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Effect of external force on the kinetics of diffusion-controlled escaping from a one-dimensional potential well

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The kinetics of diffusion-controlled escaping (DCE) from the one-dimensional potential well in the presence of external force (both static and time dependent) is analyzed in detail. It is shown that for static force the simple exponential kinetics (with the rate corresponding to the quasistatic diffusion over the barrier) is observed only in the limit of a strong force. For weak forces the nonexponential contribution to the DCE kinetics becomes significant. The general expression for the DCE kinetics in the presence of oscillating or fluctuating force is derived. With the use of this expression simple analytical formulas for the kinetics are obtained in the limits of slowly and fast oscillating or fluctuating force.

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I. INTRODUCTION

Diffusion-controlled escaping (DCE) from a potential well is the important stage of a number of chemical and physical processes in liquids [1–3] and solids [3,4] which determines kinetics of these processes. In principle, DCE can be considered as a particular type of activated rate process in which, however, the final state is delocalized in the space outside the well. Majority of works cited in Refs. [2,3] discuss three-dimensional (3D) processes.

In reality, however, DCE is very important in 1D processes as well. The important example is photoelectric carrier generation in 1D polymer semiconductors [5]. A similar problem of behavior of photogenerated electrons in 1D conductors is also discussed in Ref. [6]. Both these processes are essentially controlled by DCE from the Coulomb potential.

Recently it has been found that 1D DCE plays the important role of kink-antikink nucleation in the sine-Gordon chain, affecting the activation energy of the nucleation rate [7]. The kink-antikink interaction is known to be of the shape of the short range potential well [8], and the effect of this well shows itself considerably in kink-antikink quasiequilibrium properties. The effect of the external force on nucleation (i.e., on DCE) has also recently been discussed [9] but only quasistatic properties (rates and yields) in the presence of a static force have been considered.

It is clear that the external force strongly affects the DCE kinetics [1–3]. In general the theoretical description of this effect is rather difficult. In what follows we consider the simplest 1D DCE. To a first approximation 1D DCE in the presence of force can be treated as a diffusive passing over the cusp-shaped barrier which implies the exponential DCE kinetics. The quasistatic expression for rate of this process is well known [10–14], but it is applicable only for fairly sharp barriers.

However, the kinetics of passing over the barrier becomes fairly sophisticated in the case of the barrier of time-dependent (oscillating or fluctuating) height and/or shape [15]. An active discussion of this problem is inspired by the discovered ''resonant activation'' in passing over the a fluctuating barrier [16]. Very nontrivial mathematical aspects of the problem has attracted the attention of theorists [15,17,18], though the problem is still far from its complete solution.

It is also worth noting another problem closely related to that of the correct treatment of the time-dependent barrier mentioned above. The problem is in the correct description of DCE kinetics for relatively weak force that leads to a wide enough barrier. In this limit the substantial deviation from simple exponential kinetics is expected even for the barrier independent of time. In particular, in the absence of force DCE kinetics is known to be strongly nonexponential [19,20]. This nonexponential kinetics evidently persists in the presence of weak force, but at intermediate times (of course at very long times it is exponential). This effect together with that of the time-dependent barrier leads to the very complicated 1D DCE kinetics in general.

The kinetics of 1D DCE is analyzed in a number of articles [19–21]. The exact expression for kinetics of DCE from highly localized well in the absence of force (the parameter under consideration was the time-dependent population of the potential well) was first obtained in Ref. [19]. It was shown later that for localized and fairly deep wells the exact DCE kinetics can be reproduced in the simple model of two kinetically coupled states inside and outside the well [20]. This two-state model (TSM) is valid in the limit of fast equilibration between the well and close vicinity around the well (see below) [20]. TSM allows one to simplify the analysis of the problem significantly.

In this work within TSM we consider the kinetics of DCE from 1D potential well in the presence of external force. Both cases of static and time-dependent forces are discussed. A large variety of different types of the DCE kinetics are found depending on the relation between the well depth and force strength.

II. FORMULATION OF THE PROBLEM

The process under study is diffusion-controlled escaping of particles from the 1D potential well $u(x)$ (shown in Fig. 1) in the presence of a fairly weak external force $F(t)$ that does not change the activation energy but significantly affects the diffusive motion outside the well. Note that hereaf-

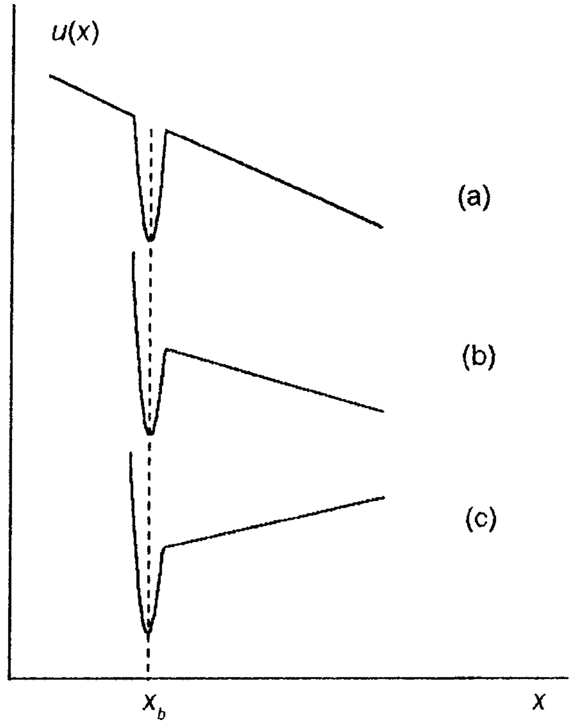

FIG. 1. The schematic picture of the potential well $u(x)$ in the presence of the external force F: (a) symmetric well $u(x)$, (b) asymmetric well $u(x)$ and repulsive force, and (c) asymmetric well $u(x)$ and attractive force.

ter all parameters of energy dimensionality will be expressed in k_BT units, i.e., we will take $k_BT=1$. In this work we consider forces of different signs and both symmetric and asymmetric (with high barrier at $x\to-\infty$) potential wells [see Figs. 1(a)–1(c)]. The potential well is assumed to be deep enough: the activation energy $u_a=-u(x_b)\gg 1$. The DCE kinetics is controlled by the distribution function $\rho(x|t)$ satisfying the Smoluchowski equation (SE)

$$\dot{\rho}=D\nabla[\nabla\rho+(\nabla u)\rho-F(t)\rho], \qquad (2.1)$$

where $\nabla=\partial/\partial x$, D is the diffusion coefficient, and $F(t)$ is the external force which is specified below. The function $\rho(x,t)$ (2.1) satisfies the boundary condition $\rho(x\to\pm\infty,t)\to 0$ and the initial condition $\rho_0(x)=\rho(x,0)=\delta(x-x_i)$ with $x_i\simeq x_b$ corresponding to the creation of particles near the bottom of the well.

A. General comments

In general, Eq. (2.1) cannot be solved analytically. However, at times t longer than the time τ_r of equilibration within the well the solution can be found in a simple analytical form [19]. This time is defined as $\tau_r=a^2/D$, where a is the characteristic size of the well that can be estimated as the distance between points at which $u(x)=-1$. It is important to note that in the considered limit of deep well the time domain $t>\tau_r$ determines the most interesting specific features of the DCE kinetics whose characteristic time is $\tau_e\approx\tau_r\exp(u_a)\gg\tau_r$ [20,21]. The solution is obtained by the expansion of the Laplace transform $\tilde{\rho}(x|E)=\int_0^\infty dt\,\exp(-Et)\rho(x|t)$ in the small parameter $\zeta=\sqrt{E\tau_r}=a\sqrt{E/D}\ll 1$ [notice that the behavior of $\rho(x|t)$ at $t>\tau_r$ is determined by that of $\tilde{\rho}(x|E)$ just in the region of E corresponding to small ζ].

