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Generalization of the Kramers–Langer theory: decay of the metastable state in the case of strongly anisotropic friction

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Abstract. The problem of escape of a classical particle from a multidimensional potential well due to the influence of random forces is studied. A new solution to the problem is obtained which shows that with fairly large friction anisotropy the qualitative picture of the process principally differs from that underlying the conventional multidimensional Kramers–Langer theory. According to the new process picture particles escape the well before reaching the saddle point; the limiting stage of the process is the particle attainment of the transition region (i.e. well dynamics), not passage through the barrier region as the conventional theory suggests. The new expression for the rate constant predicts a slower process rate in comparison with the Kramers–Langer theory. With decreasing friction anisotropy the new expression coincides with the conventional one.

1. Introduction

Dynamics of noise-induced transitions between local stable states is a problem actively being studied at the present time [1–5]. In particular, the Kramers–Langer theory (KLT) describing Brownian particle escape from a potential well under the action of random forces is widely used in the treatment of a great number of different physical and chemical phenomena [5–8]. In a more general case the noise-induced escape from attractors is studied.

Usually the escape rate from attractors is determined by the well known Arrhenius formula [2, 4]

$$\Gamma \sim \exp\left(-\frac{\Delta V}{\sigma^2}\right) \tag{1.1}$$

where ΔV is the so-called barrier height defined as the difference between the potential energies at the saddle point and at the attractor; σ^2 is the noise intensity which is assumed to be small enough that $\Delta V/\sigma^2 \gg 1$. In KLT the temperature T (in energy units) plays the role of σ^2 ane the requirement $\Delta V/\sigma^2 \gg 1$ means that the barrier height must be large in comparison with the temperature T.

In recent papers [2, 4] the idea that the relationship (1.1) is a universal law of nature is advanced. In the present paper we argue that this idea is wrong. We consider

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the activated escape process due to multidimensional Brownian motion and show that friction anisotropy can lead to strong deviations from the Arrhenius law (1.1).

In the conventional picture of particle escape from a multidimensional potential well according to KLT, it is usually believed that (1) a particle escapes the well passing via the saddle on the potential surface, (2) the process is limited by passage through the region close to the saddle point and (3) Boltzmann equilibrium is maintained in the greater part of the well. We shall show that for a wide class of potential surfaces, all these conditions are broken when friction anisotropy is large enough. In this case, a particle escapes the well before reaching the saddle and the process is limited by the particle attainment of the transition region, i.e. by well dynamics. It should be noted that any deviations from the conventional Kramers-Langer solution are due to the presence of additional small parameters in the problem under study [5].

In the present paper, which continues a series of papers [9-11], a new expression for the escape rate is obtained. This expression is correct for highly anisotropic friction when it predicts a slower escape rate than the conventional expression. Both the activation energy and the pre-exponent factor in this expression differ from conventional ones. When friction anisotropy is not too high our expression reduces to the conventional expression.

The outline of this paper is as follows. In the next section we exclude, making use of friction anisotropy, the rapidly relaxing variables from the initial multidimensional Fokker-Planck equation. As a result, we obtain an effective one-dimensional equation which describes the evolution of the distribution function over the slow variable. In sections 3 and 4, starting from this equation we calculate the escape rate for potentials of different types. For the potentials considered in section 3 the rate constant—which is calculated using the effective equation—coincides with the corresponding asymptotes of the conventional formula. In contrast, for the potentials considered in section 4 the rate constant—again calculated using the effective equation—significantly differs from the corresponding asymptote of the conventional formula. Detailed discussion of this new expression is presented in section 5. Finally, in the conclusion the basic results of the paper are summarized and the basic assumptions used in our theory are enumerated.

2. Adiabatic elimination of rapidly relaxing variables: derivation of the effective equation

Let us consider the decay of the state which, at the initial time instant $t = 0$, is localized in one of the wells of the two-dimensional double-well potential $V(x, y)$. In the present paper, for simplicity, but without loss of generality, we restrict ourselves to the two-dimensional case. Let us assume that there is a single saddle point on the potential surface and that its energy measured from the bottom of the well, ΔV, is large compared to the temperature T. Also, we shall neglect backflows, i.e. we shall consider just the decay of the distribution, not its relaxation. A large barrier height, which the particle must overcome in order to escape from the well, ensures that this process is slow compared to relaxation of the initial distribution in the well towards a quasistationary one which decays according to the $\exp(-\Gamma t)$ law.

The probability of particle escape from the potential well Γ is the least eigenvalue of the Fokker-Planck (FP) operator, $\hat{L}_{FP}$, which describes the time evolution of the distribution function $P(x, \dot{x}; y, \dot{y}; t)$ in phase space. Let us choose a coordinate system

where tensors of masses ($\hat{m}$) and friction coefficients ($\hat{\eta}$) are diagonal and write down our starting FP-equation in the form

$$-\frac{\partial P}{\partial t}=\hat{L}_{\mathrm{FP}}P \tag{2.1}$$

$$\hat{L}_{\mathrm{FP}}=\hat{L}_x+\hat{L}_y \tag{2.2}$$

$$\hat{L}_x=\dot{x}\frac{\partial}{\partial x}-\frac{1}{m_x}\frac{\partial V(x,y)}{\partial x}\frac{\partial}{\partial \dot{x}}-\frac{\eta_x}{m_x}\frac{\partial}{\partial \dot{x}}\left(\dot{x}+\frac{T}{m_x}\frac{\partial}{\partial \dot{x}}\right) \tag{2.3}$$

$$\hat{L}_y=\dot{y}\frac{\partial}{\partial y}-\frac{1}{m_y}\frac{\partial V(x,y)}{\partial y}\frac{\partial}{\partial \dot{y}}-\frac{\eta_y}{m_y}\frac{\partial}{\partial \dot{y}}\left(\dot{y}+\frac{T}{m_y}\frac{\partial}{\partial \dot{y}}\right). \tag{2.4}$$

Note that operators $\hat{L}_x$ and $\hat{L}_y$ parametrically depend on y and x, respectively. To consider just the decay problem, but not the relaxation one, we impose absorbing boundary conditions in the second well. Of course, in such a system non-conservation of probability takes place and the initial well population tends to zero with $t\to\infty$.

