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Theory of activated rate processes: Exact solution of the Kramers problem

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The Kramers theory for the escape rate of a Brownian particle from a potential well is extended to the full damping range. It is shown that the most adequate description of the underdamped Brownian motion in a deep potential well is provided by a Green function of the Fokker–Planck equation in the energy-position variables. The problem of lifetime of a particle in a single potential well is reduced to an integral equation in energy variable, with the Green function being the kernel of this equation. The straightforward solution by the Wiener–Hopf method yields an explicit expression for the lifetime, which describes the crossover from the extremely underdamped regime to that of a moderate damping. With the use of Kramer's result for moderate-to-large damping an expression for the lifetime is presented, which holds at arbitrary damping. The problem of the rate of transitions between the two minima of a double-well potential is reduced to a system of two integral equations, which is also solved by the Wiener–Hopf method. An explicit expression for the relaxation time of nonequilibrium populations of the two minima is given.

I. INTRODUCTION

This paper concerns nonlinear systems driven by random force of the white-noise type. Our interest is in nonlinear systems in which the nonlinearity leads to metastable behavior in certain ranges of the system parameters. Typical systems would be excited molecules, Josephson junctions, or logical cells.

In the metastable region one expects that deterministic stability of the metastable state corresponds in a stochastic description to a very slow activation/transition rates from the metastable to the globally stable state. Historically, such processes have interested scientists and engineers over many decades, most notably in the fields of chemical kinetics and superconducting quantum interference devices.

Metastable systems often resemble the model of a Brownian particle moving in a potential with two (or perhaps more) adjacent wells and a barrier in between, which prevents the particles from jumping over too often. In this context, Kramers' work[1] represents a milestone in the field. Since Kramers, a number of investigators have improved or extended the theory in several points. As a sample of papers we mention here the extentions to multidimensional Fokker–Planck processes,[2] to non-Markovian noise[3] and to quantum-mechanical description of activation events[4] (see also the review by Hänggy[5] and references therein).

Interest in one-dimensional Brownian motion has recently been revived by experiments with Josephson junctions.[6] In certain range of parameters these devices can be regarded as classical systems. The decay of a zero-voltage state of a junction is then completely analogous to Kramers' problem.

The aim of our paper is to give an exact solution of Kramers' problem within the whole range of damping. The paper is organized as follows.

In Sec. II we formulate the problem and briefly review the results obtained by Kramers. We believe that such a historical excursion is absolutely necessary, in view of the fact that Kramers' work is known in details only to very few people. It has already been pointed out that "some of the most important and sophisticated treatments of noise-activated escape from the metastable state ... do not reflect Kramers' understanding of the very lightly damped case,"[7] and that "Unfortunately, the advocates of many-body transition state theory seem to have been unaware of the full content of Kramers' original work."[5]

Section III is the key to the further developments, as a novel mathematical approach to description of the underdamped Brownian motion is introduced in it. The basic idea is a derivation of the Green function for the Fokker–Planck equation. An underdamped Brownian particle moves in potential well in an almost deterministic way, being only slightly perturbed by friction and random force. The total energy of the particle is the most slowly changing quantity, so in practice one needs only to find the unperturbed trajectory with a minimal energy sufficient to escape from the well and consider small perturbations of the trajectory due to thermal fluctuations and friction.

In Sec. IV we exploit the Green function derived in this approximation to transform the Fokker–Planck equation for a single potential well into an integral equation in energy variable. Section V concerns technicalities involved in solution of the integral equation. Being of the Wiener–Hopf type, it is solved therefore through the Fourier transformation with subsequent use of the Cauchy theorem. As a result we obtain an explicit expression for the decay rate in the underdamped regime [see Eqs. (2.20) and (6.1)], which describes a crossover from the extremely weak damping to a moderate one (see Fig. 2).

In Sec. VI we present one of our principal results, and Eq. (6.3) for the lifetime of a Brownian particle in a single

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potential well, which holds at arbitrary damping. In Sec. VII averaged energy of escaping particles is calculated, its dependence on damping being presented in Fig. 3.

In Sec. VIII the approach of Sec. IV and Sec. V is extended to derivation and solution of a system of two integral equations for a double-well potential, when Brownian particles can return back after several oscillations in the final well. These considerations lead us in Sec. IX to the expression (9.1) for the double-well decay rate, which holds at arbitrary damping and present the summarizing result of our work.

The decay rates derived by solution of Kramers' problem should be regarded as elementary rate constants in phenomenological equations for the well populations. In Sec. IX we present the expression (9.2) for the relaxation rate of nonequilibrium well populations. Several extentions of the developed approach are described briefly in Sec. X.

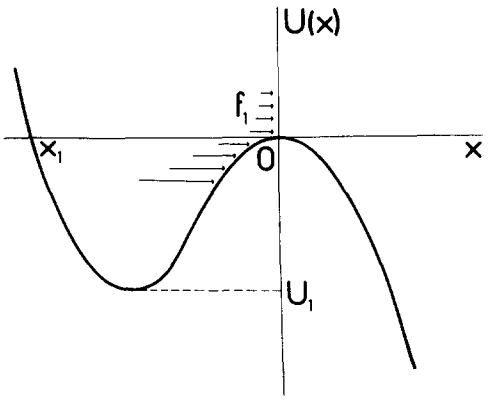

FIG. 1. Schematic representation of a one-well potential. No particles enter the potential well in the underdamped regime.

II. FORMULATION OF THE PROBLEM AND REVIEW OF PREVIOUS RESULTS

The starting point in Kramers' model is the Langevin equation

$$m\frac{d^2x}{dt^2} = -m\gamma\frac{dx}{dt} - \frac{dU(x)}{dx} + \eta(t), \tag{2.1}$$

where x is the position of a particle with the mass m, γ is the damping rate, $\eta(t)$ is stationary Gaussian force associated with the coupling to the viscous thermal bath,

$$\langle \eta(t)\eta(t')\rangle = 2m\gamma T\delta(t-t').$$

Equation (2.1) is equivalent to the Fokker–Planck equation

$$\frac{\partial F}{\partial t} + m^{-1}p\frac{\partial F}{\partial x} - \frac{\partial}{\partial p}\left[F\frac{dU}{dx} + \gamma\left(pF + mT\frac{\partial F}{\partial p}\right)\right] = 0 \tag{2.2}$$

for distribution $F(p,x,t)$ of an ensemble of noninteracting Brownian particles in momentum $p \equiv mdx/dt$ and position x.

We begin with the simplest example of the metastable state, when a Brownian particle once escaped over the barrier has no chance to return back. The corresponding one-well potential $U(x)$ is depicted in Fig. 1. The zero of the potential is chosen to be at the barrier top, located at $x = 0$. The boundary condition

$$F(p,x,t) \to 0, \quad x \to +\infty \tag{2.3}$$

reflects the initial condition that there were no particles at the outside of the barrier at $t = 0$.

From now on it will be assumed, that the depth of the well U_1 is large enough compared to T. The ratio T/U_1 is the principal small parameter of the problem. A Brownian particle trapped into a deep potential well will reside there for an exponentially long time, exceeding all the relaxation times. That is a basic point in a theory of the rate of activated processes, as it allows a sensible definition of the decaying state and introduction of the concept of the lifetime. The problem of lifetime of a particle in a potential well can then be formulated rigorously in mathematical terms.

