External force affected escape of Brownian particles from a potential well

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The effect of an external force on the kinetics of diffusion-assisted escaping of Brownian particles from a potential well is analyzed in detail. The analysis is made within the two-state model of the process which is known to be valid in the deep well limit in the absence of external force. The generalized variant of this model, taking into account the effect of the force, is shown to be quite accurate as well for some shapes of the well. Within the generalized two-state model simple expressions for the well depopulation kinetics and, in particular, for the escape rate are obtained. These expressions show that the effect of the force (F) manifests itself in the escape rate dependence on the only parameter \( \varphi = Fa/(2k_bT) \), where \( a \) is the Onzager radius of the attractive part of the well \( U(r) \), defined by the relation \( |U(a)| = k_bT \). The limiting behavior of this dependence in the cases of weak and strong force is analyzed in detail. Possible applications as well as the relation of the results of the analysis to those obtained earlier are briefly discussed.

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I. INTRODUCTION

The effect of external force on mechanisms and kinetic properties of condensed phase diffusion-assisted reaction processes is considered in a large number of works both experimentally and theoretically. The active interest of scientists to this phenomenon results from its great practical importance.

One of the most important systems, in which the external force effect is investigated very thoroughly, is recombining geminate ion pairs, undergoing relative diffusion in the external electric field. Most of theoretical studies analyze the kinetics of the processes within the simplest model, which reduces the problem to solving the Smoluchowski equation for probability distribution function (PDF) of particles diffusing in a pure Coulomb potential (with an external force) and reacting with the rate highly localized at short distances. Even in this most simple formulation the problem can, in general, be solved only numerically, though detailed analytical analysis of some simple variant of the problem have also been made for example, within the prescribed diffusion approximation.

Recent advances in time resolved investigations of charge transfer and escaping processes in fast geminate reactions and, in particular, geminate recombination of ion pairs in polar liquids, inspire further development of theoretical methods of the analysis of the considered problem. The main challenge of the theoretical studies consists in the correct description of the manifestation of specific features of the interparticle interaction (in real liquids) in the reaction kinetics in a tractable form simple enough to be suitable for applications.

In the majority of above mentioned theoretical works no specific features of the form of the interaction potential for the probe (Brownian) particles at short distances (of order of molecular size) have been taken into account. In the condensed phase, however, the distance dependence of the potential at short interparticle distances \( r \) can be strongly modified by interaction of particles under study with those of the medium. This modified interaction is usually characterized by the so called mean force potential (MFP), which in a physically reasonable form incorporates the medium effect and, in particular, discreteness of the medium at short distances. The interaction with the medium particles is known to result in the wavy behavior of the MFP at short distances. Moreover, in some systems the medium effect results in the well-type shape of the MFP at short distances (see Fig. 1) with the a markedly high barrier at distances \( r \) of order the distance of closest approach \( d \). This effect is found, for example, in the case ion pairs in polar liquids.

Concerning the applicability of well-type approximation for the real MFP shape, it is also worth mentioning the additional reasoning: from mathematical and kinetic points of view any attractive potential can be considered as well-shaped in the absence of (or low) reactivity of particles at \( r \sim d \). The only difference of this type of wells from those shown in Fig. 1 is in their urge-like shape at \( r \sim d \).

The well-type shape of the MFP (with the reaction barrier at \( r \sim d \)) results in the formation of the quasiequilibrium state within the well, which can also be considered as a cage state. In the absence of external force the kinetics of diffusion-assisted depopulation of the initially populated cage state is analyzed in detail in a number of papers. In the limit of deep well depth the problem is shown to be accurately described with the model of two kinetically coupled states: the quasiequilibrium localized state within the well and the free diffusion state outside the well.

The two-state model enables one to obtain the well depopulation kinetics in a relatively simple analytical form. This kinetics, determined by the monomolecular reactive passing over the barrier at \( r \sim d \) and escaping from well (cage), appears to be non-exponential, in general. In the limit of deep well, however, the deviation from the expo-
of which models the reaction within the well.

The main purpose of the work is to analyze the kinetics of diffusion-assisted escaping from the well in the presence of the external force \(-\mathbf{F}\), i.e. escaping from the well of the potential \(U(r) = U(r) + (\mathbf{F} \cdot \mathbf{r})\). For definiteness the force is assumed to be directed along the axis \(z\): \(\mathbf{F} = (0, 0, F)\). The analysis can conveniently be made in spherical coordinates in which \(r = (r \sin \theta \cos \phi, r \sin \theta \sin \phi, r \cos \theta)\).

The diffusive space-time evolution of the Brownian particle is described by the PDF \(\rho(r, t) \equiv \rho(r, \theta, \phi | t)\). In general, in spherical coordinates the PDF depends on all three variables \(r, \theta, \phi\). However, in the considered case of isotropic diffusion and isotropic initial condition \(\rho(r, t = 0) = \rho_0(r)\) the PDF \(\rho(r, t)\) is independent of the azimuthal angle \(\phi\) so that \(\rho(r, t) \equiv \rho(r, \theta | t)\). In our analysis we will assume that particles are created within the well at initial distance \(r_0 \sim r_b\):

\[
\rho(r, t = 0) = \left(4\pi r_i^2\right)^{-1} \delta(r - r_i), \quad (2.1)
\]

The PDF \(\rho(r, \theta | t)\) satisfies the Smoluchowski equation

\[
\dot{\rho} = \nabla_r [D(r)(\nabla_r \rho + \rho \nabla_r u_f)], \quad (2.2)
\]

where \(\nabla_r\) is the gradient operator,

\[
u = r(r) = u(r) + (f \cdot r), \quad (2.3)
\]

with \(u(r) = U(r)/(k_BT)\) and \(f = F/(k_BT)\), is the dimensionless MFP, and \(D(r)\) is the diffusion coefficient, which in our analysis is assumed to be independent of \(r\): \(D(r) = D\) [though some possible effects of \(D(r)\)-dependence can also be studied].

Note that the reaction kinetics for pairs of interacting Brownian particles, say \(a\) and \(b\), is described by the equation similar to eq. (2.2) with \(r = r_a - r_b\) and parameters expressed in terms of those for separate particles.

In the absence of force the kinetics of escaping from the spherically symmetric short range potential well \(u(r)\) is analyzied earlier. Here we extend the approach applied in these works to describe the effect of external force. This approach is based on the approximate solution of the eq. (2.2) in the limit of deep well, in which the solution can be obtained in analytical form by expansion in a small parameter \(\tau_e/\tau_f \ll 1\), where \(\tau_e \sim (a - d)^2/D\) is the time of equilibration within the well and \(\tau_f \sim \tau_e^{-u_a}\) is the time of escaping from the well.

