Delta M(s) = \int_0^\infty \Delta M(t)e^{-st} dt \tag{5.28}$$

$\Delta M(s)$  may be expanded for low and high frequencies:

$$\Delta M(s) \sim_{s \rightarrow 0} \sum_{n=0}^\infty \mu_{-(n+1)}(-s)^n \tag{5.29}$$

$$\Delta M(s) \sim_{s \rightarrow \infty} \sum_{n=0}^\infty \mu_n(-1/s)^n \tag{5.30}$$

where the expansion coefficients  $\mu_n$ , the ‘‘generalized moments,’’ are given by

$$\mu_n = (-1)^n \int_c^d g(x) \{ (L^+(x))^n \}_b f(x) dx \tag{5.31}$$

where  $\{ \}_b$  denotes operation in a space of functions that obey the adjoint reflecting boundary conditions, and  $L^+(x)$  is the adjoint Fokker–Planck operator:

$$L^+(x) = - \left\{ a(x) \frac{\partial}{\partial x} + D(x) \frac{\partial^2}{\partial x^2} \right\} \tag{5.32}$$

In view of expansions (5.29) and (5.30), we will refer to  $\mu_n, n \geq 0$ , as the high-frequency moments and to  $\mu_n, n < 0$ , as the low-frequency moments. The moment  $\mu_0$  is identical to the initial value  $\Delta M(t)$  and assumes the simple form:

$$\mu_0 = \langle f(x)g_0(x) \rangle - \langle f(x) \rangle \langle g_0(x) \rangle \tag{5.33}$$

For negative  $n$  (see Ref. 30), the following recurrent expressions for the moments  $\mu_{-n}$  may be obtained:

$$\mu_{-n} = \int_c^d \frac{4 dx}{W_{st}(x)} \int_c^x \frac{W_{st}(y)}{D(y)} \mu_{-(n-1)}(y) dy \int_c^y \frac{W_{st}(z)}{D(z)} (g_0(z) - \langle g_0(z) \rangle) dz \tag{5.34}$$

where

$$\mu_{-n}(x) = C - \int_c^x \frac{dy}{W_{st}(y)} \int_c^y \frac{2W_{st}(z)}{D(z)} \mu_{-(n-1)}(z) dz \tag{5.35}$$

where  $C$  is an integration constant, chosen to satisfy the orthogonality property. For  $n = 1$

$$\mu_{-1} = \int_c^d \frac{4dx}{W_{sr}(x)} \int_c^x \frac{W_{sr}(y)}{D(y)} (f(y) - \langle f(y) \rangle) dy \int_c^y \frac{W_{sr}(z)}{D(z)} (g_0(z) - \langle g_0(z) \rangle) dz \tag{5.36}$$

holds. Moments with negative index, which account for the low-frequency behavior of observables in relaxation processes, can be evaluated by means of simple quadratures. Let us consider now how the moments  $\mu_n$  may be employed to approximate the observable  $\Delta M(t)$ .

We want to approximate  $\Delta M(s)$  by a Padé approximant  $\Delta m(s)$ . The functional form of  $\Delta m(s)$  should be such that the corresponding time-dependent function  $\Delta m(t)$  is a series of  $N$  exponentials describing the relation of  $\Delta M(t)$  to  $\Delta M(\infty) = 0$ . This implies that  $\Delta m(s)$  is an  $[N - 1, N]$ -Padé approximant that can be written in the form

$$\Delta m(s) = \sum_{n=1}^N a_n / (\lambda_n + s) \tag{5.37}$$

or, correspondingly,

$$\Delta m(t) = \sum_{n=1}^N a_n \exp(-\lambda_n t) \tag{5.38}$$

The function  $\Delta m(s)$  should describe the low- and high-frequency behavior of  $\Delta M(s)$  to a desired degree. We require that  $\Delta m(s)$  reproduces  $N_h$  high- and  $N_l$  low-frequency moments. Because  $\Delta m(s)$  is determined by an even number of constants  $a_n$  and  $\lambda_n$ , one needs to choose  $N_h + N_l = 2N$ . We refer to the resulting description as the  $(N_h, N_l)$ -generalized-moment approximation (GMA). The description represents a two-sided Padé approximation. The moments determine the parameters  $a_n$  and  $\lambda_n$  through the relations

$$\sum_{n=1}^N a_n \lambda_n^m = \mu_m \tag{5.39}$$

where  $m = -N_l, -N_l + 1, \dots, N_h - 1$ .

Algebraic solution of Eq. (5.39) is feasible only for  $N = 1, 2$ . For  $N > 2$  the numerical solution of (5.39) is possible by means of an equivalent eigenvalue problem (for references see Ref. 30).

The most simple GMA is the  $(1, 1)$  approximation which reproduces the moments  $\mu_0$  and  $\mu_1$ . In this case, the relaxation of  $\Delta M(t)$  is approximated by a single exponential

$$\Delta M(t) = \mu_0 \exp(-t/\tau) \tag{5.40}$$

where  $\tau = \mu_{-1}/\mu_0$  is the mean relaxation time. As has been demonstrated in Ref. 30 for a particular example of rectangular barrierless potential well, this simple one-exponential approximation is often satisfactory and describes the required observables with a good precision. We should note that this is indeed so as will be demonstrated below.

## D. Differential Recurrence Relation and Floquet Approach

### 1. Differential Recurrence Relations

A quite different approach from all other presented in this review has been recently proposed by Coffey [41]. This approach allows both the MFPT and the integral relaxation time to be exactly calculated irrespective of the number of degrees of freedom from the differential recurrence relations generated by the Floquet representation of the FPE.

In order to achieve the most simple presentation of the calculations, we shall restrict ourselves to a one-dimensional state space in the case of constant diffusion coefficient  $D = 2kT/h$  and consider the MFPT (the extension of the method to a multidimensional state space is given in the Appendix of Ref. 41). Thus the underlying probability density diffusion equation is again the Fokker-Planck equation (2.6) that for the case of constant diffusion coefficient we present in the form:

$$\frac{\partial W(x, t)}{\partial t} = \frac{1}{B} \left\{ \frac{\partial}{\partial x} \left[ \frac{d\varphi(x)}{dx} W(x, t) \right] + \frac{\partial^2 W(x, t)}{\partial x^2} \right\} \quad (5.41)$$

where  $B = 2/D = h/kT$  and  $\varphi(x) = \Phi(x)/kT$  is the dimensionless potential. Furthermore, we shall suppose that  $\Phi(x)$  is the symmetric bistable potential (rotator with two equivalent sites)

$$\Phi(x) = U \sin^2(x) \quad (5.42)$$

Because the solution of Eq. (5.41) must be periodic in  $x$  that is  $W(x + 2\pi) = W(x)$ , we may assume that it has the form of the Fourier series

$$W(x, t) = \sum_{p=-\infty}^{\infty} a_p(t) e^{ipx} \quad (5.43)$$

where for convenience (noting that the potential has minima at  $0, \pi$  and a central maximum at  $\pi/2$ ) the range of  $x$  is taken as  $-\pi/2 < x < 3\pi/2$ .

On substituting Eq. (5.43) into Eq. (5.41) we have, using the orthogonality properties of the circular functions,

$$\dot{a}_p(t) + \frac{p^2}{B} a_p(t) = \frac{\sigma p}{B} [a_{p-2}(t) - a_{p+2}(t)] \quad (5.44)$$

where  $2\sigma = U/kT$ . The differential-recurrence relation for  $a_{-p}(t)$  is from Eq. (5.44)

$$\dot{a}_{-p}(t) + \frac{p^2}{B} a_{-p}(t) = \frac{\sigma p}{B} [a_{-(p-2)}(t) - a_{-(p+2)}(t)] \quad (5.45)$$

which is useful in the calculation that follows because the Fourier coefficients of the Fourier cosine and sine series, namely,

$$W(x, t) = \frac{f_0}{2} + \sum_{p=1}^{\infty} f_p(t) \cos(px) + \sum_{p=1}^{\infty} g_p(t) \sin(px) \quad (5.46)$$

corresponding to the complex series (5.43) are by virtue of Eqs. (5.44) and (5.45)

$$\begin{aligned} f_{-p}(t) = f_p(t) &= \frac{1}{\pi} \int_{-\pi/2}^{3\pi/2} W(x, t) \cos(px) dx \\ g_{-p}(t) = -g_p(t) &= -\frac{1}{\pi} \int_{-\pi/2}^{3\pi/2} W(x, t) \sin(px) dx \end{aligned} \quad (5.47)$$

Thus Eq. (5.44) need only be solved for positive  $p$ .

We also remark that Eq. (5.44) may be decomposed into separate sets of equations for the odd and even  $a_p(t)$  which are decoupled from each other. Essentially similar differential recurrence relations for a variety of relaxation problems may be derived as described in Refs. 4, 36, and 73–76, where the frequency response and correlation times were determined exactly using scalar or matrix continued fraction methods. Our purpose now is to demonstrate how such differential recurrence relations may be used to calculate mean first passage times by referring to the particular case of Eq. (5.44).

## 2. Calculation of Mean First Passage Times from Differential Recurrence Relations

In order to illustrate how the Floquet representation of the FPE, Eq. (5.44), may be used to calculate first passage times, we first take the Laplace transform of Eq. (5.41) for the probability density ( $Y(x, s) = \int_0^{\infty} W(x, t) e^{-st} dt$ ,  $\hat{a}_p(s) = \int_0^{\infty} a_p(t) e^{-st} dt$ ) which for a delta function initial distribution at  $x_0$  becomes

$$\frac{d^2 Y(x, s)}{dx^2} + \frac{d}{dx} \left[ \frac{d\varphi(x)}{dx} Y(x, s) \right] - sBY(x, s) = -B\delta(x - x_0) \quad (5.48)$$

The corresponding Fourier coefficients satisfy the differential recurrence relations

$$s\hat{a}_p(s) - \frac{\exp(-ipx_0)}{2\pi} = \frac{\sigma p}{B} [\hat{a}_{p-2}(s) - \hat{a}_{p+2}(s)] \quad (5.49)$$

The use of the differential recurrence relations to calculate the mean first passage time is based on the observation that if in Eq. (5.48) one ignores the term  $sY(x, s)$  (which is tantamount to assuming that the process is quasi-stationary, i.e., all characteristic frequencies associated with it are very small), then one has

$$\frac{d^2 Y(x, s)}{dx^2} + \frac{d}{dx} \left[ \frac{d\phi(x)}{dx} Y(x, s) \right] = -B\delta(x - x_0) \tag{5.50}$$

which is precisely the differential equation given by Risken for the stationary probability if at  $x_0$  a unit rate of probability is injected into the system; integrating Eq. (5.50) from  $x_0 - \epsilon$  to  $x_0 + \epsilon$  leads to  $G(x_0 + \epsilon) - G(x_0 - \epsilon) = 1$ , where  $G$  is the probability current given by Eq. (2.11).

The mean first passage time at which the random variable  $\xi(t)$  specifying the angular position of the rotator first leaves a domain  $L$  defined by the absorbing boundaries  $x_1$  and  $x_2$  where  $W(x, t|x_0, 0)$  and consequently  $Y(x, s = 0|x_0) \equiv Y(x, x_0)$  vanishes may now be calculated because [see Eq. (8.5) of Ref. 2]

$$T(x_0) = \int_{x_1}^{x_2} Y(x, x_0) dx \tag{5.51}$$

Here we are interested in escape out of the domain  $L$  specified by a single cycle of the potential that is out of a domain of length  $\pi$  that is the domain of the well. Because the bistable potential of Eq. (5.42) has a maximum at  $x = \pi/2$  and minima at  $x = 0, x = \pi$ , it will be convenient to take our domain as the interval  $-\pi/2 < x < \pi/2$ . Thus we will impose absorbing boundaries at  $x = -\pi/2, x = \pi/2$ . Next we shall impose a second condition that all particles are initially located at the bottom of the potential well so that  $x_0 = 0$ . The first boundary condition (absorbing barriers at  $-\pi/2, \pi/2$ ) implies that only odd terms in  $p$  in the Fourier series will contribute to  $Y(x)$ . While the second ensures that only the cosine terms in the series will contribute because there is a null set of initial values for the sine terms. Hence

$$T(x_0) = T(0)$$

is given by

$$T(0) = \int_{-\pi/2}^{\pi/2} \sum_{p=0}^{\infty} \hat{f}_{2p+1}(0) \cos(2p + 1)x dx \tag{5.52}$$

and the MFPT to go from  $-\pi/2$  to  $3\pi/2$  which is the escape time is

$$\tau_e = 2T(0) = 4 \sum_{p=0}^{\infty} \frac{(-1)^p}{2p + 1} \hat{f}_{2p+1}(0) \tag{5.53}$$

In the high barrier limit in this particular problem the inverse escape time is the Kramers' escape rate.

3. Calculation of  $\tau$  by a Continued Fraction Method

The differential recurrence relations for  $f_{2p+1}(t)$  are [4,77]

$$\dot{f}_{2p+1}(t) + \frac{(2p+1)^2}{B} f_{2p+1}(t) = \frac{\sigma(2p+1)}{B} [f_{2p-1}(t) - f_{2p+3}(t)] \tag{5.54}$$

the solution of which for  $\hat{f}_1(s)$  is [77]

$$\hat{f}_1(s) = \frac{B}{sB + (1 - \sigma) + \sigma\hat{S}_3(s)} \times \left[ f_1(0) + \sum_{p=1}^{\infty} \frac{(-1)^p}{2p+1} f_{2p+1}(0) \prod_{k=1}^p \hat{S}_{2k+1}(s) \right] \tag{5.55}$$

where the continued fraction  $\hat{S}_p(s)$  is

$$\hat{S}_p(s) = \frac{\sigma p}{sB + p^2 + \sigma p \hat{S}_{p+2}(s)} \tag{5.56}$$

and successive  $\hat{f}_p(s)$ ,  $p > 1$ , are determined from [4,77]

$$\hat{f}_p = \hat{S}_p \hat{f}_{p-2} + q_p \tag{5.57}$$

where

$$q_p = \frac{f_p(0)B - \sigma p q_{p+2}}{sB + p^2 + \sigma p \hat{S}_{p+2}} \tag{5.58}$$

whence

$$\hat{f}_3(s) = \frac{B\hat{S}_3(s)}{sB + (1 - \sigma) + \sigma\hat{S}_3(s)} \left[ f_1(0) + \sum_{p=1}^{\infty} \frac{(-1)^p}{2p+1} f_{2p+1}(0) \prod_{k=1}^p \hat{S}_{2k+1}(s) \right] - \frac{B}{\sigma} \left[ \sum_{p=1}^{\infty} \frac{(-1)^p}{2p+1} f_{2p+1}(0) \prod_{k=1}^p \hat{S}_{2k+1}(s) \right] \tag{5.59}$$

where of course the  $f_{2p+1}(0)$  are the initial values of  $f_{2p+1}(t)$ . Since  $x_0$  is not an end point in the domain of integration the initial values are

$$f_{2p+1}(0) = \frac{1}{\pi} \cos(2p+1)x_0 = \frac{1}{\pi} \tag{5.60}$$

because we suppose that  $x_0 = 0$ . All  $\hat{f}_{2p+1}(s)$  can now be written down in the manner of  $\hat{f}_1(s)$  and  $\hat{f}_2(s)$  using Eqs. (5.57) and (5.58), with the calculations being much simpler than those of the correlation time in Ref. 77 on account of the rather simple initial condition of Eq. (5.60). This is unnecessary, however, as we shall demonstrate. First we recall that for the purpose of the calculation of  $Y(x, x_0)$  the relevant quantity is the  $s = 0$  value of  $\hat{f}_{2p+1}$ . Furthermore, the  $s = 0$  value of the continued fraction  $\hat{S}_{2k+1}(s)$  is [77]

$$\hat{S}_{2k+1}(0) = \frac{\sigma/(2k + 1)}{1 + [\sigma/(2k + 1)]\hat{S}_{2k+3}(0)} \tag{5.61}$$

the solution of which, which is finite at  $\sigma = 0$ , is

$$\hat{S}_{2k+1}(0) = \frac{I_{k+(1/2)}(\sigma)}{I_{k-(1/2)}(\sigma)} \tag{5.62}$$

where  $I_{k+(1/2)}(\sigma)$  are the modified Bessel functions of the first kind of order  $k + \frac{1}{2}$ . Thus just as in Ref. 77,  $\hat{f}_1(0)$  may be written as

$$\hat{f}_1(0) = \frac{B}{2\sigma} (e^{2\sigma} - 1) \sum_{p=0}^{\infty} \frac{(-1)^p}{2p + 1} \frac{1}{\pi} L_p(\sigma) \tag{5.63}$$

where the  $L_p(\sigma)$  satisfy the recurrence relation

$$\begin{aligned} L_{p-1}(\sigma) - L_{p+1}(\sigma) &= \frac{2p + 1}{\sigma} L_p(\sigma) \\ L_p(\sigma) &= \frac{I_{p+(1/2)}(\sigma)}{I_{(1/2)}(\sigma)} \end{aligned} \tag{5.64}$$