Our calculation of the least eigenvalue of the $\hat{L}_{\mathrm{FP}}$ operator in the case of highly anisotropic friction begins with adiabatic elimination of rapidly relaxing variables. For definitiveness, we consider the x-coordinate a fast one and the y-coordinate a slow one. The eigenfunction ψ_Γ which corresponds to the least eigenvalue

$$\hat{L}_{\mathrm{FP}}\psi_\Gamma=\Gamma\psi_\Gamma \tag{2.5}$$

we present in the form

$$\psi_\Gamma(x,\dot{x};y,\dot{y})=\varphi_{\gamma(y)}(x,\dot{x}\,|\,y)g_\Gamma(y,\dot{y}). \tag{2.6}$$

Here $\varphi_{\gamma(y)}(x,\dot{x}\,|\,y)$ is the eigenfunction which corresponds to the least eigenvalue of the operator $\hat{L}_x$ with the fixed value of the slow coordinate y, $\gamma(y)$,

$$\hat{L}_x\varphi_{\gamma(y)}=\gamma(y)\varphi_{\gamma(y)}. \tag{2.7}$$

If the profile over x of the potential $V(x,y)$ with a fixed y-value is a single-well curve then $\gamma(y)=0$ and $\varphi_0(x,\dot{x}\,|\,y)$ is the equilibrium Maxwell–Boltzmann distribution over x and $\dot{x}$ in the section $V(x,y=\text{constant})$.

If this profile is a double-well curve, then $\gamma(y)\neq 0$, and is the probability per unit time of particle escape from the well due to the motion along x with a fixed y-value. Assuming that the barrier which separates the wells of a double-well profile $V(x,y=\text{constant})$ is large compared to T we can obtain the escape rate $\gamma(y)$ as a result of the solution of the one-dimensional Kramers problem [6]

$$\gamma(y)=\nu(y)\exp[-\Delta E(y)/T]. \tag{2.8}$$

The relationship between the initial potential $V(x,y)$ and the y-dependence of either the activation energy $\Delta E(y)$ or the pre-exponent $\nu(y)$ is presented in section 4. It should be recalled that we consider only the decay of the metastable state and ignore backflows of particles which have escaped the well.

Let us introduce the function $h_\Gamma(y,\dot{y})$ which describes the distribution over y and $\dot{y}$

$$h_\Gamma(y,\dot{y})=\int\psi_\Gamma(x,\dot{x};y,\dot{y})\,\mathrm{d}x\,\mathrm{d}\dot{x}$$

$$=g_\Gamma(y,\dot{y})\int\varphi_{\gamma(y)}(x,\dot{x}\,|\,y)\,\mathrm{d}x\,\mathrm{d}\dot{x}. \tag{2.9}$$

According to equations (2.2)–(2.7) this function satisfies the equation

$$\left[\dot{y}\frac{\partial}{\partial y}-\frac{1}{m_y}\frac{\mathrm{d}V_{\mathrm{eff}}(y)}{\mathrm{d}y}\frac{\partial}{\partial \dot{y}}-\frac{\eta_y}{m_y}\frac{\partial}{\partial \dot{y}}\left(\dot{y}+\frac{T}{m_y}\frac{\partial}{\partial \dot{y}}\right)+\gamma(y)\right]h_\Gamma=\Gamma h_\Gamma. \tag{2.10}$$

The effective potential $V_{\mathrm{eff}}(y)$ is connected with the intitial potential $V(x, y)$ by the relationship

$$\frac{\mathrm{d}V_{\mathrm{eff}}(y)}{\mathrm{d}y}=\frac{\int[\partial V(x, y)/\partial y]\varphi_{\gamma(y)}(x, \dot{x}\,|\,y)\,\mathrm{d}x\,\mathrm{d}\dot{x}}{\int\varphi_{\gamma(y)}(x, \dot{x}\,|\,y)\,\mathrm{d}x\,\mathrm{d}\dot{x}}. \tag{2.11}$$

Equation (2.10) is the effective equation which describes the distribution over y and $\dot{y}$. In order to simplify further calculations we shall assume that the mass m_y is not too large. Then with relatively large values of η_y—which are our interest—the distribution over the $\dot{y}$-velocities instantly relaxes towards the Maxwell distribution. *Making conventional reduction of (2.10) to an equation which describes the distribution* over the y-coordinate only we obtain [12]

$$f_\Gamma(y)=\int h_\Gamma(y, \dot{y})\,\mathrm{d}\dot{y} \tag{2.12}$$

$$\hat{L}_{\mathrm{eff}}f_\Gamma=\left\{-\mathscr{D}_y\frac{\mathrm{d}}{\mathrm{d}y}\left[\frac{\mathrm{d}}{\mathrm{d}y}+\frac{1}{T}\frac{\mathrm{d}V_{\mathrm{eff}}(y)}{\mathrm{d}y}\right]+\gamma(y)\right\}f_\Gamma=\Gamma f_\Gamma \tag{2.13}$$

where $\mathscr{D}_y=T/\eta_y$ is the diffusion coefficient.

Equations (2.10) and (2.13) are the main results of this section. In [11], with the aid of the projection operator technique, we reduced (2.1) to an effective evolution equation. This equation has the same form as (2.1), but the operator $\hat{L}_{\mathrm{FP}}$ is changed to the operator $\hat{L}_{\mathrm{eff}}$ (2.13) containing the sink term. In [11] we show that the reduction is valid if several conditions are fulfilled. Here we note the three conditions considered the most important: (*a*) potential profile $V(x, y=\text{constant})$ should be a double-well type; (*b*) $\eta_y \gg \eta_x$ (some estimations clarifying this point are presented in section 5; (*c*) friction coefficient η_y should be large enough that one could eliminate the velocity $\dot{y}$ from the initial FP equation.

It should be emphasized that we assume that the motion is diffusive along the *y-coordinate only. On the motion along the x-coordinate we do not impose any* restrictions. Variations in the friction coefficient η_x lead to changes in the sink term value, but not the form of the equation (certainly, if the above-mentioned conditions are not disturbed). These circumstances allow us to start with the multidimensional FP equation comprising both velocities $\dot{x}$, $\dot{y}$ and coordinates x, y. It is evident that such a reduction can be accomplished in the case of the multidimensional diffusion problem also. This problem is considered in recent papers [13, 14] for the two-dimensional case. In these papers a similar reduction of the initial multidimensional problem to the effective one-dimensional problem is carried out. Similarities and distinctions between both approaches and results are dealt with in [15, 16].

