The kinetics of escaping of Brownian particles from a potential well for different space dimensionality. The effect of external force.

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The kinetics of two (2D) and three (3D) dimensional diffusion-assisted escaping of Brownian particles from a potential well in the presence of an external force is analyzed in detail. The kinetics is studied within the two-state model (TSM) proposed for processes in the absence of external force. The generalized variant of this model, taking into account the force effect, is proposed which is shown to be quite accurate for some shapes of the well both for 2D and 3D processes. Within the generalized TSM simple expressions for the well depopulation kinetics and, in particular, for the escape rate are obtained. The effect of the force ($F$) is shown to manifest itself in the escape rate dependence on the only parameter $\varphi = F a / (2 k_b T)$, where $a$ is the Onsager radius of the attractive part of the well $U(r)$, defined by the relation $|U(a)| \approx k_b T$. The limiting behavior of this dependence in the cases of weak and strong force is studied in detail both in 2D and 3D processes. Some applications of obtained results to the analysis of experiments are briefly discussed.

PACS numbers: 82.20.Db, 82.20.Mj, 61.20.Lc

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 recombination process 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, in geminate recombination of ion pairs in non-polar and moderately 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 of the distance of closest approach $d$. This effect is found, for example, in the case of ion pairs in polar liquids.

Concerning the applicability of well-type approximations for the real MFPs, it is also worth mentioning the additional reason: 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 be considered as a cage. 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 two-state model (TSM), i.e. the model of two kinetically coupled states: the quasiequilibrium localized state within the well and the free diffusion state outside the well.

The TSM 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 exponential kinetics is shown to be fairly small\textsuperscript{22,23}.

In this paper we generalize the TSM to describe the effect of the external force on the well depopulation kinetics. The effect is assumed to result only from the force induced change of the rate of escaping from the well and will concentrate on the discussion of the manifestation of the force in the escaping kinetics.

Within the generalized TSM we derive simple formulas for diffusion assisted well depopulation (or escaping) kinetics in two (2D) three (3D) dimensional spaces for different models of the well shape. Moreover, taking into account that in the limit of deep well (which is of main interest of the discussion) the kinetics is close to exponential, special attention is paid to the analysis of the escape rate. The analysis shows that the specific features of the force effect on the escape rate depends on the well shape. This effect can be characterized by the rate dependence on the only parameter. In the cases of weak and strong force the limiting analytical expressions for this dependence are obtained and briefly discussed.

Some possible applications of obtained results are also discussed. It is shown that the kinetic formulas are fairly useful for the analysis of different experiments. As examples we considered recent time resolved experiments on liquid phase chemical reactions\textsuperscript{11,12,13,14}, transient photocurrents arising from dissociation of exciplexes in solutions\textsuperscript{16,17,18,25}, and the kinetics of colloidal particle trapping into and escaping from the optical force induced potential well (tweezers)\textsuperscript{26,27}.

![FIG. 1: The picture of the interaction potential $u(r)$ for two models of its shape: narrow (dashed) and wide (full) well; $a_n$ and $a_w$ are the Onsager radii for these models [defined by $u(a_n) = 1$, ($n = n, w$)], $d$ is the distances of closes approach, and $r_b$ is the coordinate of the bottom.](image)

II. FORMULATION OF THE PROBLEM

We consider the dynamics of the Brownian particle undergoing (2D or 3D) diffusive motion in a spherically symmetric MFP well $U(r) \equiv U(r)$ centered at $r = 0$, where $r$ is the vector of position of the particle. The dependence of $U(r)$ on the distance $r = |r|$ is schematically shown in Fig. 1. The MFP will be characterized by three parameters: the distance $a$ (called hereafter the Onsager radius), at which $U(a) \approx k_B T$, which is defined as:

$$a = \left( \int_{r_b}^{\infty} dr r^{-2} e^{u(r)} \right)^{-1} \quad (2.1)$$

[in Fig. 1 $a_n$ and $a_w$ denote the Onsager radii, corresponding to two models of the well shape, discussed below (in Sec. V)], the distance of closest approach $d$, and the radius $r_b$ of the bottom of the well whose energy is $U(r_b) = -U_b = -(k_B T) u_b$. At $r \sim d$ the MFP $U(r)$ is assumed to be of the shape of a barrier, diffusive passing over 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 $U_\mathbf{F} = U(r) + (\mathbf{F} \cdot \mathbf{r})$. 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 $r$, $\theta$, and $\phi$. However, in the considered case of isotropic diffusion and isotropic initial condition $\rho(r,t=0) = \rho_i(r)$ 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 $r_i \sim r_b$:

$$\rho(r,t=0) = \rho_i(r) = N_i \delta(r-r_i), \quad (2.2)$$

where $N_i = (2\pi r_i)^{-1}$ and $N_i = (4\pi r_i^2)^{-1}$ for 2D and 3D processes, respectively.

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

$$\dot{\rho} = \nabla_r [D(r)(\nabla_r \rho + \rho \nabla_r u_r)], \quad (2.3)$$

where $\nabla_r$ is the gradient operator,

$$u_r(r) = u(r) + (\mathbf{F} \cdot \mathbf{r}), \quad (2.4)$$

with $u(r) = U(r)/(k_B T)$ and $\mathbf{f} = \mathbf{F}/(k_B T)$, is the dimensionless MFP, and $D$ is the diffusion coefficient for the particle, which in our analysis is assumed to be independent of $r$ [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. (2.3) with $r = r_a - r_b$ and parameters expressed in terms of those for separate particles.22
In the absence of force the kinetics of escaping from the spherically symmetric short range potential well $u(r)$ is analyzed 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 eq. (2.3) in the limit of deep well, in which this equation can be solved analytically by expansion in the small parameter $\tau_c/\tau_e \ll 1$, where

$$\tau_c \sim (a - d)^2 / D \quad \text{and} \quad \tau_e \sim \tau_c e^{u_b} \quad (2.5)$$

are the time of equilibration within the well and the time of escaping from the well, respectively.