The leading term in Eq. (5.63) arises because

$$\begin{aligned} \frac{B}{(1 - \sigma) + \sigma\hat{S}_3(0)} &= \frac{B}{(1 - \sigma) + \sigma(I_{(3/2)}(\sigma)/I_{(1/2)}(\sigma))} \\ &= \frac{B}{2\sigma} (e^{2\sigma} - 1) \end{aligned} \tag{5.65}$$

In like manner we have

$$\hat{f}_3(0) = \frac{B\hat{S}_3(0)}{(1 - \sigma) + \sigma\hat{S}_3(0)} \frac{1}{\pi} \sum_{p=0}^{\infty} \frac{(-1)^p}{2p + 1} L_p(\sigma) - \frac{B}{\sigma\pi} \sum_{p=1}^{\infty} \frac{(-1)^p}{2p + 1} L_p(\sigma) \tag{5.66}$$



The large  $\sigma$  limit (high barrier limit,  $2\sigma = U/kT$ ) of both Eqs. (5.63) and (5.66) is the same, namely,

$$\hat{f}_1(0) = \hat{f}_3(0) \approx \frac{B}{2\sigma} \frac{e^{2\sigma}}{\pi} \sum_{p=0}^{\infty} \frac{(-1)^p}{2p+1} = \frac{B}{8\sigma} e^{2\sigma} \quad (5.67)$$

by the properties of the Riemann zeta function [78] [Eq. (5.67)] because

$$\lim_{\sigma \rightarrow \infty} L_p(\sigma) = 1$$

and because the second term in Eq. (5.66) decays as  $\sigma^{-1}$  for large  $\sigma$ . One may also deduce from Eqs. (5.57) and (5.58) that the behavior of all  $\hat{f}_{2p+1}(0)$  for large  $\sigma$  is the same. Thus we may write down  $Y(x, x_0)$  in the high barrier limit as

$$Y(x, 0) \approx \frac{B}{8\sigma} e^{2\sigma} \sum_{p=1}^{\infty} \cos(2p+1)x \quad (5.68)$$

which with Eq. (5.52) yields the following for the MFPT from  $x = 0$  to  $x = \pi/2$  or  $-\pi/2$ :

$$T_{\text{MFPT}} \approx \frac{B}{8\sigma} e^{2\sigma} \sum_{p=0}^{\infty} \frac{2(-1)^p}{2p+1} \approx \frac{\pi B}{2 \cdot 8\sigma} e^{2\sigma} \quad (5.69)$$

The escape time  $\tau_e$  out of the well that is the domain  $-\pi/2 < x < \pi/2$  is

$$\tau_e \approx 2T_{\text{MFPT}} \approx \frac{\pi B}{4 \cdot 2\sigma} e^{2\sigma} \quad (5.70)$$

in agreement with the results of the Kramers theory [Eq. (102) of Ref. 77] and the asymptotic expression for the smallest nonvanishing eigenvalue [79]. Equivalently, the escape time in this case is the MFPT from  $-\pi/2$  to  $3\pi/2$ . In the opposite limit when the potential barrier is zero, Eq. (5.53) becomes (again using the properties of the Riemann zeta and Langevin functions)

$$\tau_e = \frac{\pi^2 B}{8} \quad (5.71)$$

in agreement with the predictions of the Einstein theory of the Brownian movement as adapted to the calculation of MFPTs by Klein [80] and in contrast to the zero barrier value of the correlation time which is  $B$ .

### E. The Approach by Malakhov and Its Further Development

Another approach for computing the transition times had been proposed by Malakhov [34,35]. This approach also utilizes the definition of the desired

timescale as integral relaxation time and is based on obtaining the solution of the Laplace transformed FPE as a set with respect to small Laplace parameter  $s$  and allows us to obtain a wide variety of temporal characteristics of Markov processes with time constant drift and diffusion coefficients and for a wide variety of boundary conditions ranging from natural to periodic.

In this section we will consider this approach in detail for different types of potential profiles  $\varphi(x) = \Phi(x)/kT$ , and to avoid cumbersome calculations we present the analysis for the constant diffusion coefficient  $D = 2kT/h$ , but the results, of course, may be easily generalized for any  $D(x) \neq 0$ .

### 1. Statement of the Problem

It is convenient to present the Fokker–Planck equation in the following dimensionless form:

$$\frac{\partial W(x, t)}{\partial t} = -\frac{\partial G(x, t)}{\partial x} = \frac{1}{B} \left\{ \frac{\partial}{\partial x} \left[ \frac{d\varphi(x)}{dx} W(x, t) \right] + \frac{\partial^2 W(x, t)}{\partial x^2} \right\} \quad (5.72)$$

where  $B = 2/D = h/kT$ ,  $G(x, t)$  is the probability current, and  $\varphi(x) = 2\Phi(x)/hD = \Phi(x)/kT$  is the dimensionless potential profile.

We suppose that at initial instant  $t = 0$  all Brownian particles are located at the point  $x = x_0$ , which corresponds to the initial condition  $W(x, 0) = \delta(x - x_0)$ . The initial delta-shaped probability distribution spreads with time, and its later evolution strongly depends on the form of the potential profile  $\varphi(x)$ . We shall consider the problem for the three archetypal potential profiles that are sketched in Figs. 3–5.

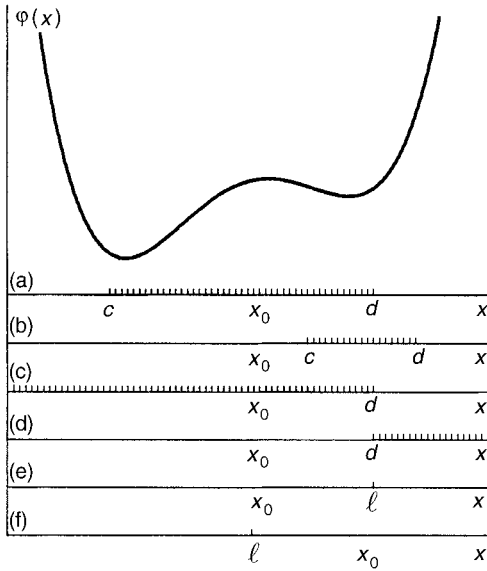
If a potential profile is of the type I (see Fig. 3) when  $\varphi(x)$  goes to plus infinity fast enough at  $x \rightarrow \pm\infty$ , there is the steady-state probability distribution

$$W(x, \infty) = Ae^{-\varphi(x)}, \quad A = 1 / \int_{-\infty}^{+\infty} \exp[-\varphi(x)] dx > 0 \quad (5.73)$$

In this case our aim is to determine *the relaxation time*  $\Theta$  that is the timescale of the probability density evolution from the initial  $W(x, 0)$  to the final value  $W(x, \infty)$  for any  $x \neq x_0$ . On the other hand we may consider the probability

$$P(t, x_0) = P(t) = \int_c^d W(x, t) dx \quad (5.74)$$

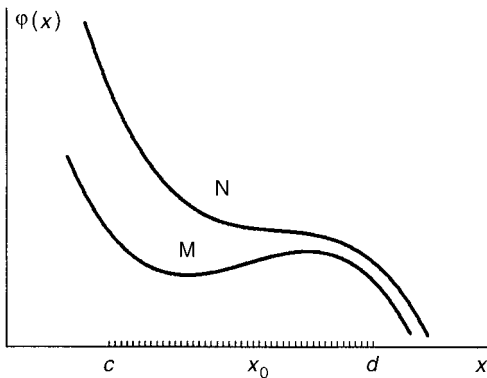
in a given interval  $[c, d]$ , which in the following we shall call *the decision interval*, and seek the relaxation time of this probability  $P(t)$  which changes from the initial value  $P(0) = \int_c^d W(x, 0) dx$  to the final one  $P(\infty) = \int_c^d W(x, \infty) dx$ . A potential



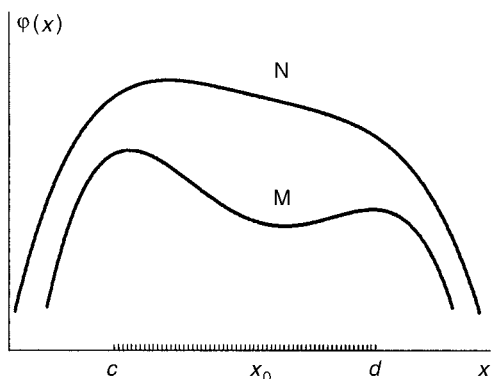
**Figure 3.** A sketch of a potential profile of type I. The  $x$  axes (a)–(f) represent various dispositions of decision intervals  $[c, d]$ ,  $[-\infty, d]$ ,  $[d, +\infty]$  and points of observation  $\ell$  with respect to the  $x_0$  coordinate of the initial delta-shaped probability distribution.

profile of type II (Fig. 4) tends fast enough to plus infinity at  $x \rightarrow -\infty$  and to minus infinity at  $x \rightarrow +\infty$ . A potential profile of type III (Fig. 5) drops to minus infinity at  $x \rightarrow \pm\infty$ . Let us note that if there is a potential profile that increases to plus infinity at  $x \rightarrow +\infty$  and decreases to minus infinity at  $x \rightarrow -\infty$ , then it may be reduced to the profile of type II by reversing of the  $x$  axis.

For potential profiles of types II and III there are no nonzero stationary probability densities because all diffusing particles in the course of time will leave the initial interval and go toward the regions where the potential  $\varphi(x)$  tends to minus infinity. In these situations we may pose two questions:



**Figure 4.** Sketches of potential profiles of type II with a metastable ( $M$ ) and a nonstable ( $N$ ) state.



**Figure 5.** Sketches of potential profiles of type III with a metastable (*M*) and a nonstable (*N*) state.

1. How long may a metastable state *M* exist in decision interval  $[c, d]$ ?
2. How long may a nonstable state *N* remain in decision interval  $[c, d]$ ?

In the first position it is reasonable to define *the decay time*  $\tau$  (or *the lifetime*  $\tau$ ) of the metastable state as the timescale of probability (5.74) evolution from the initial value  $P(0) = 1$  to the zeroth final value  $P(\infty) = 0$ .

In the second position we denote the timescale of probability (5.74) evolution from  $P(0) = 1$  to  $P(\infty) = 0$  as *the decay time*  $\tau$  of the nonstable state.

Instead of containing natural boundaries at  $x \rightarrow \pm\infty$ , all potential profiles shown in Figs. 3–5 may contain, of course, reflecting and/or absorbing boundaries whose coordinates we shall denote as  $\lambda_1, \lambda_2 : \lambda_1 \leq c < d \leq \lambda_2$ . If we consider cases with absorbing boundaries, then we arrive at an MFPT that has the same meaning: It is the timescale of the probability evolution; that is, the MFPT is actually nothing other than the decay time of a metastable or nonstable state.

Now let us define the timescales stated above in a general case as

$$\vartheta = \frac{\int_0^\infty [P(t) - P(\infty)] dt}{P(0) - P(\infty)} = \frac{\int_0^\infty [P(\infty) - P(t)] dt}{P(\infty) - P(0)} \tag{5.75}$$

for the characteristic time of probability evolution and

$$\Theta(\ell) = \frac{\int_0^\infty [W(\ell, \infty) - W(\ell, t)] dt}{W(\ell, \infty)} \tag{5.76}$$

for the relaxation time in a single point  $x = \ell \neq x_0$ . These definitions are legitimate, if variations of  $P(t)$  or  $W(\ell, t)$  are sufficiently fast so that integrals (5.75), (5.76) converge and if  $P(t)$  and  $W(\ell, t)$  during their process of tendency to  $P(\infty)$  and  $W(\ell, \infty)$  do not intersect the final values  $P(\infty)$  and  $W(\ell, \infty)$ . For the

fulfillment of the last condition, monotonic variations of  $P(t)$  and  $W(\ell, t)$  are sufficient.

Our problem is to obtain the above-stated timescales—the relaxation time, the decay time of a metastable state, and the decay time of a nonstable state—in such a way that the desired results may be expressed directly in terms of the given potential profiles  $\varphi(x)$ .

Below we provide the full resolution of this problem for potential profiles of types I, II, and III separately.

### 2. Method of Attack

We introduce into consideration the Laplace transformations of the probability density and the probability current

$$Y(x, s) = \int_0^\infty W(x, t)e^{-st} dt, \quad \hat{G}(x, s) = \int_0^\infty G(x, t)e^{-st} dt \quad (5.77)$$

Then the FPE, according to (5.72) and (5.77) and to the initial condition, may be rewritten as

$$\frac{d^2 Y(x, s)}{dx^2} + \frac{d}{dx} \left[ \frac{d\varphi(x)}{dx} Y(x, s) \right] - sBY(x, s) = -B\delta(x - x_0) \quad (5.78)$$

The Laplace transformed probability current is

$$\hat{G}(x, s) = -\frac{1}{B} \left[ \frac{d\varphi(x)}{dx} Y(x, s) + \frac{dY(x, s)}{dx} \right] \quad (5.79)$$

In Laplace transform terms the timescale (5.75) has the form

$$\vartheta = \lim_{s \rightarrow 0} \frac{s\hat{P}(s) - P(\infty)}{s[P(0) - P(\infty)]} \quad (5.80)$$

where according to (5.74) we have

$$\hat{P}(s) = \int_0^\infty P(t)e^{-st} dt = \int_c^d Y(x, s) dx$$

Integration of Eq. (5.72) with respect to  $x$  between the limits  $c$  and  $d$  leads to

$$\frac{dP(t)}{dt} = - \int_c^d \frac{\partial G(x, t)}{\partial x} dx = G(c, t) - G(d, t)$$

In the Laplace transform terms we get

$$s\hat{P}(s) - P(0) = \hat{G}(c, s) - \hat{G}(d, s) \quad (5.81)$$

Substituting (5.81) into (5.80), one obtains

$$\vartheta = \lim_{s \rightarrow 0} \frac{[P(0) - P(\infty)] - [\hat{G}(d, s) - \hat{G}(c, s)]}{s[P(0) - P(\infty)]} \quad (5.82)$$

For the relaxation time (5.76) in a single point we find in a similar manner

$$\Theta(\ell) = \lim_{s \rightarrow 0} \frac{W(\ell, \infty) - sY(\ell, s)}{sW(\ell, \infty)} \quad (5.83)$$

Thus, to obtain the timescales  $\vartheta$  and  $\Theta(\ell)$  we need to find the solution  $Y(x, s)$  of Eq. (5.78) at appropriate boundary conditions and evaluate limits (5.82) and (5.83) for  $s \rightarrow 0$ . It is precisely that way by which the various timescales for piecewise-linear and piecewise-parabolic potential profiles were derived in Refs. 32 and 33.

But now we have an arbitrary potential profile  $\varphi(x)$  in Eq. (5.78). Nobody knows a solution of this equation for any  $\varphi(x)$ . That is why we shall use another approach.

Let us note that it is not necessary to know the solution  $Y(x, s)$  as a whole, but its behavior at  $s \rightarrow 0$  only. For this reason we expand  $Y(x, s)$  and  $\hat{G}(x, s)$  in power series in  $s$ :

$$\begin{aligned} Z(x, s) &\equiv sY(x, s) = Z_0(x) + sZ_1(x) + s^2Z_2(x) + \dots \\ H(x, s) &\equiv s\hat{G}(x, s) = H_0(x) + sH_1(x) + s^2H_2(x) + \dots \end{aligned} \quad (5.84)$$

In accordance with the limit theorems of the Laplace transformation (see, e.g., Ref. 81), we obtain

$$\begin{aligned} Z_0(x) &= \lim_{s \rightarrow 0} sY(x, s) = W(x, \infty) = W_{st}(x) \\ H_0(x) &= \lim_{s \rightarrow 0} s\hat{G}(x, s) = G(x, \infty) = G_{st}(x) \end{aligned}$$

It is obvious that the steady-state quantities of the probability density  $W_{st}(x)$  and the probability current  $G_{st}(x)$  may be obtained without any difficulties at appropriate boundary conditions directly from Eq. (5.72).