Analysis of this solution shows that in the lowest order in the parameter \(\tau_e/\tau_f\) the Smoluchowski approximation (2.2) is equivalent to the model of two kinetically coupled states: the state within the well and the state of free diffusion outside the well. To clarify the main points of this model we will first briefly consider the case of the absence of the force \(\mathbf{F} = 0\).
III. TWO-STATE MODEL IN THE ABSENCE OF FORCE

Originally, the two-state model was proposed to treat the kinetics of the diffusion-assisted escaping from the well in the case $\Phi = 0$, in which the PDF $\rho(r, t)$ depends only the distance $r = |r|$: $\rho(r, t) \equiv \rho(r, t)$.

Analysis shows$^{16,17}$ that in this case in the lowest order in $\tau_r/\tau_e \ll 1$ the escaping kinetics can be described within the model of two kinetically coupled states: highly localized state within the well and free diffusion state outside the well. The evolution of the state within the well ($d < r < a$) is determined by the well population

$$n(t) = 4\pi \int_d^a \, dr \, r^2 \rho(r, t), \quad (3.1)$$

while the evolution of the state outside the well ($r > a$) is governed by the distribution function $c(r, t)$. The functions $n(t)$ and $c(r, t)$ satisfy simple kinetic equations$^{16,17}$

$$\dot{n} = S_1 \tilde{K}_+ c(a) - (K_- + w_r)n$$
$$\dot{c} = \dot{\tilde{L}}_r c + (S^{-1}_1 K_- - \tilde{K}_+) \delta(r - a), \quad (3.2a)$$

where should be solved with the initial condition

$$n(0) = 1 \quad \text{and} \quad c(r, 0) = 0 \quad (3.3)$$

[implied by eq. (2.1)] and the boundary conditions for $c(r, t)$ written as $\nabla_r c(r, t)|_{r = a} = 0$ (this condition corresponds to reflection at $r = a$) and $c(r \to \infty) = 0$. In eqs. (3.2) $S_1 = 4\pi a^2$ and

$$\dot{\tilde{L}}_r = D r^{-2} \nabla_r (r^2 \nabla_r) \quad (3.4)$$

is the radial part of the free diffusion operator, in which $\nabla_r = \partial/\partial r$. The terms proportional to $K_{\pm}$ describe the above-mentioned kinetic coupling (transitions) between the state within the well, located at $r = a$, and the free diffusion state outside the well. In the considered limit $\tau_r/\tau_e \ll 1$ the transition rates $K_{\pm}$ satisfy the relations$^{16,17}$

$$K_\pm \to \infty \quad \text{and} \quad K_-/K_+ = K_0 = a^2/Z_w, \quad (3.5)$$

where

$$Z_w = \int_{d < r < a} \, dr \, r^2 e^{-u(r)} \quad (3.6)$$

is the partition function for the well $u(r) = U(r)/(k_B T)$. Formula (3.6), obtained by comparing equilibrium solutions of eqs. (2.2) and (3.2), represents the detailed balance relation for transitions between the states of the two-state model.

The term $w_n(\epsilon)$ in eq. (3.2a) describes the effect of the first order reaction (in the well) with the rate

$$w_r = (D/Z_w) \left( \int_{r \to d} \, dr \, r^{-2} e^{u(r)} \right)^{-1}. \quad (3.7)$$

Solution of eqs. (3.2) yields$^{16,17}$

$$n(t) = \frac{1}{2\pi i} \int_{-i\infty + 0}^{i\infty + 0} \, d\epsilon \, \exp(\epsilon t) \frac{\exp(\epsilon)}{\epsilon + w_r + a^2 K_\epsilon V(\epsilon)}. \quad (3.8)$$

The function $V(\epsilon)$ is directly related to the Green’s function of the operator controlling diffusion outside the well [with the reflective boundary condition $\nabla_r g|_{r = a} = 0$]$^{16,17}$

$$G(r, r'|\epsilon) = \langle r| (\epsilon - \hat{L}_r)^{-1} |r'\rangle : \quad (3.9)$$

$$V(\epsilon) = 1/G(a, a|\epsilon) = D[a^{-1} + (\epsilon/D)^{1/2}] \quad (3.10)$$

Substitution of formula (3.10) into eq. (3.8) leads to the following formula for the well population $n(t)$.$^{17}$

$$n(t) = \frac{1}{2\pi i} \int_{-i\infty + 0}^{i\infty + 0} \, d\epsilon \, \exp(\epsilon w_a t) \frac{1}{1 + \epsilon + \gamma \epsilon^{1/2}} \quad (3.11)$$

where $\gamma = (w_r/w_0)^{1/2}(a^2 w_r/D)^{1/2}$. The rate

$$w_0 = w^0_r + w_r \quad (3.12)$$

is a sum of the rate of escaping from the well

$$w^0_r = \frac{D}{Z_w} \left( \int_{r_b}^{\infty} \, dr \, r^{-2} e^{u(r)} \right)^{-1} = D a/Z_w \quad (3.13)$$

and the rate of reaction in the well $w_r$ [see eq. (3.7)].

The function $n(t)$ (3.11) is, evidently, non-exponential. Its analytical properties are essentially determined by the parameter $\gamma \approx a l_p$, where $l_p = (D/w_0)^{1/2}$ is the average distance of diffusive motion during the lifetime $\tau_0 = w_0^{-1}$ of the particle in the well. It is easily seen that for deep wells $l_p \gg a$, and therefore $\gamma \ll 1$. The parameter $\gamma$ controls the onset of the change of the functional form of $n(t)$: $n(t) = \exp(-w_0 t)$ at $\tau \lesssim \ln(1/\gamma)$ and $n(t) \sim 1/t^{3/2}$ at $\tau \gg \ln(1/\gamma)$.

It is worth emphasizing that despite the complexity of the escaping kinetics $n(t)$, in general, it is quite close to the exponential for deep wells (for $\gamma \ll 1$, as it follows from the above expressions). Moreover, independently of the well depth average steady state characteristics of type of the time averaged kinetic parameters just coincide with those corresponding to the exponential part of the kinetics. For example, the lifetime of particles in the well

$$\tau_0 = \int_0^{\infty} \, dt \, n(t) = w_0^{-1}. \quad (3.14)$$

This means, in particular, that the steady state characteristics are quite informative and can be used in the discussion of the escaping kinetics in the more complicated case of the presence of an external forces.
IV. TWO-STATE MODEL IN THE PRESENCE OF FORCE

A. Kinetic equations

In the presence of force \( f = F/(k_BT) \neq 0 \) the potential \( u_f(r) = u(r) + (f \cdot r) \) in eq. (2.2), is not isotropic, which results in the dependence of the solution \( \rho(r, t) \) on particle polar angle \( \theta: \rho(r, t) = \rho(r, \theta(t)). \)

It is important to note that in the case \( f \neq 0 \) the two-state model is also valid for a variety of shapes of the potential well \( u(r) \) though some additional analysis of the corresponding validity criteria are certainly required.