Analysis of this solution shows that in the lowest order in the parameter $\tau_c/\tau_e$ the Smoluchowski approximation (2.3) is equivalent to the model of two kinetically coupled states: the state within the well and the state of free diffusion outside the well.

### III. TWO-STATE MODEL. 3D PROCESSES.

Originally, the TSM was proposed to treat the kinetics of diffusion-assisted escaping from the well in the case $F = 0$, in which the PDF $\rho(r, t)$ depends only the distance $r = |r|$. In the presence of force $|F| \neq 0$, however, the potential $u_F(r) = u(r) + (F \cdot r)$ in eq. (2.3), is anisotropic, which results in the dependence of the solution $\rho(r, t)$ on particle polar angle $\theta$: $\rho(r, t) \equiv \rho(r, \theta |t|)$.

It is important to note that in the case $F \neq 0$ the TSM 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.

#### A. Kinetic equations

In accordance with rigorous consideration, in the lowest order in $\tau_c/\tau_e \sim e^{-u_a} \ll 1$ 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

$$n(\theta |t|) = 4\pi \int_0^a \! dr r^2 \rho(r, \theta |t|), \quad (3.1)$$

while the evolution of the state outside the well ($r > a$) is governed by the PDF $c(r, \theta |t|)$ within the TSM 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, TSM kinetic equations, describing evolution of PDFs $n(\theta |t|)$ and $c(r, \theta |t|)$ in the presence of an external force, can be written as:

$$\dot{n} = S_a K_+(\theta) c(a |t|) + [\hat{L}_e - \{K_-(\theta) + w_r\}]n, \quad (3.2a)$$

$$\dot{c} = \hat{L}_f c + \{S_a^{-1} K_-(\theta) n - K_+(\theta) c\} \delta(r - a), \quad (3.2b)$$

where $S_a = 4\pi a^2$, 

$$\hat{L}_f = D \nabla_r (\nabla_r + f) \quad (3.3)$$

is the operator, describing 3D-diffusion outside the well, and $L_e$ 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 $K_-(\theta)$. In the considered limit $\tau_c/\tau_e \ll 1$ we will assume the transition rates $K_\pm$ to satisfy the relations:

$$K_+ \to \infty \quad \text{and} \quad K_-/(K_+ + K_-) = K_c(\theta). \quad (3.4)$$

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

Equations (3.2) should be solved with boundary conditions

$$\left(\nabla_r + f \cos \theta\right)c_{|r=a} = 0 \quad \text{and} \quad c_{|r=\infty} \to 0, \quad (3.5)$$

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. (2.2).

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

$$|l| = (l + \frac{1}{2})P_l(\cos \theta), \quad |l| = \int_0^\pi \! d\theta \sin \theta P_l(\cos \theta), \quad (3.6)$$

with $l = 0, 1, \cdots$

$$|n| = \sum_{l=0}^{\infty} n_l |l| \quad \text{and} \quad |c| = \sum_{l=0}^{\infty} c_l |l|, \quad (3.7)$$

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

$$\chi_l = \langle |l|\chi \rangle = \int_0^\pi \! d\theta \sin \theta P_l(\cos \theta) \chi(\theta). \quad (3.8)$$

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

$$|\rho_0| = (2\pi r_a^2)^{-1} |0\rangle \delta(r - r_i). \quad (3.9)$$

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 (3.12) can be solved by the method applied in 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 \( |n(t)\rangle \) and \( |c(r,t)\rangle \) [see eq. (3.17)]. The solution yields for the Laplace transform
\[
|\tilde{n}(\epsilon)| = \int_0^\infty dt e^{-\epsilon t}|n(t)\rangle : \quad (3.10)
\]
\[
|\tilde{n}(\epsilon)| = [\epsilon + w_r - \hat{L}_c + \hat{W}_c(\epsilon)]^{-1}|n_i\rangle. \quad (3.11)
\]
In this expression
\[
w_r = (D/Z_w) \left( \int_{r<d<r<a} dr r^2 e^{-u(r)} \right)^{-1}, \quad (3.12)
\]
is the rate of first order reaction in the well in which
\[
Z_w = \int_{d<r<a} dr r^2 e^{-u(r)} \quad (3.13)
\]
is the partition function for the well \( u(r) = U(r)/(k_BT) \) in the absence of force \( f = 0 \) \[3.22\]
\[
\hat{W}_c(\epsilon) = \hat{G}^{-1}(a,a|\epsilon) \hat{K}_e \quad (3.14)
\]
is the operator of the generalized \( \epsilon \)-dependent escape rate (see below), in which the equilibrium constant \( \hat{K}_e \) is the operator, indicating its dependence on the angle \( \theta \), and \( \hat{G}(a,a|\epsilon) \) is the evolution operator for diffusive motion outside the well (evaluated at \( r = r_1 = a \)):
\[
\hat{G}(a,a|\epsilon) = \langle a|e^{-(\epsilon - \hat{L}_f)}|a\rangle \quad \text{(3.15)}
\]
where \( \varphi = fa/2 \) and
\[
\hat{L}_f = D(\hat{L}_r + r^{-2} \hat{L}_\theta - 1/4 f^2)^2, \quad (3.16)
\]
is the auxiliary operator in which
\[
\hat{L}_\theta = \frac{1}{\sin \theta} \hat{\nabla}_\theta (\sin \theta \hat{\nabla}_\theta) = -\sum_{l=0}^{\infty} l(l+1)|l\rangle\langle l| \quad (3.17)
\]
and
\[
\hat{L}_r = Dr^{-2} \hat{\nabla}_r (r^2 \hat{\nabla}_r) \quad (3.18)
\]
are the operators of free orientational and radial diffusion, respectively.