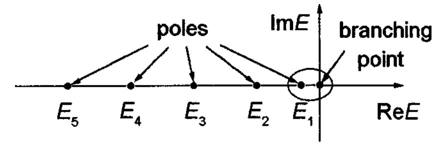

FIG. 2. The singular points of the Green's function $G(x,x'|E)$ of Eq. (2.2). Encircled are E_1-pole and the branching point at $E=0$ which mainly determine the kinetics of DCE from the deep well.

To clarify the mathematical aspects of the rigorous method and TSM it is worth adding some comments. The rigorous method is based on the reduction of Eq. (2.1) to the Schroedinger-type one

$$[(E/D+v)-\nabla^2]\sigma=D^{-1}e^{u/2}\rho_0, \qquad (2.2)$$

where $\sigma(x,E)=\tilde{\rho}(x,E)\exp[u(x)/2]$ and $v(x)=\frac{1}{4}(du/dx)^2-\frac{1}{2}d^2u/dx^2$, and the solution of this equation in the slow collision limit [22] which is defined by the inequality $\zeta\ll 1$. Equation (2.2) describes the resonance scattering of a particle by the potential $v(x)$ of the shape of the well, separated from the continuum by the high barrier [20]. The singular points of the Green's function $G(x,x'|E)=\langle x|[(E/D+v)-\nabla^2]^{-1}|x'\rangle$ of Eq. (2.2) [coinciding with those of the Green's function of Eq. (2.1)] are shown in Fig. 2. These are the poles at $E<0$ and the branching point at $E=0$ [corresponding to $\sqrt{E}$ behavior of $G(x,x'|E)$ at small E]. In the limit of deep well the first pole (closest to $E=0$) is well separated from others: $|E_1|\sim\tau_e^{-1}\ll|E_j|\sim\tau_r^{-1}$ $(j\geq 2)$. The poles at E_j $(j\geq 2)$ describe the population relaxation within the well while the pole at E_1 and the branching point (they are encircled in Fig. 2) control the DCE kinetics at $t>\tau_r$. In the lowest order in $\zeta\ll 1$ $(\sim\zeta)$ E_j poles do not influence the kinetics. The effect of these poles, i.e., the effect of population relaxation in the well on DCE kinetics, is described by higher orders of expansions in ζ.

Analysis shows [21] that TSM absolutely correctly describes the DCE kinetics obtained rigorously in the lowest order in $\zeta\ll 1$ when only the E_1 pole and the branching point are taken into account. In Ref. [21] this fact is demonstrated and discussed in detail in the case $F=0$. From a physical point of view this means that TSM correctly treats the process of reencounters with the well accompanied by subsequent quasistationary capture within and escaping from the well.

The presence of (time independent) F leads to the modification of the "potential" $v(x)$ in Eq. (2.2): $v(x)=v_F(x)=\frac{1}{4}(du/dx-F)^2-\frac{1}{2}d^2u/dx^2$, i.e., in this case the DCE kinetics is characterized by the additional "frequency" parameter $E_F=DF^2$ [the effect of time dependent $F(t)$ is analyzed in Secs. IV and V]. Following step by step the analysis of the rigorous method and TSM presented in Refs. [19–21] one can easily come to the conclusion that in the limit $E_F\ll E_j$ $(j=2,3,\ldots)$ (or $\zeta_F=a\sqrt{E_F/D}=Fa\ll 1$) both of them are again equivalent to each other in the lowest order in ζ and ζ_F. The effect of the force F in this limit manifests only in the modification of analytical properties of $G(x,x'|E)$ in the region of the E_1 pole and the branching point (this manifestation is analyzed below). The condition $\zeta_F \ll 1$ means also that the characteristic time $\tau_F = (DF^2)^{-1}$ of passing over the barrier of the potential $u(x) - Fx$ satisfies the relation $\tau_F \gg \tau_r$. In addition, this condition implies the relative weakness of the external force which does not change the shape of the well.

In the limit $\zeta_F, \zeta \ll 1$ both the rigorous method and TSM predict that the specific features of stochastic motion outside the well are represented in the Green's function $G(x,x'|E)$ by the term $\psi_f^{-1}(x,E)d\psi_f(x,E)/dx|_{x=x_b}$, where $\psi_f(x,E)$ is the solution of Eq. (2.2) describing free motion in this region [19]. Thus in both approaches the only modification of $G(x,x'|E)$ for $F \neq 0$ as compared to that for $F=0$ [19–21] reduces to the replacement of $\psi_f(x,E)$ by the solution describing the diffusion in the presence of force F. Naturally for $\zeta_F, \zeta \ll 1$ these approaches predict the same expression for the DCE kinetics.

The equivalence of the rigorous method (in the linear in ζ and ζ_F approximation) and TSM enables us to estimate the accuracy of the TSM. It is determined by the correction terms which are proportional to the high powers of ζ and ζ_F ($\sim \zeta^m$ and ζ_F^m with $m \geq 2$) which can be estimated in the rigorous method. They describe the interference between the population relaxation inside and outside the well.

In what follows we will use TSM for analysis the DCE kinetics. This model is chosen instead of the rigorous method only for the sake of the simplicity of intermediate calculations and brevity of presentation.

B. Two-state model

TSM treats DCE as a transition from the state within the well, whose population is $n(t)$, to the state outside the well described by the distribution function $c(x,t)$. The kinetic equations for $n(t)$ and $c(x,t)$ are written as

$$\dot{n} = K_+ c(0,t) - (K_- + w_r)n, \tag{2.3a}$$

$$\dot{c} = D\nabla[\nabla - F(t)]c - (K_+ c - K_- n)\delta(x). \tag{2.3b}$$

The terms proportional to $K_\pm$ describe the abovementioned kinetic coupling between the state within the well, located at $x \simeq x_b = 0$, and the state outside the well. The considered limit $\tau_r/\tau_e \ll 1$ the transition rates $K_\pm$ satisfy the relations [21]

$$K_\pm \to \infty \quad \text{and} \quad K_+/K_- = K_e = 1/Z_w, \tag{2.4}$$

where $Z_w = \int_w dx e^{-u(x)}$ is the partition function for the well.

Equations (2.3) should be solved with the initial condition

$$n(0) = 1 \quad \text{and} \quad c(x,0) = 0. \tag{2.5}$$

As to the boundary conditions for $c(x,t)$, it is different for symmetric [Fig. 1(a)] and symmetric [Figs. 1(b),1(c)] well: for symmetric well these conditions are given by $c(x \to \pm\infty) = 0$, while for asymmetric one they are written as $\partial c/\partial x - Fc|_{x=0} = 0$ and $c(x \to \infty) = 0$.

In Eqs. (2.3) we also took into account the first order reaction in the well (with the rate w_r) represented by the term $w_r n$ in the first of Eqs. (2.3). The reaction can be treated as a diffusive passing over reactive barrier at small $x < x_b$ near the bottom of the well.