In the following sections we use equation (2.10) and (2.13) for calculation of the least eigenvalue Γ of the starting operator $\hat{L}_{\mathrm{FP}}$ under highly anisotropic friction. In a further section we show that in the case of potentials with a single-well profile $V(x, y=\text{constant})$ this eigenvalue coincides with asymptotes $\eta_y \to \infty$ of the conventional KLT formula. In contrast, in the case of potentials with a double-well profile $V(x, y=$ constant) we obtain a new solution of the problem which differs considerably from such asymptote. In section 5 we point out the range of friction coefficient η_y over

which significant departures of the escape rate Γ from predictions of the conventional KLT formula take place.

3. Escape rate calculation based on the effective equation: no sink case

In the case under study here the profile $V(x, y = \text{constant})$ is a single-well curve and the Maxwell-Boltzmann distribution over x and $\dot{x}$ with each magnitude of the slow coordinate y sets in as a result of the rapid relaxation, i.e.

$$\varphi_0(x, \dot{x}\,|\,y) \propto \exp\left[-\frac{m_x \dot{x}^2}{2T} - \frac{V(x, y)}{T}\right]. \tag{3.1}$$

The potential $V(x, y = \text{constant})$ has a minimum, its position $x_0(y)$ being determined from the equation

$$\frac{\partial V(x, y)}{\partial x} = 0. \tag{3.2}$$

When calculating the effective potential $V_{\text{eff}}(y)$ we assume that in the fairly wide vicinity of the point $x_0(y)$ the potential $V(x, y)$ is a quadratic function of x

$$V(x, y) \simeq V_0(y) + \tfrac{1}{2}\varkappa(y)[x - x_0(y)]^2 \tag{3.3}$$

where

$$V_0(y) = V(x_0(y), y) \qquad \varkappa(y) = \left.\frac{\partial^2 V(x, y)}{\partial x^2}\right|_{x_0(y)}. \tag{3.4}$$

Equation (2.11), (3.1) and (3.3) lead to an effective potential of the form

$$V_{\text{eff}}(y) = V_0(y) + \frac{T}{2}\ln\frac{\varkappa(y)}{\tilde{\varkappa}} \tag{3.5}$$

where $\tilde{\varkappa}$ is an arbitrary constant which fixes the zero of energy. Let us discuss the potential $V_{\text{eff}}(y)$ in more detail. It is possible to show that it is a double-well curve, its minima being at the points y_i and y_f, and the maximum at the point y_{sp} where y_i, y_f and y_{sp} are the values of the y-coordinate at the initial and final wells and the saddle point in the potential $V(x, y)$, respectively.

Thus, in the case under consideration, as a result of adiabatic elimination of the fast variable we come to the one-dimensional Kramers problem in the potential $V_{\text{eff}}(y)$. This problem is described by (2.10) with $\gamma(y) = 0$. In this case the expression for the escape rate gives the Kramers formula [6]

$$\Gamma = \frac{1}{2\pi}\left(\frac{V''_{\text{eff}}(y_i)}{|V''_{\text{eff}}(y_{\text{sp}})|}\right)^{1/2}\left[\sqrt{\left(\frac{\eta_y}{2m_y}\right)^2 + \frac{|V''_{\text{eff}}(y_{\text{sp}})|}{m_y}} - \frac{\eta_y}{2m_y}\right]\exp\left(-\frac{\Delta V_{\text{eff}}}{T}\right). \tag{3.6}$$

Let us show that this expression coincides with the asymptote $\eta_y \to \infty$ of the conventional KLT expression for the escape rate. The latter expression has the form [7, 17]

$$\Gamma_e = \frac{1}{2\pi}\left(\frac{\det \hat{V}^{\text{w}}}{|\det \hat{V}^{\text{sp}}|}\right)^{1/2} H \exp(-\Delta V/T) \tag{3.7}$$

where $\hat{V}^{w}$ and $\hat{V}^{sp}$ are the matrices of the second derivatives of the potential at the well bottom and at the saddle point, H is the single positive root of the equation

$$\det(\hat{m}H^2+\hat{\eta}H+\hat{V}^{sp})=0. \tag{3.8}$$

With $\eta_y \to \infty$ the positive root of (3.8) is determined by different formulae depending on the sign of the matrix element V_{xx}^{sp}

$$H=\frac{1}{2m_y}\left(\sqrt{\eta_y^2+\frac{4m_y}{V_{xx}^{sp}}|\det \hat{V}^{sp}|}-\eta_y\right) \qquad \text{if } V_{xx}^{sp}>0 \tag{3.9}$$

$$H=\frac{1}{2m_x}(\sqrt{\eta_x^2+4m_x|V_{xx}^{sp}|}-\eta_x) \qquad \text{if } V_{xx}^{sp}<0. \tag{3.10}$$

In the case under study when sections $V(x, y=\text{constant})$ are single-well curves and $V_{xx}^{sp}=\varkappa(y_{sp})>0$, it is easy to see that (3.6) coincides with (3.7) in which H is determined by (3.9).

Let us point out the principle difference between equations (3.9) and (3.10) for the H-quantity and, hence, the difference between the conventional escape rate expressions for potential surfaces $V(x, y)$ with $V_{xx}^{sp}>0$ and $V_{xx}^{sp}<0$. If $V_{xx}^{sp}>0$ according to (3.7) and (3.9) the escape rate decreases with an increase in the friction coefficient η_y and tends to zero with $\eta_y \to \infty$ as $1/\eta_y$. In contrast, if $V_{xx}^{sp}<0$ according to (3.7) and (3.10) escape rate does not depend on the friction coefficient η_y along the slow coordinate. This fact contradicts general qualitative ideas. Indeed, with the presence of a slow coordinate particles escape the well in the following manner: the rapid coordinates adjust themselves to the slow one and the process is limited by the slow motion. Therefore, the 'true' escape rate should decrease with increasing η_y. In the following section we derive a new formula for the escape rate in the case of potentials with $V_{xx}^{sp}<0$ which is free from this obvious defect.