Noteworthy is that for the initial condition \( |n_i\rangle = (1/2\pi)|0\rangle \).

In what follows we will restrict ourselves to the analysis of the well depopulation kinetics \( \tilde{n}(t) \), whose Laplace transform is given by
\[
\tilde{n}(\epsilon) = 2\pi \int_0^\pi d\theta \sin \theta \tilde{n}(\theta,\epsilon) = 2\pi \langle 0|\tilde{n}(\epsilon)|0\rangle \quad (3.19)
\]
\[
= \langle 0|\epsilon + w_r - \hat{L}_c + \hat{W}_c(\epsilon)|0\rangle. \quad (3.20)
\]

C. General formulas

Formulas (3.15) \[3.17\] allow us to evaluate the operator \( \hat{G}^{-1}(a,a|\epsilon) \) in analytical form and, therefore, analyze the behavior of \( \hat{n}_0(\epsilon) \) relatively easily.

In the evaluation it is worth taking into account the useful relation which simplifies the differential operator in the radial space:
\[
\langle a|e^{-(\epsilon - \hat{L}_f)}|a\rangle = \langle a|e^{-(\epsilon - \hat{L}_f)}|a\rangle, \quad (3.20)
\]
where
\[
\hat{L}_f = D(\nabla^2_r + r^{-2} \hat{L}_\theta - 1/4 f^2). \quad (3.21)
\]
The evolution operator \( \langle a|e^{-(\epsilon - \hat{L}_f)}|a\rangle \) can be obtained in analytical form \[3.26\] with the use of two linearly independent operator solutions \( \hat{\psi}_-(r) \) and \( \hat{\psi}_+(r) \) of equation
\[
(\epsilon - \hat{L}_f)\hat{\psi}_\pm = 0 \quad (3.22)
\]
in which the operator \( \hat{L}_\theta \) is treated as a parameter. These solutions satisfy two boundary conditions corresponding to those given in eq. \( 3.5 \) [after change of variable \( c(r) = e^{-(fr\cos \theta)/2} \psi(r) \)]
\[
(\nabla_r + \frac{1}{2} f\omega)\hat{\psi}_- |r = a = 0 \quad \text{and} \quad \hat{\psi}_+ |r \to \infty \to 0, \quad (3.23)
\]
where
\[
\omega = \sum_{l,l'=0}^\infty |l\rangle\langle l| \cos \theta |l'|\langle l'| \quad (3.24)
\]
is the matrix representation of the function \( \cos \theta \). The matrix elements \( \langle l| \cos \theta |l'\rangle = \langle l|f_1(\cos \theta)|l'\rangle \) are evaluated analytically \[3.26\] 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 Bessel functions \( \hat{K}_{l+1/2}(x) \) and \( \hat{I}_{l+1/2}(x) \)
\[
\hat{X}(r) = \sqrt{r} \sum_{l=0}^\infty |l\rangle X_{l+1/2}(\varphi_x r/a)|l\rangle, \quad (X = I, K): \quad (3.25)
\]
\[
\hat{\psi}_+(r) = \hat{K}(r), \quad \hat{\psi}_-(r) = \hat{I}(r) + \hat{K}(r)\hat{\kappa}, \quad (3.26)
\]
where \( \varphi = fa/2 \),
\[
\varphi_x = \varphi \sqrt{1 + \epsilon/\epsilon f}, \quad \epsilon f = Df^2/4 = (D/a^2)\varphi^2, \quad (3.27)
\]
and \( \hat{\kappa} \) is the matrix determined by the boundary condition at \( r = a \) [see eq. \( 3.29 \)]:
\[
\hat{\kappa} = [\nabla_r \hat{K}(r) - \hat{q}\hat{K}(r)]^{-1} |\hat{q}\hat{I}(r) - \nabla_r \hat{I}(r)|_{r=a}, \quad (3.28)
\]
in which
\[
\hat{q} = a^{-1}(1 - \varphi \omega) \equiv a^{-1}(1 - \varphi \cos \theta). \quad (3.29)
\]
It is worth noting that the matrices $\hat{K}$ and $\hat{I}$ do not commute with the operator $\hat{\omega}$ and, therefore, the order of matrices in expressions (3.22)-(3.28) 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 representation of the evolution operator $\langle r | (\epsilon - \hat{\lambda}_f)^{-1} | r_i \rangle$ in terms of non-commuting solutions $\hat{\psi}_+(r)$ and $\hat{\psi}_-(r)$ is proposed and thoroughly discussed in ref. [29]. This representation generalizes the well known one for scalar solutions $\psi_+(r)$ and $\psi_-(r)$. In general, the proposed representation is fairly cumbersome. In the particular case of solutions given by eq. (3.25), however, it reduces to a more simple one:

$$\langle r | (\epsilon - \hat{\lambda}_f)^{-1} | r_i \rangle = \hat{g}(r, r_i) + \hat{K}(r)\hat{K}(r_i)W_{\hat{K}}^{-1}$$  \hspace{1cm} (3.30) 

In this formula

$$W_{\hat{K}} = D[\nabla_r \hat{I}(r)\hat{K}(r) - \nabla_r \hat{K}(r)\hat{I}(r)] = D$$  \hspace{1cm} (3.31) 

is the Wronskian of two solutions and 

$$\hat{g}(r, r_i) = [\hat{K}(r)\hat{I}(r_i)\theta(r - r_i) + \hat{I}(r)\hat{K}(r_i)\theta(r_i - r)]W_{\hat{K}}^{-1}$$  \hspace{1cm} (3.32) 

is the evolution operator for $\hat{\kappa} = 0$ in which $\theta_H(x)$ is the Heaviside step function.