In the case of time-independent (static) force F Eqs. (2.3) can be solved by the Laplace transformation in time. Solution leads to the following formula for the well population $n(t)$:

$$n(t) = \frac{1}{2\pi i}\int_{-i\infty+0}^{i\infty+0} dE \frac{e^{Et}}{E + w_r + K_e V(E)}. \tag{2.6}$$

In this formula the function $V(\epsilon)$ is directly related to the Green's function of the operator which controls diffusion outside the well

$$g(x,x_i|E) = \langle x|[E - D(\nabla^2 - F\nabla)]^{-1}|x_i\rangle: \tag{2.7}$$

$$V(E) = 1/g(0,0|E). \tag{2.8}$$

In addition to the time dependence of the well population $n(t)$ the steady state characteristics such as the total yield of escaping Y_e and reaction $Y_r = 1 - Y_e$ are of certain interest for analysis of the problem and possible applications. They can be easily represented in terms of the life time in the well:

$$\tau_w = \int_0^\infty dt\, n(t), \tag{2.9}$$

$$Y_e = 1 - Y_r = 1 - w_r \tau_w. \tag{2.10}$$

Formulas (2.9) and (2.10) are applicable both for static and time- dependent forces. In the case of static F, however, the simple expression for τ_w can be derived using Eq. (2.6):

$$\tau_w = 1/[w_r + K_e V(0)]. \tag{2.11}$$

Formulas (2.6)–(2.8) show that for static force F the problem of calculating the DCE kinetics $n(t)$ reduces to the evaluation of the Green's function (2.7) and subsequent calculation of the inverse Laplace transform (2.6). The case of force depending on time is much more complicated. It will be analyzed in detail in Secs. IV and V.

III. STATIC EXTERNAL FORCE

Prior to discussion of the DCE kinetics we need to note that in the case of asymmetric well the effect of the external force on kinetics is essentially different for $F > 0$ [Fig. 1(b)] and $F < 0$ [Fig. 1(c)]. The repulsive force ($F > 0$) enhances the escape of particles from the well and subsequent diffusion apart from the well, whereas the attractive force ($F < 0$) prevents diffusion of particles to infinity giving rise to the formation of the equilibrium state in the potential $u(x) + |F|x$ [see Fig. 1(c)]. Kinetics of depopulation of the well is, naturally, different in these two cases and in what follows we will discuss them separately though the formal mathematical expressions for $n(t)$ are close in both cases. We start our discussion of the DCE kinetics with the simplest case of the absence of external force ($F = 0$) investigated earlier in Ref. [20].

A. The absence of external force

For $F=0$ one gets $g_s(x,x_i|E)=(2kD)^{-1}e^{-k|x-x_i|}$ and $g_a(x,x_i|E)=(2kD)^{-1}[e^{-k|x-x_i|}+e^{-k(x+x_i)}]$, where $k(E)=\sqrt{E/D}$, for symmetric (s) and asymmetric (a) well, respectively. Correspondingly, according to the definition (2.8), for symmetric and asymmetric wells

$$V_\nu(E)=Dp_\nu k(E)\quad(\nu=s,a),\tag{3.1}$$

where $p_s=2$, $p_a=1$, and $k(E)=\sqrt{E/D}$.

Substitution of the expression (3.1) into Eq. (2.6) leads to the following formula for the DCE kinetics $n_\nu(t)$ $(\nu=s,a)$ [20]:

$$n_\nu^0(t)=\frac{1}{2\pi i}\int_{-i\infty+0}^{i\infty+0}\frac{du\,\exp(u\tau)}{u+\alpha_\nu^0\sqrt{u}+1}$$
$$=\frac{z_+^0\Phi(z_+^0\sqrt{\tau})-z_-^0\Phi(z_-^0\sqrt{\tau})}{z_+^0-z_-^0},\tag{3.2}$$

where $\tau=w_rt$, $\alpha_\nu^0=p_\nu K_e\sqrt{D/w_r}$, $z_\pm^0=\frac{1}{2}\alpha_\nu^0\pm i\sqrt{1-\frac{1}{4}(\alpha_\nu^0)^2}$, and $\Phi(z)=[1-\mathrm{erf}(z)]e^{z^2}$. The parameters $z_\pm^0$ are the roots of equation $z^2-\alpha_\nu^0z+1=0$.

Specific features of the DCE kinetics $n_\nu^0(t)$ (3.2) are analyzed in detail in Refs. [20,21]. In general this kinetics is nonexponential and, in particular, at long times $t\gg1/w_r$ it is of inverse power type: $n_\nu^0(t)\sim1/t^{3/2}$. In the limit of small $\alpha_\nu^0\ll1$, however, more detailed analysis of the kinetics is possible.

The analysis shows [20,21] that at small times $\tau=w_rt<\ln(1/\alpha_\nu^0)$ the kinetics is exponential, $n_\nu^0(t)=\exp(-w_rt)$, while at large times $\tau>\ln(1/\alpha_\nu^0)$ it is of inverse power type, $n_\nu^0(t)=\alpha_\nu^0/[2\sqrt{\pi}(w_rt)^{3/2}]$. In the absence of reaction ($w_r\to0$), however the kinetics is completely nonexponential: $n_\nu^0(t)=\Phi(\sqrt{\epsilon_1t})$, where $\epsilon_1=DK_e^2$. This formula also predicts inverse power type behavior of $n_\nu^0(t)$ at large t but different from that mentioned above: $n_\nu^0(t)\simeq1/\sqrt{\pi\epsilon_1t}$.

It is seen that even in the absence of the external force a large variety of different types of the DCE kinetics occur. The effect of a force clearly leads to some additional interesting specific features of this kinetics.

B. The presence of external force

1. General formulas

In the case $F\neq0$ the Green's functions $G_\nu(x,x_i|E)$ can easily be obtained analytically both for symmetric ($\nu=s$) and asymmetric ($\nu=a$) wells. Substitution of these functions into Eq. (2.8) gives

$$V_s(E)=2D\varkappa(E)\quad\text{and}\quad V_a(E)=D[\tfrac{1}{2}F+\varkappa(E)]\tag{3.3}$$

with $\varkappa(E)=\sqrt{(E+\frac{1}{4}DF^2)/D}$. Thus the DCE kinetics $n_\nu(t)$ $(\nu=s,a)$ is represented as

$$n_\nu(t)=\frac{1}{2\pi i}e^{-\epsilon_0\tau}\int_{-i\infty+\epsilon_0}^{i\infty+\epsilon_0}\frac{d\epsilon\,\exp(\epsilon\tau)}{\epsilon-S_\nu+\alpha_\nu\sqrt{\epsilon}},\tag{3.4}$$

where $S_\nu=\mathrm{sgn}(w_\nu)$ and

$$\tau=|w_\nu|t\tag{3.5}$$

is the dimensionless time in which the characteristic rate w_ν $(\nu=s,a)$ is expressed in terms of the rate parameters of the model

$$w_r,\quad w_0=DF^2/4,\quad\text{and}\quad w_e=DF/Z_w:\tag{3.6}$$

$$w_s=w_0-w_r\quad\text{and}\quad w_a=w_0-w_r-w_e/2.\tag{3.7}$$

In addition, in formula (3.4) there are two dimensionless parameters

$$\epsilon_0=w_0/|w_\nu|\quad\text{and}\quad\alpha_\nu=p_\nu(w_e/2\sqrt{w_0|w_\nu|})\tag{3.8}$$

(with $p_s=2$ and $p_a=1$) that essentially determine the specific features of $n_\nu(t)$.

The behavior of $n_\nu(t)$ substantially depends on the sign of w_ν. The fact is that in the case of positive w_ν there exists the pole of the integrand in Eq. (3.4) in the interval $0\leqslant\epsilon\leqslant\epsilon_0$ (at $\epsilon=\sqrt{z_p}$, where z_p is the positive root of equation $z^2+\alpha_\nu z-1=0$), which gives rise to the contribution to n_ν exponentially depending on time. For negative w_ν, however, this pole is absent and, the DCE kinetics is nonexponential in general.