Similarly to the case of the absence of force, in any variant of the anisotropic two-state model (for \( f \neq 0 \)) the kinetics is also described by two functions: the population \( n(\theta|t) \) within the well and the PDF \( c(r, \theta|t) \) of particles outside the well. These functions, however, depend on the polar angle \( \theta \). Within the two-state model the effect of the force \( f \) shows itself in the dependence of kinetic parameters on \( \theta \). The form of this dependence is determined by the particular variant of the model.

In general, two-state kinetic equations, describing evolution of PDFs \( n(\theta|t) \) and \( c(r, \theta|t) \) in the presence of an external force, can be written by analogy with eqs. (3.2):

\[
\begin{align*}
\dot{n} &= S_I K_+(\theta) c(a|t) + [\hat{L}_c - (K_-(\theta) + w_r)]n, \quad (4.1a) \\
\dot{c} &= \hat{L}_f c + [S_I^{-1} K_-(\theta) n - K_+(\theta)] \delta(r - a), \quad (4.1b)
\end{align*}
\]

where

\[
\hat{L}_f = D \nabla_r (\nabla_r + f)
\]

is the operator, describing diffusion outside the well, and \( \hat{L}_c \) is the Smoluchowski operator in \( \{\theta\} \)-space which controls orientational relaxation of the PDF in the well.

The essential difference of anisotropic equations from isotropic ones consists in the orientation dependence of rates, \( K_+(\theta) \) and \( K_-(\theta) \). Below, in accordance with eq. (3.2), in the considered limit \( \tau_r/\tau_c \ll 1 \) we will assume the transition rates \( K_{\pm} \) to satisfy the relations:

\[
K_\pm \to \infty \quad \text{and} \quad K_-(\theta)/K_+(\theta) = K_\epsilon(\theta).
\]

(4.3)

Therefore in this limit \( \theta \)-dependence of rates \( K_{\pm}(\theta) \) show itself in that of the equilibrium constant: \( K_\epsilon(\theta) \). The form of the function \( K_\epsilon(\theta) \) is determined by the shape of the well. Some model well shapes and corresponding \( K_\epsilon(\theta) \) dependences, as well as applicability of the corresponding two-state models, are discussed below.

Equations (4.1) should be solved with boundary conditions

\[
(\nabla_r + f \cos \theta)c|_{r=a} = 0 \quad \text{and} \quad c|_{r-\infty} = 0,
\]

(4.4)

first of which describes reflection of particles (diffusing in the state outside the well) at \( r = a \). The initial condition is assumed to be isotropic and given by eq. (2.1).

In what follows it will be convenient to represent functions \( n(\theta|t) \) and \( c(r, \theta|t) \) in the form of vectors \( |n(t)\rangle \) and \( |c(r, t)\rangle \), whose components are obtained by expansion of these functions in the orthonormal basis of properly normalized Legendre polynomials (spherical functions):

\[
\begin{align*}
|Y_l\rangle &= (l + 1/2) P_l(c \cos \theta), \quad (4.5a) \\
\langle Y_l| &= \int_0^\pi d\theta \sin \theta P_l(c \cos \theta) \ldots \quad (4.5b)
\end{align*}
\]

with \( l = 0, 1, \ldots \):

\[
|\mathbf{n}\rangle = \sum_{l=0}^{\infty} n_l |Y_l\rangle \quad \text{and} \quad |\mathbf{c}\rangle = \sum_{l=0}^{\infty} c_l |Y_l\rangle,
\]

(4.6)

where for any vector \( |\chi(\theta)\rangle, \quad (\chi = n, c) \), its components \( \chi_l \) are defined by

\[
\chi_l = \langle Y_l|\chi\rangle = \int_0^\pi d\theta \sin \theta P_l(c \cos \theta) \chi(\theta).
\]

(4.7)

In term of this vector representation the initial condition can conveniently be written in the form, explicitly displaying its independence of orientation:

\[
|\rho_i\rangle = (2\pi r_i^2)^{-1} |Y_0\rangle \delta(r - r_i).
\]

(4.8)

As for the initial condition, it is worth noting, in addition, that in the most realistic limit of orientational relaxation within the well much faster than the escaping from the well the escaping kinetics is insensitive to the orientational dependence of the initial condition.

B. Escaping kinetics

Equations (4.1) can be solved by the method, applied above in the case of the absence of force, but with the use of expansion of \( n(\theta|t) \) and \( c(r, \theta|t) \) in spherical functions \( |Y_l\rangle \), i.e. vector representation \( |\mathbf{n}(t)\rangle \) and \( |\mathbf{c}(r|t)\rangle \) [see eq. (4.6)]. The solution yields for the Laplace transform

\[
|\tilde{\mathbf{n}}(\epsilon)\rangle = \int_0^\infty dt e^{-\epsilon t} |\mathbf{n}(t)\rangle : \quad (4.9)
\]

\[
|\tilde{\mathbf{n}}(\epsilon)\rangle = \langle \epsilon + w_r + \hat{L}_c + a^2 \mathring{V}(\epsilon) \hat{K}_\epsilon \rangle^{-1} |\mathbf{n}_i\rangle,
\]

(4.10)

where for the initial condition \( |\mathbf{n}_i\rangle = (1/2\pi)|Y_0\rangle \). In this expression the equilibrium constant \( \hat{K}_\epsilon \) is the operator, which indicates its dependence on the orientation angle \( \theta \), and

\[
\mathring{V} = \hat{G}^{-1}(a, a|\epsilon)
\]

(4.11)

is the operator in the space of \( |Y_l\rangle \)-states, expressed in terms of the evolution operator for diffusive motion outside the well (evaluated at \( r = r_i = a \)):

\[
\hat{G}(a, a|\epsilon) = \langle a| (\epsilon - \hat{L}_f)^{-1} \rangle a
\]

\[
e^{-\epsilon \cos \theta} \langle a| (\epsilon - \hat{L}_f)^{-1} \rangle a e^{\epsilon \cos \theta}, \quad (4.12)
\]
in which \( \varphi = fa/2 \) and
\[
\hat{\Lambda}_f = D(\hat{L}_r + r^{-2}\hat{L}_\theta - \frac{1}{4}f^2),
\]
with
\[
\hat{L}_\theta = (1/\sin \theta) \nabla_\theta [\sin \theta (\nabla_\theta)].
\]

In the expression (4.13) \( \hat{L}_r \) is the operator of radial diffusion, defined in eq. (3.3), and \( \hat{L}_\theta \) is the operator of free orientational diffusion, diagonal in \( |Y_l\rangle \)-basis:
\[
\hat{L}_\theta = -\sum_{l=0}^{\infty} l(l+1)|Y_l\rangle \langle Y_l|.
\]

In what follows we will mainly restrict ourselves to the analysis of the total population of the well \( n_0(t) \), for the Laplace transform of which one gets the expression
\[
\hat{n}_0(\epsilon) = 2\pi \int_0^\pi d\theta \sin \theta \hat{n}(\theta, \epsilon) \equiv 2\pi \langle Y_0 | \hat{n} | Y_0 \rangle = \langle Y_0 | [w_r + \hat{L}_c + a^2 \hat{V}(\epsilon) \hat{K}_e]^{-1} | Y_0 \rangle,
\]
where \( \hat{n}(\theta, \epsilon) \) and \( \hat{n}_0 \) are the matrix representation of the function \( \cos \theta \).