The validity of the expression (3.30) can be verified by direct substitution to equation inhomogeneous variant of eq. (3.22) with delta-function in the right hand side.

For the particular case $r = r_i = a$ formula (3.30) yields

$$\langle a | (\epsilon - \hat{\lambda}_f)^{-1} | a \rangle = D^{-1}[\hat{q} + \hat{q}_K(\epsilon)]^{-1}$$  \hspace{1cm} (3.33) 

where

$$\hat{q}_K(\epsilon) = -\nabla_r \hat{K}(r)/\hat{K}(r)|_{r=a} = \sum_{l=0}^{\infty} |l\rangle q_{K_l}(\epsilon) |l\rangle$$  \hspace{1cm} (3.34) 

with

$$q_{K_l}(\epsilon) = a^{-1}[I + \varphi_l \hat{K}_{l-} \varphi_l]/K_{l+} \varphi_l]$$.  \hspace{1cm} (3.35) 

Substituting the expression (3.33) into eq. (3.22) and then into eqs. (3.16) and (3.14) we obtain formula

$$\hat{G}^{-1}(a, a|\epsilon) = D[\hat{q} + e^{-\varphi \cos \theta}\hat{q}_K(\epsilon)e^{\varphi \cos \theta}]$$  \hspace{1cm} (3.36) 

For our 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:

$$\hat{L}_c = D_c[\sin \theta \nabla_{\theta}\sin \theta + \nabla_{\theta} \tilde{u}]],$$  \hspace{1cm} (3.37) 

where $D_c \sim D/r_0^2$ is the orientational diffusion coefficient $\tilde{u}(\theta)$ is the effective orientational potential which is determined by the shape of the well (see below).

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 $D_c \gg \tau_e^{-1}$. This relation means that after some time $\sim \tau_e = D_c^{-1}$ of orientational relaxation (of the initial population in the well) the vector of well population $|\hat{n}(t)\rangle$ remains close to the equilibrium one $|\Psi_e\rangle$ during the process:

$$|\hat{n}(t)\rangle \approx \bar{n}(t)|\Psi_e\rangle,$$  \hspace{1cm} (3.38) 

where

$$|\Psi_e\rangle = Z^{-1}_{\theta} e^{-\bar{u}_e(\theta)}, \quad Z_{\theta} = \int_0^\pi d\theta \sin \theta e^{-\bar{u}_e(\theta)}.$$  \hspace{1cm} (3.39) 

Note that within bra-ket notation the adjoint vector $\langle \psi_e|$ coincides with $|\Psi_e\rangle$ and is given by formula

$$\langle \psi_e | = (0) = \int_0^\pi d\theta \sin \theta \ldots,$$  \hspace{1cm} (3.40) 

which can be verified by the relation $\langle \psi_e | \hat{L}_c = 0$ directly following from the definition of $\hat{L}_c$ [see eq. (3.37)]. 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 $||W_{\hat{K}}|| \sim w_0$. In such a case in the lowest order in the parameter $w_0/D_c \ll 1$ we can significantly simplify the general expression for $\bar{n}_0(\epsilon)$ [eq. (3.19)] and thus for the inverse average lifetime $\tilde{\omega}_0 = \tau_0^{-1} = \bar{n}_0^{-1}(0)$ as follows:

$$\bar{n}(\epsilon) = [\epsilon + \bar{w}_r + \bar{w}_c(\epsilon)]^{-1} \quad \text{and} \quad \tilde{\omega}_0 = \bar{w}_r + \bar{w}_c,$$  \hspace{1cm} (3.41) 

where

$$\bar{w}_e(\epsilon) = \langle \psi_e | \hat{W}_c(\epsilon) |\psi_e\rangle \quad \text{and} \quad \bar{w}_e = \bar{w}_c(0).$$  \hspace{1cm} (3.42) 

Equation (3.41) presents the main result of the work for the kinetics of the well depopulation in the limit of fast orientational relaxation.

The depopulation kinetics predicted by formulas (3.41) and (3.42) essentially depends on the shape of the potential well which determines the orientational potential $\bar{u}(\theta)$ in the Smoluchowski-type operator $\hat{L}_c$ [see eq. (3.37)] and, therefore, the equilibrium state $|\Psi_e\rangle$. In our work we will consider two realistic models of the well shape in which simple analytical expressions well depopulation kinetics can be obtained.

### E. Application of 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 \(a = a_w\)), for which \(a - d \ll d\) and the time of equilibration within the well \(\tau_e \sim (a - d)^2/D \ll a^2/D \ll \tau_c\), where \(\tau_c\) is the time of escaping from the well [see eq. (2.23)].