Relaxation of an arbitrary initial distribution of particles interacting with the thermal bath is a two-stage process. After a comparatively short time the distribution of particles inside the potential well and in a vicinity of the barrier approaches its steady-state form. The next stage of relaxation is a purely exponential decay of the distribution as a whole, caused by escapes of the particles over the barrier,

$$F(p,x,t) = F(p,x)\exp(-t/\tau). \tag{2.4}$$

The steady-state distribution $F(p,x)$ could be found from the equation

$$\tau^{-1}F - m^{-1}p\frac{\partial F}{\partial x} + \frac{\partial}{\partial p}\left[F\frac{dU}{dx} + \gamma\left(pF + mT\frac{\partial F}{\partial p}\right)\right] = 0 \tag{2.5}$$

which is obtained by inserting Eq. (2.4) into Eq. (2.2). Solution of Eq. (2.5) is unnormalizable

$$\int F(p,x)dpdx = \infty$$

as $F(p,x)$ diverges at $x \to +\infty$. One encounters the same problem also in the quantum tunneling theory.[8] The straightforward solution of Eq. (2.2) with any reasonable initial condition like Eq. (2.3) is well normalizable and tends to the solution (2.4) of Eq. (2.5), but the larger x the slower. Below we consider $F(p,x)$ only inside the well and in a close vicinity of the barrier.

The distribution function approaches the thermal equilibrium as we move away from the barrier into the initial well,

$$F(p,x,t) = \frac{N\Omega_1}{2\pi T}\exp[-(\epsilon + U_1)/T], \quad -\epsilon \gg T, \tag{2.6}$$

where

$$\epsilon = \frac{p^2}{2m} + U(x) \tag{2.7}$$

is the total energy, taken with respect to the barrier top, $N(t)$ is the number of particles in the well. The main contribution to the normalization condition

$$\int_{-\infty}^{0} dx \int_{-\infty}^{+\infty} F(p,x,t)dp = N(t)$$

comes from a region near the bottom of the well, where the potential can be represented by a harmonic oscillator

$$U(x) \approx -U_1 + \tfrac{1}{2}m\Omega_1^2 (x - x_m)^2$$

of frequency $\Omega_1 = [m^{-1}U''(x_m)]^{1/2}$, x_m being the location of the potential minimum.

The flux of particles

$$J = \int_{-\infty}^{+\infty} m^{-1} p F(p,x,t)\,dp \tag{2.8}$$

does not depend on x in a neighborhood of the barrier top as long as $|U(x)| \ll U_1$, and through the particle number conservation $dN/dt = J$ is related to the lifetime of a particle

$$\tau^{-1} = J/N. \tag{2.9}$$

Below we shall use this relation to calculate τ^{-1}. The first term in Eq. (2.5) is negligibly small. Hence, the steady-state distribution obeys the equation

$$m^{-1} p \frac{\partial F}{\partial x} - \frac{\partial}{\partial p}\left[F\frac{dU}{dx} + \gamma\left(pF + mT\frac{\partial F}{\partial p}\right)\right] = 0 \tag{2.10}$$

with the boundary condition (2.3) and asymptotics (2.6).

In the case of an inverted oscillator potential

$$U(x) = -\tfrac{1}{2}m\omega^2 x^2.$$

Kramers has found an exact solution of the above formulated problem

$$F(p,x) = \text{const} \cdot \exp\left(-\frac{p^2}{2mT} + \frac{m\omega^2 x^2}{2T}\right) \times \int_{x - \lambda p/m\omega^2}^{+\infty} \exp\left(-\frac{m\omega^2 \xi^2}{2\gamma\lambda T}\right) d\xi, \tag{2.11}$$

where

$$\lambda = (\omega^2 + \tfrac{1}{4}\gamma^2)^{1/2} - \tfrac{1}{2}\gamma. \tag{2.12}$$

The upper limit of integration is chosen to be infinity in view of the condition (2.3). The integral in Eq. (2.11) becomes a constant, if

$$\frac{\lambda p}{m\omega^2} - x \gg \left(\frac{\gamma\lambda T}{m\omega^2}\right)^{1/2}. \tag{2.13}$$

In this region of variables the function $F(p,x)$ approaches an equilibrium one.

The solution (2.11) has enabled Kramers to find an escape probability per unit time. Namely, one could find the normalization factor in Eq. (2.11) by comparison with Eq. (2.6). Then, using Eqs. (2.8) and (2.9) one would obtain

$$\tau^{-1} = \frac{\Omega_1}{2\pi}\left[\left(1 + \frac{\gamma^2}{4\omega^2}\right)^{1/2} - \frac{\gamma}{2\omega}\right] e^{-U_1/T}. \tag{2.14}$$

Introducing the fluxes J^R and J^L of particles with right- and left-hand side directions of momentum, in analogy with Eq. (2.8) and with the use of Eq. (2.11) one could easily obtain a probability of recrossings

$$\frac{J^L}{J^R} = 1 - \left(1 + \frac{\gamma^2}{4\omega^2}\right)^{-1/2}. \tag{2.15}$$

The rigorous condition of validity of the above obtained results will be given below. A simplified condition is that solution (2.11) approaches the equilibrium distribution at such x, where the inverted oscillator approximation for the potential still holds. One should bear in mind that at sufficiently large negative momenta p the function $F(p,x)$ will always be far from the equilibrium one due to depopulation of this region of the phase space [see Eq. (2.11)]. The condition (2.6) should only be satisfied for energies below the barrier top, when

$$\frac{p^2}{2m} - \frac{m\omega^2 x^2}{2} < 0.$$

This inequality together with Eq. (2.13) yields

$$-x \gg \frac{(\gamma\lambda T/m)^{1/2}}{\omega(\omega - \lambda)}. \tag{2.16}$$

The last condition gives an estimation of a spatial region, where the equilibrium distribution of particles is only negligibly perturbed by their escapes over the barrier. At large and moderate dampings $\gamma \gtrsim \omega$ the condition (2.16) with account of Eq. (2.12) yields

$$-x \gg (T/m\omega^2)^{1/2}.$$

This means that $F(p,x)$ deviates from the equilibrium function in a rather narrow region of x, where $|U(x)| \sim T \ll U_1$.

However, in the underdamped regime $\gamma \ll \omega$ the condition (2.16) simplifies to

$$-x \gg (\omega/\gamma)^{1/2}(T/m\omega^2)^{1/2}$$

and $F(p,x)$ becomes nonequilibrium in a much broader region, so that with $\gamma \to 0$ the inverted oscillator approximation for $U(x)$ shall inevitably be broken. The width of a typical potential well by the order of magnitude is about $(U_1/m\omega^2)^{1/2}$. The condition of validity of Eq. (2.14) for τ^{-1} in the underdamped regime then becomes

$$\gamma \gg \omega T/U_1. \tag{2.17}$$

To conclude the discussion based on the solution (2.11), we write down the equation for τ^{-1} in the underdamped limit of Eq. (2.14) as

$$\tau^{-1} = \frac{\Omega_1}{2\pi}\exp\left(-\frac{U_1}{T}\right), \quad \omega \gg \gamma \gg \omega T/U_1. \tag{2.18}$$

We have derived the lower limit of validity of the last equation in a rather formal manner. Now it is worthwhile to discuss the physical meaning of these results. It can easily be seen that in the limit of $\gamma \to 0$ the integral in Eq. (2.11) goes over into $\theta(p - m\omega x)$ where θ is the standard step function. The distribution $F(p,x)$ describes, therefore, the equilibrium flux of particles towards the barrier and the flux of particles reflected from the barrier. The particles with energies above the barrier top escape from the well, whereas those with energies below the barrier top are reflected from the barrier. It is physically evident, that at $\gamma = 0$ no equilibrium flux towards the barrier is possible, as a nonvanishing interaction with the thermal bath only enables particles to climb up the energy scale from the bottom of the well to the top of the barrier. We realize, therefore, that Eq. (2.14) is inapplicable in the limit of $\gamma \to 0$, because it ignores the effects of depopulation below the barrier top.