4. Escape rate calculation based on the effective equation: problem with a sink-term

We begin our escape rate calculation in the case of potentials $V(x, y)$ whose profile over x, $V(x, y=\text{constant})$, with actual y-values is a double-well curve, by establishing the relationships between the potential $V(x, y)$ with the sink term (2.8) and the effective potential $V_{eff}(y)$. It should be noted that for such potentials $V_{xx}^{sp}<0$. Let us designate the coordinates at the bottom of the left and right wells, and the top of the barrier which separates them in the section $V(x, y=\text{constant})$, by $x_0(y)$, $x_1(y)$ and $x_b(y)$, respectively. They are the roots of the equation

$$\frac{\partial V(x, y)}{\partial x}=0 \tag{4.1}$$

and $x_0(y)<x_b(y)<x_1(y)$. The activation energy $\Delta E(y)$, which depends on the y-coordinate, is determined by the expression

$$\Delta E(y)=V_b(y)-V_0(y) \tag{4.2}$$

where

$$V_b(y)=V(x_b(y), y) \qquad V_0(y)=V(x_0(y), y). \tag{4.3}$$

It is possible to show that the potentials $V_0(y)$ and $V_b(y)$ are single-well curves which have their minima at the points $y = y_w$ and $y = y_{sp}$, respectively, where y_w and y_{sp} are the values of the y-coordinate at the bottom of the initial well and at the saddle point, respectively. The pre-exponent $\nu(y)$ in equation (2.8) according to the Kramers formula, has the form [6]

$$\nu(y) = \frac{1}{2\pi}\left[\frac{\varkappa_0(y)}{|\varkappa_b(y)|}\right]^{1/2}\left[\sqrt{\left(\frac{\nu_x}{2m_x}\right)^2 + \frac{|\varkappa_b(y)|}{m_x}} - \frac{\eta_x}{2m_x}\right] \tag{4.4}$$

where

$$\varkappa_0(y) = V''_{xx}(x_0(y), y) \qquad \text{and} \qquad \varkappa_b(y) = V''_{xx}(x_b(y), y).$$

The basic contribution to the integrals in (2.11) for $V_{eff}(y)$ is made in the vicinity of point $x_0(y)$ where the function $\varphi_{\gamma(y)}(x, \dot{x}\,|\,y)$ is close to the Boltzmann distribution. Utilizing the quadratic expansion over x of the potential $V(x, y = \text{constant})$ in this vicinity

$$V(x, y) \simeq V_0(y) + \tfrac{1}{2}\varkappa_0(y)[x - x_0(y)]^2 \tag{4.5}$$

we obtain the following expression for the effective potential

$$V_{eff}(y) = V_0(y) + \frac{T}{2}\ln\frac{\varkappa_0(y)}{\varkappa_0(y_w)}. \tag{4.6}$$

In equation (4.6) the zero of potential energy is fixed in such a way that in the vicinity of the point y_w the potentials $V_{eff}(y)$ and $V_0(y)$ coincide.

Thus, we have established relations between all the parameters which enter into the effective equation (2.13) with friction coefficients and initial multidimensional potential $V(x, y)$. Let us go to direct calculations of the escape rate based on this equation.

A number of papers [18-21] are devoted to an analysis of the decay kinetics of a state whose evolution is described by the diffusion equation with a sink term of the form

$$-\frac{\partial f}{\partial t} = \hat{L}_{eff} f = \left\{-\mathscr{D}_y \frac{\partial}{\partial y}\left[\frac{\partial}{\partial y} + \frac{1}{T}\frac{\mathrm{d}V_{eff}(y)}{\mathrm{d}y}\right] + \gamma(y)\right\} f \tag{4.7}$$

where $f(y, t)$ is the distribution function over the y-coordinate at the time instant t. This equation takes account of the competition between the two processes: relaxation towards the Boltzmann distribution in the potential $V_{eff}(y)$ and decay due to the sink $\gamma(y)$ which destroys this distribution. Kinetics is easily calculated only in the two limiting cases when $\mathscr{D}_y = 0$ and $\mathscr{D}_y \to \infty$.

In the first case ($\mathscr{D}_y = 0$, relaxation is frozen) the probability of the particle staying in the well during the time interval t (the so-called survival function)

$$Q(t) = \int f(y, t)\,\mathrm{d}y \tag{4.8}$$

changes with time according to the law

$$Q(t) = \int f(y, 0)\exp[-\gamma(y)t]\,\mathrm{d}y. \tag{4.9}$$

In this case the decay has a multiexponential nature and depends on the initial distribution $f(y, 0)$. Equilibrium in the well is not reached and particles do not escape from the well through the saddle.

In the other limiting case, $\mathscr{D}_y \to \infty$, relaxation instantly restores the equilibrium distribution in the potential $V_{\text{eff}}(y)$

$$f_e(y) \propto \exp[-V_{\text{eff}}(y)/T]. \tag{4.10}$$

Here, the decay is a single-exponential $Q(t) = Q(0)\exp(-\Gamma t)$, where the escape rate Γ has the form

$$\Gamma = \Gamma_e = \int \gamma(y) f_e(y)\, dy \Big/ \int f_e(y)\, dy. \tag{4.11}$$

In the general case the decay is described by the multiexponential law

$$Q(t) = \sum_{n=1}^{\infty} c_n \exp(-\lambda_n t) \tag{4.12}$$

where λ_n are the eigenvalues of the effective evolution operator $\hat{L}_{\text{eff}}$ (2.13), numbered *in the order of their increase*, c_n *are the decomposition coefficients of the initial* distribution $f(y, 0)$ over eigenfunctions of the conjugated operator

$$\hat{L}^+_{\text{eff}} = -\mathscr{D}_y\left[\frac{d^2}{dy^2} - \frac{1}{T}\frac{dV_{\text{eff}}(y)}{dy}\frac{d}{dy}\right] + \gamma(y). \tag{4.13}$$

Equation (4.12) shows that for the single-exponential decay it is necessary to satisfy two conditions, the first being the gap in the spectrum of eigenvalues of the operator $\hat{L}_{\text{eff}}$: $\lambda_1 \ll \lambda_2$. This condition reflects the fact that quasistationary distribution—which decays according to the single-exponential law $\exp(-\lambda_1 t)$—sets in during the time interval of the order λ_2^{-1} which is small compared to the typical time interval of its subsequent decay λ_1^{-1}. The second condition is expressed by the inequality

$$c_1 \gg \sum_{n=2}^{\infty} c_n.$$

Actually, it is the demand for the initial distribution which guarantees the single-exponential decay of the overwhelming majority of the assembly subsystems. Further, we assume that this condition is fulfilled.