After some algebraic manipulations the expression (3.4) can be represented in the following form:

$$n_\nu(t)=n_0e^{-\epsilon_\nu\tau}+e^{-\epsilon_0\tau}I_\nu(\alpha_\nu,\tau),\tag{3.9}$$

where $\tau=|w_\nu|t$,

$$\epsilon_\nu=\epsilon_0-(\sqrt{1+\tfrac{1}{4}\alpha_\nu^2}-\tfrac{1}{2}\alpha_\nu)^2,\tag{3.10}$$

$$n_0=\left(1-\frac{\alpha_\nu}{\sqrt{4+\alpha_\nu^2}}\right)\theta(w_\nu),\tag{3.11}$$

and

$$I_\nu(\alpha,\tau)=\frac{2\alpha}{\pi}\int_0^\infty dv\frac{v^2\exp(-v^2\tau)}{(v^2+S_\nu)^2+\alpha^2v^2}$$
$$=\frac{z_+\Phi(z_+\sqrt{\tau})-z_-\Phi(z_-\sqrt{\tau})}{z_++S_\nu z_-}.\tag{3.12}$$

In Eqs. (3.9)–(3.12) $\theta(w)$ is the Heaviside step function, $S_\nu=\mathrm{sgn}(w_\nu)$, $z_+=\sqrt{S_\nu+\frac{1}{4}\alpha^2}+\frac{1}{2}\alpha$, $z_-=S_\nu(\sqrt{S_\nu+\frac{1}{4}\alpha^2}-\frac{1}{2}\alpha)$, and

$$\Phi(z)=[1-\mathrm{erf}(z)]e^{z^2}.\tag{3.13}$$

In its general structure the expression (3.12) is similar to formula (3.2), however, the presence of the additional term $S_\nu=\mathrm{sgn}(w_\nu)$ in Eq. (3.12) leads to a very large variety of different analytical properties of the DCE kinetics in the case $F\neq0$ discussed below.

2. Analysis of different limits

Prior to the discussion of various limits it is worth making some general comments. Formula (3.9) predicts that $n_\nu(0) = n_0 + I_\nu(\alpha_\nu, 0) = 1$ in accordance with the initial condition (2.5). The first term n_0 is non-zero only for $w_\nu > 0$. This means that at $w_\nu > 0$ the analytical properties of the function $I_\nu(\alpha,\tau)$ strongly differ from those at $w_\nu < 0$. In particular, for $w_\nu > 0$ $I_\nu(\alpha,0)$ depends on α and smaller than 1, whereas for $w_\nu < 0$ $I_\nu(\alpha,0) = 1$. In addition, at $w_\nu > 0$ $I_\nu(\alpha,\tau)$ is the nonexponential function of τ for all τ, while at $w_\nu < 0$ it is exponential at $\tau < \tau_c = \ln(1/\alpha)$ and nonexponential at $\tau > \tau_c$ in agreement with results of Sec. III A.

a. Strong repulsive external force $F > 0$

The limit of strong repulsive force $F > 0$ is defined by

$$w_\nu > 0 \quad \text{and} \quad w_0 \gg w_e, w_r. \tag{3.14}$$

In this limit the first exponential term in formula (3.9) is dominating: $n_0 \simeq 1$, and the rate w_d of the (exponential) well depopulation is a sum of the reaction and DCE rates

$$w_d = \epsilon_\nu w_\nu \simeq w_r + w_e \tag{3.15}$$

both for symmetric and asymmetric wells. The expression for DCE rate w_e (3.6), naturally, coincides with the rate of diffusive passing over the cusp-shaped barrier when the force in the state of reagents is much larger than that in the state of products [3,14]. The expression (3.15) is actually the particular case of the general formula for the depopulation rate w_d valid in the limit sharp barrier outside the well:

$$w_d \simeq w_r + K_e V_\nu(0) \tag{3.16}$$

which can easily be seen from the expression (2.6).

b. Repulsive force $(F > 0)$ of intermediate strength

This case corresponds to

$$w_\nu > 0 \quad \text{and} \quad w_0 \sim w_e, w_r. \tag{3.17}$$

(1) In general, at these conditions both terms in formula (3.9) are of comparable absolute value. However, since $\epsilon_\nu < w_0$ and $I_\nu(\alpha,\tau)$ is the decreasing function of τ the long time asymptotic behavior of $n_\nu(t)$ is completely determined by the first exponential term

$$n(t) \approx n_0 e^{-\epsilon_\nu |w_\nu| t} \quad \text{for} \quad t \gg w_e^{-1}, w_r^{-1}. \tag{3.18}$$

Compared to the previous case (a), however, the corresponding pre-exponential factor n_0, given by Eq. (3.11), is smaller than 1, and the DCE rate $\epsilon_\nu |w_\nu|$ [see Eq. (3.10)] is lower than w_e. The decrease of the absolute value of the DCE rate $\epsilon_\nu |w_\nu|$ with the decrease of the force strength results evidently from the increase of the number of returning trajectories as the slope F of the cusp-shaped barrier near the well becomes less steep.

(2) In the special case of relatively weak force, when $w_\nu > 0$ but $w_\nu \ll w_e$, the pre-exponential factor n_0 is very small: $n_0 \ll 1$, and $\epsilon_\nu \simeq \epsilon_0$. In this limit the initial stage of the DCE kinetics is described by the second non-exponential term $\sim I_\nu(\alpha_\nu, \tau)$ of the expression (3.9).

In the case $w_\nu > 0$ but $w_\nu \ll w_e$ the DCE kinetics has the following specific features.

(a) For $w_\nu \neq 0$ at short times no simple approximations for the nonexponential function $I_\nu(\alpha,\tau)$ occur, and one needs to use the general expression (3.12). At long times τ, however, it is of inverse power type $I_\nu(\alpha,\tau) \simeq \alpha/(2\sqrt{\pi}\tau^{3/2})$, so that

$$n_\nu(t) \sim t^{-3/2} \exp(-w_0 t). \tag{3.19}$$

(b) At $w_\nu \to 0$ the expression for $n_\nu(t)$ simplifies since in this case $n_0 = 0$ and $I_\nu(\alpha,\tau) = \Phi(\alpha\sqrt{\tau}) = [1 - \mathrm{erf}(\alpha\sqrt{\tau})] e^{\alpha^2 \tau}$. Thus for very small w_ν

$$n_\nu(t) = [1 - \mathrm{erf}(\gamma_\nu \sqrt{w_0 t})] \exp[-(1-\gamma_\nu^2) w_0 t], \tag{3.20}$$

where $\gamma_\nu = \alpha_\nu \sqrt{w_\nu / w_0} = p_\nu (w_e / 2 w_0)$. Formula (3.20) predicts the following long time behavior of $n_\nu(t)$: $n_\nu(t) \sim t^{-1/2} \exp[-(1-\gamma_\nu^2) w_0 t]$.