Considering motion of a Brownian particle in the extremely underdamped regime as an almost conservative one, with a very slow diffusion on the energy axis, Kramers obtained[1]

$$\tau^{-1}=\frac{\gamma S_1}{T}\frac{\Omega_1}{2\pi}e^{-U_1/T}, \tag{2.19}$$

where S_1 is the action per one oscillation of a particle with the zero total energy,

$$S_1=2\int_{x_1}^{0}[-2mU(x)]^{1/2}dx,$$

x_1 being the left-hand side turning point, $U(x_1)=0$. By the order of magnitude $S_1\sim U_1/\omega$. Note, that in contrast to Eq. (2.19), where S_1 depends on the shape of the potential in a whole, Eq. (2.14) involves the shape of the potential well only through its curvatures at the initial minimum and at the barrier top. The frequency Ω_1 is inevitably involved into both Eq. (2.14) and Eq. (2.19), as it is a measure of the phase space available at the initial minimum, and thus of the density which has to be depleted here by the flux escaping over the barrier.

The region of validity of Eq. (2.19),

$$\gamma\ll T/S_1\sim\omega T/U_1$$

does not overlap with that of Eq. (2.14) [see Eq. (2.17)], they are separated by an interval of dampings $\gamma\sim\omega T/U_1$. To calculate τ in this region means to bridge up the whole range of γ, and thus, to obtain a complete solution of the problem.

In a series of papers attempts have been made at solving the outlined problem (see, e.g., Ref. 5 and references therein). Unfortunately, these attempts involved unjustified assumptions about distribution function, and results obtained in such ways represent only *ad hoc* interpolations between the two Kramers' results.

In the present paper a rigorous relationship for τ^{-1} valid at arbitrary dampings is found. No model assumptions have been used, the only small parameter of the problem being T/U_1. In what follows we shall systematically neglect algebraically small corrections of order T/U_1 compared to 1, retaining only the leading order term in a low temperature expansion.

It is convenient to factorize the decay rate into two parts,

$$\tau^{-1}=A\frac{\Omega_1}{2\pi}e^{-U_1/T}. \tag{2.20}$$

Dependence on the coupling to the thermal bath is absorbed into the factor A, while the second factor describes an equilibrium property of the system and does not require knowledge of the dynamics. It is shown below that in the underdamped regime A depends on the sole parameter

$$\delta_1\equiv\gamma S_1,$$

the loss of energy per one oscillation of a particle with energy close to the barrier height. The anticipated expression for A should describe the crossover from

$$A=\delta_1/T,\quad \delta_1\ll T \tag{2.21}$$

to

$$A=1,\quad T\ll\delta_1\ll U_1 \tag{2.22}$$

[see Eqs. (2.19) and (2.18)].

On the other hand, at $\delta_1\gtrsim U_1$, when $\omega\sim\gamma$, the prefactor A depends only on the ratio γ/ω,

$$A=\left(1+\frac{\gamma^2}{4\omega^2}\right)^{1/2}-\frac{\gamma}{2\omega}, \tag{2.23}$$

as it is seen from Eq. (2.14). Once a functional form of A describing the crossover between Eq. (2.21) and Eq. (2.22) is known, the naive product of it with Eq. (2.23) will give the prefactor A within the whole damping range in a low temperature limit $T/U_1\ll 1$.

III. GREEN FUNCTION OF THE FOKKER–PLANCK EQUATION IN THE UNDERDAMPED REGIME

The purpose of this section is to demonstrate that the underdamped Brownian motion in a deep potential well can be adequately described in terms of a Green function of the Fokker–Planck equation. In the next section this approach will be extended to derivation of an integral equation, the derived below Green function being its kernel.

In accordance with Kramers' results we assume that the flux over the barrier is carried by particles with energies ϵ in a close vicinity of the barrier top

$$\epsilon\lesssim T.$$

The scale of the potential energy exceeds greatly both the thermal energy and the friction-induced energy loss per one oscillation,

$$U_1\gg T,\delta_1.$$

Therefore, the deterministic dynamics of the escape process is only slightly perturbed by friction and the random force. As the total energy ϵ is the most slowly varying quantity, it is convenient to use it as a new variable instead of the momentum p. The price we pay for this convenience is that now we have to treat the right- and left-going particles separately. The Fokker–Planck equation (2.10) may be transformed via substitutions

$$\begin{aligned}
&p=\pm\{2m[\epsilon-U(x)]\}^{1/2}\equiv p_\pm(\epsilon,x),\\
&\left.\frac{\partial}{\partial p}\right|_x=m^{-1}p_\pm(\epsilon,x)\left.\frac{\partial}{\partial\epsilon}\right|_x\quad\text{for } p\gtrless 0,\\
&\left.\frac{\partial}{\partial x}\right|_p=\left.\frac{\partial}{\partial x}\right|_\epsilon+\frac{dU}{dx}\left.\frac{\partial}{\partial\epsilon}\right|_x,\\
&f^{R,L}(\epsilon,x)=F[p_\pm(\epsilon,x),x].
\end{aligned} \tag{3.1}$$

To proceed further we observe that one can put $\epsilon=0$ in the relationship for $p_\pm(\epsilon,x)$. Indeed, our basic trajectory corresponds directly to $\epsilon=0$, and the leading contributions to escapes come from particles in a narrow range of energies $|\epsilon|\sim T$. Furthermore, the main part of particle trajectories lies inside the well, where $|U(x)|\gg|\epsilon|$. In this approximation the Fokker–Planck equation of interest takes on the form

$$\frac{\partial f}{\partial x}=\pm[-2mU(x)]^{1/2}\gamma\frac{\partial}{\partial\epsilon}\left[f^{R,L}+T\frac{\partial f^{R,L}}{\partial\epsilon}\right] \tag{3.2}$$

with coefficients independent on ϵ. Close to the left-hand side turning point we have

$$f^R(\epsilon,x)=f^L(\epsilon,x),\quad |x-x_1|\ll x_1, \tag{3.3}$$

whereas close to the barrier top $f^R=f^L$ only for $\epsilon<0$. The function f^L vanishes for $\epsilon>0$, as there are no particles going over the barrier into the well.