In our method for the solution of equation (2.13), which is put forward below, specific features of the sink term are used. The main peculiarity of the sink term is its fast growth with y. Near the well bottom of the effective potential the sink force is negligibly small and the distribution $f_\Gamma(y)$ in this region is close to the equilibrium distribution. With an increase in y the sink force grows exponentially which leads to an appreciable depletion of the distribution $f_\Gamma(y)$ (compared with the Boltzmann distribution) due to particle escape. As long as the depleted region is far enough from the well bottom, the decay kinetics is of single-exponential nature since particle escape from the well occurs much more slowly than relaxation in the well.

In order to calculate the least eigenvalue Γ let us present equation (2.13) in the form

$$-\mathscr{D}_y \frac{d}{dy}\left[f_e \frac{d}{dy}(f_\Gamma/f_e)\right] + \gamma(y) f_\Gamma = \Gamma f_\Gamma. \tag{4.14}$$

Let us integrate this equation from $-\infty$ up to the point $\bar{y}$. Choice of the point $\bar{y}$ we specify below. Here, we indicate that the point $\bar{y}$ is chosen far enough to the right of the well bottom, $y_w < \bar{y}$ (we take that $y_w < y_{sp}$), so that the normalization condition can be written in the form

$$\int_{-\infty}^{\infty} f_\Gamma(y)\, dy \simeq \int_{-\infty}^{\bar{y}} f_\Gamma(y)\, dy \simeq 1. \tag{4.15}$$

As a result, we obtain the following expression for the escape rate

$$\Gamma \simeq \int_{-\infty}^{\bar{y}} \gamma(y) f_\Gamma(y)\, dy - \mathscr{D}_y \{ f_e(y) \frac{d}{dy} [f_\Gamma(y)/f_e(y)] \}_{y=\bar{y}}. \tag{4.16}$$

To obtain the escape rate Γ from formula (4.16) it is necessary to know the function $f_\Gamma(y)$ with $y \leqslant \bar{y}$, and its first derivative at the point $\bar{y}$, $f'_\Gamma(\bar{y})$. For calculation of this eigenfunction we use a method initiated by Kramers [6] and which was discussed in detail in a recent review article [22]. Its main idea takes into account the fact that Γ is very close to zero, and consists in constructing the eigenfunction $f_\Gamma(y)$ from the solutions of the stationary equation with $\Gamma = 0$. We shall see that our choice of the point $\bar{y}$ is made in such a way that in calculating $f_\Gamma(y)$ for $y < \bar{y}$ we can neglect the sink term $\gamma(y)$ in the operator $\hat{L}_{\text{eff}}$ (2.13). As a result, the equation determining $f_\Gamma(y)$ for $y < \bar{y}$ takes the form

$$\left\{ \frac{d}{dy} \left[\frac{d}{dy} + \frac{1}{T} \frac{dV_{\text{eff}}(y)}{dy} \right] \right\} f_\Gamma(y) = 0. \tag{4.17}$$

This equation has two linearly independent solutions: equilibrium distribution in the potential $V_{\text{eff}}(y)$, $f_e(y)$, and

$$f_e(y) \int^{y} \exp[V_{\text{eff}}(y')/T]\, dy'.$$

The eigenfunction $f_\Gamma(y)$ is presented in the form of a linear combination of these two solutions

$$f_\Gamma(y) = f_e(y) \left\{ 1 + A \int_{y_0}^{y} \exp[V_{\text{eff}}(y')/T]\, dy' \right\} \qquad y \leqslant \bar{y}. \tag{4.18}$$

Here, A is a constant which will be determined from the requirement of matching of (4.18) at the point $\bar{y}$ with the expression for $f_\Gamma(y)$ which is true for $y \geqslant \bar{y}$. The point y_0 is taken in such a way that it is between the well bottom and the point $\bar{y}$, far away from each of them, i.e. $y_w < y_0 < \bar{y}$. It should be noted that the point y_0 does not enter into the final expression for the escape rate.

Now, let us calculate the function $f_\Gamma(y)$ for $y \geqslant \bar{y}$. Here, we present the function $f_\Gamma(y)$ in the form

$$f_\Gamma(y) = \chi_\Gamma(y) \exp[-V_{\text{eff}}(y)/2T] \tag{4.19}$$

and, as a result, pass to the Schrödinger-type equation for the function $\chi_\Gamma(y)$

$$\hat{\mathscr{H}} \chi_\Gamma = \Gamma \chi_\Gamma \tag{4.20}$$

$$\hat{\mathscr{H}} = -\mathscr{D}_y \frac{d^2}{dy^2} + [W(y) + \gamma(y)]. \tag{4.21}$$

The term $W(y)$ in the 'potential energy' in Hamiltonian $\hat{\mathscr{H}}$ is linked to the potential $V_{\text{eff}}(y)$ by the relationship

$$W(y) = \mathscr{D}_y \left[-\frac{1}{2T} V''_{\text{eff}}(y) + \left(\frac{1}{2T} V'_{\text{eff}}(y) \right)^2 \right] \tag{4.22}$$

Let us define our choice of the point $\bar{y}$. The general view of the potential energy function in the Hamiltonian (4.21) prompts us to choose as $\bar{y}$ the value of the y-coordinate where both terms in the potential energy are equal:

$$W(\bar{y}) = \gamma(\bar{y}). \tag{4.23}$$

With $y < \bar{y}$ the distribution $f_\Gamma(y)$ is close to equilibrium $f_e(y)$ since here $W(y) \gg \gamma(y)$. This fact justifies disregarding the sink term in (4.17). In the appendix we show that for a wide range of $\bar{y}$-values the growth rate of the sink term $\gamma(y)$ greatly exceeds the growth rate of the competing contribution to the potential energy, $W(y)$ for $y \geqslant \bar{y}$. For this reason with $y > \bar{y}$, $\gamma(y) \gg W(y)$, the distribution $f_\Gamma(y)$ is appreciably depleted compared with the equilibrium distribution, due to particle escape.