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 \(f d \ll 1\) while \(f a \geq 1\)). 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. (3.41) for the well depopulation kinetics. In our study, in addition to this formula we will also use the representation for \(e^{\pm \varphi \cos \theta}\) in terms of expansion in spherical functions \(P_l(\cos \theta)\):

\[
e^{\pm \varphi \cos \theta} = \sum_{l=0}^{\infty} (\pm 1)^l (l + \frac{1}{2}) I_{l + \frac{1}{2}}(\varphi) P_l(\cos \theta). \tag{3.43}
\]

1. Narrow-well shape

In the case of narrow well, when \(a - d \ll d\), 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 \(u_l(\theta)\) on the orientation angle \(\theta\):

\[
\ddot{u}_l(\theta) \approx u_f(r_b, \theta) \approx u_f + f a \cos \theta \tag{3.44}
\]

with \(f = |f| > 0\), and the force effect on free diffusion in the state outside the well. In eq. (3.43) 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 \(f r_b \approx f a\).

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 \(K_e(\theta)\) on the angle \(\theta\). In such a case \(K_e(\theta)\) is given by the relation \(22, 23, 22\):

\[
K_e(\theta) = K_e^0 = a^2/Z_w, \tag{3.45}
\]

in which the effective partition function \(Z_w\) is given by eq. (3.13), 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. (3.43). This is because the external force leads to the identical change of both the bottom energy \(\ddot{u}_b(\theta) \approx \ddot{u}_b + f a \cos \theta\) and the energy of the free diffusion state at \(r = a\): \(u_f(a, \theta) \approx f a \cos \theta\).

The potential \(\ddot{u}_b(\theta)\) determines the kinetics of orientational relaxation of the population in the well, which is described by the Smoluchowski operator \(3.37\) with

\[
\ddot{u}(\theta) = \ddot{u}_b(\theta) - \ddot{u}_b = 2 \varphi \cos \theta, \quad \text{where} \quad \varphi = fa/2. \tag{3.46}
\]

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

\[
|\Psi\rangle = e^{-\frac{2 \varphi \cos \theta}{Z_0(\varphi)}} \text{ with } Z_0(\varphi) = \frac{\sinh(2\varphi)}{\varphi}. \tag{3.47}
\]

Substitution of formulas (3.47) and (3.43) into the expression (3.42) yields for the function \(w_\epsilon(\epsilon)\):

\[
w_\epsilon(\epsilon)/w^0_\epsilon = Q(\epsilon) = \frac{1}{2} + \varphi \coth(2\varphi) + S(\varphi, \epsilon). \tag{3.48}
\]

In this formula \(22, 23\)

\[
w^0_\epsilon = w^0_\epsilon = w_\epsilon(\varphi = 0, \epsilon = 0) = Da/Z_w \tag{3.49}
\]

is the escape rate in the absence of a force and

\[
S(\varphi, \epsilon) = \frac{2\pi}{\varphi} Z_0(\varphi) \sum_{l=0}^{\infty} (l + \frac{1}{2}) I_{l + \frac{1}{2}}^2(\varphi) q_l(\varphi), \tag{3.50}
\]

where

\[
q_l(\varphi) = a q_{1l}(\epsilon) = l + \varphi K_{l - \frac{1}{2}}(\varphi)/K_{l + \frac{1}{2}}(\varphi). \tag{3.51}
\]

The function \(w_\epsilon(\epsilon) = w^0_\epsilon Q(\epsilon)\) is fairly complicated so that, in general, the depopulation \(n(t)\) can hardly be obtained in analytical form. In the considered limit of deep well, however, the main \(\epsilon\) dependent contribution \(\sim \varphi^2\) comes from the term with \(l = 0\) of the sum in eq. (3.50).

The \(\epsilon\)-dependence of other terms with \(l \geq 1\), which are of higher order in \(\varphi \sim \varphi^2\), can be neglected by taking \(\varphi \approx \varphi_\epsilon = \varphi\). In so doing one gets

\[
S(\varphi, \epsilon) \approx \tilde{S}(\varphi) + \varphi^{-1} \tanh(\varphi)/\varphi - \varphi, \tag{3.52}
\]

where:

\[
\tilde{S}(\varphi) = \frac{2\pi}{\varphi} \left[ \frac{1}{Z_0(\varphi)} \sum_{l=0}^{\infty} (l + \frac{1}{2}) I_{l + \frac{1}{2}}^2(\varphi) q_l(\varphi) \right]. \tag{3.53}
\]

and

\[
w_\epsilon(\epsilon) \approx \tilde{w}_\epsilon + \tilde{w}_\epsilon [(1 + \epsilon/\epsilon_f)^{1/2} - 1] \tag{3.54}
\]

with \(\tilde{w}_\epsilon = w_\epsilon(\epsilon = 0) = w^0_\epsilon Q(0)\) [see eq. (3.12)],

\[
\epsilon_f = (D/a^2)\varphi^2, \quad \text{and} \quad w_\epsilon = w^0_\epsilon \tanh \varphi. \tag{3.55}
\]

The inverse Laplace transformation of \(\tilde{n}(\epsilon)\) yields \(22\):

\[
\tilde{n}(\epsilon) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} dt \exp[\epsilon(ut)] \frac{1 + \epsilon + \gamma(\epsilon_f + \epsilon)^{1/2}}{1 + \epsilon + \gamma(\epsilon_f + \epsilon)^{1/2}}. \tag{3.56}
\]
where $\varepsilon_f = \varepsilon_f / w, w = \tilde{w}_0 - \varphi = w_r + \tilde{w}_e - \varphi$, and

$$\tilde{\gamma} = \sqrt{\frac{w_0^2}{w} \tanh \frac{\varphi}{w} \gamma_e \text{ with } \gamma_e = \sqrt{\frac{a^2 w_0^2}{D}}}. \quad (3.57)$$

The kinetics (3.56) can be expressed in terms of error functions. In the absence of force formula (3.56), naturally, reduces to that obtained earlier for $\varphi = 0$.

$$\bar{n}_{\varphi=0}(t) = \frac{1}{2\pi i} \int_{-i\infty+0}^{i\infty+0} d\varepsilon \frac{\exp[\varepsilon \psi_0 t]}{1 + \varepsilon + \gamma_0 \varepsilon^{1/2}}. \quad (3.58)$$

where $w_0 = w(\varphi = 0) = w_r + w_0^0$ and $\gamma_0 = \tilde{\gamma}_{\varphi=0} = (w_0^0/w_0)^{1/2} \gamma_e$.