Equation (3.3) takes on a more convenient form after introduction of the action s along the basic trajectory instead of the particle position x. The relationship between s and x is defined by the differential equation

$$\frac{ds}{dx} = \pm [-2mU(x)]^{1/2}. \tag{3.4}$$

We arrive then at an equation

$$\frac{\partial f(\epsilon,s)}{\partial s} = \gamma \frac{\partial}{\partial \epsilon}\left[f(\epsilon,s) + T\frac{\partial f(\epsilon,s)}{\partial \epsilon}\right], \tag{3.5}$$

which describes diffusion and uniform drift in the energy space. Note, that propagation along the basic trajectory is parametrized not by time or position, as in more familiar cases, but by the action s.

Equation (3.5) enables one to find a relationship between the functions f at different actions,

$$f(\epsilon,s) = \int_{-\infty}^{+\infty} g(\epsilon-\epsilon',s-s')f(\epsilon',s')d\epsilon', \tag{3.6}$$

where g is the Green function of Eq. (3.5), which satisfies an initial condition

$$g(\epsilon-\epsilon',0) = \delta(\epsilon-\epsilon').$$

Solution of Eq. (3.5) for g gives

$$g(\epsilon-\epsilon',s) = (4\pi T\gamma s)^{-1/2}\exp\left[-\frac{(\epsilon-\epsilon'+\gamma s)^2}{4T\gamma s}\right]. \tag{3.7}$$

Quite naturally, the Gaussian random forces induce the Gaussian distribution of variation of the energy. The mean energy loss $\langle\epsilon'-\epsilon\rangle$ is connected with the mean square value of $\epsilon - \langle\epsilon\rangle$ by the fluctuation–dissipation theorem,

$$\langle(\epsilon-\langle\epsilon\rangle)^2\rangle = 2T(\epsilon'-\langle\epsilon\rangle) = 2T\gamma s,$$

where the brackets $\langle\cdots\rangle$ denote averaging over the distribution (3.7).

The advantage of introduction of the action s instead of the particle position x is that s increases steadily along the oscillatory trajectory, whereas assignment of x is insufficient to specify different cycles of motion.

A word of caution about the upper indices R and L, which were suppressed in Eq. (3.6), is in order. In the simplest case we insert into the integrand of Eq. (3.6) the function f^L. In the left-hand side of this equation we get then the function f^L at the interval of trajectory before the left-hand side turning point x_1, and the function f^R after reflection of the particles. Situation at the barrier top is somewhat more complicated, because only particles with energy $\epsilon<0$ are reflected, whereas those with $\epsilon>0$ escape over the barrier forever.

An obvious implication of Eq. (3.6) is that in the underdamped regime the distribution of particles throughout the potential well can be easily found from the distribution at a certain x. Transformation from the action s back to the position x is defined by integration of Eq. (3.4).

In view of the oscillatory nature of the motion in a well it is rather likely that, if complemented by a proper boundary condition to account for the escape of particles from the well, the integral relationship (3.6) can well be transformed into a closed integral equation.

IV. INTEGRAL EQUATION FOR DISTRIBUTION FUNCTION IN A SINGLE POTENTIAL WELL

In this section we use Eq. (3.6) to derive an integral equation for the distribution function, which under certain conditions is equivalent to the Fokker–Planck equation. One of these conditions, already derived above, $\gamma \ll \omega$, concerns the validity of Eq. (3.6). In this regime Eqs. (3.4) and (3.6) determine the distribution function $f(x,\epsilon)$ within the whole potential well, once this function is known at a certain point in the well.

To transform the relationship (3.6) into an integral equation we need additional information about behavior of the potential $U(x)$ at the outside of the barrier. The simplest situation is that of a single potential well, when after surmounting the barrier particles accelerate down its outer slope and never return back into the initial well. In this case Eq. (2.15) gives an estimation of probability of recrossings, caused by interaction with the thermal bath,

$$\frac{J^L}{J^R} \approx \frac{\gamma^2}{8\omega^2} \ll 1.$$

Hence, we shall neglect the recrossings of the barrier. In terms of the functions $f^{R,L}(\epsilon,x)$ this means that $f^L(\epsilon,0) = 0$. Close to the barrier top the flux of the left-going particles arises only due to reflections from the barrier of the right going particles with $\epsilon<0$. This gives the following relationship between f^R and f^L:

$$\begin{aligned} &f^L[\epsilon,x(\epsilon)] = f^R[\epsilon,x(\epsilon)], \quad \epsilon<0; \\ &f^L(\epsilon,0) = 0, \quad \epsilon>0, \end{aligned} \tag{4.1}$$

where $x(\epsilon)$ is a root of equation

$$U(x) = \epsilon, \quad x_m < x < 0, \tag{4.2}$$

corresponding to the right-hand side turning point at the given energy. It should be emphasized that Eq. (4.1) plays a role of a boundary condition, because: (1) it connects the functions f^R and f^L at negative energies; (2) it specifies the problem by the statement, that there are no left-going particles directly at the barrier top.

Particles with different ϵ are reflected at different $x(\epsilon)$ but for $\epsilon \sim T$ this difference is small compared to the size of the potential well,

$$|x(-T)| \approx (2T/m\omega^2)^{1/2} \ll |x_1|.$$

We can assume, therefore, that all these particles propagate along trajectories very close to the basic trajectory ($\epsilon \approx 0$) and can be described by the same Green function (3.7). One could doubt whether the motion of all the particles can be described by the unique function (3.7) as particles with different energies oscillate with different periods, moreover, the period of oscillation diverges as $\ln(U_1/|\epsilon|)$ with $\epsilon \to 0$. The answer is that we consider a probabilistic problem and are interested, therefore, in evolution of the distribution function rather than in dynamics of individual particles. Periods of oscillation do not enter in our problem altogether, as the probabilistic evolution, governed by Eq. (3.7), depends only on the action s along the basic trajectory. In a more technical term, if we introduce the action $S(\epsilon)$ per one oscillation,

$$S(\epsilon)=\oint\{2m[\epsilon-U(x)]\}^{1/2}dx, \quad \epsilon<0$$

we could see, that at small energies

$$S(0)-S(\epsilon)\approx 2\pi|\epsilon|/\Omega(\epsilon)\sim|\epsilon/\omega|\ln(U_1/|\epsilon|), \quad |\epsilon|\ll U_1,$$

where $\Omega(\epsilon)$ is the energy-dependent oscillation frequency. We can safely neglect the difference between $S(0)$ and $S(\epsilon)$, as it could only give small corrections of the order of $T/U_1\ll 1$. In this way we arrive at the basic parameter of the problem

$$S_1\equiv S(0)=\oint[-2mU(x)]^{1/2}dx$$
$$=2\int_{x_1}^{0}[-2mU(x)]^{1/2}dx,$$

which has already appeared in Sec. II in discussion of Kramers' results.

The purpose of the above considerations was to explain why Eq. (3.6) with the action s, corresponding to $\epsilon=0$, could be exploited to describe evolution of $f(\epsilon,s)$ with $|\epsilon|\sim T$. Now we will proceed further with derivation of an integral equation.