In our solution of equation (4.20) with $y \geqslant \bar{y}$ we use the exponential growth of the sink term and introduce two simplifying assumptions. We suggest that with $y \geqslant \bar{y}$

$$W(y) \simeq W(\bar{y}) = \text{constant} \qquad \gamma(y) = \gamma \exp[s(y-\bar{y})] \tag{4.24}$$

where $\gamma = \gamma(\bar{y})$ and $s = s(\bar{y}) = \gamma'(\bar{y})/\gamma(\bar{y})$, since the function $\chi_\Gamma(y)$ rapidly tends to zero with $y > \bar{y}$. As a result, (4.20) takes the form

$$\frac{d^2\chi_\Gamma}{dy^2} - \frac{\gamma}{\mathscr{D}_y}\left\{1 - \frac{\Gamma}{\gamma} + \exp[s(y-\bar{y})]\right\}\chi_\Gamma = 0 \qquad y > \bar{y}. \tag{4.25}$$

Here we take into account that, according to the definition of the point $\bar{y}$ (4.23), $W(\bar{y}) = \gamma(\bar{y}) = \gamma$. The solution of this equation, tending to zero with $y \to \infty$, has the form [23]

$$\chi_\Gamma(y) = BK_\mu(z) \qquad z = \mu \exp[s(y-\bar{y})/2] \tag{4.26}$$

where B is an arbitrary constant and $K_\mu(z)$ is the modified Bessel function [23]

$$\mu = \mu(\bar{y}) = \frac{2}{s}\sqrt{\frac{\gamma}{\mathscr{D}_y}}. \tag{4.27}$$

Here we take into account the fact that the ratio Γ/γ is much smaller than unity.

The constants A and B entering into equation (4.18) and (4.26) can be determined from the requirements of continuity of the function $f_\Gamma(y)$ and its first derivative at the point $\bar{y}$. As a result, we obtain

$$A = A(\bar{y}) = -\frac{V_{\text{eff}}(\bar{y})}{T}\exp[-V_{\text{eff}}(\bar{y})/T]h(\mu) \tag{4.28}$$

where the function $h(\mu)$ has the form

$$h(\mu) = \frac{K_{\mu-1}(\mu)}{K_{\mu+1}(\mu)}. \tag{4.29}$$

With $\mu > 0$ $h(\mu)$ is the positive monotonically decreasing function satisfying the inequality $h(\mu) \leqslant 1$, equality being reached at $\mu = 0$.

Now, having the explicit expression for the function $f_\Gamma(y)$ with $y \leqslant \bar{y}$, we can find the desired eigenvalue from equation (4.16). As a result, we obtain

$$\Gamma = \Gamma_1 + \Gamma_2 + \Gamma_3 \tag{4.30}$$

$V_{\text{eff}}(y)$ by the relationship

$$W(y) = \mathscr{D}_y\left[-\frac{1}{2T}V''_{\text{eff}}(y) + \left(\frac{1}{2T}V'_{\text{eff}}(y)\right)^2\right] \tag{4.22}$$

Let us define our choice of the point $\bar{y}$. The general view of the potential energy function in the Hamiltonian (4.21) prompts us to choose as $\bar{y}$ the value of the y-coordinate where both terms in the potential energy are equal:

$$W(\bar{y}) = \gamma(\bar{y}). \tag{4.23}$$

Assuming that in the vicinity of the well bottom the potential $V_{\text{eff}}(y)$ is quadratic and calculating the integral in (4.33) we obtain

$$\Gamma_3 = h(\mu)\Gamma_{\text{FPT}}(\bar{y}) \tag{4.34}$$

where $\Gamma_{\text{FPT}}(\bar{y})$ is the inverse first passage time from the point $y < \bar{y}$ to the point $\bar{y}$, averaged over the positions of the starting point y with the Boltzmann weight [24]

$$\Gamma_{\text{FPT}}(\bar{y}) = \frac{\mathscr{D}_y V''_{\text{eff}}(y_w)}{T} \sqrt{\frac{V_{\text{eff}}(\bar{y}) - V_{\text{eff}}(y_w)}{\pi T}} \exp\left[-\frac{V_{\text{eff}}(\bar{y}) - V_{\text{eff}}(y_w)}{T}\right]. \tag{4.35}$$

Here we also take account of (4.28) for A. One can show that Γ_2 and Γ_3 have the relationship.

$$\Gamma_2 = -\frac{\mu}{4}\Gamma_3. \tag{4.36}$$

As a result, we can present equation (4.32) for the escape rate in the form

$$\Gamma = \int_{-\infty}^{\bar{y}} \gamma(y) f_e(y)\, dy + \left(1 - \frac{\mu}{4}\right) h(\mu)\Gamma_{\text{FPT}}(\bar{y}). \tag{4.37}$$

This expression for the process rate is one of the main results of the present paper. Its detailed analysis is presented in the following section. The simplified version of (4.37) was first obtained in our paper [10]. In [10], in the second term, the factor $(1-\mu/4)h(\mu)$ is equal to unity, i.e. it is suggested that $\mu = 0$.

5. Discussion

Analysis of equation (4.37) begins by noting that according to this expression the escape rate is determined by the position of the point $\bar{y}$ in a single-valued manner. In turn the $\bar{y}$-position is a function of the friction coefficient η_y in accordance with (4.23). With $\bar{y} \to \infty$, $\Gamma_{\text{FPT}}(\bar{y}) \to 0$ and (4.37) takes the form (see (4.11))

$$\Gamma = \Gamma_e = \int_{-\infty}^{\infty} \gamma(y) f_e(y)\, dy. \tag{5.1}$$

Substituting in (5.1) the explicit expressions for the functions $\gamma(y)$ and $f_e(y)$ we make sure that the escape rate Γ_e coincides with asymptote $\eta_y \to \infty$ of the conventional KLT formula, i.e. with equation (3.7) in which the factor H is determined by equation (3.10). The main contribution to the integral (5.1) is made in the vicinity of the y_{sp} point. This means that particles escape the well passing via the saddle, i.e. the qualitative process picture on which KLT is based takes place.