Inserting (5.84) into (5.82), we obtain

$$\begin{aligned} \vartheta = \lim_{s \rightarrow 0} \left\{ \frac{[P(0) - P(\infty)] - [H_1(d) - H_1(c)]}{s[P(0) - P(\infty)]} \right. \\ \left. - \frac{[H_2(d) - H_2(c)]}{[P(0) - P(\infty)]} - s \frac{[H_3(d) - H_3(c)]}{[P(0) - P(\infty)]} - \dots \right\} \end{aligned}$$

Here it is taken into account that for all profiles in question the steady-state probability current  $H_0(x)$  equals 0 for any finite  $x$ .

As will be demonstrated below for all profiles the following condition takes place

$$H_1(d) - H_1(c) = P(0) - P(\infty) \tag{5.85}$$

Consequently, the desired timescale reads as follows:

$$\vartheta = \frac{H_2(c) - H_2(d)}{P(0) - P(\infty)} \tag{5.86}$$

Substituting (5.84) into (5.83), we find the relaxation time in a single point:

$$\Theta(\ell) = -\frac{Z_1(\ell)}{W(\ell, \infty)} = -\frac{Z_1(\ell)}{Z_0(\ell)} \tag{5.87}$$

Hence, to attain our aim it is necessary to calculate functions  $H_2(x)$  and  $Z_1(x)$ . Inserting (5.84) into (5.78) and (5.79), it is easy to write the following equations:

$$\frac{d}{dx} \left( \frac{dZ_0}{dx} + \phi'Z_0 \right) = 0 \tag{a}$$

$$\frac{d}{dx} \left( \frac{dZ_1}{dx} + \phi'Z_1 \right) = BZ_0 - B\delta(x - x_0) \tag{b} \tag{5.88}$$

$$\frac{d}{dx} \left( \frac{dZ_2}{dx} + \phi'Z_2 \right) = BZ_1 \tag{c}$$

⋮ ⋮

$$H_0 = -\frac{1}{B} \left[ \frac{dZ_0}{dx} + \phi'Z_0 \right] \tag{a}$$

$$H_1 = -\frac{1}{B} \left[ \frac{dZ_1}{dx} + \phi'Z_1 \right] \tag{b} \tag{5.89}$$

$$H_2 = -\frac{1}{B} \left[ \frac{dZ_2}{dx} + \phi'Z_2 \right] \tag{c}$$

⋮ ⋮

From (5.88) and (5.89) we obtain

$$\frac{dH_0}{dx} = 0 \tag{a}$$

$$\frac{dH_1}{dx} = -Z_0 + \delta(x - x_0) \tag{b} \tag{5.90}$$

$$\frac{dH_2}{dx} = -Z_1 \tag{c}$$

⋮ ⋮





where

$$F(x) = A \int_{-\infty}^x e^{-\varphi(v)} dv \tag{5.93}$$

is the integral distribution function for the probability density  $W_{st}(x)$ .

It is easy to see that

$$H_1(d) - H_1(c) = \begin{cases} -A \int_c^d e^{-\varphi(v)} dv + 1 = P(0) - P(\infty), & c < x_0 < d \\ -A \int_c^d e^{-\varphi(v)} dv = P(0) - P(\infty), & x_0 < c < d \end{cases}$$

Thus, condition (5.85) is true for potential profiles of type I, and therefore the relaxation time  $\Theta$  is really found according to (5.86).

The function  $H_2(x)$  may be found from (5.91c) taking into account (5.92) and (5.93):

$$H_2 = C_1 F(x) + B \int_{-\infty}^x e^{-\varphi(u)} du \int_{-\infty}^u e^{\varphi(v)} [1(v - x_0) - F(v)] dv + C_2$$

where  $C_1$  and  $C_2$  are arbitrary constants, which must be defined from boundary conditions  $H_2(\pm\infty) = 0$ . As the result, we have  $C_2 = 0$  and

$$C_1 = -B \int_{-\infty}^{+\infty} e^{-\varphi(u)} du \int_{-\infty}^u e^{\varphi(v)} [1(v - x_0) - F(v)] dv$$

Consequently,

$$H_2(x) = B \left\{ \int_{-\infty}^x e^{-\varphi(u)} du \int_{-\infty}^u e^{\varphi(v)} [1(v - x_0) - F(v)] dv - F(x) \int_{-\infty}^{+\infty} e^{-\varphi(u)} du \int_{-\infty}^u e^{\varphi(v)} [1(v - x_0) - F(v)] dv \right\} \tag{5.94}$$

By changing the integration order, one obtains

$$H_2(c) - H_2(d) = \frac{B}{A} \left\{ P(\infty) \int_{-\infty}^{+\infty} e^{\varphi(v)} [1(v - x_0) - F(v)] [1 - F(v)] dv - P(\infty) \int_{-\infty}^c e^{\varphi(v)} [1(v - x_0) - F(v)] dv - \int_c^d e^{\varphi(v)} [1(v - x_0) - F(v)] [F(d) - F(v)] dv \right\} \tag{5.95}$$

*The Initial Probability Distribution Is Within the Decision Interval.* After some transformations taking into account that  $c < x_0 < d$ , we obtain finally from (5.95) and from (see (5.86))

$$\Theta = \frac{H_2(c) - H_2(d)}{1 - P(\infty)}$$

the following quantity of the relaxation time for the situation depicted in Fig. 3(a):

$$\begin{aligned} \Theta = \frac{B}{A(1 - P_\infty)} & \left\{ (1 - P_\infty) \int_c^d e^{\varphi(v)} F(v) [1 - F(v)] dv \right. \\ & + P_\infty \int_{-\infty}^c e^{\varphi(v)} F^2(v) dv + P_\infty \int_d^\infty e^{\varphi(v)} [1 - F(v)]^2 dv \\ & \left. - (1 - F_2) \int_c^{x_0} e^{\varphi(v)} F(v) dv - F_1 \int_{x_0}^d e^{\varphi(v)} [1 - F(v)] dv \right\} \end{aligned} \quad (5.96)$$

where  $F_1 = F(c)$ ,  $F_2 = F(d)$ , and  $P_\infty \equiv P(\infty)$ .

In the particular case where  $c = -\infty$  ( $F(d) = P_\infty$ ,  $F(c) = 0$ ) the relaxation time is given by

$$\begin{aligned} \Theta = \frac{B}{A} & \left\{ \int_{x_0}^d e^{\varphi(v)} F(v) [1 - F(v)] dv + \frac{P_\infty}{(1 - P_\infty)} \int_d^\infty e^{\varphi(v)} [1 - F(v)]^2 dv \right. \\ & \left. - \int_{-\infty}^{x_0} e^{\varphi(v)} F^2(v) dv \right\} \end{aligned} \quad (5.97)$$

If, on the other hand,  $d = \infty$  ( $F(d) = 1$ ,  $F(c) = 1 - P_\infty$ ) from (5.96), one finds

$$\begin{aligned} \Theta = \frac{B}{A} & \left\{ \int_c^{x_0} e^{\varphi(v)} F(v) [1 - F(v)] dv + \frac{P_\infty}{(1 - P_\infty)} \int_{-\infty}^c e^{\varphi(v)} F^2(v) dv \right. \\ & \left. - \int_{x_0}^\infty e^{\varphi(v)} [1 - F(v)]^2 dv \right\} \end{aligned} \quad (5.98)$$

In the case of the symmetry of the potential profile with respect to the coordinate of the initial distribution  $x_0$  (which may be taken as  $x_0 = 0$ ) and of the symmetrical decision interval  $[-d, +d]$  from (5.96), one can obtain the following expression for the relaxation time:

$$\Theta = \frac{B}{A_1} \left\{ \int_0^d e^{\varphi(v)} f(v) [1 - f(v)] dv + \frac{P_\infty}{(1 - P_\infty)} \int_d^\infty e^{\varphi(v)} [1 - f(v)]^2 dv \right\} \quad (5.99)$$

where a new function is introduced:

$$f(x) = A_1 \int_0^x e^{-\varphi(v)} dv, \quad A_1^{-1} = \int_0^\infty e^{-\varphi(v)} dv, \quad P_\infty = f(d)$$

As may be shown, the same relaxation time (5.99) will take place if the initial distribution is located in an immediate vicinity of the origin (i.e., when  $x_0 = +0$ ) and when the reflecting wall is sited at the point  $x = 0$ .

In the situation where there are two reflecting walls at the points  $\lambda_1 = 0$  and  $\lambda_2 = \lambda$  and the decision interval is  $[c = 0, d]$ , so that  $0 < x_0 < d < \lambda$ , expression (5.96) becomes ( $F_1 = 0, F_2 = P_\infty$ )

$$\Theta = \frac{B}{A_2} \left\{ \int_0^d e^{\varphi(v)} \psi(v) [1 - \psi(v)] dv + \frac{P_\infty}{(1 - P_\infty)} \int_d^\lambda e^{\varphi(v)} [1 - \psi(v)]^2 dv - \int_0^{x_0} e^{\varphi(v)} \psi(v) dv \right\} \quad (5.100)$$

where

$$\psi(x) = A_2 \int_0^x e^{-\varphi(v)} dv, \quad A_2^{-1} = \int_0^\lambda e^{-\varphi(v)} dv, \quad P_\infty = \psi(d)$$

*The Initial Probability Distribution Lies Outside the Decision Interval.* In this case, which is depicted in Fig. 3(b), the chosen points  $c$  and  $d$  satisfy the inequalities  $x_0 < c < d$ . Because of  $P(0) = 0$  the relaxation time is now [see (5.86)]

$$\Theta = \frac{H_2(d) - H_2(c)}{P_\infty} \quad (5.101)$$

The numerator of this fraction is represented by (5.95) as before, but due to the above-mentioned inequalities the relaxation time is expressed by another formula ( $F_1 = F(c), F_2 = F(d)$ ):

$$\Theta = \frac{B}{A} \left\{ \int_{-\infty}^{+\infty} e^{\varphi(v)} F(v) [1 - F(v)] dv - \int_{-\infty}^{x_0} e^{\varphi(v)} F(v) dv - \int_d^\infty e^{\varphi(v)} [1 - F(v)] dv - \frac{1}{F_2 - F_1} \int_c^d e^{\varphi(v)} [1 - F(v)] [F(v) - F_1] dv \right\} \quad (5.102)$$

In particular case where  $d = \infty$  ( $F_2 = 1$ ,  $P_\infty = 1 - F_1$ )

$$\Theta = \frac{B}{A} \left\{ \int_{x_0}^c e^{\varphi(v)} F(v) [1 - F(v)] dv + \frac{F_1}{1 - F_1} \int_c^\infty e^{\varphi(v)} [1 - F(v)]^2 dv - \int_{-\infty}^{x_0} e^{\varphi(v)} F(v)^2 dv \right\} \quad (5.103)$$

*The Relaxation Time in a Single Point.* We turn now to formula (5.87). The function  $Z_1(x)$  may be obtained in two ways: First, one can solve Eq. (5.88b), second, one can use Eq. (5.90c) keeping in mind that the function  $H_2(x)$  is already obtained [see formula (5.94)] and in addition it satisfies the required boundary conditions ( $H_2(\pm\infty) = 0$ ).

The second way is shorter. From (5.90c) and (5.94) we have

$$-Z_1(x) = \frac{dH_2(x)}{dx} = Be^{-\varphi(x)} \left\{ \int_{-\infty}^x e^{-\varphi(v)} [1(v - x_0) - F(v)] dv - A \int_{-\infty}^{+\infty} e^{-\varphi(u)} du \int_{-\infty}^u e^{\varphi(v)} [1(v - x_0) - F(v)] dv \right\}$$

Hence, according to (5.87) and by changing the order of integration in the last integral, the relaxation time may be expressed as

$$\Theta(\ell) = \frac{B}{A} \left\{ \int_{-\infty}^{\ell} e^{\varphi(v)} [1(v - x_0) - F(v)] dv - \int_{-\infty}^{+\infty} e^{\varphi(v)} [1(v - x_0) - F(v)][1 - F(v)] dv \right\} \quad (5.104)$$

Considering the relaxation time at the point  $x = \ell > x_0$  [Fig. 3(e)], one obtains the following after some transformations:

$$\Theta(\ell) = \frac{B}{A} \left\{ \int_{-\infty}^{+\infty} e^{\varphi(v)} F(v) [1 - F(v)] dv - \int_{-\infty}^{x_0} e^{\varphi(v)} F(v) dv - \int_{\ell}^{\infty} e^{\varphi(v)} [1 - F(v)] dv \right\} \quad (5.105)$$

It is easy to check that the same relaxation time may be derived from expression (5.102) for  $c \leq \ell \leq d$  at  $c \rightarrow \ell$ ,  $d \rightarrow \ell$ .

For the case where  $\ell < x_0$  [Fig. 3(f)] from (5.104) after some transformations, it follows that the relaxation time takes the form

$$\Theta(\ell) = \frac{B}{A} \left\{ \int_{-\infty}^{+\infty} e^{\varphi(v)} F(v) [1 - F(v)] dv - \int_{-\infty}^{\ell} e^{\varphi(v)} F(v) dv - \int_{x_0}^{\infty} e^{\varphi(v)} [1 - F(v)] dv \right\} \quad (5.106)$$

When comparing (5.106) with (5.105), it becomes evident that these expressions coincide to make the interchange  $x_0 \leftrightarrow \ell$ . This fact demonstrates the so-called *reciprocity principle*: In any linear system, some effect does not vary if the source (at position  $x = x_0$ ) and the observation point ( $x = \ell$ ) will be interchanged. The linearity of our system is represented by the linearity of the Fokker–Planck equation (5.72).

#### 4. Basic Results Relating to Decay Times

*Potential Profiles of Type II.* Consider now the potential profiles of type II, which may represent the occurrence of the metastable state or the nonstable state (Fig. 4) and which tend to plus infinity at  $x \rightarrow -\infty$  and to minus infinity at  $x \rightarrow +\infty$ . The boundary conditions are now  $G(-\infty, t) = 0$  and  $W(+\infty, t) = 0$ . For this reason all functions  $H_k(x)$  must be zero at  $x = -\infty$  and all functions  $Z_k(x)$  must be zero at  $x = +\infty$ . For such potential profiles the nonzero steady-state distributions do not exist and consequently  $Z_0(x) \equiv 0$ .

As for probability  $P(t) = \int_c^d W(x, t) dx$ , where  $c < x_0 < d$ , it is evident that  $P(0) = 1$  and  $P(\infty) = 0$ . From (5.86) it follows that (denoting  $\tau$  as the decay time of the metastable state or the decay time of the unstable state)

$$\tau = H_2(c) - H_2(d) \quad (5.107)$$

From Eq. (5.90b) we get  $H_1(x) = 1(x - x_0)$  and consequently condition (5.85) is fulfilled. From Eq. (5.91c) one can find

$$\frac{dH_2(x)}{dx} = e^{-\varphi(x)} \left[ C_1 + B \int_{-\infty}^x e^{\varphi(v)} 1(v - x_0) dv \right] \quad (5.108)$$

where  $C_1$  is an arbitrary constant.

Because  $Z_1(x) = -dH_2(x)/dx$  [see Eq. (5.90c)] must be zero at  $x = +\infty$ , we obtain

$$C_1 = -B \int_{-\infty}^{+\infty} e^{\varphi(v)} 1(v - x_0) dv = -B \int_{x_0}^{+\infty} e^{\varphi(v)} dv$$

Consequently, the integration of Eq. (5.108) gives

$$H_2(x) = B \left\{ \int_{-\infty}^x e^{-\varphi(u)} du \int_{-\infty}^u e^{\varphi(v)} 1(v - x_0) dv - \int_{x_0}^{+\infty} e^{\varphi(v)} dv \cdot \int_{-\infty}^x e^{-\varphi(v)} dv \right\} + C_2$$

Because of  $H_2(-\infty) = 0$ , an arbitrary constant  $C_2$  must be zero.