Moreover, since the escaping kinetics appears to be fairly close to the exponential (see Sec. III), to characterize the process it is sufficient to calculate the mean inverse lifetime \( \tilde{n}_0 \) of particles in the well defined by eq. (3.14):
\[
\tilde{n}_0 = \hat{n}_0(0) = \langle Y_0 | [w_r + \hat{L}_c + a^2 \hat{V}(0) \hat{K}_e]^{-1} | Y_0 \rangle.
\]

### C. General formulas

Formulas (4.12) (4.13) allow us to evaluate the operator \( \hat{V}(\epsilon) \) in analytical form and, therefore, analyze the behavior of \( \hat{n}_0(\epsilon) \) and \( \tilde{n}_0 \) relatively easily.

In the evaluation it is worth taking into account the useful relation which simplifies the differential operator in the radial space:
\[
\langle a | (\epsilon - \hat{\Lambda}_f)^{-1} | a \rangle = \langle a | (\epsilon - \hat{\lambda}_f)^{-1} | a \rangle,
\]
where
\[
\hat{\lambda}_f = D(\nabla_r^2 + r^{-2}\hat{L}_\theta - \frac{1}{4}f^2).
\]

The evolution operator \( \langle a | (\epsilon - \hat{\lambda}_f)^{-1} | a \rangle \) can be obtained in analytical form using the technique of two linearly independent solutions \( \psi_-(r) \) and \( \psi_+(r) \) of the equation
\[
(\epsilon - \hat{\lambda}_f) \psi_\pm = 0
\]
in which the operator \( \hat{L}_\theta \) is treated as a parameter. These solutions satisfy two boundary conditions corresponding to those given in eq. (4.13) [after change of variable \( c(r) = e^{-(fr \cos \theta)/2}(r) \)]
\[
(\nabla_r + \frac{1}{2}f\hat{\omega}) \hat{\psi}_-|_{r=a} = 0 \quad \text{and} \quad \hat{\psi}_+|_{r=0} \rightarrow 0,
\]
where
\[
\hat{\omega} = \sum_{l,m=0}^{\infty} |Y_l\rangle \langle Y_l| \cos \theta |Y_m\rangle \langle Y_m|,
\]
is the matrix representation of the function \( \cos \theta \). The matrix elements \( \langle Y_l| \cos \theta |Y_m\rangle = \langle Y_l| P_0(\cos \theta) |Y_m\rangle \) are evaluated analytically, though the corresponding formulas will not be needed in our further analysis.

Both solutions \( \hat{\psi}_+(r) \) and \( \hat{\psi}_-(r) \) are expressed in terms of matrices of modified Bessel functions:
\[
\hat{K}(r) = \sqrt{r} \sum_{l=0}^{\infty} |Y_l\rangle K_{l+\frac{1}{2}}(kr) \langle Y_l|,
\]
\[
\hat{I}(r) = \sqrt{r} \sum_{l=0}^{\infty} |Y_l\rangle I_{l+\frac{1}{2}}(kr) \langle Y_l|,
\]
\[
\hat{\psi}_+(r) = \hat{K}(r), \quad \hat{\psi}_-(r) = \hat{I}(r) + \hat{\hat{K}}(r)\hat{\kappa},
\]
where
\[
k(\epsilon) = \sqrt{(f/2)^2 + \epsilon/D}
\]
and \( \hat{\kappa} \) is the matrix determined by the boundary condition at \( r = a \) [see eq. (4.24)]:
\[
\hat{\kappa} = [\nabla_r \hat{K}(r) - \hat{q}\hat{K}(r)]^{-1}[\hat{q}\hat{I}(r) - \nabla_r \hat{I}(r)]|_{r=a},
\]
in which
\[
\hat{q} = a^{-1}(1 - \varphi \hat{\omega}) \equiv a^{-1}(1 - \varphi \cos \theta),
\]
with \( \varphi = fa/2 \).

It is worth noting that the matrices \( \hat{K} \) and \( \hat{I} \) do not commute with \( \hat{\omega} \) and, therefore, the order of matrices in the products of the matrices in expressions (4.25) - (4.27) is important. As a result of these special commutation properties of the matrices, the matrix solutions \( \hat{\psi}_+(r) \) and \( \hat{\psi}_-(r) \) do not commute either.

The general representation of the evolution equation \( \hat{r}((\epsilon - \hat{\lambda}_f)^{-1} | r_i \rangle \) in terms of non-commuting solutions \( \hat{\psi}_+(r) \) and \( \hat{\psi}_-(r) \) is proposed and thoroughly discussed in ref. [20]. This representation generalizes the one well known in the case of scalar solutions \( \hat{\psi}_+(r) \) and \( \hat{\psi}_-(r) \).

In general, the proposed representation is fairly complicated, however, in the particular case of solutions given by eqs. (4.23) and (4.24) it reduces to a more simple one:
the Wronskian of two solutions which is a scalar function similar to eq. (4.20) but with delta-function where

We need to specify the operator \( \hat{L}_c \) describing orientational relaxation in the well. Naturally it should be of the Smoluchowski-like form:

\[
\hat{L}_c = D_c(\sin \theta)^{-1} \nabla_\theta [\sin \theta (\nabla_\theta + \nabla_\theta \bar{u})],
\]

(4.35)

where \( D_c \) is the orientational diffusion coefficient \( \bar{u}(\theta) \) is the effective orientational which is determined by the shape of the well (see below).

For the sake generality, we will not assume any relation of the value of \( D_c \) with that of \( \bar{D} \) outside the well (type of \( D_c \approx D/r_c^2 \)).

Moreover, in the considered limit of large well depth it is quite natural to assume that orientational relaxation is much faster than well depopulation.