Up to now there are two characteristic values of the y-coordinate: y_w and y_{sp}. The condition $\bar{y} \to \infty$ means that $\bar{y} > y_{sp}$. However, if $\bar{y} < y_{sp}$ but $\bar{y} > y_w$, the second term in (4.37) is dominant and the escape rate takes the form

$$\Gamma \simeq (1-\mu/4)h(\mu)\Gamma_{\text{FPT}}(\bar{y}). \tag{5.2}$$

If, additionally, μ is close to zero, then

$$\Gamma \simeq \Gamma_{\text{FPT}}(\bar{y}). \tag{5.3}$$

In accordance with these formulae we note the following: first, in those situations when (5.3) is applicable, the particles escape the well before they reach the saddle

since $\bar{y} < y_{sp}$. Second, in this case the process is determined by the well dynamics, not passage through the barrier region as is assumed in the conventional process picture. Equation (4.35) for $\Gamma_{FPT}(\bar{y})$ suggests this unambiguously since all the quantities entering into it are characterized by the dynamics in the well. It should be noted that equation (5.3) for the escape rate as an alternative to the conventional KLT formula was first obtained in our paper [9].

Thus, (4.37) for the escape rate comprises both the conventional regime—when particles escape from the well via the saddle on the potential surface—and the new decay regime when $\Gamma \propto \Gamma_{FPT}(\bar{y})$ and particles escape the well before they reach the saddle.

Analysis of the equations obtained is considerably simplified if we specify the forms of potentials. In typical situations when in the region of both the well bottom and the saddle point, quadratic expansions are true and the potentials $V_{eff}(y)$, $V_0(y)$ and $V_b(y)$ have the form

$$V_{eff}(y) = V_0(y) = \tfrac{1}{2}k_0 y^2 \qquad V_b(y) = \Delta V + \tfrac{1}{2}k_b(y - y_{sp})^2. \tag{5.4}$$

Here and below we employ the system of coordinates whose origin is at the bottom of the initial well, i.e. $y_w = 0$. The parameters k_0 and k_b in (5.4) are expressed through the parameters of the initial potential $V(x, y)$ by the relationships

$$k_0 = \frac{\det \hat{V}^w}{V_{xx}^w} \qquad k_b = \frac{\det \hat{V}^{sp}}{V_{xx}^{sp}}. \tag{5.5}$$

The values k_0 and k_b are positive since $\det \hat{V}^w$ and V_{xx}^w are both positive and $\det \hat{V}^{sp}$ and V_{xx}^{sp} are both negative. Substituting $V_{eff}(y)$ (5.4) in (4.22) we obtain

$$W(y) = \frac{1}{\tau_{\mathscr{D}}}\left(-\frac{1}{2} + \frac{k_0}{4T}y^2\right) \tag{5.6}$$

where $\tau_{\mathscr{D}} = T/\mathscr{D}_y k_0 = \eta_y/k_0$ is the characteristic time of diffusion relaxation in the potential $V_{eff}(y)$. We shall also assume that in the sink term (2.8) the pre-exponent does not depend on y, and the activation energy (4.2) has the form

$$\Delta E(y) = \Delta V + \tfrac{1}{2}k_b(y - y_{sp})^2 - \tfrac{1}{2}k_0 y^2 \tag{5.7}$$

and with the actual y-values is positive and decreases with increasing y. In this case the sink force $\gamma(y)$ grows with y.

In the framework of these assumptions equation (4.37) for the escape rate takes the form

$$\Gamma = \frac{1}{2}\left[1 + \operatorname{erf}\left(\sqrt{\frac{k_b}{2T}}(\bar{y} - y_{sp})\right)\right]\Gamma_e + \left(1 - \frac{\mu}{4}\right)h(\mu)\Gamma_{FPT}(\bar{y}). \tag{5.8}$$

Here

$$\Gamma_e = \nu\sqrt{\frac{k_0}{k_b}}\exp\left(-\frac{\Delta V}{T}\right) \tag{5.9}$$

$$\Gamma_{FPT}(\bar{y}) = \frac{1}{\tau_{\mathscr{D}}}\sqrt{\frac{V_0(\bar{y})}{\pi T}}\exp\left[-\frac{V_0(\bar{y})}{T}\right] \tag{5.10}$$

where $\operatorname{erf}(z) = (2/\sqrt{\pi})\int_0^z \exp(-\xi^2)\,d\xi$ is the integral of errors [23]. The μ-value according to (4.27) is determined by the relationship

$$\mu = \mu(\bar{y}) = \frac{k_0\bar{y}}{k_0\bar{y} + k_b(y_{sp} - \bar{y})}. \tag{5.11}$$

Finally, (4.23)—from which the position of the point $\bar{y}$ is determined—can be presented in the form

$$2\nu\tau_{\mathscr{D}} = \frac{V_0(\bar{y})}{T}\exp\left[\frac{V_b(\bar{y}) - V_0(\bar{y})}{T}\right]. \tag{5.12}$$

Here we take into account the fact that the ratio $V_0(\bar{y})/T$ is much greater than unity with the $\bar{y}$-values under consideration. Generally speaking (5.12) has three roots, however, two of them—which are near the well bottom—have nothing to do with the subject. Using (5.12) we can write the important relationship

$$\Gamma_{\mathrm{FPT}}(\bar{y}) \simeq \frac{2}{\sqrt{\pi}}\sqrt{\frac{k_b}{k_0}}\sqrt{\frac{T}{V_0(\bar{y})}}\exp\left[-\frac{k_b(\bar{y}-y_{\mathrm{sp}})^2}{2T}\right]\Gamma_{\mathrm{e}} \tag{5.13}$$

which shows that $\Gamma_{\mathrm{FPT}}(\bar{y})$ is always smaller than the asymptote $\eta_y \to \infty$ of the conventional expression Γ_{e} if the point $\bar{y}$ is not too close to the well bottom.

The expressions obtained allow us to specify the conditions under which the new decay regime takes place. The conventional KLT formula (3.7) is correct if

$$\bar{y} - y_{\mathrm{sp}} \gg \sqrt{T/k_b}. \tag{5.14}$$

The region where the escape rate is considerably smaller than that predicted by the conventional formulae is determined by the requirement

$$\bar{y} \leqslant y_{\mathrm{sp}} \tag{5.15}$$

but $\bar{y} > y_{\mathrm{w}}$. At the boundary of the region—where $\bar{y} = y_{\mathrm{sp}}$—the escape rate (5.8) is approximately two times lower than Γ_{e}.