The relationship (4.1) will be of crucial importance in this derivation, as it connects the distribution of the left-going particles f^L at the inner right-hand side slope of the barrier with the distribution of the right-going particles. We begin with introduction of a new function

$$f(\epsilon)=f^R(\epsilon,0), \quad \epsilon>0;$$
$$f(\epsilon)=f^R[\epsilon,x(\epsilon)], \quad \epsilon<0,$$

where $x(\epsilon)$ is defined by Eq. (4.2). The function $f(\epsilon)$ gives the rate of escapes for $\epsilon>0$ and the rate of reflections from the barrier for $\epsilon<0$. The reflected particles make up a distribution of the left-going particles f^L [see Eq. (4.1)]. These particles propagate to the left-hand side turning point, where they are reflected again. At this moment the function f^L changes over into the function f^R [see Eq. (3.3)]. Propagating backwards across the well these particles should reach the barrier and reproduce the initial distribution $f(\epsilon)$. That is precisely the condition Eq. (3.6) has to be complemented by to be transformed into an integral equation for the function $f(\epsilon)$.

Evidently, evolution of the particle distribution in vicinity of the closed basic trajectory is governed by the Green's function

$$g(\epsilon-\epsilon')=g(\epsilon-\epsilon',S_1)$$
$$=(4\pi\delta_1 T)^{-1/2}\exp\left[-\frac{(\epsilon-\epsilon'+\delta_1)^2}{4T\delta_1}\right], \tag{4.3}$$

where $\delta_1\equiv\gamma S_1$ is the energy loss per one oscillation. Now we are in the position to write down our principal integral equation

$$f(\epsilon)=\int_{-\infty}^{0}g(\epsilon-\epsilon')f(\epsilon')d\epsilon'. \tag{4.4}$$

The lower limit of integration is extended to infinity in view of a rapid convergence of the integral.

The boundary condition deep in the potential well is

$$f(\epsilon)=\frac{\Omega_1}{2\pi T}e^{-(\epsilon+U_1)/T}, \quad -\epsilon\gg T. \tag{4.5}$$

Hereafter the distribution function is normalized to one particle in the well [see Eq. (2.6)]. Then, by virtue of Eqs. (2.8), (2.9) the decay rate is given by

$$\tau^{-1}=J=\int_0^{+\infty}f(\epsilon)d\epsilon. \tag{4.6}$$

Here we have used the identity $m^{-1}pdp\equiv d\epsilon$ and taken into account that in the underdamped regime only positive momenta contribute to the integral in Eq. (2.8).

Equations (4.3)–(4.6) are completely equivalent to the initial Eqs. (2.3), (2.6), and (2.8)–(2.10) in the region of $\gamma\sim\omega T/U_1$, when $\delta_1\sim T$. In the extremely underdamped regime $\delta_1\ll T$ Eq. (4.4) simplifies down to a differential equation

$$\delta_1\frac{d}{d\epsilon}\left(f+T\frac{df}{d\epsilon}\right)=0, \quad \delta_1\ll T, \tag{4.7}$$

subject to the boundary conditions of Eq. (4.5) and

$$f(0)=0. \tag{4.8}$$

Integration of Eq. (4.4) over positive ϵ yields in the same approximation

$$\tau^{-1}=-\delta_1 T\left.\frac{df}{d\epsilon}\right|_{\epsilon=0}. \tag{4.9}$$

Equations (4.7)–(4.9) have been first derived by Kramers,[1] his final result for τ^{-1} being Eq. (2.19).

Next we proceed to solution of Eq. (4.4) at arbitrary δ_1/T.

V. THE WIENER–HOPF METHOD IN KRAMERS' PROBLEM

Equation (4.4) represents a one-sided convolution equation. To solve it by the Wiener–Hopf method[9] we introduce the one-sided Fourier transformations

$$\varphi^{\pm}(\lambda)=\frac{2\pi}{\Omega_1}e^{U_1/T}\int_{-\infty}^{+\infty}f(\epsilon)\theta(\pm\epsilon)$$
$$\times\exp[(i\lambda+\tfrac{1}{2})\epsilon/T]d\epsilon. \tag{5.1}$$

Comparison of Eqs. (2.20), (4.6), and (5.1) yields

$$A=\varphi^{+}(i/2). \tag{5.2}$$

The boundary condition (4.5) shows that $\varphi^{-}(\lambda)$ has a pole,

$$\varphi^{-}(\lambda)=\frac{-i}{\lambda+i/2}, \quad |\lambda+i/2|\ll 1. \tag{5.3}$$

After the Fourier transformation of Eq. (4.4) we arrive at a Wiener–Hopf equation

$$\varphi^{+}(\lambda)+\varphi^{-}(\lambda)=g(\lambda)\varphi^{-}(\lambda), \tag{5.4}$$

where

$$g(\lambda)=\exp\left[-\frac{\delta_1}{T}\left(\lambda^2+\frac{1}{4}\right)\right]$$

is the Fourier tranformed counterpart of Eq. (4.3). It is convenient to rewrite Eq. (5.4) as

$$\varphi^{+}(\lambda)+G(\lambda)\varphi^{-}(\lambda)=0, \tag{5.5}$$

where

$$G(\lambda)\equiv 1-\exp\left[-\frac{\delta_1}{T}\left(\lambda^2+\frac{1}{4}\right)\right]. \tag{5.6}$$

The functions $\varphi^+(\lambda)$ and $\varphi^-(\lambda)$, defined by Eq. (5.1), are analytical in the upper and lower half-planes of complex λ, the only exception being the pole (5.3) of $\varphi^-(\lambda)$. To explain the Wiener–Hopf method in some details, we rewrite Eq. (5.5) as

$$\ln[-\varphi^+(\lambda)]=\ln\varphi^-(\lambda)+\ln G(\lambda)$$

and with the use of the Cauchy theorem decompose $\ln G(\lambda)$ into two terms, analytical in the corresponding half-planes of λ, arriving at the equation

$$\ln[-\varphi^+(\lambda)]-\ln G^+(\lambda)=\ln\varphi^-(\lambda)+\ln G^-(\lambda), \tag{5.7}$$

where

$$\ln G^{\pm}(\lambda)=\pm\frac{1}{2\pi i}\int_{-\infty}^{+\infty}\frac{\ln G(\lambda')}{\lambda'-\lambda\mp i0}\,d\lambda. \tag{5.8}$$

The functions $G^{\pm}(\lambda)$ are entire functions which have no zeros in the half-planes $\mathrm{Im}\,\lambda>0$ and $\mathrm{Im}\,\lambda<0$ and tend to unity when $\lambda\to\infty$. Naturally, we have

$$G^+(\lambda)G^-(\lambda)\equiv G(\lambda). \tag{5.9}$$

As the functions in the left and in the right-hand side of Eq. (5.7) are analytical in different half-planes of complex λ, they should be equal to an entire function, which is to be chosen to satisfy Eq. (5.3). In this way arrive at the following solution of Eq. (5.5):

$$\varphi^+(\lambda)=\frac{iG^+(\lambda)G^-(-i/2)}{\lambda+i/2},\qquad \varphi^-(\lambda)=-\frac{iG^-(-i/2)}{G^-(\lambda)(\lambda+i/2)}. \tag{5.10}$$

Insertion of Eq. (5.10) into Eq. (5.2) gives

$$A=|G^+(i/2)|^2. \tag{5.11}$$

Here we have used the fact that $G^+(i/2)$ is complex conjugated to $G^-(-i/2)$. Equation (5.11) together with Eqs. (5.8) and (5.6) gives an exact solution of the Kramers' problem in the underdamped regime.