### D. Fast orientational relaxation in the well

The fast orientational relaxation limit implies that \( D_c \gg \bar{w}_0 \), where \( \bar{w}_0 \) is the rate of depopulation of the well defined in eq. (4.14). This relation means that after some time \( \tau_c \approx D_c^{-1} \) of orientational relaxation (of

\[
\langle r(\epsilon - \hat{L}_f)^{-1} r_i \rangle = -D^{-1}[\hat{K}(r)I(r_i)\theta_H(r-r_i) + I(r)\hat{K}(r_i)\theta_H(r_i-r) + \hat{K}(r)\theta_H(r_i-r_i)]/W(\hat{K}, I).
\]

(4.29)

In this expression \( \theta_H(x) \) is the Heaviside step function and

\[
W(\hat{K}, I) = \nabla_r \hat{K}(r)I(r) - \nabla_r I(r) \hat{K}(r)
\]

(4.30)
is the Wronskian of two solutions which is a scalar function \( W(\hat{K}, I) = -1 \). The validity of the expression [4.29] can easily be verified by direct substitution of it to equation similar to eq. [4.20] but with delta-function in the right hand side.

For the particular case \( r = r_i \) a formula [4.29] yields

\[
\langle a | (\epsilon - \hat{L}_f)^{-1} | a \rangle = D^{-1}[\hat{q} - \hat{q}_K(\epsilon)]^{-1},
\]

(4.31)

where

\[
\hat{q}_K(\epsilon) = \nabla_r \hat{K}(r)/\hat{K}(r)|_{r=a} = \sum_{l=0}^{\infty} |Y_l\rangle q_{K_l}(\epsilon)\langle Y_l|
\]

(4.32)

with

\[
q_{K_l}(\epsilon) = (l/a) + k(\epsilon)K_{l-\frac{1}{2}}(k(\epsilon)a)/K_{l+\frac{1}{2}}(k(\epsilon)a).
\]

(4.33)

Substituting the expression [4.31] into eq. [4.18] and then into eqs. [4.13] and [4.11] we obtain fairly simple formula for \( \hat{V}(\epsilon) \):

\[
\hat{V}(\epsilon) = D e^{-\varphi \cos \theta} [\hat{q} - \hat{q}_K] e^{\varphi \cos \theta} = D \left[ a^{-1} (1 - \varphi \cos \theta) - e^{-\varphi \cos \theta} \hat{q}_K e^{\varphi \cos \theta} \right] (4.34)
\]

For out further analysis of the escaping kinetics \( n_0(t) \) we need to specify of the operator \( \hat{L}_c \) describing orientational relaxation in the well. Naturally it should be of the Smoluchowski-like form:

\[
\hat{L}_c = D_c(\sin \theta)^{-1} \nabla_\theta [\sin \theta (\nabla_\theta + \nabla_\theta \bar{u})],
\]

(4.35)

where \( D_c \) is the orientational diffusion coefficient \( \bar{u}(\theta) \) is the effective orientational which is determined by the shape of the well (see below).

For the sake generality, we will not assume any relation of the value of \( D_c \) with that of \( \bar{D} \) outside the well (type of \( D_c \approx D/r_c^2 \)).

Moreover, in the considered limit of large well depth it is quite natural to assume that orientational relaxation is much faster than well depopulation.

### D. Fast orientational relaxation in the well

The fast orientational relaxation limit implies that \( D_c \gg \bar{w}_0 \), where \( \bar{w}_0 \) is the rate of depopulation of the well defined in eq. (4.14). This relation means that after some time \( \tau_c \approx D_c^{-1} \) of orientational relaxation (of the initial population in the well) the vector of well population \( |n(t)\rangle \) remains close to the equilibrium one \( |\Psi_e\rangle \) during the process:

\[
|n(t)\rangle \approx n_0(t)|\Psi_e\rangle,
\]

(4.36)

where

\[
|\Psi_e\rangle = Z^{-1}_\theta e^{-\bar{u}n(\theta)}, \quad Z_\theta = \int_0^\pi d\theta \sin \theta e^{-\bar{u}n(\theta)}.
\]

(4.37)

Note that with in bra-ket notation the adjoint vector \( |\psi_e\rangle \) coincides with \( |Y_0\rangle \) and is given by formula

\[
|\Psi_e\rangle = |Y_0\rangle = \int_0^\pi d\theta \sin \theta \ldots,
\]

(4.38)

which can be confirmed by the relation \( \langle \Psi_e|\hat{L}_c|0\rangle = 0 \) directly following from the definition of \( \hat{L}_c \) [see eq. (4.35)]. With the use of this formula one can easily find that \( |\psi_e\rangle \) satisfies the normalization condition \( \langle \Psi_e|\Psi_e\rangle = 1 \).

In what follows we will restrict ourselves to the analysis of the escaping kinetics just in this limit of fast orientational relaxation.

For fast orientational relaxation the splitting \( \delta L_c \) of eigenvalues of the operator \( \hat{L}_c (\delta L_c \sim D_c) \) is much larger than \( a^2\|\hat{V}\hat{K}_c\| \sim w_c \). In such a case in the lowest order in the parameter \( w_c/D_c \ll 1 \) we can significantly simplify the general expressions (4.10) and (4.11) for \( n_0(\epsilon) \) and the inverse average lifetime \( \bar{w}_0 = \tau_0^{-1} = \bar{n}_0^{-1}(\epsilon) \), respectively, as follows:

\[
\bar{n}_0(\epsilon) = [\epsilon + w_c + a^2\langle \Psi_e|\hat{V}(\epsilon)\hat{K}_c|\Psi_e\rangle]^{-1},
\]

(4.39)

and

\[
\bar{w}_0 = \tau_0^{-1} = \bar{n}_0^{-1}(\epsilon) = w_c + a^2\langle \Psi_e|\hat{V}(0)\hat{K}_c|\Psi_e\rangle.
\]

(4.40)

Equation (4.39) presents the main result of the work for the kinetics of the well depopulation in the limit of fast orientational relaxation.

Formula (4.39) shows that, in general, in the fast orientational relaxation limit the escaping kinetics \( n_0(t) \) is non-exponential, however, as it has been mentioned above in Sec. III in the considered case of deep wells its deviation from exponential is very small and, therefore, the kinetics can quite accurately be characterized by the only parameter, the mean lifetime \( \bar{w}_0 \) or the corresponding mean rate \( \bar{w}_0 = \tau_0^{-1} \). For this reason, in what follows we will mainly discuss these two parameters.

Moreover, below we will concentrate on the second term in square brackets in eq.(4.40):

\[
w_c = a^2\langle \Psi_e|\hat{V}(0)\hat{K}_c|\Psi_e\rangle,
\]

(4.41)
which can be interpreted as the mean escape rate.