Equation (5.12) determines how the position of the point $\bar{y}$ changes with change in the friction coefficient η_y. Analysis of this equation shows that the $\bar{y}$-point shifts deeper into the well with increasing η_y (more precisely, with an increase in the product $\nu\tau_{\mathscr{D}}$ in the left-hand side of (5.12)). The product $\Gamma_{\mathrm{e}}\tau_{\mathscr{D}}$ is a more convenient control parameter for the problem than $\nu\tau_{\mathscr{D}}$. With the help of this parameter the inequality (5.15) determining the region where escape rate deviations from the conventional formulae are considerable can be presented in the form

$$\Gamma_{\mathrm{e}}\tau_{\mathscr{D}} \geqslant \sqrt{\frac{k_0}{k_b}}\frac{\varepsilon_0}{2}\exp(-\varepsilon_0) \qquad \varepsilon_0 = V_0(y_{\mathrm{sp}})/T. \tag{5.16}$$

There is another limiation on the application of equations (4.37) and (5.8) for the escape rate, namely that the $\bar{y}$-point must not be too close to the well bottom†. More precisely, this condition requires satisfaction of the inequalities

$$\frac{V_0(\bar{y})}{T} \gg 1 \qquad \text{i.e.} \quad \bar{y} \gg \sqrt{T/k_0}. \tag{5.17}$$

These inequalities are equivalent to a restriction on the dimensionless control parameter $\Gamma_{\mathrm{e}}\tau_{\mathscr{D}}$ of the form

$$\Gamma_{\mathrm{e}}\tau_{\mathscr{D}} \ll \sqrt{\frac{k_0}{k_b}}\exp\left[\frac{k_b y_{\mathrm{sp}}^2}{2T}\right]. \tag{5.18}$$

† If this condition is not fulfilled the decay kinetics has a multiexponential nature (see section 4).

Thus, the region of the $\Gamma_e\tau_{\mathcal{D}}$-parameter where our new solution leads to considerable escape rate deviations from the conventional predictions is given by the inequalities

$$\sqrt{\frac{k_0}{k_b}}\frac{\varepsilon_0}{2}\exp(-\varepsilon_0) \ll \Gamma_e\tau_{\mathcal{D}} \ll \sqrt{\frac{k_0}{k_b}}\exp\left[\frac{k_b y_{sp}^2}{2T}\right]. \tag{5.19}$$

It should be noted that the parameter $\Gamma_e\tau_{\mathcal{D}}$ is a complex construction. It depends on the friction anisotropy and also on other problem parameters such as temperature, potential, etc. To study the dependences in detail it is necessary to concretize the model. This will be done in a further paper.

In concluding this section let us point out the most important feature of the revised escape rate (4.37), (5.8): the rate tends to zero with an increase in η_y (at fixed η_x) in contrast with the conventional expression which tends to a finite value with $\eta_y \to \infty$ (see (3.7), (3.10)). To verify the presence of such a feature it is necessary to take into account the relationship between the friction coefficient and the $\bar{y}$-point position which is set up by equation (5.12).

6. Concluding remarks

In the paper a new solution of the noise-induced escape problem is obtained. This solution shows that if friction anisotropy is strong enough particles escape the well before reaching the saddle on the potential surface. In this case the process is limited not by passage across the barrier top but by reaching the transition region, i.e. by the well dynamics. When the friction anisotropy is not too large the conventional solution of the problem, i.e. the Kramers–Langer theory is correct.

The new solution predicts considerably smaller escape rate values than the conventional one if friction anisotropy is strong enough. Additionally, our theory shows that with very strong friction anisotropy when condition (5.18) is disturbed, the decay kinetics has a multiexponential character and depends on the initial state of the system (see section 4).

Such a state of affairs seems to us particularly interesting in two respects. The first aspect is connected with the opinion repeatedly quoted in the literature that the only condition which guarantees the single-exponential character of decay kinetics is the barrier height requirement, i.e. $\Delta V/T \gg 1$ [5]. Our theory shows that this opinion is wrong: the transition from a single exponent decay to a multiexponent decay occurs as a result of a change in friction anisotropy, although the requirement $\Delta V/T \gg 1$ in this case is fulfilled.

Secondly, our analysis shows limitations of the viewpoint that noise-induced escape from attractors always occurs via the saddle on the potential surfaces. We show that there are situations in which particles escape from the well before they reach the saddle, in spite of the fact that the condition $\Delta V/T \gg 1$ is met.

In conclusion, we reiterate the conditions under which our new solution is true. These conditions represent the requirements which are placed upon both the friction coefficients and the potential surface. The friction must be sufficiently anisotropic to ensure the existence of the slow mode. However, this anisotropy must not be too strong, otherwise, the decay has a multiexponential character. As regards the potential surface, it should be noted that it must have double-well sections with fixed values of slow coordinate over a wide range of these values. Also, the second well must be

deeper than the first so that neglecting the return of particles which escape the first well is valid.

Appendix

Let us compare the growth rates of the competing contributions to the 'potential energy' in the Hamiltonian (4.21), $W(y)$ and $\gamma(y)$, at the point $\bar{y}$ determined from (4.23). For this purpose we use the potential $V(x, y)$ studied in section 5. Let us consider logarithmic derivatives

$$\left.\frac{\mathrm{d} \ln \gamma(y)}{\mathrm{d}y}\right|_{\bar{y}} = s(\bar{y}) = \frac{k_b(y_{\mathrm{sp}} - \bar{y}) + k_0 \bar{y}}{T} \tag{A1}$$

and

$$\left.\frac{\mathrm{d} \ln W(y)}{\mathrm{d}y}\right|_{\bar{y}} = \frac{k_0 \bar{y}}{T(-1 + k_0 \bar{y}^2/2T)}. \tag{A2}$$

Comparison of these equations shows that over a wide range of $\bar{y}$-positions the growth rate of the sink term $\gamma(y)$ significantly exceeds the growth rate of the competing term $W(y)$ at this point. This relation between the growth rates breaks down in two cases: (1) the approach of the $\bar{y}$-position close to the well bottom, $\bar{y} \sim \sqrt{T/k_0}$; and (2) with $\bar{y} \gg y_{\mathrm{sp}}$.

In the first case the decay has a multiexponential character and our new expression for the escape rate does not 'work'. In the second case our method of problem treatment does not 'work'. These $\bar{y}$-positions correspond to friction coefficients η_y for which it is not reasonable to assume that the y-coordinate is a slow one. In such situations the procedure of adiabatic elimination of fast variables leading to our basic equations (2.10) and (2.13) is not applicable. In this case the escape rate Γ is determined by the conventional KLT formula.

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