c. Weak repulsive external force $F > 0$

In the case of weak force, when

$$w_\nu < 0, \tag{3.21}$$

the first exponential term in Eq. (3.9) is absent and the DCE kinetics is determined by the second term $\sim I_\nu(\alpha_\nu, \tau)$. It is easily seen that at $w_\nu < 0$ the behavior of $I_\nu(\alpha,\tau)$ is similar to that of $n_\nu^0(t)$ with $w_r \neq 0$ [see Eq. (3.2)] which describes the DCE kinetics in the absence of external force. In particular, in the limit $\alpha_\nu \ll 1$ there are two well distinguishable stages of the DCE kinetics. At relatively short times $t < t_c = |w_\nu|^{-1} \ln(1/\alpha_\nu)$ kinetics is exponential:

$$n_\nu(t) \simeq \exp[-(w_0 - w_\nu) t] = \exp[-(w_r + w_e/2) t], \tag{3.22}$$

while at longer times $t > t_c$ kinetics is nonexponential:

$$n_\nu(t) \simeq (\alpha_\nu / 2\sqrt{\pi}) (|w_\nu| t)^{-3/2} \exp(-w_0 t). \tag{3.23}$$

Note that $w_\nu < 0$ means that $w_r + w_e/2 > w_0$ and the decrease of $n_\nu(t)$ becomes slower as time t changes from $t < t_c$ to $t > t_c$. It is worth noting also that according to Eq. (3.22) at $t < t_c$ the DCE rate equals $w_e/2$ rather than w_e as in the case of strong force [see Eq. (3.16)]. Naturally, in the limit $F \to 0$ the formulas (3.22) and (3.23) reduce to those corresponding to the case of the absence of external force (see Sec. III A).

d. Attractive external force $F < 0$

For $F < 0$ the DCE kinetics n_ν is also described by the general expression (3.9). It is clear from this expression that the change of F sign does not change the DCE kinetics for symmetric well. In the case of asymmetric well the DCE kinetics for $F < 0$ strongly differs from that for $F > 0$. This strong dependence results from the fact that in the expression (3.7) for w_a the sign of the rate w_e depends on the sign of F and for $F < 0$ the rate $w_e < 0$. The negative sign of w_e leads to some important specific features of the kinetics $n_a(t)$.

(1) In the strong external field limit, when $|w_e| \ll w_0$, the depopulation rate

$$\epsilon_a = w_r, \tag{3.24}$$

i.e., the DCE rate is zero. This result is quite natural.

(2) In the absence of reaction ($w_r=0$) the first term in the expression for $n_a(t)$ (3.9) is always independent of time, i.e., the rate $\epsilon_a=0$, no matter how strong the external force is. The absolute value of this term

$$n_0=4w_0/(|w_e|+4w_0)=|F|Z_w/(1+|F|Z_w) \quad (3.25)$$

determines the statistical weight of the well in the equilibrium state in the potential $u(x)+|F|x$.

e. Escaping yield

The escaping and reaction yields defined by Eq. (2.10) are given by the universal formula

$$Y_e^s=1-Y_r^s=\frac{w_e}{w_r+w_e}, \quad (3.26a)$$

$$Y_e^a=1-Y_r^a=\frac{w_e}{w_r+(w_e+|w_e|)/2}, \quad (3.26b)$$

and do not provide any information on details of the DCE kinetics discussed above. Moreover these relations can be misinterpreted since they coincide with those predicted in the simple exponential model for escaping kinetics which, in reality, is only observed in the limit of strong force (See Eqs. (3.15) and (3.24)].

IV. OSCILLATING EXTERNAL FORCE

In general the analysis of the DCE kinetics in the presence of time-dependent force is very complicated. For harmonically oscillating force, however, the problem can be reduced to that for static force and thus solved by the method developed above.

A. General expressions

In the case of harmonically oscillating force $F(t)=F_0\cos(\omega_0 t)$ one can find the functions $n(t)$ and $c(x,t)$, satisfying Eqs. (2.3), in terms of expansion in Floquet states [24], which are usually applied in analyzing the dynamics of periodically driven systems [25]

$$n(t)=\sum_{m=-\infty}^{\infty}\int_0^{\omega_0}d\omega\, N_m(\omega)e^{-i(\omega+m\omega_0)t}, \quad (4.1)$$

$$c(x,t)=\sum_{m=-\infty}^{\infty}\int_0^{\omega_0}d\omega C_m(x,\omega)e^{-i(\omega+m\omega_0)t}. \quad (4.2)$$

Substituting these function in Eqs. (2.3) one gets the matrix equations for the vectors

$$\mathbf{N}(\omega)=\{N_m(\omega)\} \text{ and } \mathbf{C}(x,\omega)=\{C_m(x,\omega)\}: \quad (4.3)$$

$$i\hat{\Omega}\mathbf{N}=K_+\mathbf{C}(0)-(K_-+w_r)\mathbf{N}+\mathbf{N}_i, \quad (4.4a)$$

$$i\hat{\Omega}\mathbf{C}=D\nabla(\nabla-F_0\hat{f})\mathbf{C}-(K_+\mathbf{C}-K_-\mathbf{N})\delta(x), \quad (4.4b)$$

in which $\mathbf{C}(0)=\mathbf{C}(x=0,\omega)$, $\mathbf{N}_i=\{1\}$ is the vector of initial population [see Eq. (2.5)] represented in the vector space of $\mathbf{N}$, and the matrices $\hat{\Omega}$ and $\hat{f}$ are given by

$$\Omega_{jk}=(\omega+j\omega_0)\delta_{jk} \text{ and } f_{jk}=\tfrac{1}{2}(\delta_{j+1,k}+\delta_{j-1,k}). \quad (4.5)$$

Equations (4.4) should be solved with the boundary conditions $\mathbf{C}(x\to\pm\infty)=0$ and $\mathbf{C}(x\to\infty)=0$; $\partial\mathbf{C}/\partial x-F_0\hat{f}\mathbf{C}|_{x=0}=\mathbf{0}$ for symmetric and asymmetric well, respectively.

Solution of these equations in the limit (2.4) yields

$$\mathbf{N}(\omega)=\hat{G}(\omega)\mathbf{N}_i, \quad (4.6)$$

where

$$\hat{G}(\omega)=[i\hat{\Omega}(\omega)+w_r+K_e\hat{V}(\omega)]^{-1}. \quad (4.7)$$

In the expression for $\hat{G}(\omega)$

$$\hat{V}(\omega)=1/\hat{g}(0,0|\omega) \quad (4.8)$$

with $\hat{g}(x,x_i|\omega)=\langle x|[i\hat{\Omega}(\omega)-D(\nabla^2-F_0\hat{f}\nabla)]^{-1}|x_i\rangle$.

The Green's function $\hat{g}(x,x_i|\omega)$ and thus the matrix $\hat{V}(\omega)$ can be calculated analytically by the methods developed in Ref. [23]:

$$\hat{V}_s(\omega)=2D\hat{\varkappa}(\omega) \text{ and } \hat{V}_a(\omega)=D[\tfrac{1}{2}F_0\hat{f}+\hat{\varkappa}(\omega)] \quad (4.9)$$

with $\hat{\varkappa}(\omega)=\sqrt{[i\hat{\Omega}(\omega)+\frac{1}{4}DF_0^2\hat{f}^2]/D}$, for symmetric ($s$) and asymmetric ($a$) wells

The final formulas (4.8) and (4.9) are suitable for the analysis of the DCE kinetics $n_\nu(t)$. It is obtained by substitution of the vector $\mathbf{N}_\nu(\omega)$ into the relation (4.1).

B. Limiting cases

In general, Eqs. (4.1)–(4.9) enable one to calculate the DCE kinetics $n_\nu(t)$ only numerically. However, the limits of slow and fast force oscillations can easily be analyzed analytically.