To apply formulas (4.39)-(4.41) one need to specify the shape of the potential well which determines the orientational potential $\tilde{u}(\theta)$ in the Smoluchowski-type operator $\hat{L}_e$ [see eq. (3.33)] and, therefore, the equilibrium state $|\Psi_e\rangle$. In our work we will consider two realistic models of the well shape in which relatively simple analytical expressions for the mean rate $\bar{w}_0 = \bar{\tau}_0^{-1}$ and, in particular, for $w_e$ can be obtained.

V. APPLICATION OF GENERAL RESULTS

In this section we will analyze the specific features of mean escape rate $w_e$ for two variants of the well shape:

1) Narrow well shape (shown in Fig. 1 by dashed line with $a = a_n$), for which $a - d \ll d$ and the time of equilibration within the well $\tau_e \sim (a - d)^2/D \ll a^2/D \ll \tau_e$, where $\tau_e \sim \bar{\tau}_0^{-1}$ [see eq. (3.44)] is the time of escaping from the well;

2) The wide well shape (full line in Fig. 1 with $a = a_w$), corresponding to a small distance of closest approach $d \ll a$ (in which of the main interest is the region $fd \ll 1$ while $fa \geq 1$). This shape is schematically shown in Fig. 1 by full line with $a = a_w$.

The analysis will be made in the above-discussed limit of fast orientational relaxation in the well with the use of eq. (1.39) for the well depopulation kinetics. In our study, in addition to this formula and other ones derived above, we will also use the representation for $e^{\pm \varphi \cos \theta}$ in terms of expansion in spherical functions $P_l(\cos \theta)$:

$$e^{\pm \varphi \cos \theta} = \sqrt{\frac{2\pi}{\varphi}} \sum_{l=0}^{\infty} (\pm 1)^l (l + \frac{1}{2}) I_{l+\frac{1}{2}}(\varphi) P_l(\cos \theta). \quad (5.1)$$

A. Narrow-well shape

In the case of narrow well, when $a - d < d$, the well is of the shape of attractive well layer near the distance of closest approach $d$. In this limit within the wide region force strengths $f < 1/(a - d)$ we can neglect the effect of the force on the radial shape of the well and take into consideration only the dependence of well depth $\tilde{u}(\theta)$ on the orientation angle $\theta$:

$$\bar{u}_b(\theta) \approx u(r_b, \theta) \approx u_b + f a \cos \theta \quad (5.2)$$

with $f = |f| > 0$, and the force effect on free diffusion in the state outside the well. In eq. (5.2) we took into account the smallness of the width of the well, $a - d \ll d$, which leads to the high accuracy of the relation $f r_b \approx a$.

It is important to note that the small value of the well width and, therefore, fast equilibration of the well population in radial direction, ensures the validity of the description of the kinetics in terms of the angular coordinate dependent well population $n(\theta|t)$ introduced above. Noteworthy is also that the negligible force affected change of the well shape results in the absence of the dependence of the detailed balance relation and the equilibrium constant [see eq. (3.3)] on the angle $\theta$, i.e $K_e = K_0^e$. In other words, the effective partition function $Z_w$, which governs the constant $K_e$, is still given by eq. (3.33), i.e. is controlled by the shape of the potential $u(r)$ without external force, despite possible strong force effect on the energy of the bottom predicted by eq. (5.2). This is because the external force leads to the identical change of both the bottom energy $\bar{u}_b(\theta) \approx u_b + f a \cos \theta$ and the energy of the free diffusion state at $r = a$: $u_f(a, \theta) \approx f a \cos \theta$.

The potential $\bar{u}_b(\theta)$ determines the kinetics of orientational relaxation of the population in the well, which is described by the Smoluchowski operator (4.33) with

$$\bar{u}(\theta) = \tilde{u}_b(\theta) - u_b = 2\varphi \cos \theta, \quad \text{where } \varphi = fa/2. \quad (5.3)$$

In this case the equilibrium state within the well is written as

$$|\Psi_e\rangle = Z_0^{-1}(\varphi) e^{-2\varphi \cos \theta} \quad (5.4)$$

with

$$Z_0(\varphi) = \sinh(2\varphi)/\varphi. \quad (5.5)$$

Substitution of formulas (5.4) and (5.1) into the expression (4.41) yields for the mean escape rate $w_e(\varphi)$, expressed in terms of the universal function $Q_n(\varphi)$:

$$w_e(\varphi)/w_{e_n}^0 = Q_n(\varphi) = \frac{1}{2} + \varphi \coth(2\varphi) + S_n(\varphi). \quad (5.6)$$

In this formula $w_{e_n}^0$ is the escape rate in the absence of a force [see eq. (5.19)], $\varphi = fa/2$, and

$$S_n(\varphi) = 2Z_0^{-1}(\varphi)(\pi/\varphi) \sum_{l=0}^{\infty} (l + 1/2) I_{l+1/2}(\varphi) q_l(\varphi) \quad (5.7)$$

with $Z_0(\varphi)$ defined in eq. (5.4) and

$$q_l(\varphi) = a q_{K_l} = l + \varphi K_{l-\frac{1}{2}}(\varphi)/K_{l+\frac{1}{2}}(\varphi). \quad (5.8)$$

Formula (5.6) shows that the force effect on the rate is characterized by the only parameter $\varphi = fa/2$. The numerical calculated universal function $Q_n(\varphi)$ which describes this effect is displayed in Fig. 2a. In addition, some limiting specific features of the behavior of $Q_n(\varphi)$ can be revealed with simple analytical expressions.

a. Weak force limit. In the limit of weak external force, when $\varphi = fa/2 \ll 1$, in two lowest orders in $\varphi$ the mean escape rate $w_e$ can be calculated using only the first term (with $l = 0$) in the sum $S_n(\varphi)$ in the expression (5.7) and $Q(\varphi) = w_e(\varphi)/w_{e_n}^0$:

$$Q_n(\varphi) = Q_n^w(\varphi) \approx 1 + \varphi = 1 + fa/2. \quad (5.9)$$

b. Strong force limit. In the opposite case $\varphi = fa/2 \gg 1$, denoted as the strong external force limit, the analysis
In deriving eq. (5.10) we used the expression for one-dimensional estimation with the use of eq. (5.7) by truncation function. The limiting results obtained above for \( \varphi \ll 1 \) and \( \varphi \gg 1 \) can be combined into a simple algebraic interpolation formula

\[
Q_n(\varphi) \approx Q_n^l(\varphi) = \frac{1}{2} + \frac{\varphi e^{2\varphi}}{\sinh(2\varphi)} + \frac{\varphi^2}{6 + 2\varphi^2} \tag{5.11}
\]

which reproduces function \( Q_n(\varphi) \), numerically evaluated using eqs. (5.6)-(5.8), with accuracy \( \sim 3\% \) (see Fig. 2a).