Here we are not going to discuss general properties of kinetics $\bar{n}(t)$ but restrict ourselves to the qualitative analysis of its asymptotic behavior at short and long times in the limit $\gamma_e \ll 1$, corresponding to the case of deep potential well, and in the most realistic case of relatively weak force, in which $\varepsilon_f < 1$, i.e. $D/w < 4/f^2$. In this limit at relatively short times $t < w^{-1} \ln(1/\gamma_\varphi) \sim \tilde{w}_0^{-1} \ln(1/\gamma_0)$ the kinetics is exponential.

$\bar{n}(t) \approx e^{-\psi_0 t} (\tilde{w}_0 = w_r + \tilde{w}_e)$. In the opposite limit $t \gg w^{-1} \ln(1/\gamma_\varphi)$ the dependence $\bar{n}(t)$ is non-exponential.

$\bar{n}(t) \sim t^{-3/2} \varepsilon^{-1/4} t^4$.

As expected, in the absence of force ($\varepsilon_f = 0$) the kinetics at long times becomes of inverse type power, which is determined by long trajectories of particles diffusing freely outside the well. Note that for weak force the parameter $\varepsilon_f$ is small: $\varepsilon_f \sim \varphi^2$, and can be neglected. This means that in the weak force limit the accuracy of the kinetics $\bar{n}(t)$ coincides with that for $\varphi = 0$ in which $w = \tilde{w}_0$. Detailed analysis of specific features of the kinetics predicted by formulas (3.59) and (3.57) is made in ref. [24].

It is easily seen that that in the considered limit of deep well the non-exponential inverse power tail of the kinetics $n_0(t)$ is small. Moreover the effect of this tail tends to zero as the value of the force is increased. In such a case the effect of force $\varphi$ on the escaping kinetics is reduced to that on the mean escape rate $\bar{w}_e(\varphi) = w_e(\varepsilon = 0, \varphi)$

$$\bar{w}_e(\varphi) / w_e = \tilde{Q}_n(\varphi) = \frac{1}{2} + \varphi \coth(2\varphi) + \tilde{S}(\varphi). \quad (3.59)$$

Formula (3.59) shows that the force effect on the rate is characterized by the only parameter $\varphi = fa/2$. The numerical calculated universal function $\tilde{Q}_n(\varphi)$ which describes this effect is displayed in Fig. 2a. In addition, some limiting specific features of the behavior of $\tilde{Q}_n(\varphi)$ 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 estimated using only the first term (with $l = 0$) in the sum $\tilde{S}(\varphi)$ in the expression (3.59) for $\tilde{Q}_n(\varphi) = n_0(\varphi)$:

$$\bar{Q}_n(\varphi) = \bar{Q}_n(\varphi) \approx 1 + \varphi = 1 + fa/2. \quad (3.60)$$

b. Strong force limit. In the opposite case $\varphi = fa/2 \gg 1$, denoted as the strong external force limit, the analysis of the dependence $w_e(\varphi)$ with the use of eq. (3.59) is more complicated. However, the corresponding limiting dependence can easily be derived taking into account that in the limit $\varphi \gg 1$ the escaping process is, actually, one-dimensional, for which the $\tilde{Q}_n(\varphi)$-factor is given by:

$$\tilde{Q}_n(\varphi) = \tilde{Q}_n^*(\varphi) \approx 2\varphi = fa. \quad (3.61)$$

In deriving eq. (3.61) we used the expression for one-dimensional escape rate $w_1 = Df/Z^{(1)}_w$, in which $Z^{(1)}_w = \int_{d<r<a} dr e^{-w(r)} \approx Z_w/a^2$ is the one-dimensional partition function.

Note that this relation is also confirmed by the semi-quantitative estimation with the use of eq. (3.56) by truncating the sum at $l = l^* \sim \sqrt{\varphi} \gg 1$ and then summing up the terms which mainly contribute to $\tilde{S}(\varphi)$.

c. Interpolation formula. The limiting results obtained above for $\varphi \ll 1$ and $\varphi \gg 1$ can be combined into a simple algebraic interpolation formula

$$\tilde{Q}_n(\varphi) \approx Q^{(1)}_n(\varphi) = 1 + \varphi(2 - e^{-\varphi}) \quad (3.62)$$

which reproduces function $\tilde{Q}_n(\varphi)$, numerically evaluated using eqs. (3.59) and (3.57), with accuracy $\sim 3\%$ (see Fig. 2a).
2. Wide-well shape

Another form of the well shape, in which analysis of the escape rate \( w_e \) can be made analytically, corresponds to the small distance of closest approach, or large \( a \), for which \( d \sim r_b \ll a \). In this case in a fairly wide region of relatively strong force \( f < 1/d, 1/r_b \) the escape kinetics is fairly accurately described by the TSM (3.24).

It is important to note that the inequality \( f r_b < 1 \) 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:

\[
|\Psi_e(\varphi)\rangle = |0\rangle. \tag{3.63}
\]

This, in turn, means that the partition function \( Z_w \) is independent of the angle \( \theta \) and is given by eq. (3.13).