After some transformations we have

$$H_2(x) = B \begin{cases} \int_{x_0}^x e^{\varphi(v)} dv \int_v^x e^{-\varphi(u)} du - \int_{x_0}^{\infty} e^{\varphi(v)} dv \cdot \int_{-\infty}^x e^{-\varphi(u)} du, & x > x_0 \\ - \int_{x_0}^{\infty} e^{\varphi(v)} dv \cdot \int_{-\infty}^x e^{-\varphi(u)} du, & x < x_0 \end{cases}$$

Hence, according to (5.107), taking into account that  $c < x_0 < d$ , we finally arrive at the exact expression of the escape time of the Brownian particles from decision interval  $[c, d]$  for an arbitrary potential profile  $\varphi(x)$  of type II (Fig. 4):

$$\tau = B \left\{ \int_{x_0}^d e^{\varphi(v)} dv \int_c^v e^{-\varphi(u)} du + \int_d^{\infty} e^{\varphi(v)} dv \cdot \int_c^d e^{-\varphi(u)} du \right\} \quad (5.109)$$

In the case where the absorbing boundary is at  $x = \lambda_2 > d$ , expression (5.109) takes the form

$$\tau = B \left\{ \int_{x_0}^d e^{\varphi(v)} dv \int_c^v e^{-\varphi(u)} du + \int_d^{\lambda_2} e^{\varphi(v)} dv \cdot \int_c^d e^{-\varphi(u)} du \right\} \quad (5.110)$$

For the decision interval extended to the absorbing boundary ( $d = \lambda_2$ ) from (5.110), one obtains

$$\tau = B \int_{x_0}^{\lambda_2} e^{\varphi(v)} dv \int_c^v e^{-\varphi(u)} du \quad (5.111)$$

If, in addition,  $c = -\infty$ , we have come to the MFPT

$$\tau = B \int_{x_0}^{\lambda_2} e^{\varphi(v)} dv \int_{-\infty}^v e^{-\varphi(u)} du \equiv T(x_0, \lambda_2) \quad (5.112)$$

that we have already mentioned. In other words, the MFPT coincides with the decay time of the state existing in decision interval  $[-\infty, \lambda_2]$ .

For the decision interval  $[-\infty, d]$ , escape time (5.109) reads

$$\tau = T(x_0, d) + B \left\{ \int_d^\infty e^{\varphi(v)} dv \cdot \int_{-\infty}^d e^{-\varphi(u)} du \right\} \tag{5.113}$$

We obtain  $\tau > T(x_0, d)$ . Such, indeed, is the case, because the escape of the Brownian particles from the decision interval is more rapid when the absorbing wall is at  $x = d$  than it is in the presence of the comparatively slowly dropping potential profile (see Fig. 4).

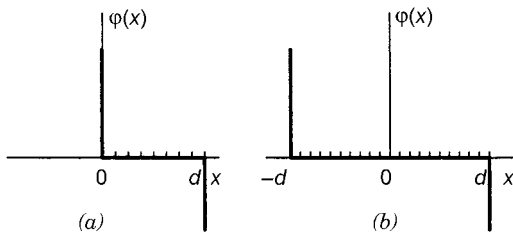
In the case where the reflecting wall and the absorbing wall are at the ends of the decision interval  $[c, d]$ , the decay time

$$\tau = B \int_{x_0}^d e^{\varphi(v)} dv \int_c^v e^{-\varphi(u)} du \tag{5.114}$$

obtained from (5.110) coincides with the MFPT.

We now call attention to an interesting paradoxical fact: For two different situations we have obtained the same decay times represented by formulas (5.111) and (5.114). It is obvious that the processes of changing the probability  $P(t) = \int_c^d W(x, t) dx$  from  $P(0) = 1$  to  $P(\infty) = 0$  in the two above-mentioned situations must be distinct because of various potential profiles  $\varphi(x)$  for  $x < c$ . What is the reason for this coincidence of the decay times? This occurrence is due to integral properties of the timescales defined by (5.75). Different behaviors of  $P(t)$  may lead to the same  $\vartheta$ .

Let us consider, for example, two simplest cases where this fact takes place (Fig. 6). There are two different potential profiles (a) and (b) with  $x_0 = +0$  and with the same decision interval  $[0, d]$ . The decay time of the metastable state arranged in the decision interval according to (5.111) and (5.114) is the same and equals  $\tau = d^2/D$ . At the same time, it is clear that evolutions of  $P(t)$  are different. In case (b), decreasing of the probability is precisely faster because of the fastest outcome of the initial distribution from the decision interval to the left.



**Figure 6.** The simplest example of two different [(a) and (b)] potential profiles with the same lifetime  $\tau$ .

*Potential Profiles of Type III.* We now direct our attention to the potential profiles of type III (Fig. 5). The boundary conditions are now  $W(\pm\infty) = 0$ . Consequently, all functions  $Z_k(x)$  must be zero at  $x = \pm\infty$ . As before,  $Z_0(x) \equiv 0$ ,  $P(t) = \int_c^d W(x, t) dx$ ,  $c < x_0 < d$ ,  $P(0) = 1$ ,  $P(\infty) = 0$ , and

$$\tau = H_2(c) - H_2(d)$$

The calculation of  $H_1(x)$  from Eq. (5.90b) gives

$$H_1(x) = 1(x - x_0) + C_1$$

where an arbitrary constant  $C_1$  remains unknown because we do not know boundary conditions on the functions  $H_k(x)$ . At the same time, condition (5.85) is fulfilled.

The calculation of  $dH_2(x)/dx$  from Eq. (5.91c) results in

$$\frac{dH_2(x)}{dx} = e^{-\varphi(x)} \left[ C_2 + B \int_{-\infty}^x e^{\varphi(v)} [1(v - x_0) + C_1] dv \right]$$

Taking into account Eq. (5.90c), we can determine arbitrary constants  $C_1$  and  $C_2$  from the boundary conditions:  $-Z_1(\pm\infty) = \frac{dH_2(x)}{dx} \Big|_{x=\pm\infty} = 0$ . This leads to

$$C_1 = - \int_{x_0}^{+\infty} e^{\varphi(v)} dv \Big/ \int_{-\infty}^{+\infty} e^{\varphi(v)} dv, \quad C_2 = -B \int_{-\infty}^{+\infty} e^{\varphi(v)} [1(v - x_0) + C_1] dv$$

and to

$$H_2(x) = -B \left\{ \int_{-\infty}^x e^{-\varphi(u)} du \int_u^{+\infty} e^{\varphi(v)} [1(v - x_0) + C_1] dv \right\} + C_3$$

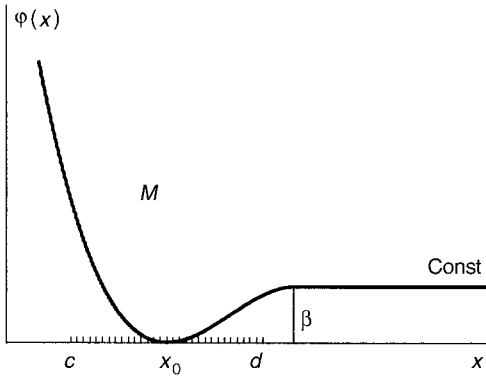
Therefore, independently of the value of an arbitrary constant  $C_3$ , we obtain

$$\tau = B \int_c^d e^{-\varphi(u)} du \int_u^\infty e^{\varphi(v)} [1(v - x_0) + C_1] dv$$

By reversing the order of the integrals, we arrive at the net expression for the decay time for the situation depicted in Fig. 5:

$$\begin{aligned} \tau = B \left\{ f_1 \cdot \int_{x_0}^d e^{\varphi(v)} dv \int_c^v e^{-\varphi(u)} du - f_2 \cdot \int_c^{x_0} e^{\varphi(v)} dv \int_c^v e^{-\varphi(u)} du \right. \\ \left. + f_1 \cdot \int_d^\infty e^{\varphi(v)} dv \cdot \int_c^d e^{-\varphi(u)} du \right\} \end{aligned} \tag{5.115}$$





**Figure 7.** An example of the potential profile with the metastable state (*M*) for which the convergence condition is disrupted.

where

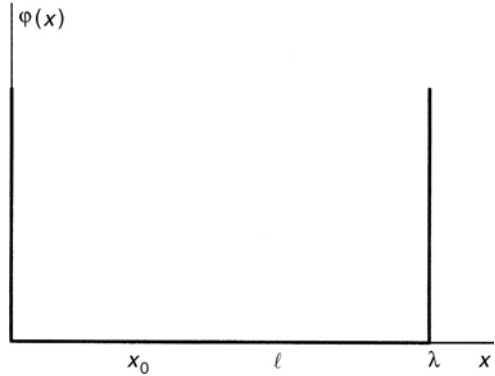
$$f_1 = \int_{-\infty}^{x_0} e^{\varphi(v)} dv/f_3, \quad f_2 = \int_{x_0}^{\infty} e^{\varphi(v)} dv/f_3, \quad f_3 = \int_{-\infty}^{\infty} e^{\varphi(v)} dv \quad (5.116)$$

5. *Some Comments and Interdependence of Relaxation and Decay Times*

*Convergence Condition.* Let us return to the convergence condition of integrals (5.75) and (5.76). Consider, for example, the potential profile depicted in Fig. 7 and let us try to calculate the decay time of the metastable state *M* in accordance with (5.75). It is easy to verify that for this potential profile  $\vartheta = \infty$ , that is, the integral in (5.75) diverges, though the probability  $P(t)$  varies from  $P(0) = 1$  to  $P(\infty) = 0$ . The important matter is that this probability changes from the initial value to the final one slowly enough. To determine the time characteristics for such profiles it is necessary to use another approach (see, e.g., Refs. 82–84), defining the relaxation time at the level 1/2 (5.12).

It is very interesting to note that in this case the factor  $e^{2\beta}$  arises in the escape time instead of the Kramers' factor  $e^\beta$ . This circumstance is associated with the good possibility for the Brownian particles to diffuse back to the potential well from a flat part of the potential profile, resulting in strong increasing of the escape time from the well (see, e.g., Ref. 83).

*Monotony Condition.* Let us turn back to the monotony condition of the variations of  $P(t)$  or  $W(\ell, t)$ . If, for example, the point  $\ell$  is arranged near  $x_0$ , where the initial probability distribution  $W(x, 0) = \delta(x - x_0)$  is located, the probability density  $W(\ell, t)$  early in the evolution may noticeably exceed the final value  $W(\ell, \infty)$ . For such a situation the relaxation time  $\Theta(\ell)$  according to (5.76) may take not only a zero value, but also a negative one. In other words,



**Figure 8.** A rectangular potential well.

nonmonotony of  $P(t)$  or  $W(\ell, t)$  leads in accordance with (5.75) and (5.76) to defective results. We analyze this situation with aid of a simple example.

Consider the potential profile depicted in Fig. 8. At the points  $x = 0$  and  $x = \lambda$  the reflecting walls are arranged. The relaxation time at the point  $\ell$  may be calculated with the aid of (5.105), taking into account that  $\varphi(x) = 0$ ,  $x \in [0, \lambda]$ :

$$\Theta(\ell) = \frac{B}{A} \left\{ \int_0^\lambda F(v)[1 - F(v)] dv - \int_0^{x_0} F(v) dv - \int_\ell^\lambda [1 - F(v)] dv \right\} \quad (5.117)$$

Here

$$A^{-1} = \int_0^\lambda dv = \lambda, \quad F(v) = A \int_0^v d\xi = v/\lambda$$

As a result we have ( $B = 2/D$ )

$$\Theta(\ell) = \frac{\lambda^2}{3D} \left\{ 1 - 3\left(\frac{x_0}{\lambda}\right)^2 - 3\left(1 - \frac{\ell}{\lambda}\right)^2 \right\} \quad (5.118)$$

Three terms in (5.117) correspond to three terms in (5.118).

We have obtained the relaxation time—that is, the time of attainment of the equilibrium state or, in other words, the transition time to the stationary distribution  $W(\ell, \infty)$  at the point  $\ell$  in the rectangular potential profile. This time depends on the delta-function position  $x_0$  and on the observation point location  $\ell$ .

The relaxation time is maximal for  $x_0 = 0$  and  $\ell = \lambda$ —that is, when  $x_0$  and  $\ell$  are widely spaced. If the distance between  $x_0$  and  $\ell$  decreases, the relaxation time goes down.

But if the distance between  $x_0$  and  $\ell$  is too small, expression (5.118) may give  $\Theta(\ell) = 0$  or even  $\Theta(\ell) < 0$ . What does it mean? This signals that the condition of monotonic variation of  $W(\ell, t)$  from zero to  $W(\ell, \infty)$  is broken and that the obtained values of the relaxation times are false.

The special investigation has shown that, in particular, for  $x_0 = 0$  the relaxation time defined by (5.118) is true for  $\ell/\lambda \geq 0.5$ . At the same time it would be reasonable to take the first term in (5.118)—that is,  $\Theta = \lambda^2/3D$ —as an upper bound for the relaxation time in the rectangular well to avoid the difficulties with the possible nonmonotonic behavior of the  $W(\ell, t)$  regardless of the values  $x_0$  and  $\ell$ .

The same reasoning may be extended on all above-obtained results regarding relaxation times, but with some care especially when there are no any potential barriers between  $x_0$  and the observation point.

*Some Common Interdependence of Relaxation Times.* Consider an arbitrary disposition of the initial distribution point  $x_0$  and the boundary point  $d$  [see Fig. 3(c,d)]. We may take into account two decision intervals  $I_1 = [-\infty, d]$  and  $I_2 = [d, +\infty]$  and define two probabilities:

$$P_1(t) = \int_{-\infty}^d W(x, t) dx, \quad P_2(t) = \int_d^{\infty} W(x, t) dx$$

In line with these probabilities, we may introduce into consideration two relaxation times  $\Theta_1$  and  $\Theta_2$  according to a common definition (5.75). From the evident equality  $P_1(t) + P_2(t) = 1$ , it follows that  $\Theta_1 = \Theta_2$  for both  $d > x_0$  and  $d < x_0$ .

If there is the symmetrical potential profile  $\varphi(x) = \varphi(-x)$  and the initial distribution is located at the origin (i.e.,  $x_0 = 0$ ), then all results concerning the relaxation times will be the same as for the potential profile in which the reflecting wall is at  $x = 0$  and at  $x_0 = +0$ . This coincidence of the relaxation times may be proven in a common case taking into account that the probability current at  $x = 0$  is equal to zero at any instant of time.

*Interdependence Between Relaxation and Decay Times.* Consider the potential profile of type I which is symmetrical with respect to  $x = d > 0$  and where the initial distribution is located at  $x_0 = 0$  and the decision interval is  $[-\infty, d]$  (see Appendix). The relaxation time that follows from (5.97) is

$$\Theta = \frac{B}{A} \left\{ \int_0^d e^{\varphi(v)} F(v) [1 - F(v)] dv - \int_{-\infty}^0 e^{\varphi(v)} F^2(v) dv + \frac{F(d)}{1 - F(d)} \int_d^{\infty} e^{\varphi(v)} [1 - F(v)]^2 dv \right\}$$

This formula may be transformed into

$$\Theta = \frac{B}{A} \left\{ \int_0^d e^{\varphi(v)} F(v) dv - \int_{-\infty}^d e^{\varphi(v)} F^2(v) dv + \frac{F(d)}{1-F(d)} \int_d^{\infty} e^{\varphi(v)} [1-F(v)]^2 dv \right\}$$

Because of the potential profile symmetry we have  $F(d) = 1/2$ ,  $F(d-z) = 1 - F(d+z)$  and the second integral goes to  $\int_d^{\infty} e^{\varphi(v)} [1-F(v)]^2 dv$ . As a result, we have

$$\Theta = \frac{B}{A} \int_0^d e^{\varphi(v)} F(v) dv = B \int_0^d e^{\varphi(v)} dv \int_{-\infty}^v e^{-\varphi(u)} du = T(0, d) \quad (5.119)$$

Thus, we have proven the so-called *principle of conformity* which was demonstrated for an arbitrary symmetrical potential profile of type I by another more complicated way in Refs. 70 and 85.

Consider the bistable one-level system with symmetrical potential profile  $\varphi(x) = \varphi(-x)$  with respect to the origin, where the potential barrier of the height  $\beta$  is located (Fig. 9). According to the principle of conformity and (5.119) the relaxation time  $\Theta$  of this bistable system (the decision interval is  $[-\infty, 0]$ ) is equal to

$$\Theta = B \int_{-d}^0 e^{\varphi(v)} dv \int_{-\infty}^v e^{-\varphi(u)} du = T(-d, 0)$$

If we will locate the absorbing wall at the point  $x = d$  (the dashed line in Fig. 9), the MFPT  $T(-d, d)$  reads

$$T(-d, d) = B \int_{-d}^d e^{\varphi(v)} dv \int_{-\infty}^v e^{-\varphi(u)} du$$

After some transformations using the symmetrical properties of the potential profile, one finds

$$T(-d, d) = 2T(-d, 0) + \tau_0$$

where

$$\tau_0 = 2B \int_0^d e^{\varphi(v)} dv \int_0^v e^{-\varphi(u)} du$$

It may be shown that for the high enough potential barrier  $\beta \gg 1$  the quantity  $\tau_0$  is significantly smaller than  $2T(-d, 0)$  and we arrive at

$$\Theta = \frac{1}{2}T(-d, +d) \quad (5.120)$$

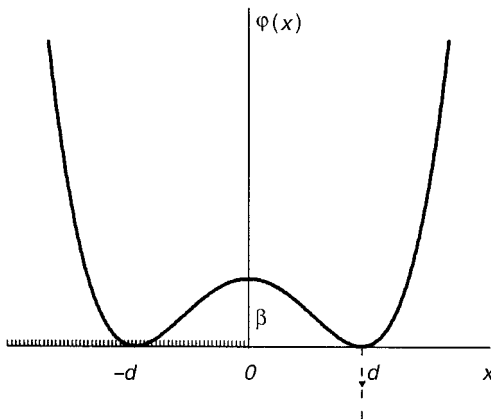
Expression (5.120) means that the relaxation time in an arbitrary symmetrical one-level bistable system is two times smaller than the MFPT  $T(-d, +d)$ —that is, two times smaller than the decay time of the metastable state—shown with the dashed line taken into account in Fig. 9.