VI. LIFETIME OF A BROWNIAN PARTICLE IN A SINGLE POTENTIAL WELL

Insertion of Eq. (5.8) for $G^+(\lambda)$ into Eq. (5.11) yields the final result for the prefactor A,

$$A=\exp\left(\frac{1}{2\pi}\int_{-\infty}^{+\infty}\ln\left\{1-\exp\left[-\frac{\delta_1}{T}\left(\lambda^2+\frac{1}{4}\right)\right]\right\}\times\frac{d\lambda}{\lambda^2+\frac{1}{4}}\right). \tag{6.1}$$

This expression can be represented in several equivalent forms,

$$A(\Delta)=\exp\left\{\frac{2}{\pi}\int_0^{\pi/2}\ln[1-\exp(\Delta/4\cos^2 x)]\,dx\right\} \tag{6.1a}$$

$$=\exp\left\{-2\pi^{-1/2}\sum_{n=1}^{\infty}n^{-1}\,\mathrm{erfc}[(n\Delta)^{1/2}/2]\right\} \tag{6.1b}$$

$$=\Delta\exp\left\{(\Delta/\pi)^{1/2}\sum_{n=0}^{\infty}\frac{\zeta(\frac{1}{2}-n)}{n!(2n+1)}(-\Delta/4)^n\right\};\qquad \Delta\equiv\delta_1/T, \tag{6.1c}$$

where

$$\mathrm{erfc}(x)=\int_x^{+\infty}e^{-y^2}dy$$

is the error integral, $\zeta(z)$ is the Riemann zeta function, $\zeta(1/2)=-1.46$. The series in Δ in Eq. (6.1c) converges inside the circle $|\Delta|=8\pi$. The asymptotics of $A(\Delta)$ may be obtained from Eq. (6.1b) for $\delta_1\gg T$ and from Eq. (6.1c) for $\delta_1\ll T$,

$$A(\Delta)=1-2(\pi\Delta)^{-1/2}e^{-\Delta/4},\quad \Delta\gg 1, \tag{6.2a}$$

$$A(\Delta)=\Delta[1+\zeta(1/2)(\Delta/\pi)^{1/2}]\approx\Delta-0.82\Delta^{3/2},\quad \Delta\ll 1. \tag{6.2b}$$

The curve A vs Δ is shown in Fig. 2.

As one would have expected, A is nonanalytical at $\Delta=0$ which reflects the principal change of the properties of the system with alteration of the sign of γ.

A final expression for the lifetime of a Brownian particle in a single potential well may be written down directly as a product of Eq. (6.1) and Eq. (2.14),

$$\tau^{-1}=\frac{\Omega_1}{2\pi}\left[\left(1+\frac{\gamma^2}{4\omega^2}\right)^{1/2}-\frac{\gamma}{2\omega}\right]A\left(\frac{\gamma S_1}{T}\right)e^{-U_1/T}. \tag{6.3}$$

In the intermediate-to-overdamped regime $\gamma S_1\gg T$ Eq. (6.3) differs from Eq. (2.14) only by terms $\sim\exp(-\gamma S_1/4T)$. In the intermediate-to-underdamped regime $\gamma\ll\omega$ the factor (2.23) brings in Eq. (6.3) a relative error of order γ/ω, which is as small as T/U_1 at $\gamma S_1\sim T$. Hence, the product of Eq. (6.1) and Eq. (2.14) gives correctly the leading order term in a low temperature expansion of the particle lifetime in the whole damping range. Equation (6.3) depends on five quantities: U_1, Ω_1, ω, S_1, and γ, which completely specify the metastable state of a Brownian particle in a single potential well. Extension to a double-well potential is given in Sec. VIII.

VII. AVERAGE ENERGY OF ESCAPING PARTICLES

Energy distribution of escaping particles is given by the inverse Fourier transform

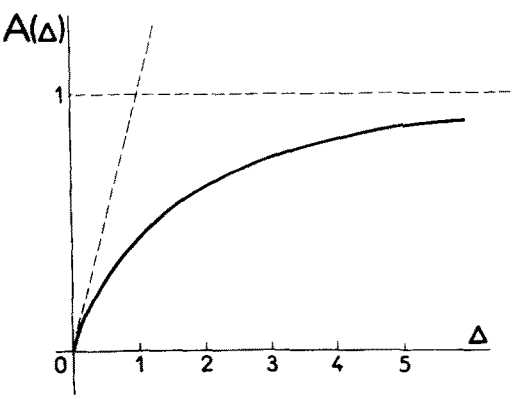

FIG. 2. Dependence of the prefactor A in Eq. (6.1) on the reduced dissipation $\Delta\equiv\gamma S_1/T\equiv\delta_1/T$.

$$f(\epsilon)=\frac{\Omega_1}{4\pi^2 T}\int_{-\infty}^{+\infty}\varphi^{+}(\lambda)\exp\left[-\left(i\lambda+\frac{1}{2}\right)\frac{\epsilon}{T}\right]d\lambda, \tag{7.1}$$

where $\varphi^{+}(\lambda)$ is given by Eqs. (5.8) and (5.10). Unfortunately, only numerical evaluation of the integral in Eq. (7.1) is possible, as $\varphi^{+}(\lambda)$ cannot be represented in a simple analytical form. That can already be seen from complicated structure of Eq. (6.2) for the prefactor $A(\Delta)$, which equals $\varphi^{+}(\lambda)$ at $\lambda=i/2$. A comparatively simple expression can be obtained only for the average energy of escaping particles

$$\bar{\epsilon}=\int_0^{+\infty}f(\epsilon)\epsilon\,d\epsilon\Big/\int_0^{+\infty}f(\epsilon)d\epsilon.$$

With the use of Eq. (5.1) we get

$$\bar{\epsilon}=T\frac{d\ln\varphi^{+}(\lambda)}{d\lambda}\Big|_{\lambda=i/2}$$
$$=1+\frac{2}{\pi}\int_0^{\pi/2}(1-2\cos^2 x)\times\ln[1-\exp(-\Delta/4\cos^2 x)]dx;$$
$$\Delta\equiv\delta_1/T.$$

The dependence of $\bar{\epsilon}/T$ on the ratio δ_1/T is shown in Fig. 3. In the limiting cases one obtains

$$\bar{\epsilon}/T=1-2(\pi\Delta)^{-1/2}e^{-\Delta/4};\quad \Delta\gg 1, \tag{7.2a}$$

$$\bar{\epsilon}/T=-\zeta(1/2)(\Delta/\pi)^{1/2}\approx 0.82\Delta^{1/2},\quad \Delta\ll 1. \tag{7.2b}$$

At $\delta_1\gg T$ the distribution $f(\epsilon)$ is a Boltzmann one and $\bar{\epsilon}=T$. At $\delta_1\ll T$ average energy of escaping particles is small and so is $f(\epsilon)$,

$$\bar{\epsilon}\sim(\delta_1 T)^{1/2},\quad f(0)\sim\frac{\Omega_1\delta_1}{T^2}e^{-U_1/T}.$$

The last expression gives an estimation of $f(0)$, which has earlier been taken to be vanishingly small [see Eq. (4.8)].