The effect of force, however, manifests itself in the anisotropy of the activation energy of escaping \( u_a(\theta) \):

\[
u_a(\theta) \approx u_f(\theta, a) \approx u_b + 2\varphi \cos \theta, \quad (\varphi = fa/2), \tag{3.64}
\]

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

\[
K_e(\theta) = K_e^0 e^{-2\varphi \cos \theta}, \tag{3.65}
\]

where \( K_e^0 \) is the isotropic equilibrium constant in the absence of external force given by eq. (3.64).

Formula (3.65) calls for some additional comments especially concerning its applicability. The fact is that the value of \( K_e(\theta) \) at each particular \( \theta \) is determined assuming local quasiequilibrium of the population outside and inside the well in the region close to \( r = a \) 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 \( \varphi = fa/2 \ll 1 \) the time of passing over the escape barrier width \( \delta_b \sim \min\{a, f^{-1}\} \) (the width of the region of transition from the inner part of the well to the outer one), \( \tau_e \sim \delta^2_b/D \) is comparable with the time of reorientation \( \tau_e \sim a^2/D \). It is worth noting, however, that the accuracy of quasiequilibrium assumption becomes better with increasing \( f \) since the for \( \varphi = fa/2 \gg 1 \) the width \( \delta_b \ll a \) and, correspondingly, \( \tau_e \ll \tau_e \).

The above-mentioned arguments lead us to the conclusion that in the considered limit of small radius of the well bottom the TSM 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 (3.41), (3.42), 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 \( K_e(\theta) \) of type of eq. (3.42) over the isotropic equilibrium state is similar to the average over the equilibrium distribution (3.41), except for the partition function \( Z_0(\varphi) \) [eq. (3.44)], which should be replaced by \( Z_0(\varphi \rightarrow 0) = 2 \) corresponding to the isotropic distribution. These simple algebraic manipulations result in the following expression for \( w_e(\varphi) \)

\[
\bar{w}_e(\varphi)/w^0_{e_n}(\varphi) = \bar{Q}_w(\varphi) = \frac{1}{2} Z_0(\varphi) e^{-2\varphi} \bar{Q}_n(\varphi) \tag{3.66}
\]

where \( Z_0(\varphi) \) and \( Q_n(\varphi) \) are determined in eqs. (3.47) and (3.59), respectively, and

\[
w^0_{e_n}(\varphi) = w^0_{e} e^{2\varphi} \tag{3.67}
\]

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

\[
u^* = u_a(\theta = \pi) = u_b - 2\varphi. \tag{3.68}
\]

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 \( \varphi \rightarrow \infty \). 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 \( \varphi \rightarrow \infty \), looking unexpected at first sight, can be understood by simple analysis (see below).

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

\[
\bar{Q}_w(\varphi) = \bar{Q}_w(\varphi \ll 1) \approx 1 - \varphi. \tag{3.69}
\]

Such a behavior of \( Q_w(\varphi) \) results from using the \( \varphi \)-dependent normalizing rate \( w^0_{e_n} \sim e^{2\varphi} \) (instead of \( w^0_{e_n} = w^0_{e} \)) in the definition of \( Q_w(\varphi) \).

2b. Strong force limit. In the opposite limit \( \varphi = fa/2 \gg 1 \) 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 Arrhenius-type expression for \( w_e \), at \( \varphi \gg 1 \) it monotonically decreases approaching the asymptotic value \( 1/2 \).

The obtained \( Q_w(\varphi) \)-dependence at \( \varphi \rightarrow \infty \) can easily be understood by taking into account that, according to formula (3.65), in the case of wide well for strong external forces the flux of escaping particles is highly localized in a small region of orientations \( \delta \theta = \pi - \theta \lesssim 1/\sqrt{\varphi} \ll 1 \). 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 \( J_\varphi \sim \varphi \), as it follows from eq. (3.61), so that \( Q_w(\varphi) \sim s_c J_\varphi \sim \text{const} \). The exact estimation can be obtained just by substitution of the corresponding limiting expression (3.61) into eq. (3.60):

\[
\tilde{Q}_w^b(\varphi) = \frac{1}{2} Z_0(\varphi) e^{-2\varphi} \tilde{Q}_n^b(\varphi) |_{\varphi \gg 1} = \frac{1}{2} \tag{3.70}
\]

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. (3.62):

\[
\tilde{Q}_w(\varphi) \approx \tilde{Q}_n^b(\varphi) = \frac{1}{2} Z_0(\varphi) e^{-2\varphi} \tilde{Q}_n^b(\varphi). \tag{3.71}
\]

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

### IV. ESCAPING KINETICS IN 2D CASE

In this section we briefly discuss the kinetics of force affected two dimensional escaping of Brownian particles from the well.

The formal analysis of the 2D problem is very similar to that in the 3D cases made above. The differences reduce to a few changes of analytical forms of dependences on the parameters of the model.

First, the 2D TSM equations are similar to 3D eqs. (3.2) but with 2D variants of parameters and operators: \( S_n = 2\pi a \), \( L_f = D \nabla_\varphi (\nabla_\varphi + f) \) is the operator describing 2D diffusive motion outside the well, and \( L_c = D_c \nabla_\theta (\nabla_\theta + \nabla_\varphi u_\varphi(\theta)) \) is the operator of orientational (circular) diffusion in the circular 2D space. The analytical form of the equilibrium constant \( K_c(\theta) \) is also somewhat different from those discussed above in 3D case (see below) 3.13.34

Similar to 3D case the orientation dependent population of the well \( n(\theta,t) \) and PDF of particles outside the well \( c(r,\theta,t) \) are conveniently represented as vectors by expanding them in basis of vectors

\[
|l| = N_l \cos(l\theta), \quad |l| = \int_0^\pi d\theta \cos(l\theta), \ldots, \quad (l \geq 0), \quad (4.1)
\]

where \( N_{l\geq1} = 1/\pi \) and \( N_0 = 1/(2\pi) \).