This is concerned with the fact that in the case of the relaxation time, roughly speaking only *half of all* Brownian particles should leave the initial potential minimum to reach the equilibrium state, while for the profile of the decay time case *all* particles should leave the initial minimum. Expression (5.120), of course, is true only in the case of the sufficiently large potential barrier, separating the stable states of the bistable system, when the inverse probability current from the second minimum to the initial one may be neglected (see Ref. 33).

The comparison with known results (e.g., Refs. 2, 20, 21, 86, and 87) for variety of examples of metastable, bistable and periodic potentials was done in Refs. 32–35 and 85.

### 6. Derivation of Moments of Transition Time

In this section we restrict our consideration by potentials of type II only (in this case moments of transition time are moments of decay time). The approach, considered above for derivation of the mean transition time may also be used to obtain higher moments, given by Eq. (5.1).



**Figure 9.** A potential profile of type I representing a one-level bistable system. The dashed line shows the absorbing wall.

Let us write in the explicit form the expressions for functions  $H_n(x)$  (we remind that  $H(x, s) = s\hat{G}(x, s) = H_0(x) + sH_1(x) + s^2H_2(x) + \dots$ ) using the boundary conditions  $W(+\infty, t) = 0$  and  $G(-\infty, t) = 0$  ( $H_1(x) = 1(x - x_0)$ ):

$$\begin{aligned}
 H_2(x) &= -B \int_{-\infty}^x e^{-\varphi(v)} \int_v^{\infty} e^{\varphi(y)} 1(y - x_0) dy dv \\
 H_n(x) &= -B \int_{-\infty}^x e^{-\varphi(v)} \int_v^{\infty} e^{\varphi(y)} H_{n-1}(y) dy dv, \quad n = 3, 4, 5, \dots
 \end{aligned}
 \tag{5.121}$$

As one can check, from formula (5.1) (taking the integral by parts and Laplace transforming it using the property  $P(x_0, 0) - s\hat{P}(x_0, s) = \hat{G}(d, s) - \hat{G}(c, s)$  together with the expansion of  $H(x, s)$  via  $H_n(x)$ ), one can obtain the following expressions for moments of decay time [88]:

$$\begin{aligned}
 \tau_1(c, x_0, d) &= -(H_2(d) - H_2(c)) \\
 \tau_2(c, x_0, d) &= 2(H_3(d) - H_3(c)) \\
 \tau_3(c, x_0, d) &= -2 \cdot 3(H_4(d) - H_4(c)), \dots \\
 \tau_n(c, x_0, d) &= (-1)^n n! (H_{n+1}(d) - H_{n+1}(c))
 \end{aligned}
 \tag{5.122}$$

From these recurrent relations, one obtains the following expression for the second moment in the case  $c = -\infty$  ( $c < x_0 < d$ ):

$$\begin{aligned}
 \tau_2(-\infty, x_0, d) &= 2B^2 \left\{ [\tau_1(-\infty, x_0, d)]^2 \right. \\
 &\quad + \int_{-\infty}^d e^{-\varphi(x)} dx \cdot \int_{x_0}^{\infty} e^{\varphi(v)} \int_d^v e^{-\varphi(u)} \int_u^{\infty} e^{\varphi(z)} dz du dv \\
 &\quad \left. - \int_{x_0}^d e^{-\varphi(x)} \int_{x_0}^x e^{\varphi(v)} \int_d^v e^{-\varphi(u)} \int_u^{\infty} e^{\varphi(z)} dz du dv dx \right\}
 \end{aligned}
 \tag{5.123}$$

where  $\tau_1(-\infty, x_0, d)$  is the first moment:

$$\begin{aligned}
 \tau_1(-\infty, x_0, d) &= B \left\{ \int_{-\infty}^d e^{-\varphi(x)} dx \cdot \int_{x_0}^{\infty} e^{\varphi(v)} dv \right. \\
 &\quad \left. - \int_{x_0}^d e^{-\varphi(x)} \int_{x_0}^x e^{\varphi(v)} dv dx \right\}
 \end{aligned}
 \tag{5.124}$$

Instead of analyzing the structure and the properties of the second and higher moments, in the next section, we will perform analysis of temporal evolution of the survival probability.

7. *Timescales of Evolution of Averages and Correlation Time*

Analogically, one can apply the considered approach to derive timescales of evolution of averages [89] and correlation time [90,91]. We will search for the average  $m_f(t)$  in the form

$$m_f(t) = \langle f(x) \rangle = \int_{-\infty}^{+\infty} f(x)W(x,t) dx \tag{5.125}$$

As we have mentioned above, the FPE (5.72) is a continuity equation. To obtain necessary average  $m_f(t)$  (5.125), let us multiply it by the function  $f(x)$  and integrate with respect to  $x$  from  $-\infty$  to  $+\infty$ . Then we get

$$\frac{dm_f(t)}{dt} = - \int_{-\infty}^{+\infty} f(x) \frac{\partial G(x,t)}{\partial x} dx \tag{5.126}$$

This is already an ordinary differential equation of the first order ( $f(x)$  is a known deterministic function), but nobody knows how to find  $G(x,t)$ .

Let us define the characteristic scale of time evolution of the average  $m_f(t)$  as an integral relaxation time:

$$\tau_f(x_0) = \frac{\int_0^{\infty} [m_f(t) - m_f(\infty)] dt}{m_f(0) - m_f(\infty)} \tag{5.127}$$

Definition (5.127) as before is general in the sense that it is valid for any initial condition. But here we restrict ourselves by the delta-shaped initial distribution and consider  $\tau_f(x_0)$  as a function of  $x_0$ . For arbitrary initial distribution the required timescale may be obtained from  $\tau_f(x_0)$  by separate averaging of both numerator and denominator  $m_f(0) - m_f(\infty)$  over initial distribution, because  $m_f(0)$  is also a function of  $x_0$ .

The restrictions of the definition (5.127) are the same as before: It gives correct results only for monotonically evolving functions  $m_f(t)$  and  $m_f(t)$  should fastly enough approach its steady-state value  $m_f(\infty)$  for convergence of the integral in (5.127).

Performing Laplace transform of formula (5.127), Eq. (5.126) (Laplace transformation of (5.126) gives:  $sm_f(s) - m_f(0) = - \int_{-\infty}^{+\infty} f(x)[\partial \hat{G}(x,s)/\partial x] dx$ , where  $m_f(s) = \int_0^{\infty} m_f(t)e^{-st} dt$ ) and combining them, we obtain

$$\begin{aligned} \tau_f(x_0) &= \lim_{s \rightarrow 0} \frac{sm_f(s) - m_f(\infty)}{s[m_f(0) - m_f(\infty)]} \\ &= \lim_{s \rightarrow 0} \frac{m_f(0) - m_f(\infty) - \int_{-\infty}^{+\infty} f(x)[\partial \hat{G}(x,s)/\partial x] dx}{s[m_f(0) - m_f(\infty)]} \end{aligned} \tag{5.128}$$

where  $\hat{G}(x,s)$  is the Laplace transformation of the probability current  $\hat{G}(x,s) = \int_0^{\infty} G(x,t)e^{-st} dt$ .

Introducing the function  $H(x, s) = s\hat{G}(x, s)$  and expanding it into power series in  $s$ , we restrict our computation by obtaining  $H_2(x)$  only, since it can be demonstrated that

$$\tau_f(x_0) = -\frac{\int_{-\infty}^{+\infty} f(x) dH_2(x)}{[m_f(0) - m_f(\infty)]} \quad (5.129)$$

Substituting the concrete form of  $H_2(x)$  (5.94) into formula (5.129), one can obtain the characteristic scale of time evolution of any average  $m_f(t)$  for arbitrary potential such that  $\varphi(\pm\infty) = \infty$ :

$$\begin{aligned} \tau_f(x_0) = & \frac{B}{m_f(0) - m_f(\infty)} \left\{ \int_{-\infty}^{\infty} f(x) e^{-\varphi(x)} \int_{x_0}^x e^{\varphi(u)} F(u) du dx \right. \\ & - A \int_{-\infty}^{\infty} f(x) e^{-\varphi(x)} dx \int_{-\infty}^{\infty} e^{-\varphi(x)} \int_{x_0}^x e^{\varphi(u)} F(u) du dx \\ & + A \int_{-\infty}^{\infty} f(x) e^{-\varphi(x)} dx \int_{x_0}^{\infty} e^{-\varphi(x)} \int_{x_0}^x e^{\varphi(u)} du dx \\ & \left. - \int_{x_0}^{\infty} f(x) e^{-\varphi(x)} \int_{x_0}^x e^{\varphi(u)} du dx \right\} \quad (5.130) \end{aligned}$$

where  $F(x)$  is expressed by

$$F(u) = \int_{-\infty}^u e^{-\varphi(v)} dv / \int_{-\infty}^{+\infty} e^{-\varphi(v)} dv \quad (5.131)$$

and  $A = 1 / \int_{-\infty}^{+\infty} e^{-\varphi(x)} dx$ .

Analogically, the correlation time as evolution time of the correlation function  $K_x(t) = \langle x(t')x(t'+t) \rangle$  [90] or the correlation time of more general function  $K_f(t) = \langle f(x(t'))f(x(t'+t)) \rangle$  (in Ref. 91 the correlation time of  $\sin(x(t))$  has been computed) may be obtained. Here we present the correlation time of  $K_x(t) = \langle x(t')x(t'+t) \rangle$  [90] defined as

$$\tau_c = \frac{1}{\sigma^2} \int_0^{\infty} [K_x(t) - \langle x \rangle^2] dt \quad (5.132)$$

where  $\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2$ . As can be demonstrated [90], the correlation time is given by

$$\tau_c = \frac{B}{A\sigma^2} \int_{-\infty}^{+\infty} e^{\varphi(u)} [H(u) - \langle x \rangle F(u)]^2 du \quad (5.133)$$



where

$$H(x) = \int_{-\infty}^x uW(u) du, \quad \langle x \rangle = H(\infty), \quad \sigma^2 = \int_{-\infty}^{+\infty} (u - \langle u \rangle)^2 W(u) du$$

$$W(x) = Ae^{-\varphi(x)}, \quad A = 1 / \int_{-\infty}^{+\infty} e^{-\varphi(x)} dx$$

One can check that this result coincides with the result by Risken and Jung (5.24) for the case of constant diffusion coefficient.

## VI. TIME EVOLUTION OF OBSERVABLES

### A. Time Constant Potentials

It is known that when the transition of an overdamped Brownian particle occurs over a potential barrier high enough in comparison with noise intensity  $\Delta\Phi/kT \gg 1$ , time evolution of many observables (e.g., the probability of transition or the correlation function) is a simple exponent  $\sim \exp(-t/\tau)$  [2,15], where  $\tau$  is the corresponding timescale (the mean transition time or the correlation time). Such representation of an observable is evident, for example, from the method of eigenfunction analysis. In this case the corresponding timescale (mean transition time) gives complete information about the probability evolution. The boundaries of validity of exponential approximation of the probability were studied in Refs. 24 and 30. In Ref. 24 the authors extended the mean first passage time to the case of “radiation” boundary condition and for two barrierless examples demonstrated good coincidence between exponential approximation and numerically obtained probability. In a more general case the exponential behavior of observables was demonstrated in Ref. 30 for relaxation processes in systems having steady states. Using the approach of “generalized moment approximation,” the authors of Ref. 30 obtained the exact mean relaxation time to steady state (see Section V.C), and for particular example of a rectangular potential well they demonstrated good coincidence of exponential approximation with numerically obtained observables. They considered in Ref. 30 an example where the rectangular well did not have a potential barrier, and the authors of that paper supposed that their approach (and the corresponding formulas) should also give good approximation in tasks with diffusive barrier crossing for different examples of potentials and in a wide range of noise intensity.

In this section we will analyze the validity of exponential approximation of observables in wide range of noise intensity [88,89,91,92].

#### 1. Time Evolution of Survival Probability

Let us perform the analysis of temporal evolution of the probability  $P(t, x_0)$  of a Brownian particle, located at the point  $x_0$  ( $t = 0$ ) within the interval  $(c, d)$ , to be

at the time  $t > 0$  inside the considered interval:  $P(t, x_0) = \int_c^d W(x, t) dx$  (survival probability). We suppose that  $c$  and  $d$  are arbitrary chosen points of an arbitrary potential profile  $\varphi(x)$ , and boundary conditions at these points may be arbitrary:  $W(c, t) \geq 0$  and  $W(d, t) \geq 0$ , and we restrict our consideration by profiles of type II (Fig. 4).

The corresponding moments of decay time were obtained above (5.122). Let us analyze in more detail their structure. One can represent the  $n$ th moment in the following form:

$$\tau_n(c, x_0, d) = n! \tau_1^n(c, x_0, d) + r_n(c, x_0, d) \tag{6.1}$$

This is a natural representation of  $\tau_n(c, x_0, d)$  due to the structure of recurrent formulas (5.121), which is seen from the particular form of the first and the second moments given by (5.123) and (5.124). Using the approach, applied in the paper by Shenoy and Agarwal [93] for analysis of moments of the first passage time, it can be demonstrated that in the limit of a high barrier  $\Delta\varphi \gg 1$  ( $\Delta\varphi = \Delta\Phi/kT$  is the dimensionless barrier height) the remainders  $r_n(c, x_0, d)$  in formula (6.1) may be neglected. For  $\Delta\varphi \approx 1$ , however, a rigorous analysis should be performed for estimation of  $r_n(c, x_0, d)$ . Let us suppose that the remainders  $r_n(c, x_0, d)$  may be neglected in a wide range of parameters, and below we will check numerically when our assumption is valid.

The cumulants [2,43] of decay time  $\varkappa_n$  are much more useful for our purpose to construct the probability  $P(t, x_0)$ —that is, the integral transformation of the introduced probability density of decay time  $w_\tau(t, x_0)$  (5.2). Unlike the representation via moments, the Fourier transformation of the probability density (5.2)—the characteristic function—decomposed into the set of cumulants may be inversely transformed into the probability density.

Analogically to the representation for moments (6.1), a similar representation can be obtained for cumulants  $\varkappa_n$ :

$$\varkappa_n(c, x_0, d) = (n - 1)! \varkappa_1^n(c, x_0, d) + R_n(c, x_0, d) \tag{6.2}$$

It is known that the characteristic function  $\Theta(\omega, x_0) = \int_0^\infty w_\tau(t, x_0) e^{j\omega t} dt$  ( $j = \sqrt{-1}$ ) can be represented as the set of cumulants ( $w_\tau(t, x_0) = 0$  for  $t < 0$ ):

$$\Theta(\omega, x_0) = \exp \left[ \sum_{n=1}^\infty \frac{\varkappa_n(c, x_0, d)}{n!} (j\omega)^n \right] \tag{6.3}$$

In the case where the remainders  $R_n(c, x_0, d)$  in (6.2) (or  $r_n(c, x_0, d)$  in (6.1)) may be neglected, the set (6.3) may be summarized and inverse Fourier transformed:

$$w_\tau(t, x_0) = \frac{e^{-t/\tau}}{\tau} \tag{6.4}$$

where  $\tau$  is the mean decay time [34,35] ( $\tau(c, x_0, d) \equiv \tau_1 \equiv \bar{x}_1$ ):

$$\tau(c, x_0, d) = B \left\{ \int_{x_0}^d e^{\varphi(x)} \int_c^x e^{-\varphi(v)} dv dx + \int_d^\infty e^{\varphi(x)} dx \int_c^d e^{-\varphi(v)} dv \right\} \quad (6.5)$$

This expression is a direct transformation of formula (5.124), where now  $c$  is arbitrary, such that  $c < x_0 < d$ .