1. Slowly oscillating force

The limit of slow oscillations of $F(t)$ is defined by the inequality

$$w_e, DF_0^2 \gg \omega_0. \quad (4.10)$$

In this limit the DCE kinetics can most easily be analyzed for strong external forces $F_0\gg 1/Z_w$ [see the second of inequalities (3.14)]. In this case

$$\hat{G}_s(\omega)=[i\hat{\Omega}+w_r+w_e|\hat{f}|]^{-1}, \quad (4.11a)$$

$$\hat{G}_a(\omega)=[i\hat{\Omega}+w_r+\tfrac{1}{2}w_e(\hat{f}+|\hat{f}|)]^{-1}. \quad (4.11b)$$

In the expressions (4.11) $w_e=DF_0/Z_w$ and $|\hat{f}|=\sqrt{\hat{f}^2}$.

It is easily seen that the kinetics $n_\nu(t)$ obtained using the matrix expressions (4.11) can be equivalently calculated by solution of simple kinetic equations valid in the strong force limit:

$$\dot{n}_s=-[w_r+w_e|\cos(\omega_0 t)|]n_s \quad (4.12a)$$

$$\dot{n}_a = -[w_r + w_e\theta(\cos(\omega_0 t))]n_a, \tag{4.12b}$$

where $\theta(y)$ is the step function. The solutions of these equations can be represented as follows:

$$n_\nu(t) = \exp\{-[w_r t + \phi_\nu(t) + \psi_\nu(t)]\} \quad (\nu = s,a). \tag{4.13}$$

Here $\phi_{s,a}(t)$ are the bounded functions

$$\phi_s(t) = (w_e/\omega_0)\sin(\omega_0 t)\{2\theta[\cos(\omega_0 t)] - 1\} \tag{4.14a}$$

$$\phi_a(t) = (w_e/\omega_0)\sin(\omega_0 t)\theta[\cos(\omega_0 t)]. \tag{4.14b}$$

The unbounded functions

$$\psi_s(t) = 2\psi_a(t) = (2w_e/\omega_0)[\varphi], \tag{4.15}$$

where $[x] = x - \{x\}$ is the integral part of x and $\varphi = (\omega_0 t/\pi) + 1/2$, determine the decrease of $n_\nu(t)$: at $t \gg 1/\omega_0$ the average well depopulation rate is given by

$$\overline{w_d^s} = w_r + 2w_e/\pi \quad \text{and} \quad \overline{w_d^a} = w_r + w_e/\pi \tag{4.16}$$

for symmetric and asymmetric well, respectively.

2. Fast oscillating force

In the limit of fast oscillating force, when

$$w_e, DF_0^2 \ll \omega_0, \tag{4.17}$$

in Eqs. (4.4) coupling between ''eigenstates'' $|j\rangle$ of the matrix $\hat{\Omega}$, caused by the nondiagonal matrix $F_0\hat{f}$, can be neglected. In this case the main nonoscillating part of the DCE kinetics is determined by the inverse Fourier transformation of the matrix element

$$\hat{G}_{\nu_{00}}(\omega) = [i\omega + w_r + p_\nu DK_e\varkappa_0(\omega)]^{-1}, \tag{4.18}$$

where p_ν $(\nu = s,a)$ is defined in Eq. (3.8) and $\varkappa_0(\omega) = \sqrt{[i\omega + \frac{1}{4}DF_0^2\hat{f}^2{}_{00}]/D}$, i.e., $\varkappa_0(\omega) = \sqrt{(i\omega + \frac{1}{8}DF_0^2)/D}$. In derivation of formula for $\varkappa_0(\omega)$ we took into account that $\hat{f}_{jj}^2 = 1/2$.

After the evident change of integration path in the integral of the inverse Fourier transformation we arrive at formula (3.4) for the DCE kinetics in the presence of static force $(1/\sqrt{2})F_0$ [which is, actually, $F(t)$ averaged over the oscillation period $F_0 = \sqrt{\langle F^2(t)\rangle}$], i.e., with the following parameters:

$$w_0 = \tfrac{1}{8}DF_0^2, \quad w_e = \frac{DF_0}{\sqrt{2}Z_w}, \quad w_s = w_\nu = w_0 - w_r. \tag{4.19}$$

The specific features of the kinetics (3.4) have been discussed in detail in Sec. III. Here we only note that, according to formulas (4.18) and (4.19), in the limit (4.17) both for symmetric and asymmetric wells the DCE kinetics in the presence of oscillating force reduces to that of Eq. (3.4) corresponding to the symmetric well and static average force, but with different parameters α: $\alpha_s = 2\alpha_a$. In other words, the fast oscillating force results in a similar effect on DCE for both types of wells, but with the DCE rate for symmetric well about two times larger than for the similar asymmetric one (with the same Z_w).

V. FLUCTUATING EXTERNAL FORCE

We will analyze the effect of fluctuating external force in the Markovian approximation [26] which enable one to simplify the problem reducing it to solving the system of differential equations usually called the stochastic Liouville equation [27]. Nevertheless, most of results obtained in this section are fairly general and independent of the applied approximation.

A. Markovian approximation

In the Markovian approximation for force fluctuations the two coupled equations (2.3) are replaced by two coupled systems of equations [similar to Eqs. (4.4)] for the vectors $\mathbf{n}(t) = \{n_j(t)\}$ and $\mathbf{c}(x,t) = \{c_j(x,t)\}$ whose components describe the evolution of the system in the states $|j\rangle$ corresponding to the different values of the force. In what follows, for the sake of convenience we will also use bra and ket notations for the vectors $\mathbf{n}(t) \equiv |\mathbf{n}(t)\rangle$ and $\mathbf{c}(x,t) \equiv |\mathbf{c}(x,t)\rangle$. These systems of equations (called the stochastic Liouville equation) are written as

$$\dot{\mathbf{n}} = K_+\mathbf{c}(0) - (K_- + w_r - \hat{W}_f)\mathbf{n}, \tag{5.1a}$$

$$\dot{\mathbf{c}} = D\nabla(\nabla - \hat{F})\mathbf{c} - \hat{W}_f\mathbf{c} - (K_+\mathbf{c} - K_-\mathbf{n})\delta(x). \tag{5.1b}$$

Here $\hat{F}$ is the matrix of forces diagonal in the basis $|j\rangle$: $F_{jj'} = F_j\delta_{jj'}$, and the matrix $\hat{W}_f$ describes the transitions between states $|j\rangle$ resulting in the fluctuations of force. The solution of Eqs. (5.1) satisfies the boundary conditions $\mathbf{c}(x \to \pm\infty) = 0$ and $\mathbf{c}(x \to \infty) = 0$; $\partial\mathbf{c}/\partial x - \hat{F}\mathbf{c}|_{x=0} = 0$ for symmetric and asymmetric well, respectively.