In a recent paper[7] an attempt has been made to solve Kramers' problem at $\delta_1\sim T$ by inclusion in Eq. (4.7) an additional loss term due to escapes from the well. In the extremely underdamped regime this approach gives

$$\left.\begin{aligned}A_{\mathrm{BHL}}(\Delta)&=\Delta-\Delta^{3/2}\\ \bar{\epsilon}_{\mathrm{BHL}}/T&=\Delta^{1/2}\end{aligned}\right\}\quad \Delta\ll 1,$$

if we chose parameter α, introduced in the papers by Büttiker, Harris, and Landauer[7,10] to be unity, so as to have $A=1$ at $\delta_1\gg T$. We see, that these results differ from Eqs. (6.2b) and (7.2b) only by numerical factor $|\zeta(1/2)|\pi^{-1/2}\approx 0.82$, which is rather close to unity. However, the distinction between the two approaches is clearly emphasized by our respective results for $\Delta\gg 1$. Results given by Eqs. (6.2a) and (7.2a) exhibit a sharp dropoff of corrections $\sim\exp(-\Delta/4)$, whereas those of BHL yield relative corrections of the order of Δ^{-1}.

VIII. DOUBLE-WELL POTENTIAL

Now we turn to a more general situation when beyond the barrier there is another well with a finite depth, as shown in Fig. 4. In this case there is a finite probability for the particle to return into the initial well after visiting the final well. This possibility is nonnegligible only in the underdamped regime, when the particle that entered the final well loses its energy so slowly, that after several oscillations fluctuations may still throw it back over the barrier.

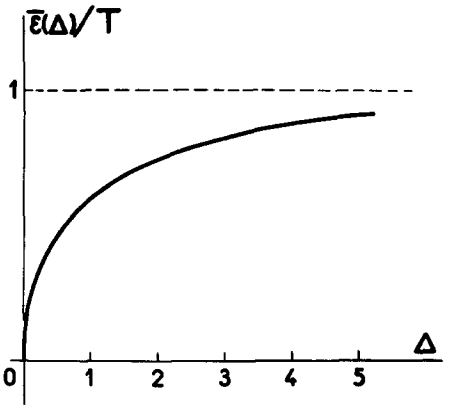

FIG. 3. Dependence of the averaged energy of escaping particles on the reduced dissipation $\Delta\equiv\gamma S_1/T\equiv\delta_1/T$.

To take account of this process we introduce, in analogy with Eq. (2.10), the distributions $f_1(\epsilon)$ and $f_2(\epsilon)$ of the particles, moving towards the barrier from the respective wells. In analogy with Eq. (4.3) we introduce also the Green's functions of the Fokker–Planck equation for these two wells,

$$g_j(\epsilon-\epsilon')=(4\pi\delta_j T)^{-1/2}\exp[-(\epsilon-\epsilon'+\delta_j)^2/4\delta_j T],$$
$$\delta_j\equiv\gamma S_j,$$

where S_j is the action per one oscillation of the particle with $\epsilon=0$ in the well j ($j=1,2$),

$$S_1=2\int_{x_1}^{0}[-2mU(x)]^{1/2}dx,$$
$$S_2=2\int_{0}^{x_2}[-2mU(x)]^{1/2}dx.$$

To write down a system of integral equations for the functions $f_1(\epsilon), f_2(\epsilon)$ by analogy with Eq. (4.4) one should realize that there are now two distinct contributions to, say, $f_1(\epsilon)$. One of them is given by particles reflected from the

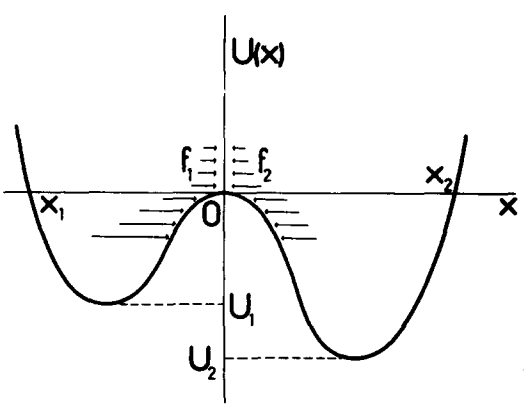

FIG. 4. Schematic representation of a double-well potential.

barrier one period earlier with distribution $f_1(\epsilon)\theta(-\epsilon)$, the other is given by particles which have passed over the barrier one period earlier with distribution $f_2(\epsilon)\theta(\epsilon)$. The full system of equations is then

$$f_1(\epsilon) = \int_{-\infty}^{+\infty} g_1(\epsilon-\epsilon') \times [f_1(\epsilon')\theta(-\epsilon') + f_2(\epsilon')\theta(\epsilon')]d\epsilon';$$
$$f_2(\epsilon) = \int_{-\infty}^{+\infty} g_2(\epsilon-\epsilon') \times [f_2(\epsilon')\theta(-\epsilon') + f_1(\epsilon')\theta(\epsilon')]d\epsilon'.$$

The boundary condition (4.5) for $f_1(\epsilon)$ is still retained, whereas $f_2(\epsilon)$ has no Boltzmann tail deep in the well 2, as initially there were no particles in this well. Following the definition (5.1), we introduce the Fourier transforms $\varphi_1^{\pm}(\lambda)$ and $\varphi_2^{\pm}(\lambda)$ of $f_1(\epsilon)$ and $f_2(\epsilon)$. These new functions obey the system of equations

$$\varphi_1^+(\lambda) + \varphi_1^-(\lambda) = [1-G_1(\lambda)][\varphi_1^-(\lambda) + \varphi_2^+(\lambda)],$$
$$\varphi_2^+(\lambda) + \varphi_2^-(\lambda) = [1-G_2(\lambda)][\varphi_2^-(\lambda) + \varphi_1^+(\lambda)], \tag{8.1}$$

where

$$G_j(\lambda) \equiv 1 - \exp[-\Delta_j(\lambda^2 + 1/4)], \quad \Delta_j \equiv \delta_j/T. \tag{8.2}$$

As above, $\varphi_1^+(\lambda)$ is analytical in the upper half-plane, whereas $\varphi_1^-(\lambda)$ has in the lower half-plane only a pole at $\lambda = -i/2$ with the residue $-i$. The functions $\varphi_2^+(\lambda)$ and $\varphi_2^-(\lambda)$ are analytical in the upper and in the lower half-planes of λ.