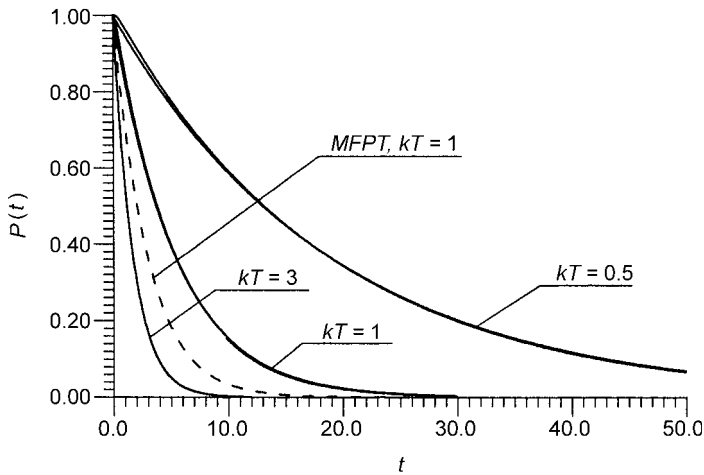
Probably, a similar procedure was previously used (see Refs. 1 and 93–95) for summation of the set of moments of the first passage time, when exponential distribution of the first passage time probability density was demonstrated for the case of a high potential barrier in comparison with noise intensity.

Integrating probability density (6.4), taking into account definition (5.2), we get the following expression for the survival probability  $P(t, x_0)$  ( $P(0, x_0) = 1$ ,  $P(\infty, x_0) = 0$ ):

$$P(t, x_0) = \exp(-t/\tau) \quad (6.6)$$

where mean decay time  $\tau$  is expressed by (6.5). Probability (6.6) represents a well-known exponential decay of a metastable state with a high potential barrier [15]. Where is the boundary of validity of formula (6.6) and when can we neglect  $r_n$  and  $R_n$  in formulas (6.1) and (6.2)? To answer this question, we have considered three examples of potentials having metastable states and have compared numerically obtained survival probability  $P(t, x_0) = \int_c^d W(x, t) dx$  with its exponential approximation (6.6). We used the usual explicit difference scheme to solve the FPE (5.72), supposing the reflecting boundary condition  $G(c_b, t) = 0$  ( $c_b < c$ ) far above the potential minimum and the absorbing one  $W(d_b, t) = 0$  ( $d_b > d$ ) far below the potential maximum, instead of boundary conditions at  $\pm\infty$ , such that the influence of phantom boundaries at  $c_b$  and  $d_b$  on the process of diffusion was negligible. The first considered system is described by the potential  $\Phi(x) = ax^2 - bx^3$ . We have taken the following particular parameters:  $a = 2$  and  $b = 1$ , which lead to the barrier height  $\Delta\Phi \approx 1.2$ ,  $c = -2$ ,  $d = 2a/3b$ , and  $kT = 0.5; 1; 3$  (in computer simulations we set the viscosity  $h = 1$ ). The corresponding curves of the numerically simulated probability and its exponential approximation are presented in Fig. 10. In the worse case when  $kT = 1$  the maximal difference between the corresponding curves is 3.2%. For comparison, there is also presented a curve of exponential approximation with the mean first passage time (MFPT) of the point  $d$  for  $kT = 1$  (dashed line). One can see that in the latter case the error is significantly larger.

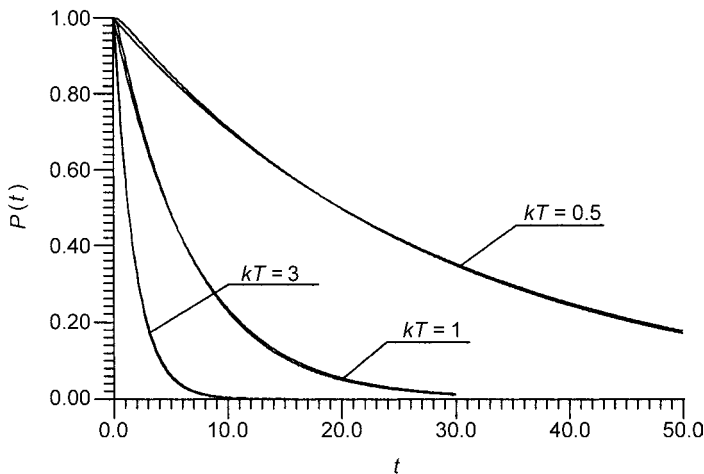
The second considered system is described by the potential  $\Phi(x) = ax^4 - bx^5$ . We have taken the following particular parameters:  $a = 1$  and  $b = 0.5$ , which lead to the barrier height  $\Delta\Phi \approx 1.3$ ,  $c = -1.5$ ,  $d = 4a/5b$ , and  $kT = 0.5; 1; 3$ . The corresponding curves of the numerically simulated probability and its



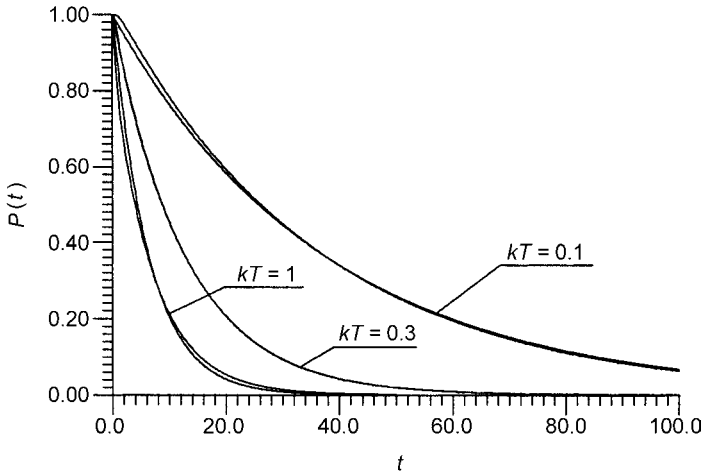
**Figure 10.** Evolution of the survival probability for the potential  $\Phi(x) = ax^2 - bx^3$  for different values of noise intensity; the dashed curve denoted as MFPT (mean first passage time) represents exponential approximation with MFPT substituted into the factor of exponent.

exponential approximation are presented in Fig. 11. In the worse case ( $kT = 1$ ) the maximal difference between the corresponding curves is 3.4%.

The third considered system is described by the potential  $\Phi(x) = 1 - \cos(x) - ax$ . This potential is multistable. We have considered it in the interval  $[-10, 10]$ , taking into account three neighboring minima. We have taken



**Figure 11.** Evolution of the survival probability for the potential  $\Phi(x) = ax^4 - bx^5$  for different values of noise intensity.



**Figure 12.** Evolution of the survival probability for the potential  $\Phi(x) = 1 - \cos(x) - ax$  for different values of noise intensity.

$a = 0.85$ , which leads to the barrier height  $\Delta\Phi \approx 0.1$ ,  $c = -\pi - \arcsin(a)$ ,  $d = \pi - \arcsin(a)$ ,  $x_0 = \arcsin(a)$ , and  $kT = 0.1; 0.3; 1$ . The corresponding curves of the numerically simulated probability and its exponential approximation are presented in Fig. 12. In difference with two previous examples, this potential was considered in essentially longer interval and with smaller barrier. The difference between curves of the numerically simulated probability and its exponential approximation is larger. Nevertheless, the qualitative coincidence is good enough.

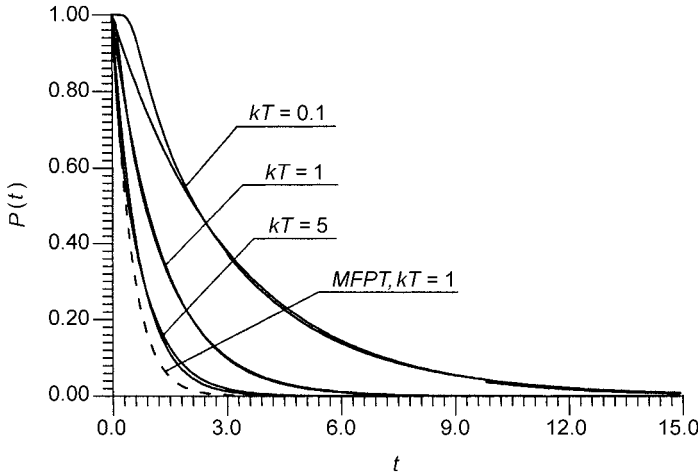
Finally, we have considered an example of metastable state without potential barrier:  $\Phi(x) = -bx^3$ , where  $b = 1$ ,  $x_0 = -1$ ,  $d = 0$ ,  $c = -3$ , and  $kT = 0.1; 1; 5$ . A dashed curve is used to present an exponential approximation with the MFPT of the point  $d$  for  $kT = 1$  (Fig. 13). It is seen that even for such an example the exponential approximation [with the mean decay time (6.5)] gives an adequate description of the probability evolution and that this approximation works better for larger noise intensity.

## 2. Temporal Evolution of Averages

Once we know the required timescale of the evolution of an average, we can present the required average in the form

$$m_f(t) = (m_f(0) - m_f(\infty)) \exp(-t/\tau_f(x_0)) + m_f(\infty) \quad (6.7)$$

The applicability of this formula for several examples of the time evolution of the mean coordinate  $m(t) = \langle x(t) \rangle$  will be checked below.



**Figure 13.** Evolution of the survival probability for the potential  $\Phi(x) = -bx^3$  for different values of noise intensity; the dashed curve denoted as MFPT (mean first passage time) represents exponential approximation with MFPT substituted into the factor of exponent.

As an example of the description presented above, let us consider the time evolution of a mean coordinate of the Markov process:

$$m(t) = \langle x(t) \rangle = \int_{-\infty}^{+\infty} xW(x, t) dx \tag{6.8}$$

The characteristic timescale of evolution of the mean coordinate in the general case may be easily obtained from (5.130) by substituting  $x$  for  $f(x)$ . But for symmetric potentials  $\varphi(x) = \varphi(-x)$  the expression of timescale of mean coordinate evolution may be significantly simplified ( $m(\infty) = 0$ ):

$$\tau_m(x_0) = \frac{B}{x_0} \left\{ \int_0^{+\infty} xe^{-\varphi(x)} dx \cdot \int_0^{x_0} e^{\varphi(u)} du + \int_0^{x_0} xe^{-\varphi(x)} \int_{x_0}^x e^{\varphi(u)} du dx \right\} \tag{6.9}$$

If  $x_0 = 0$ , it is not difficult to check that  $\tau_m(x_0) = 0$ .

Let us consider now some examples of symmetric potentials and check the applicability of exponential approximation:

$$m(t) = \langle x(t) \rangle = x_0 \exp(-t/\tau_m(x_0)) \tag{6.10}$$

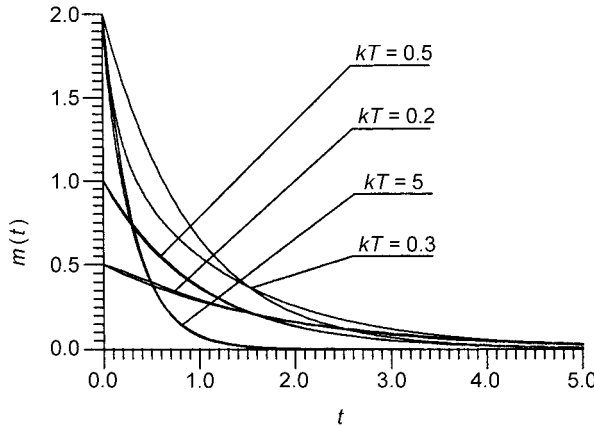
First, we should consider the time evolution of the mean coordinate in the monostable parabolic potential  $\varphi(x) = ax^2/2$  (linear system), because for this

case the time evolution of the mean is known:

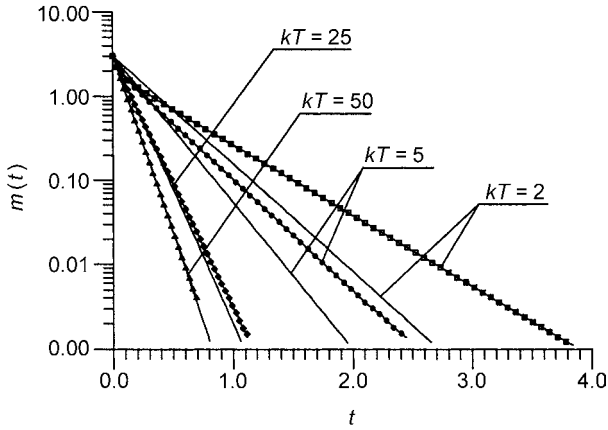
$$m_{\text{par}}(t) = x_0 \exp(-at/B) \quad (6.11)$$

where  $a = a'/kT$  and  $B = h/kT$ , so  $\tau_{\text{par}} = B/a$  for the linear system and does not depend on noise intensity and the coordinate of initial distribution  $x_0$ . On the other hand,  $\tau_m(x_0)$  is expressed by formula (6.9). Substituting parabolic potential  $\varphi(x) = ax^2/2$  in formula (6.9), making simple evaluations and changing the order of integrals, it can be easily demonstrated that  $\tau_m(x_0) = B/a = h/a' = \tau_{\text{par}}$ , so for purely parabolic potential the time of mean evolution (6.9) is independent of both noise intensity and  $x_0$ , which is required. This fact proves the correctness of the used approach.

The second considered example is described by the monostable potential of the fourth order:  $\Phi(x) = ax^4/4$ . In this nonlinear case the applicability of exponential approximation significantly depends on the location of initial distribution and the noise intensity. Nevertheless, the exponential approximation of time evolution of the mean gives qualitatively correct results and may be used as first estimation in wide range of noise intensity (see Fig. 14,  $a = 1$ ). Moreover, if we will increase noise intensity further, we will see that the error of our approximation decreases and for  $kT = 50$  we obtain that the exponential approximation and the results of computer simulation coincide (see Fig. 15, plotted in the logarithmic scale,  $a = 1$ ,  $x_0 = 3$ ). From this plot we can conclude that the nonlinear system is “linearized” by a strong noise, an effect which is qualitatively obvious but which should be investigated further by the analysis of variance and higher cumulants.



**Figure 14.** Evolution of the mean coordinate in the potential  $\Phi(x) = x^4/4$  for different values of noise intensity.



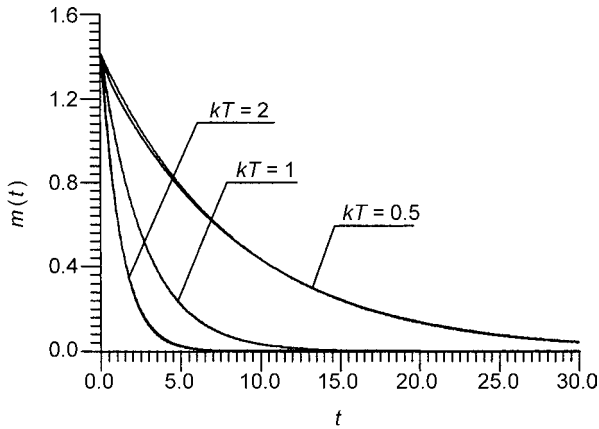
**Figure 15.** Evolution of the mean coordinate in the potential  $\Phi(x) = x^4/4$  for different values of noise intensity (logarithmic scale).

The third considered example is described by the bistable potential—the so-called “quartic” potential:  $\Phi(x) = ax^4/4 - bx^2/2$ . In this case the applicability of exponential approximation also significantly depends on the coordinate of initial distribution. If  $x_0$  is far from the potential minimum, then there exist two characteristic timescales: fast dynamic transition to potential minimum and slow noise-induced escape over potential barrier. In this case the exponential approximation gives a not-so-adequate description of temporal dynamics of the mean; however, it may be used as a first estimation. But if  $x_0$  coincides with the potential minimum, then the exponential approximation of the mean coordinate differs only a few percent from results of computer simulation even in the case when noise intensity is significantly larger than the potential barrier height (strongly nonequilibrium case) (see Fig. 16,  $a = 1$ ,  $b = 2$ ,  $x_0 = 1.414$ ). If, however, we consider the case where the initial distribution  $x_0$  is far from the potential minimum, but the noise intensity is large, we will see again as in the previous example that essential nonlinearity of the potential is suppressed by strong fluctuations and the evolution of the mean coordinate becomes exponential (see Fig. 17, plotted in the logarithmic scale,  $a = 1$ ,  $b = 2$ ,  $x_0 = 2.5$ ).