Equations (5.1) should be solved with the initial condition

$$|\mathbf{c}(x,0)\rangle = 0 \quad \text{and} \quad |\mathbf{n}(0)\rangle = |0\rangle, \tag{5.2}$$

where $|0\rangle$ is the equilibrium eigenvector of the matrix $\hat{W}_f$, i.e., $\hat{W}_f|0\rangle = \langle 0|\hat{W}_f = 0$. The vectors $|0\rangle$ and $\langle 0|$ can be represented in terms of expansion in the bases $|j\rangle$ and $\langle j|$, respectively:

$$|0\rangle = \sum_j \overline{p_j}|j\rangle \quad \text{and} \quad \langle 0| = \sum_j \langle j|, \tag{5.3}$$

where $\overline{p_j} = \langle j|0\rangle$ is the equilibrium probability to find the system in the state $|j\rangle$. Note that, in general, $\langle 0| \neq |0\rangle^+$ because the matrix $\hat{W}_f$ is non-Hermitian. For convenience of our further discussion let us also introduce the projection operator on the equilibrium state $|0\rangle$:

$$\hat{P}_0 = |0\rangle\langle 0|. \tag{5.4}$$

The DCE kinetics $n_\nu(t)=\langle 0|\mathbf{n}_\nu(t)\rangle$ for symmetric ($\nu=s$) and asymmetric ($\nu=a$) wells can be obtained by solution of Eqs. (5.1) by means of the Laplace transformation which gives

$$n_\nu(t)=\langle 0|\mathbf{n}_\nu(t)\rangle=\frac{1}{2\pi i}\int_{-i\infty+0}^{i\infty+0}d\varepsilon\, e^{\varepsilon t}\langle 0|\hat{G}_\nu(\varepsilon)|0\rangle \quad (\nu=s,a), \quad (5.5)$$

where

$$\hat{G}_\nu(\varepsilon)=[\varepsilon+w_r+\hat{W}_f+K_e\hat{V}_\nu(\varepsilon)]^{-1}, \quad (5.6)$$

with

$$\hat{V}_\nu(\varepsilon)=1/\hat{g}_\nu(0,0|\varepsilon) \quad (5.7)$$

and $\hat{g}_\nu(x,x_i|\varepsilon)=\langle x|[\varepsilon+\hat{W}_f-D(\nabla^2-\hat{F}\nabla)]^{-1}|x_i\rangle$. The matrix $\hat{V}_\nu(\varepsilon)$ can be obtained analytically by the method proposed in Ref. [23] as in the case of oscillating force

$$\hat{V}_s(\varepsilon)=2D\hat{\varkappa}(\varepsilon) \quad \text{and} \quad \hat{V}_a(\varepsilon)=D[\tfrac{1}{2}D\hat{F}+\hat{\varkappa}(\varepsilon)] \quad (5.8)$$

in which $\hat{\varkappa}(\omega)=\sqrt{(\varepsilon+\hat{W}_f+\frac{1}{4}D\hat{F}^2)/D}$.

The formulas (5.4)–(5.8) enable one to analyze the specific features of the DCE kinetics in some limits quite easily.

B. Analysis of limits

1. Slowly fluctuating force

The slow fluctuation limit is defined by

$$w_e, D\overline{F^2}\gg\|W_f\|, \quad (5.9)$$

where $\overline{F^2}=\Sigma_j\overline{p}_jF_j^2$ is the average square of the force. Similar to the case of oscillating force here we will assume that the external force is strong enough: $\sqrt{\overline{F^2}}\gg 1/Z_w$, so that the DCE kinetics is described by the fluctuating DCE rate. In this limit

$$\hat{V}_s(\varepsilon)=|\hat{W}_e|/K_e \quad \text{and} \quad \hat{V}_a(\varepsilon)=\tfrac{1}{2}(\hat{W}_e+|\hat{W}_e|)/K_e \quad (5.10)$$

with $\hat{W}_e=D\hat{F}/Z_w$ and $|\hat{W}_e|=\sqrt{\hat{W}_e^2}$. The expressions for $\hat{G}_\nu(\varepsilon)$ with $\hat{V}_\nu$ (5.10) correspond to the simple first order DCE kinetics but with fluctuating DCE rate W_e.

In general, the calculation of the DCE kinetics in the slow fluctuation limits requires some matrix operations. Here we will restrict ourselves to the discussion of limiting situations

a. Quasistatic fluctuations

In the quasistatic limit, when $\|\hat{W}_e\|\gg\|\hat{W}_f\|$, one can neglect the fluctuation matrix $\hat{W}_f$. In this case the inverse Laplace transformation (5.5) yields for $n_\nu(t)$:

$$n_\nu(t)=\langle 0|\exp(-\hat{W}_e^\nu t)|0\rangle=\sum_j \overline{p}_j\exp[-W_e^\nu(j)t], \quad (5.11)$$

where $W_e^s(j)=D|F_j|/Z_w$ and $W_e^a(j)=DF_j\theta(F_j)/Z_w$. It is clear that in general the quasistatic DCE kinetics predicted by Eq. (5.11) is strongly nonexponential.

b. Relatively fast fluctuations

This limit is defined by inequality $\|\hat{W}_e\|\ll\|\hat{W}_f\|$. In this case $\hat{G}_s\simeq[\varepsilon+w_r+\overline{|W_e|}]^{-1}$ and $\hat{G}_a\simeq[\varepsilon+w_r+\frac{1}{2}(\overline{W}_e+\overline{|W_e|})|0\rangle]^{-1}$, and therefore for both types of wells: symmetric (s) and asymmetric (a), the DCE kinetics is exponential:

$$n_s(t)\simeq\exp[-(w_r+\overline{|W_e|})t], \quad (5.12a)$$

$$n_a(t)\simeq\exp[-w_rt-\tfrac{1}{2}(\overline{W}_e+\overline{|W_e|})t]. \quad (5.12b)$$

Hereafter we use the notation $\overline{A}$ for the average of matrix elements of any matrix $\hat{A}$

$$\overline{A}=\langle 0|\hat{A}|0\rangle=\sum_j \overline{p}_jA_j \quad (5.13)$$

in which the probabilities $\overline{p}_j$ are defined in Eq. (5.3).

2. Fast fluctuating force

In the opposite limit of fast force fluctuations, when

$$w_e, D\overline{F^2}\ll\|W_f\|, \quad (5.14)$$

the fluctuations are averaged out. This leads to the strong simplification of formula for $\hat{G}_\nu$ $(\nu=s,a)$:

$$\hat{G}_\nu(\varepsilon)=[\varepsilon+w_r+2p_\nu DK_e\varkappa_0(\varepsilon)]^{-1}\hat{P}_0, \quad (5.15)$$

where $p_s=2p_a=2$ and $\varkappa_0(\varepsilon)=\sqrt{(\varepsilon+\frac{1}{4}D\overline{F^2})/D}$ (remember that $\overline{F^2}=\Sigma_j\overline{p}_jF_j^2$).

The expression (5.15) shows that, similar to the case of fast oscillating force (see Sec. IV B 2), in the limit of fast force fluctuations the DCE kinetics reduces to that for the (average) static force and symmetric well no matter whether the original well $u(x)$ is symmetric or asymmetric. The only difference between symmetric and asymmetric wells is in the amplitude factor $p_{s,a}$ of the term $\sim\varkappa$ in formula for $G_{s,a}$. This means that in the fast fluctuation limit the specific features of the DCE kinetics are the same as those for static force (Sec. III).

3. Two-state model of force fluctuations

Here we will analyze the general expressions obtained above in the simple two-state model of Markovian fluctuations of the force F. In this model the matrix $\hat{W}_f$ is given by

$$\hat{W}_f=w_f(\hat{E}-|0\rangle\langle 0|)=w_f(\hat{E}-\hat{P}_0), \quad (5.16)$$

where $\hat{E}$ is the unity matrix, $\langle 0|=(1,1)$, and $|0\rangle=\frac{1}{2}(1,1)^\top$. This definition means that the probabilities $\overline{p}_1=\overline{p}_2=1/2$. The force matrix $\hat{F}$ is taken in the simplest form

$$F_{jj'}=(-1)^{j-1}F_0\delta_{jj'}, \quad (5.17)$$

so that $\overline{F}=\langle 0|\hat{F}|0\rangle=0$. It is worth emphasizing the important property of the matrix $\hat{F}$ (5.17): $\hat{F}^2=F_0^2\hat{E}$.