### B. Wide-well shape

Another form of the well shape, in which analysis of the escape rate \( w_\epsilon \) can be made analytically, corresponds to the small distance of closest approach, or large \( a \), for which \( d \sim r_h \ll a \). In this case in a fairly wide region of relatively strong force \( f < 1/d, 1/r_h \) the escape kinetics is fairly accurately described by the two-state model (4.11).

It is important to note that the inequality \( f r_h < 1 \) ensures quite high accuracy of the approximation neglecting the effect of force on the well shape in the region near the bottom. In this approximation, the quasiequilibrium population distribution within the well is isotropic:

\[
|\Psi_e\rangle = |Y_0\rangle. \tag{5.12}
\]

This, in turn, means that the partition function \( Z_w \) is independent of the angle \( \theta \) and is given by eq. (3.9). The effect of force, however, manifests itself in the anisotropy of the activation energy of escaping \( u_\epsilon(\theta) \):

\[
u_\epsilon(\theta) \approx \nu(\theta, a) \approx u_\epsilon + 2\varphi \cos \theta, \quad (\varphi = fa/2), \tag{5.13}
\]

which, in turn, leads to the anisotropy of the detailed balance relation, i.e. the anisotropy of the equilibrium constant

\[
K_\epsilon(\theta) = K_0 \epsilon e^{-2\varphi \cos \theta}, \tag{5.14}
\]

where \( K_0 \epsilon \) is the isotropic equilibrium constant in the absence of external force given by eq. (5.13).

Formula (5.14) calls for some additional comments especially concerning its applicability. The fact is that the value of \( K_\epsilon(\theta) \) at each particular \( \theta \) is determined assuming local quasiequilibrium of the population outside and inside the well in the region close to \( \theta = a \) at this \( \theta \). In general, it is difficult to justify the existence of the quasiequilibrium in the considered limit, unlike the limit of narrow well discussed above. This is because for \( \varphi = fa/2 \lesssim 1 \) the time of passing over the escaping barrier width \( \delta_0 \sim \min\{a, f^{-1}\} \) (the width of the region of transition from the inner part of the well to the outer one), \( \tau_0 \sim \delta_0^2/D \) is comparable with the time of reorientation \( \tau_\infty \sim a^2/D \). It is worth noting, however, that the accuracy of quasiequilibrium assumption becomes better with increasing \( f \) since the for \( \varphi = fa/2 \gtrsim 1 \) the width \( \delta_0 \ll a \) and, correspondingly, \( \tau_0 \ll \tau_\infty \).

The above-mentioned arguments lead us to the conclusion that in the considered limit of small radius of the
well bottom the two-state model with $\theta$-dependent equilibrium constant $K_e(\theta)$ gives quite reasonable interpolation formula for the kinetics of the escaping process and, in particular, for the escape rate $w_e$, which correctly describes both the limit of weak and strong external force. Further analysis (see below) will confirm this statement.

Formula for the escaping kinetics can straightforwardly be derived with the use of general formulas (5.9), (5.10), and some results obtained above in the limit of narrow potential well. The fact is that, in the mathematical form, the average of any operator multiplied by angular dependent equilibrium constant (5.14) over the isotropic equilibrium state (5.12) is similar to the average over the equilibrium distribution (5.4), except for the partition function $Z_0(\varphi)$ [eq. (5.5)], which should be replaced by $Z_0(\varphi \to 0) = 2$ corresponding to the isotropic distribution. These simple algebraic manipulations result in the following expression for $w_e(\varphi)$

$$w_e(\varphi)/w_{e_0}^0(\varphi) = Q_w(\varphi) = \frac{1}{2}Z_0(\varphi)e^{-2\varphi}Q_n(\varphi)$$  

(5.15)

where $Z_0(\varphi)$ and $Q_n(\varphi)$ are determined in eqs. (5.9) and (5.10), respectively, and

$$w_{e_0}^0(\varphi) = w_{e_0}e^{2\varphi}$$  

(5.16)

is the escape rate in the absence of the external force but with the activation energy $u_{e_0}^*$, corresponding to the orientation $\theta = \pi$ (most favorable for escaping):

$$u_{e_0}^* \equiv u_0(\theta = \pi) = u_b - 2\varphi.$$  

(5.17)

As in the case of narrow potential well the dependence of $w_e$ on the force $f$ is expressed in terms of that on the only parameter $\varphi$. The characteristic function $Q_w(\varphi)$, which determines the pre-exponential factor in the activation type dependence of $w_e(\varphi)$, is displayed in Fig. 2b. The numerical results show that $Q_w(\varphi)$ monotonically decreases (with increasing $\varphi$) from $Q_w = 1$ at $\varphi = 0$ to $Q_w = 1/2$ at $\varphi \to \infty$. This behavior is markedly different from that of $Q_n(\varphi)$ although the specific features of $Q_w(\varphi)$-dependence are essentially determined by those of $Q_n(\varphi)$. Some of features of the function $Q_w(\varphi)$, for example saturation at $\varphi \to \infty$, looking unexpected at first sight, can be understood by simple analysis (see below).

a. Weak force limit. In the weak force limit the behavior of $Q_w(\varphi)$ at $\varphi = f a/2 \ll 1$ differs form that obtained above for $Q_n(\varphi)$ (i.e., for narrow potential well): $Q_w(\varphi)$ decreases with increasing $\varphi$, so that at $\varphi \ll 1$

$$Q_w^0(\varphi) = Q_w(\varphi \ll 1) \approx 1 - \varphi.$$  

(5.18)

Such a behavior of $Q_w(\varphi)$ results from the $\varphi$-dependent normalizing rate $w_{e_0}^0 \to e^{2\varphi}$ (instead of $w_{e_0}^0 = w_e^0$) in the definition of $Q_w(\varphi)$.

b. Strong force limit. In the opposite limit $\varphi = f a/2 \gg 1$ the force strongly affects the average escape rate $w_e$, first of all, because it significantly changes the activation energy of the rate $w_e$. As for $Q_w(\varphi)$, which characterizes the pre-exponential factor of the corresponding Arrenius-type expression for $w_e$, at $\varphi \gg 1$ it monotonically decreases approaching the asymptotic value 1/2.