### 3. Discussion of Applicability of Single Exponential Approximation

Temporal behavior of the correlation function was studied in Ref. 91 using a particular example of the correlation function of  $\sin x(t)$  in a periodic potential with periodic boundary conditions. In that case the use of single exponential approximation had also given a rather adequate description. The considered

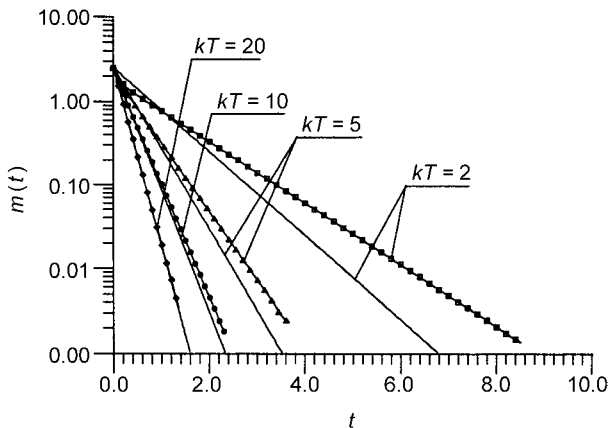




**Figure 16.** Evolution of the mean coordinate in the potential  $\Phi(x) = x^4/4 - x^2$  for different values of noise intensity with initial distribution located in the potential minimum.

examples of observables lead to the following conclusions about the possibility to use single exponential approximation:

1. The single exponential approximation works especially well for observables that are less sensitive to the location of initial distribution, such as transition probabilities and correlation functions.
2. In all other cases it is usually enough to apply a double exponential approximation to obtain the required observable with a good precision,



**Figure 17.** Evolution of the mean coordinate in the potential  $\Phi(x) = x^4/4 - x^2$  for different values of noise intensity with initial distribution located far from a potential minimum (logarithmic scale).

and one can have recourse to a two-sided Padé approximation as suggested in Ref. 30.

3. The exponential approximation may lead to a significant error in the case when the noise intensity is small, the potential is tilted, and the barrier is absent (purely dynamical motion slightly modulated by noise perturbations). But, to the contrary, as it has been observed for all considered examples, the single exponential approximation is more adequate for a noise-assisted process: either (a) a noise-induced escape over a barrier or (b) motion under intensive fluctuations.

### **B. Time Periodic Potentials: Resonant Activation and Suprathreshold Stochastic Resonance**

Investigation of nonlinear dynamical systems driven by noise and periodic signal is an important topic in many areas of physics. In the past decade several interesting phenomena, such as resonant activation [96], stochastic resonance [97], ratchet effect [98,99], noise-enhanced stability of unstable systems [61], and field-induced stabilization of activation processes [100], have been observed in these systems. In particular, for underdamped systems driven by periodic signals, the effect of resonant activation was reported by many authors (see Ref. 96 and references therein). The phenomenon consists of a decrease of the decay time of metastable state (or, equivalently, increase of decay rate) at certain frequencies of the periodic signal. For overdamped systems the resonant activation was first observed in the case of stochastically driven barriers fluctuating according to some probability distribution [101–105] and, recently, for barriers that are either (a) deterministically flipping between two states [105] or (b) continuously (sinusoidally) driven [100]. In the deterministic continuous case, however, the study was limited to the case of small driving amplitudes.

The application of methods described above with the help of adiabatic approximation allows us to study different characteristics of Markov processes subjected to driving signals. The use of exact mean transition times (instead of Kramers' time) helps to obtain an analytical description of probability evolution for arbitrary noise intensity and arbitrary amplitude of the driving signal, and such approximate description provides good coincidence with computer simulation results up to driving frequencies of the order of cutoff frequency of the system and even allows us to predict the effect of resonant activation for the case of a strong periodic driving (we call the “strong” or “suprathreshold” driving the case when the driving amplitude exceeds the static threshold amplitude).

As an example, let us consider again a system with a metastable state described by the potential of type II (Fig. 4) [106] (an example with the potential of type I was considered in Ref. 107):

$$\varphi(x, t) = (-bx^3 + ax^2 + Ax \cos(\omega t + \psi))/kT \quad (6.12)$$

with  $\psi$  an arbitrary phase. The particle is initially located in the potential well near the minimum. In the course of time the potential barrier moves up and down and the probability to find a particle in the minimum tends to zero. Again we are interested in the evolution of the survival probability:

$$P(t) = \int_{-\infty}^d W(x, t) dx \quad (6.13)$$

where  $d$  is the coordinate of the barrier top at the instant of time when the barrier height has its maximal value.

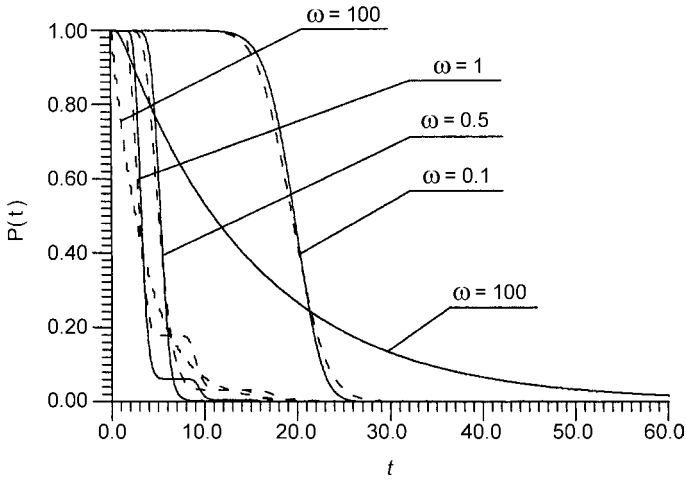
For the analysis of the resonant activation effect in the considered system it is suitable to use as monitoring characteristic the first moment of the expansion of the survival probability (6.13). If one decomposes the probability to the set of moments as was done above for time-constant potentials, it can be demonstrated that  $\tau(\omega)$  defined as

$$\tau(\omega) = \frac{\int_0^{\infty} [P(t) - P(\infty)] dt}{[P(0) - P(\infty)]} \quad (6.14)$$

is the first moment of such expansion [the mean decay time (MDT)]. In the considered case,  $\tau(\omega)$  correctly describes the probability evolution (a comparison of some characteristic scale of the probability evolution, e.g., decrease of the probability  $e$  times, and the MDT provides rather good coincidence both for the case of zero initial phase of driving and for the phase averaged characteristics).

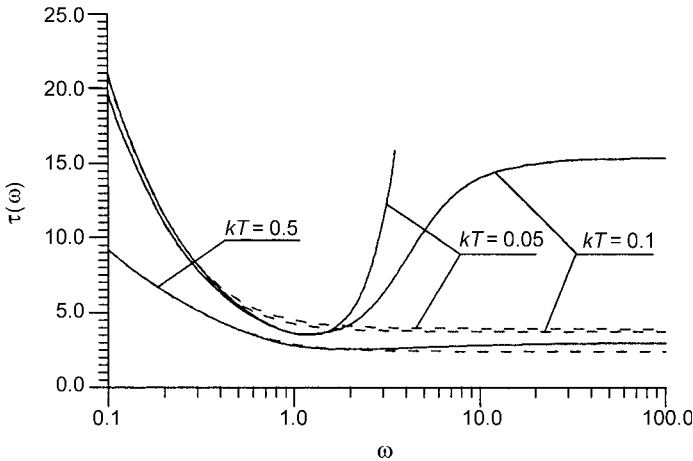
In computer simulations the probability  $P(t)$  is obtained by solving the FPE with the potential (6.12) for the following parameter values  $d = (a + \sqrt{a^2 + 3Ab})/3b$ ,  $a = 1$ ,  $b = 1$ ,  $A = 1, 0.3, 0.1$ . For convenience we take the initial distribution located at  $x_0 = 0 \neq x_{\min}$  (the phenomenon is quite insensitive to the location of the initial condition). Let us consider first the case of zero phase  $\psi = 0$ . With this choice the potential barrier at the initial instant of time has maximal height and is decreasing during the first half of the period. The probability evolution for  $\psi = 0$  is depicted in Fig. 18 for  $kT = 0.1$ ,  $A = 1$  (strong driving) and for different values of the frequency, from which it is clear that the decay of metastable state occurs earlier for  $\omega \approx 1$  than for other values. This manifestation of the resonant activation is also seen in Fig. 19 where the mean decay time for different values of the noise intensity is presented. We see that the resonant activation is almost absent at large noise intensities (for  $kT = 1$  the effect has the order of error) and becomes stronger when the noise intensity is decreased.

The complete curve  $\tau(\omega)$  in Fig. 19 is difficult to describe analytically, but one can have recourse to the adiabatic approximation. This approximation has been used in the context of stochastic resonance by many authors [96,108]. Here



**Figure 18.** Evolution of the survival probability for different values of frequency of the driving signal,  $kT = 0.1$ ,  $A = 1$ . Solid lines represent results of computer simulation, and dashed lines represent an adiabatic approximation (6.15).

we remark that the part of the curve  $\tau(\omega)$  for  $0 \leq \omega \leq 1$  may be well-described by a modified adiabatic approximation that allows us to extend the usual analysis to arbitrary driving amplitudes and noise intensities. To this end the probability to find a particle at the time  $t$  in the potential minimum takes the



**Figure 19.** The mean decay time as a function of frequency of the driving signal for different values of noise intensity,  $kT = 0.5, 0.1, 0.05$ ,  $A = 1$ . The phase is equal to zero. Solid lines represent results of computer simulation, and dashed lines represent an adiabatic approximation (6.15).

form

$$P(x_0, t) = \exp \left\{ - \int_0^t \frac{1}{\tau_p(x_0, t')} dt' \right\} \quad (6.15)$$

where  $\tau_p(x_0, t')$  is the exact mean decay time [34,35] obtained for the corresponding time-constant potential:

$$\tau_p(x_0) = B \left\{ \int_{x_0}^{r^d} e^{\varphi(y)} \int_{-\infty}^y e^{-\varphi(x)} dx dy + \int_d^{\infty} e^{\varphi(y)} dy \int_{-\infty}^{r^d} e^{-\varphi(x)} dx \right\} \quad (6.16)$$

[Note that with respect to the usual adiabatic analysis we have *ad hoc* substituted the approximate Kramers' time by the exact one, Eq. (6.16), and found a surprisingly good agreement of this approximate expression with the computer simulation results in a rather broad range of parameters.]

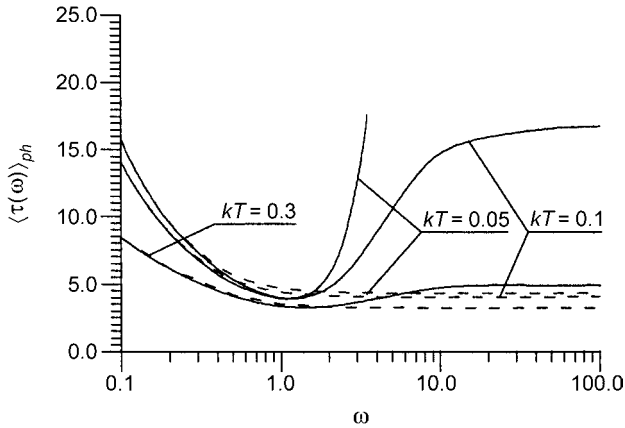
The corresponding curves derived from Eqs. (6.15) and (6.16) are reported in Figs. 18 and 19 as dashed lines, from which we see that there is a good agreement between the modified adiabatic approximation and the numerical results up to  $\omega \sim 1$ . Moreover, the approximation improves with the increase of the noise intensity. This could be due to the fact that the adiabatic approximation [96,108] is based on the concept of instantaneous escape, and for higher noise intensity the escape becomes faster.

In the opposite limit,  $\omega \gg 1$ ,  $\tau(\omega)$  can be described by formula (6.16), with the potential (6.12) averaged over the period of the driving signal. Therefore we can obtain the following empirical expressions for the “amplitude” of the resonant activation effect for  $\omega = 0$ ,  $\omega = \infty$ :

$$\tau_0 = \frac{\tau_p(x_0)}{\tau_a(x_0, \infty)}, \quad \tau_\infty = \frac{\tau_p(x_0, \bar{\varphi}(x, t))}{\tau_a(x_0, \infty)} \quad (6.17)$$

where  $\tau_a(x_0, \infty)$  denotes the minimal value of  $\tau(\omega)$  which is approximately equal to the value given by adiabatic approximation at  $\omega \rightarrow \infty$  and  $\bar{\varphi}(x, t)$  denotes potential (6.12) averaged over the period. It is important to note that the resonant activation effect can be predicted on the basis of asymptotic consideration in the ranges  $0 < \omega < 1$  and  $\omega \gg 1$  without having to rely on computer simulations because the following relations take place:  $\tau(\omega \approx 1) < \tau(\omega = 0)$ ,  $\tau(\omega \approx 1) < \tau(\omega = \infty)$ .

Similar analysis of the MDT may be performed for arbitrary initial phase  $\psi \neq 0$ . We note that, depending on the initial phase,  $\tau(\omega)$  may vary significantly (especially in the low-frequency limit). This is due to the fact that the height of the potential barrier at initial instant of time has a large variation (from zero to some maximal value). Because in real experiments the initial phase is usually

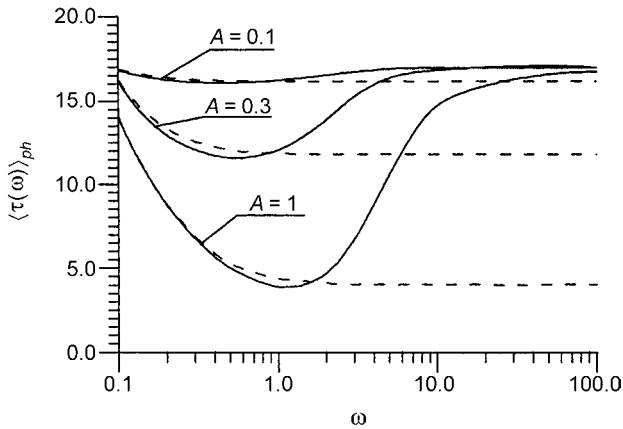


**Figure 20.** The phase-averaged mean decay time as a function of frequency of the driving signal for different values of noise intensity,  $kT = 0.3, 0.1, 0.05$ ,  $A = 1$ . Solid lines represent results of computer simulation, and dashed lines represent adiabatic approximation (6.15).

not accessible, one has to consider it as an uniformly distributed random variable, so that it is natural to average the mean decay time upon the initial phase distribution  $\langle \tau(\omega) \rangle_{ph}$ . This is done in Fig. 20, from which we see that  $\langle \tau(\omega) \rangle_{ph}$  has the same qualitative behavior as for  $\psi = 0$  (see Fig. 19) and therefore the observed effect is rather independent of the phase.

It is worth to remark, that the curves of the MDT for different values of noise intensity ( $kT < 0.1$ ) actually coincide with the one for  $kT = 0$  in the frequency range, corresponding to the minimum of the curve  $\tau(\omega)$  ( $\omega \sim 1$ ) (see Figs. 19 and 20). This means that in this region of parameters the fluctuations are suppressed by the strong external signal, and, therefore, tuning a real device in this regime may significantly decrease noise-induced errors.

We have also investigated the dependence of the phase-averaged mean decay time on the amplitude of the driving signal. This is shown in Fig. 21 where the phase-averaged MDT is reported for different values of the driving amplitude. From this figure we see that the phenomenon exists also for relatively small values of the amplitude ( $A = 0.3, 0.1$ ) for which no transitions occur in the absence of noise. As has been demonstrated in Ref. 106, the location of the minimum  $\omega_{\min}$  of  $\langle \tau(\omega) \rangle_{ph}$ , as well as the value of the minimum of  $\langle \tau(\omega) \rangle_{ph}$ , significantly depends on  $kT$ . On the other hand, for very small amplitudes the resonant activation is significantly reduced and the corresponding frequency where the minimum of  $\tau(\omega)$  occurs decreases toward  $\omega \sim 0.5$ . In this region, however, a description of the phenomenon can be done in terms of the theory developed in Refs. 109—112 and the results coincide with the conclusions, reported in Ref. 96.



**Figure 21.** The phase-averaged mean decay time as a function of frequency of the driving signal for different values of the amplitude,  $A = 1, 0.3, 0.1, kT = 0.1$ . Solid lines represent results of computer simulation, and dashed lines represent an adiabatic approximation (6.15).