In the model (5.16), (5.17)

$$\hat{\varkappa}(\varepsilon)=q_f(\varepsilon)\hat{E}+[q_0(\varepsilon)-q_f(\varepsilon)]\hat{P}_0, \tag{5.18}$$

where $q_f=\sqrt{(\varepsilon+w_f+\frac{1}{4}DF_0^2)/D}$ and $q_0=\sqrt{(\varepsilon+\frac{1}{4}DF_0^2)/D}$. Substitution of this relation into Eq. (5.6) gives after some matrix manipulations

$$\langle 0|\hat{G}_s|0\rangle=1/X_s, \tag{5.19a}$$

$$\langle 0|\hat{G}_a|0\rangle=1/[X_a+\tfrac{1}{4}(w_e^2/X_f)]. \tag{5.19b}$$

Here $w_e=DF_0/Z_w$ and

$$X_\nu(\varepsilon)=\varepsilon+w_r+\tfrac{1}{2}p_\nu DK_e q_0(\varepsilon), \tag{5.20}$$

$$X_f(\varepsilon)=\varepsilon+w_r+w_f+\tfrac{1}{2}DK_e q_f(\varepsilon) \tag{5.21}$$

(remember that $p_s=2$ and $p_a=1$).

In general, formula (5.19) for $\langle 0|\hat{G}_\nu(\varepsilon)|0\rangle$ is rather complicated to apply for calculating the DCE kinetics with Eq. (5.5), but it is quite suitable for analysis of some particular cases.

(a) First, note that the two-state model (5.16) predicts no effect of the force fluctuations on DCE from the symmetric well, i.e., the DCE kinetics in this case is the same both for fluctuating and for static forces. It is easily seen from approximate limiting expressions (5.11) and (5.12), as well as from general formula (5.19) (G_s is independent of X_f).

(b) For asymmetric wells the strong effect of force fluctuations on kinetics is predicted by formula (5.19). The corresponding inverse Laplace transform of $\langle 0|\hat{G}_a(\varepsilon)|0\rangle$ can hardly be obtained analytically in general. In the case of relatively fast fluctuations, however, when $w_e=DF_0/Z_w \ll w_f$, one can neglect ε-dependence of X_f taking

$$X_f\simeq X_f^0=w_r+w_f+\tfrac{1}{2}DK_e q_f(0). \tag{5.22}$$

In this limit the fluctuating force leads to the additional DCE with the rate $\delta w_e=\frac{1}{4}(w_e^2/X_f^0)$, and the total DCE kinetics $n_a(t)$ reduces to that for static force but with renormalized reaction rate as it is seen from Eqs. (5.5), (5.19), and (3.4).

(c) The two-state model (5.16) enables one to obtain simple expressions for the DCE yield Y_e [Eq. (2.10)] in the presence of fluctuating force. Remind that in the case of symmetric well the two-state model predicts no effect of fluctuations and the DEC yield Y_e^s is the same as for the static repulsive force $F=F_0$. For the asymmetric well

$$Y_e^a=1-Y_r^a=1-w_r[w_r+\tfrac{1}{2}w_e+\tfrac{1}{4}(w_e^2/X_f^0)]^{-1}. \tag{5.23}$$

This formula is valid for any values of parameters of the model. The effect of force fluctuations on the DCE yield is described by the terms $\sim w_e$ and $\sim w_e^2$ in the right hand side of Eq. (5.23).

VI. CONCLUSION

In this work we have thoroughly analyzed the specific features of the kinetics of diffusion-controlled escaping (DCE) from the 1D potential well in the presence of time-independent (static), oscillating or fluctuating external force. The force is assumed to be relatively weak: it significantly affects diffusion outside the well, but does not change the activation energy. The cases of symmetric and asymmetric potential well are considered (see Fig. 1). Some general conclusions of this work concerning specific features of the DCE kinetics in the fast and slow oscillation or fluctuation limits are similar to those obtained in Refs. [17,18] (mainly corresponding to the case of strong field). In our analysis special attention has been paid to the weak field limit in which some peculiarities of the kinetics are found.

A large variety of types of the DCE kinetics $n_\nu(t)$ for symmetric ($\nu=s$) and asymmetric ($\nu=a$) potential wells has been found for static fields. The important parameter that controls the change of kinetics is the ratio $\xi=w_0/w_e$ of the escaping time $1/w_e=Z_w/(DF)$ and the characteristic time $1/w_0=1/(DF^2)$ of diffusion over the cusp-shaped barrier of the potential $u(x)-Fx$. For $\xi\ll 1$, i.e., for strong fields, the DCE kinetics is described by the first order equations (4.12). In the opposite limit $\xi\gg 1$ (weak fields) the kinetics is strongly nonexponential similar to the case of the absence of force [20,21].

The effect of force oscillations and fluctuations on the DCE kinetics is also analyzed. Simple analytical expressions for the functions $n_{s,a}(t)$ are obtained in the limits of slow and fast oscillations and fluctuations of force. In both limits the DCE kinetics is shown to be nonexponential, in general. In particular, in the fast oscillations/fluctuation limit the kinetics of DCE from symmetric and asymmetric wells reduces to that corresponding to the case of static force and symmetric well.

The expressions for the DCE yield Y_e are derived in the cases of static and fluctuating external force. The yield appears to be insensitive to the details of the DCE kinetics in the presence of static force. In the case of fluctuating force it gives interesting information about the dependence of the DCE kinetics on fluctuation correlation time.

The DCE yield Y_e in the presence of oscillating field can be represented in the form of matrix expression $Y_e=\mathbf{N}_i^\top\hat{G}(\omega=0)\mathbf{N}_i$, where $\mathbf{N}_i$ and $\hat{G}(\omega)$ are defined in Sec. IV A. The yield Y_e gives some important information about the effect of oscillating force on the DCE kinetics. Unfortunately, in general, the evaluation of Y_e is possible only numerically.

In this article we restricted ourselves mainly to the general analysis of the developed method and consideration of the most interesting limits. This method, however, offers some interesting possibilities of further investigations of the specific features of DCE kinetics.

(1) The results of this work are very important for description of the kinetic properties of kink-antikink ensembles [7,9]. So far the effect of geminate DCE kinetics analyzed in this article on the kinetic characteristics of multiparticle systems such as the correlation functions has not been studied rigorously enough although this effect is expected to be

fairly strong in the limit of strong interaction between particles.

(2) Here we discussed only the influence of a weak force which does not change the escaping activation energy u_b. Some effects of a stronger force, however, can also be interpreted within the approach developed. In particular, one can easily take into account the oscillations or fluctuations of the activation energy if they are not accompanied by the change of the shape of the potential at the dissociation threshold. In this case TSM is still applicable though one should assume that the rate of capture into the well K_+ [see Eq. (2.4)] is scalar value (i.e., K_+ is independent of time) while $\hat{K}_- = K_+\hat{Z}_w$ is the matrix in one of spaces described in Secs. IV and IV (representing the time dependent K_-). This approach is very close to that considered in some other models which are discussed in connection with various problems of the theory of stochastic resonance [15]

(3) The method developed can also be applied to the model of two kinetically coupled wells [21] which is equivalent to that of diffusive passing over the square barrier separating two narrow wells (see also Ref. [18]). Within this model one can describe the effect of fluctuating activation energy with the use of the abovementioned modification of the rate constant K_-.

(4) It is of special interest to analyze the effects of nonadiabaticity on the stochastic processes. This problem is of certain importance for the theory of stochastic resonances [28]. The proposed method makes it possible to get some new insight into the problem. For example, it enables one to treat it in the simple model of coupled narrow wells.

The work on some of the problems described in this list is currently in progress. The results of this work will be presented later in separate publications.

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