The system (8.1) is reduced into two independent Wiener–Hopf equations:

$$\varphi^+(\lambda) + \frac{G_1(\lambda)G_2(\lambda)}{G_{12}(\lambda)}\varphi^-(\lambda) = 0,$$
$$\psi^+(\lambda) + \psi^-(\lambda) = 0, \tag{8.3}$$

where

$$\varphi(\lambda) \equiv \varphi_1(\lambda) - \varphi_2(\lambda),$$
$$\psi(\lambda) \equiv G_1(\lambda)\varphi_1(\lambda) + G_2(\lambda)\varphi_2(\lambda), \tag{8.4}$$
$$G_{12}(\lambda) \equiv 1 - \exp[-(\Delta_1+\Delta_2)(\lambda^2+1/4)].$$

We are only interested in the first of Eqs. (8.3), as the flux over the barrier is given by

$$\tau^{-1} = \int_0^{+\infty} [f_1(\epsilon) - f_2(\epsilon)]d\epsilon \tag{8.5}$$

so that we arrive at

$$A = \varphi_1^+(i/2) - \varphi_2^+(i/2) = \varphi^+(i/2). \tag{8.6}$$

After factorization of $G_1(\lambda)$, $G_2(\lambda)$, and $G_{12}(\lambda)$ in an analogy with Eqs. (5.8), (5.9) one gets

$$\varphi^+(\lambda) = i\frac{G_1^-(-i/2)G_2^-(-i/2)G_1^+(\lambda)G_2^+(\lambda)}{(\lambda+i/2)G_{12}^-(-i/2)G_{12}^+(\lambda)} \tag{8.7}$$

and a similar expression for $\varphi^-(\lambda)$. From Eqs. (8.6) and (8.7) it follows that the prefactor $A(\Delta_1,\Delta_2)$ for a double-well potential in the underdamped regime may be written down through the function $A(\Delta)$ introduced earlier by Eq. (6.1),

$$A(\Delta_1,\Delta_2) = \frac{A(\Delta_1)A(\Delta_2)}{A(\Delta_1+\Delta_2)}. \tag{8.8}$$

The result takes such a simple form by virtue of the kernels $G_1(\lambda)$, $G_2(\lambda)$, and $G_{12}(\lambda)$ being given by the same function (6.1) with different Δ's.

IX. DECAY RATE WITHIN THE WHOLE DAMPING RANGE

The final relationship for the decay rate of the metastable state **1** may be written as a product of Eqs. (8.8) and (2.23). The result is

$$\tau_1^{-1} = \frac{\Omega_1}{2\pi}\left[\left(1+\frac{\gamma^2}{4\omega^2}\right)^{1/2} - \frac{\gamma}{2\omega}\right] \times \frac{A(\gamma S_1/T)A(\gamma S_2/T)}{A[\gamma(S_1+S_2)/T]} e^{-U_1/T}. \tag{9.1}$$

This result holds at arbitrary damping γ. The final state of the particle is specified by the only parameter S_2, which influences the decay rate of the state **1** only in the underdamped regime. Equation (9.1) goes over into Eq. (6.3) for a single potential well at $S_2 \gg S_1$. For symmetric double-well potential one has $S_1 = S_2$. Expansion of Eq. (9.1) in the underdamped limit gives then the coefficient of the $(\gamma S_1/T)^{3/2}$ term, which agrees to five significant figures with the result of numerical calculations.[11]

As the difference of the depths of the initial and final potential wells does not enter the calculations, the dynamic prefactor is symmetric in the well indices. Equation (9.1) with Ω_1 and U_1 substituted by Ω_1 and U_2 gives the rate of fluctuational transitions τ_2^{-1} from the well 2 into the well 1. Oscillatory approximation at the bottom of the well is by no means restrictive. In the case of an arbitrary well one only needs to normalize correctly the equilibrium function (2.6). Thus, our results describe completely the activated decay rates of a one-dimensional metastable state.

The lifetimes τ_1 and τ_2 derived by solution of Kramers' problem, should be used as elementary rate constants in phenomenological equations for the well populations

$$dN_1/dt = -N_1/\tau_1 + N_2/\tau_2,$$
$$dN_2/dt = N_1/\tau_1 - N_2/\tau_2.$$

These equations conserve the total population $N_{12} + N_2$. Their solution is given by

$$N_1(t) = \frac{N_1(0)\left[1+\frac{\Omega_1}{\Omega_2}\exp\left(\frac{U_2-U_1}{T}-\frac{t}{\tau}\right)\right] + N_2(0)\left[1-\exp\left(-\frac{t}{\tau}\right)\right]}{1+\frac{\Omega_1}{\Omega_2}\exp\left(\frac{U_2-U_1}{T}\right)},$$

where

$$\tau^{-1}=\tau_1^{-1}+\tau_2^{-1}=\left[\left(1+\frac{\gamma^2}{4\omega^2}\right)^{1/2}-\frac{\gamma}{2\omega}\right]\frac{A(\gamma S_1/T)A(\gamma S_2/T)}{A\left[\gamma(S_1+S_2)/T\right]}\left[\frac{\Omega_1}{2\pi}e^{-U_1/T}+\frac{\Omega_2}{2\pi}e^{-U_2/T}\right] \tag{9.2}$$

is the relaxation rate of nonequilibrium populations of the two wells.

X. SUMMARY AND CONCLUSIONS

In 1940 Kramers has calculated the escape rate of a Brownian particle from a single one-dimensional potential well in two regimes of damping. The Kramers result in the moderate-to-large damping regime has been successfully extended to multidimensional Brownian motion,[2] to non-Markovian processes[3] and to dissipative quantum mechanical tunneling systems.[4] In contrast to that, Kramers' result for the extremely underdamped regime has not been improved for more than four decades, as the problem of the underdamped Brownian motion lacked a general method of attack. In the meantime, manufacturing of the high-quality Josephson junctions has revived the interest in the underdamped decay rates.[6]

In this paper we have presented a novel mathematical approach to description of the underdamped Brownian motion in deep potential wells. In a general case of a many-valley potential this approach allows a reduction of the Fokker–Planck equation to a system of integral equations in energy variable, which after the Fourier transformation are similar to the Wiener–Hopf equation. We have considered above the cases of a single potential well and of a double-well potential, when these equations can be explicitly solved by the Wiener–Hopf method.

Some of the technical points of the present paper have already been employed by one of the present authors (V.I.M.) in an analysis of the tilted periodic potential problem.[12] Of the results thus obtained it is worthwhile to mention a calculation of the fluctuational current–voltage characteristics and the lifetime of zero-voltage states in the high-quality Josephson junctions.[12] Moreover, the quantum tunneling effects at the barrier top can be naturally incorporated into the calculations.[13]

A brief account of the above described Green function method has been published elsewhere.[14] In this paper a formal solution of a problem of the tilted periodic potential with allowance for quantum effects at the top of the barrier has been presented, omitting all the technicalities.

Recently there has been a great deal of activity on the problem of non-Markovian activated processes, where one encounters memory friction and Gaussian colored (nonwhite) noise. For the equilibrium state the latter is exemplified by the Johnson–Nyquist noise. These effects become significant, if typical spacing of the energy levels in a potential well is comparable to temperature, $\hbar\Omega_1 \sim T$. On the other hand, effects of the quantum penetration at the barrier top become nonnegligible, when $\hbar\omega \sim T$. In considerations of papers[13,14] it has implicitly been assumed that $\Omega_1 \ll \omega$, so that the results obtained there are only applicable to rather wide potential wells with a steep barrier top.

A general case of arbitrary relation between Ω_1 and ω, when both the Johnson–Nyquist noise inside a potential well and the quantum tunneling effects at the barrier top should be taken into account, has been considered by Larkin and Ovchinnikov.[15] They derived an integral equation seemingly identical to that obtained earlier,[13] effects of the Johnson–Nyquist noise being absorbed into a modified kernel, which represents a Green's function for the Wigner distribution function and coincides with the Green's function (4.3) of the Fokker–Planck equation only in the classical limit $\hbar\Omega_1 \ll T$.

The above presented solution of the Kramers problem in the underdamped regime and the list of related problems do demonstrate quite clearly that the Green's function approach to the Fokker–Planck equation is a most adequate one for quantitative description of the underdamped Brownian motion.

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