The obtained $Q_w(\varphi)$-independence at $\varphi \to \infty$ can easily be understood by taking into account that, according to formula (5.14), in the case of wide well the strong external force causes significant localization of the flux of escaping particles in a small region of orientations $\delta \theta = \pi - \theta < 1/\sqrt{\varphi} \ll 1$. The escape rate is determined by the total flux $J_e$ through this region of size $s_e \sim (\delta \theta)^2 \sim \varphi^{-1}$. In the strong force limit $\varphi \gg 1$ the flux $J_e \sim \varphi$, as it follows from eq. (5.10), so that $Q_w(\varphi) \sim s_e J_e \sim \text{const}$. The exact estimation can be obtained just by substitution of the corresponding limiting expression (5.10) into eq. (5.15):

$$Q_w^* = \frac{1}{2}Z_0(\varphi)e^{-2\varphi}Q_n^*(\varphi),$$  

(5.19)

Similarly to the narrow well limit, in the case of wide well for large $\varphi$ the escape rate is determined by the quasi-one-dimensional flux of escaping particles. The mechanism of formation of the one-dimensional flux is, however, somewhat different in both cases: for narrow wells the transition to the one dimensional regime results from high localization of the well population in the small region at $\theta \sim \pi$, while for wide wells this transition is caused by strong localization of favorable transition rates in this region.

c. Interpolation formula. A simple interpolation expression for $Q_w(\varphi)$ can be derived, for example, with the use of similar formula for $Q_n(\varphi)$ presented in eq. (5.11):

$$Q_w(\varphi) \approx Q_n^i(\varphi) = \frac{1}{2}Z_0(\varphi)e^{-2\varphi}Q_n^i(\varphi).$$  

(5.20)

Quite satisfactory accuracy ($\sim 3\%$) of this formula is demonstrated in Fig. 2b.

VI. SUMMARY AND CONCLUDING REMARKS

This work concerns detailed theoretical study of the effect of the external force $f = F/(k_B T)$ on the kinetics of depopulation of a deep potential well. The well is assumed to be isotropic and highly localized (short range). Though, detailed analysis showed that fairly deep potential well resulted, for example, from the Coulomb interaction (at large $r$) can also be considered as highly localized in some conditions.

Fairly simple matrix expression for the kinetics of the well depopulation is obtained, which predicts strong effect of external force on the kinetics. Moreover, in general, the kinetics is predicted to be non-exponential.

In our work we have concentrated on the analysis in the most physically reasonable limit of fast orientational relaxation of the PDF in the well. In this limit the analytical expression for the depopulation kinetics is derived which predicts the kinetics to be close to the exponential and the total depopulation rate to be a sum of reaction and escape rates. In our work we have mainly studied...
the specific features of the escape rate \( w_e \), whose value appears to significantly depend on shape of the well. Simple analytical expressions for \( w_e(f) \) are obtained for two limiting types of wells: narrow wells of type of well layer at a distance of closest approach \( d \) (for which \( a - d \ll a \)) and deep wells with small distance \( d \ll a \).

In the case of narrow well the effect of the force on the escape rate is fairly strong but shows itself only in the preexponential factor of the Arrhenius-type dependence of the rate, i.e. no strong effect on the activation energy is predicted. On the contrary, in the case of wide well (\( d \ll a \)) the force affects not only preexponential factor but the activation energy as well.

It is worth noting that the effect of an external force on the diffusion-assisted processes in the presence of interaction between particles are studied in a number of works (see, for example, refs. [1] and [7]). Especially comprehensively the force effect (electric field effect) is analyzed in the case of ion pair recombination reaction, i.e. in the case of the Coulomb interaction between particles.

Unfortunately it is practically impossible to compare the results our analysis with those obtained earlier, since the earlier works mainly concerned with processes in potentials without well at short distances, the reactivity is usually assumed to be high. In particular, in the case of ion pair recombination processes the recombination kinetics is considered to be determined by diffusive motion in the pure Coulomb potential. It is, nevertheless, interesting to note that in the small field limit \( f a \ll 1 \) the force effect on the probability \( P_e(f) \) of escape from the Coulomb potential, found in ref. [4], is independent of the initial distance between ions and is represented in the form \( P_e(f) \approx P_e(f = 0)(1 + f a/2) \), which is in apparent agreement with the field dependence of the escape rate obtained in our works [see eqs. (5.9) and (5.18)].

Noteworthy is also that in the strong force limit the escaping process becomes nearly one-dimensional in both cases of well shape considered. In this limit the escaping rate is determined by the one-dimensional flux from the small region of favorite orientations corresponding to \( \theta \sim \pi \). This fact allows one to easily improve the considered two-state model, in which the effect of the force on the location of top of the barrier (assumed to be at \( r = a \)) is neglected. Moreover, in the strong force limit one can also take into account the smoothness of the shape of the realistic barrier near the top, which in the two-state model is actually assumed to be of cuff shape.

Concerning possible applications of formulas obtained, note that the most convenient for experimental analysis is not the force dependent inverse mean lifetime \( \tilde{\omega}_0(\varphi) \) [see eq. (1.10)], but the difference \( \tilde{\omega}_0^w(\varphi) - \tilde{\omega}_0^0(\varphi) = w_e(\varphi) - w_0^0 \), which is independent of the rate \( w_e \), of reaction within the well (assumed to be independent of \( \varphi \)). The corresponding dimensionless parameters

\[
\delta Q_n(\varphi) = [\tilde{\omega}_0^w(\varphi) - \tilde{\omega}_0^0(\varphi)]/w_0^0(\varphi), \quad (\nu = n, w), \tag{6.1}
\]

are directly related to \( Q_e(\varphi) \):

\[
\delta Q_n(\varphi) = Q_n(\varphi) - 1, \quad \delta Q_w(\varphi) = Q_w(\varphi) - e^{-2\varphi}. \tag{6.2}
\]

The behavior of \( \delta Q_n(\varphi) \) is, clearly, similar to that of \( Q_n(\varphi) \) except for evident displacement along the ordinate axis. As for \( \delta Q_w(\varphi) \)-dependence, shown in Fig. 3, its form is essentially different from that of \( Q_w(\varphi) \): at \( \varphi \to 0 \) the function \( \delta Q_w(\varphi) \approx \varphi \) is similar to \( \delta Q_n(\varphi) \), while \( \delta Q_w(\varphi \to \infty) = 1/2 \). Moreover \( \delta Q_w(\varphi) \) has a maximum (though not very pronounced) at \( \varphi = \varphi_m \approx 2.0 \).

It is of great interest to compare these theoretical predictions with experimental results of type of those given in refs. [7-14] but in the presence of electric field.

Concluding our brief discussion we would like to note that in this work we restricted ourselves to the analysis of the most realistic limit of fast orientational relaxation within the well. In reality, however, with the use of general formula (4.16) one can also describe the manifestation of finiteness of the orientation relaxation time. The case, in which the effect of finiteness is largest, of course, corresponds to \( L_c = 0 \), i.e. the absence of orientational relaxation. In this case the angular dependence of the equilibrium rate \( [K_e(\theta)] \), evidently, results in the highly non-exponential well depopulation kinetics \( n_0(t) \), which can be approximated by the sum of exponentially decreasing (monomolecular) contributions with \( \theta \)-dependent rates, coming from different orientations. With the use of obtained formulas there will be no difficulties to analyze this case as well, when needed.

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