It is intuitively obvious that this phenomenon should also exist in systems having steady states (e.g., in a system described by “quartic” potential that has been intensively studied in the context of stochastic resonance), but it is more natural to investigate the resonant properties of signal-to-noise ratio (SNR) in those cases [113].

Consider a process of Brownian diffusion in a potential profile  $\varphi(x, t) = \Phi(x, t)/kT$ :

$$\varphi(x, t) = (bx^4 - ax^2 + xA \sin(\omega t + \psi))/kT \tag{6.18}$$

where  $\psi$  is initial phase. The quantity of our interest is the SNR. In accordance with Ref. 97 we denote SNR as

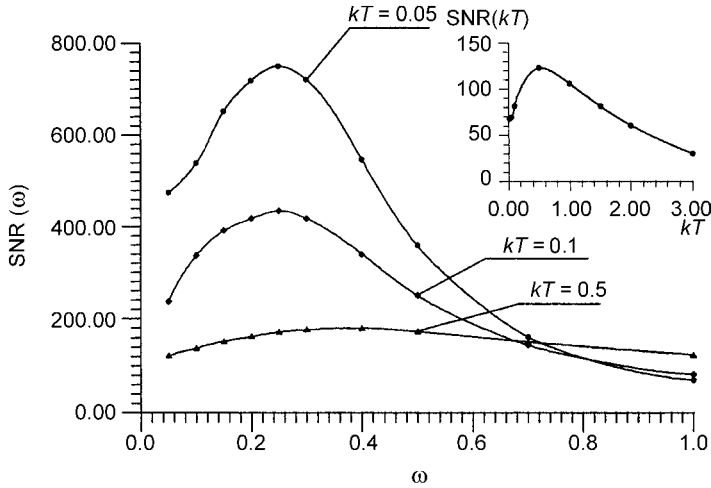
$$\text{SNR} = \frac{1}{S_N(\omega)} \lim_{\Delta\Omega \rightarrow 0} \int_{\omega - \Delta\Omega}^{\omega + \Delta\Omega} S(\Omega) d\Omega \tag{6.19}$$

where

$$S(\Omega) = \int_{-\infty}^{+\infty} e^{-i\Omega\tau} K[t + \tau, t] d\tau \tag{6.20}$$

is the spectral density,  $S_N(\omega)$  is noisy pedestal at the driving frequency  $\omega$ , and  $K[t + \tau, t]$  is the correlation function:

$$K[t + \tau, t] = \langle\langle x(t + \tau)x(t) \rangle\rangle \tag{6.21}$$



**Figure 22.** Signal-to-noise ratio as a function of driving frequency. *Inset:* SNR as a function of  $kT$ .

where the inner brackets denote the ensemble average and the outer brackets indicate the average over initial phase  $\psi$ .

In computer simulations we had chosen the following parameters of the potential:  $b = 1$ ,  $a = 2$ . With such a choice the coordinates of minima equal  $x_{\min} = \pm 1$ , the barrier height in the absence of driving is  $\Delta\Phi = 1$ , the critical amplitude  $A_c$  is around 1.5, and we have chosen  $A = 2$  to be far enough from  $A_c$ . In order to obtain the correlation function  $K[t + \tau, t]$  we solved the FPE (2.6) numerically, using the Crank–Nicholson scheme.

In order to study the resonant behavior of spectral density, let us plot the SNR as function of driving frequency  $\omega$ . From Fig. 22 one can see, that SNR as function of  $\omega$  has strongly pronounced maximum. The location of this maximum at  $\omega = \omega_{\max}$  approximately corresponds to the timescale matching condition:  $\omega_{\max} \approx \pi/\tau_{\min}$ , where  $\tau_{\min}$  is the minimal transition time from one state to another one.

When the driving frequency is higher than the cutoff frequency of the system,  $\omega \geq \omega_c$ , noise helps the particle to move to another state and the conventional stochastic resonance may be observed (see the inset of Fig. 22 for  $\omega = 1$ ). Therefore, for the case of strong periodic driving, the signal-to-noise ratio of the bistable system as well as the mean decay time of a metastable state demonstrate resonant behavior as function of frequency of the driving signal, which reflects the same origin of these phenomena.

In conclusion, we note that the practical application of phenomena of resonant activation and suprathreshold stochastic resonance provide an



intriguing possibility to tune a concrete device in a regime with minimal noise-induced error.

## VII. CONCLUSIONS

In the frame of the present review, we discussed different approaches for description of an overdamped Brownian motion based on the notion of integral relaxation time. As we have demonstrated, these approaches allow one to analytically derive exact time characteristics of one-dimensional Brownian diffusion for the case of time constant drift and diffusion coefficients in arbitrary potentials and for arbitrary noise intensity. The advantage of the use of integral relaxation times is that on one hand they may be calculated for a wide variety of desirable characteristics, such as transition probabilities, correlation functions, and different averages, and, on the other hand, they are naturally accessible from experiments.

Another important thing is that in many situations for the considered diffusion processes these characteristic timescales give a rather good description of observables via utilization of single exponential approximation. The exponential approximation works especially well for observables that are less sensitive to the location of initial distribution, such as transition probabilities and correlation functions. In all other cases it is usually enough to apply double exponential approximation to obtain the required observable with a good precision, and one can have recourse to the two-sided Padé approximation as suggested in Ref. 30. The exponential approximation may lead to a significant error in the case where the noise intensity is small, the potential is tilted, and the barrier is absent (purely dynamical motion slightly modulated by noise perturbations). To the contrary, as has been observed for all considered examples, the single exponential approximation is more adequate for a noise-assisted process: either (a) noise-induced escape over a barrier or (b) motion under intensive fluctuations. Moreover, these temporal characteristics are useful for the description of diffusion processes in time-dependent potentials, where one can have recourse to adiabatic approximation and obtain an adequate description of an observable up to the cutoff frequency of the considered system.

Finally we note that the presented approaches may be easily generalized for the case of multidimensional systems with axial symmetry. The generalization for arbitrary multidimensional potentials had been discussed in Refs. 41 and 114.

## Acknowledgments

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Research (Project N 00-02-16528, Project N 99-02-17544, and Project N 00-15-96620) and by the Ministry of High Education of Russian Federation (Project N 992874).

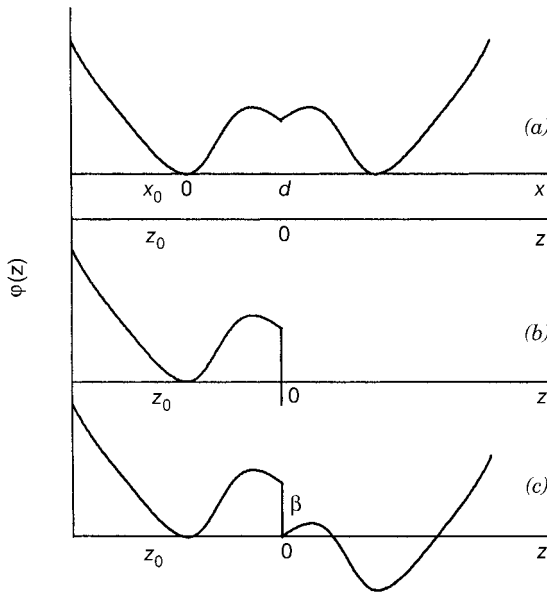
**APPENDIX: THE PRINCIPLE OF CONFORMITY**

We consider the process of Brownian diffusion in a potential  $\varphi(x)$ . The probability density of a Brownian particle is governed by the FPE (5.72) with delta-function initial condition. The moments of transition time are given by (5.1).

Let us formulate the principle of conformity:

The moments of transition time of a dynamical system driven by noise, described by arbitrary potential  $\varphi(x)$  such that  $\varphi(\pm\infty) = \infty$ , symmetric relatively to some point  $x = d$ , with initial delta-shaped distribution, located at the point  $x_0 < d$  [Fig. A1(a)], coincides with the corresponding moments of the first passage time for the same potential, having an absorbing boundary at the point of symmetry of the original potential profile [Fig. A1(b)].

Let us prove that formula (4.19) (in this particular case for  $c = -\infty$ ) not only gives values of moments of FPT of the absorbing boundary, but also expresses moments of transition time of the system with noise, described by an arbitrary symmetric with respect to the point  $d$  potential profile.



**Figure A1.** Potential profiles illustrating the principle of conformity.

Superpose the point of symmetry of the dimensionless potential profile with the origin of the coordinate  $z = x - d$  such that  $\varphi(-z) = \varphi(z)$  and put  $z_0 = x_0 - d < 0$ . For the Laplace-transformed probability density  $Y(z, s) = \int_0^\infty W(z, t)e^{-st} dt$  from Eq. (5.72) we may write the following equation:

$$\frac{d^2 Y(z, s)}{dz^2} + \frac{d}{dz} \left[ \frac{d\varphi(z)}{dz} Y(z, s) \right] - sBY(z, s) = -B\delta(z - z_0) \quad (9.1)$$

Note that the probability current in Laplace transform terms is

$$\hat{G}(z, s) = \int_0^\infty G(z, t)e^{-st} dt = -\frac{1}{B} \left[ \frac{d\varphi(z)}{dz} Y(z, s) + \frac{dY(z, s)}{dz} \right] \quad (9.2)$$

Suppose that we know two linearly independent solutions  $U(z) = U(z, s)$  and  $V(z) = V(z, s)$  of the homogeneous equation corresponding to (9.1) (i.e., when the right-hand side of Eq. (9.1) is equal to zero), such that  $U(z) \rightarrow 0$  at  $z \rightarrow +\infty$  and  $V(z) \rightarrow 0$  at  $z \rightarrow -\infty$ . Because of symmetry of the function  $\varphi(z)$ , these independent solutions may be also chosen as symmetrical, such that  $U(-z) = V(z)$ ,  $U(0) = V(0)$ ,  $[dU(z)/dz]_{z=0} = -[dV(z)/dz]_{z=0} < 0$ . In this case the general solution of Eq. (9.1) may be represented as follows:

$$Y(z, s) = \begin{cases} Y_1(z) + y^-(z), & z \leq z_0 \\ Y_1(z) + y^+(z), & z_0 \leq z \leq 0 \\ Y_2(z), & z \geq 0 \end{cases} \quad (9.3)$$

where

$$\begin{aligned} Y_1(z) &= C_1 V(z), & Y_2(z) &= C_2 U(z) \\ y^-(z) &= \frac{B}{W[z_0]} U(z_0) V(z), & y^+(z) &= \frac{B}{W[z_0]} V(z_0) U(z) \end{aligned}$$

Here  $W[z] = U(z) \frac{dV(z)}{dz} - V(z) \frac{dU(z)}{dz}$  is Wronskian, and  $C_1$  and  $C_2$  are arbitrary constants that may be found from the continuity condition of the probability density and the probability current at the origin:

$$Y_1(0) + y^+(0) = Y_2(0), \quad \hat{G}(z = -0, s) = \hat{G}(z = +0, s) \quad (9.4)$$

Calculating from (9.4) the values of arbitrary constants and putting them into (9.3), one can obtain the following value for the probability current Laplace transform  $\hat{G}(z, s)$  (9.2) at the point of symmetry  $z = 0$ :

$$\hat{G}(0, s) = \frac{V(z_0)}{W[z_0]} \left[ \frac{dV(z)}{dz} \right]_{z=0} \quad (9.5)$$

Actually, we can prove the principle of conformity step-by-step for all moments of transition time (5.4),(5.5), and so on, but it is more simple to prove it for the probability density of transition time  $w_\tau(t, z_0)$  (5.2). Taking the Laplace transform from the expression (5.2) and noting that  $s\hat{Q}(s, z_0) - Q(0, z_0) = \hat{G}(0, s)$ , one can obtain the following formula for  $w_\tau(s, z_0)$ :

$$w_\tau(s, z_0) = \frac{s\hat{Q}(s, z_0) - Q(0, z_0)}{Q(\infty, z_0) - Q(0, z_0)} = \frac{\hat{G}(0, s)}{Q(\infty, z_0) - Q(0, z_0)} \quad (9.6)$$

where  $\hat{Q}(s, z_0) = \int_0^\infty Y(z, s) dz$  is the Laplace-transformed decay probability. In our particular case  $Q(0, z_0) = 0$ ,  $Q(\infty, z_0) = 1/2$ , because the steady-state probability density  $W(z, \infty)$  will spread symmetrically from both sides of the point of symmetry  $z = 0$ . Thus, combining (9.6) and (9.5) we obtain the following formula for the Laplace-transformed probability density of transition time:

$$w_\tau(s, z_0) = \frac{2V(z_0)}{W[z_0]} \left[ \frac{dV(z)}{dz} \right]_{z=0} \quad (9.7)$$

Before finding the Laplace-transformed probability density  $w_T(s, z_0)$  of FPT for the potential, depicted in Fig. A1(b), let us obtain the Laplace-transformed probability density  $w_\tau(s, z_0)$  of transition time for the system whose potential is depicted in Fig. A1(c). This potential is transformed from the original profile [Fig. A1(a)] by the vertical shift of the right-hand part of the profile by step  $\beta$  which is arbitrary in value and sign. So far as in this case the derivative  $d\varphi(z)/dz$  in Eq. (9.1) is the same for all points except  $z = 0$ , we can use again linear-independent solutions  $U(z)$  and  $V(z)$ , and the potential jump that equals  $\beta$  at the point  $z = 0$  may be taken into account by the new joint condition at  $z = 0$ . The probability current at this point is continuous as before, but the probability density  $W(z, t)$  has now the step, so the second condition of (9.4) is the same, but instead of the first one we should write  $Y_1(0) + y^+(0) = Y_2(0)e^{-\beta}$ . It gives new values of arbitrary constants  $C_1$  and  $C_2$  and a new value of the probability current at the point  $z = 0$ . Now the Laplace transformation of the probability current is

$$\hat{G}(0, s) = \frac{2V(z_0)}{W[z_0](1 + e^{-\beta})} \left[ \frac{dV(z)}{dz} \right]_{z=0} \quad (9.8)$$

One can find that for the potential depicted in Fig. A1(c) the quantity  $Q(\infty, z_0)$  has been also changed and now equals  $Q(\infty, z_0) = 1/(1 + e^{-\beta})$ , while the quantity of  $Q(0, z_0)$  certainly, as before, is  $Q(0, z_0) = 0$ . It is easy to check that the substitution of new values of  $\hat{G}(0, s)$  and  $Q(\infty, z_0)$  into formula (9.6) gives the same formula (9.7) for  $w_\tau(s, z_0)$ . Putting now  $\beta = \infty$ —that is, locating the

absorbing boundary at the point  $z = 0$  ( $x = d$ )—we obtain the same formula (9.7), not for the probability density of the transition time but for the probability density of FPT  $w_T(s, z_0)$ . It is known that if the Laplace transformations of two functions coincide, then their origins coincide too. So, if we substitute the coinciding probability densities  $w_\tau(t, z_0)$  and  $w_T(t, z_0)$  into formula (5.1) [see formulas (5.2) and (5.3)] for the cases of the symmetric potential profile and the profile with the absorbing boundary at the point of symmetry, we should obtain equal values for the moments of transition time and FPT.

Thus, we have proved the principle of conformity for both probability densities and moments of the transition time of symmetrical potential profile and FPT of the absorbing boundary located at the point of symmetry.

It is obvious that moments of FPT to the point 0 are the same for the profiles depicted in Fig. A1. For moments of transition time, this coincidence is not so easily understandable, and the fact that the principle of conformity is valid for the potential depicted in Fig. A1(c) leads to an unusual conclusion: Neither the quantity nor the sign of the potential step  $\beta$  influences the moments of the transition time.

For the mean transition time, this fact may be explained in the following way: If the transition process is going from up to down, then the probability current is large, but it is necessary to fill the lower minimum by the larger part of the probability to reach the steady state; if the transition process is going from down to up, then the probability current is small, and it is necessary to fill the upper minimum by the smaller part of the probability to reach the steady state.

The difference in the quantities of currents is completely compensated by quantities of final probabilities of reaching the steady state.

An interested reader can easily check the principle of conformity numerically and see that if the probability of the FPT  $Q_T(t, x_0)$  [Fig. A1(b)] is known, then the decay probability  $Q_\tau(t, x_0)$  [Fig. A1(a)] is expressed as  $Q_\tau(t, x_0) = [1 + Q_T(t, x_0)]/2$ .

Note finally that the principle of conformity, proved for delta-shaped initial distribution of the probability density, may also be extended to arbitrary initial distributions located within the considered interval  $W(x, 0) = W_{in}(x)$ ,  $x \in (c, d)$ .

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