The solution of (2D) TSM equations for vectors \( |n(t)\rangle \) and \( |c(r,t)\rangle \) by the method applied in the 3D case yields for \( \delta_0(\epsilon) = \int_0^\pi d\theta \bar{n}(\theta,\epsilon) = \langle 0|\bar{n}(\epsilon) \rangle \) the expression (3.19). In the fast orientational relaxation limit this expression, naturally, reduces to formula (3.11). In both these equations the operator \( \hat{W}_c(\epsilon) \) is given by eq. (3.14) in which

\[
\hat{G}^{-1}(a,a|\epsilon) = D e^{-\varphi \cos \theta} \hat{q}_K(\epsilon) e^{\varphi \cos \theta} - \frac{1}{2} f \cos \theta, \tag{4.2}
\]

where \( \hat{q}_K(\epsilon) = \sum_{l=0}^\infty |l| q_{K_l}(\epsilon)/|l| \) with

\[
q_{K_l}(\epsilon) = e^{-1} [l + \varphi K_{l-1}(\varphi)/K_l(\varphi)]. \tag{4.3}
\]

With the use of thus obtained general expressions and the relation \( e^{\pm \varphi \cos \theta} = I_0(\varphi) + 2 \sum_{l=1}^\infty I_l(\varphi) \cos(l\theta) \tag{4.4} \)

one can derive relatively simple formulas for the depopulation kinetics \( r_0(t) \) within two models of the well shape discussed in Sec. IIIID: the models of narrow and wide well.

It is worth noting that the kinetics of 2D diffusion-assisted reactions are essentially different from that of 3D processes because 2D diffusion is recurrent while 3D one is transient. In the particular case of diffusion-assisted escaping from the well the recurrent nature of 2D diffusion manifests itself in strongly non-exponential escaping kinetics even in the case of deep well. Moreover in the absence of external force \( \bar{w}_c = w_c(\epsilon = 0) = \langle \Psi_c|\bar{W}_c(\epsilon = 0)|\Psi_c \rangle = 0 \), i.e. the probability of escaping from the well is zero and escaping is always reversible (which is quite natural for recurrent process).

This, in turn, means that unlike 3D escaping processes, in the absence of force, the efficiency of 2D ones cannot be characterized by the only parameter. The external force, however, results in the irreversible escaping flux which shows itself in \( \bar{w}_c(\varphi \neq 0) \neq 0 \) and nearly exponential escaping kinetics approaching the exponential with the increase of force. Below we will restrict ourselves to the evaluation the mean escape rate \( \bar{w}_c(\varphi) \) describing the force effect on the escape process, which, as we have already mentioned above, is getting closer to exponential with increasing the force \( \varphi \).

#### A. Narrow-well shape

In the 2D case of narrow wells \( a - d \ll d \), which is defined similarly to the 3D case (see Sec. III.E.1.), in the large region of forces \( f \) the force effect reduces to the change of the quasiequilibrium distribution within the well. The corresponding 2D quasiequilibrium state \( |\Psi_c(\epsilon)\rangle \) can be written as

\[
|\Psi_c(\epsilon)\rangle = I_0^{-1}(2\varphi) e^{-2\varphi \cos \theta}. \tag{4.5}
\]

With the use of this expression and formulas, derived above, we get

\[
\bar{w}_c(\varphi)/w_{c,n}^* = \tilde{Q}_n(\varphi) = \varphi I_1(2\varphi)/I_0(2\varphi) + \tilde{S}_p(\varphi), \tag{4.6}
\]

where

\[
w_{c,n}^* = D/Z_w^{(2)}, \quad \text{with} \quad Z_w^{(2)} = \int_{d < r < a} dr \, r e^{-u(r)}. \tag{4.7}
\]
is the auxiliary parameter of dimensionality of rate and

\[ \tilde{S}(\varphi) = \varphi I_0^{-1}(2\varphi) \sum_{i=0}^{\infty} \zeta_i I_i^2(\varphi) K_{i-1}(\varphi) K_i^{-1}(\varphi), \tag{4.8} \]

with \( \zeta_0 = 1 \) and \( \zeta_{\geq 1} = 2 \).

The numerically calculated dependence \( \bar{w}_e(\varphi) \) is displayed in Fig. 3. As expected \( \bar{w}_e(\varphi \to 0) \to 0 \). In the opposite limit \( \varphi \gg 1 \) we get the dependence

\[ \bar{w}_e(\varphi \gg 1)/w_{e\infty}^* \approx 2\varphi = fa \tag{4.9} \]

similar to that obtained in the 3D case and corresponding to the 1D escaping mechanism (see Fig. 3). To clarify this statement note that for narrow wells \( Z_{w}^{(2)} \approx a Z_{w}^{(1)} \), where \( Z_{w}^{(1)} = \int_{d<r<a} dr e^{-u(r)} \) is the 1D partition function, and therefore \( \bar{w}_e(\varphi \gg 1) \approx 2\varphi w_{e\infty}^* = fa(D/Z_{w}^{(2)}) \approx Df/Z_{w}^{(1)} \).

### B. Wide-well shape

The opposite limit of (2D) wide wells \((a-d \gg d)\), defined by analogy to the 3D case (Sec. III.E.2), can be treated with the use of formulas obtained in the narrow-well case. To do that one should take into account, similarly to the 3D case, that in the wide-well limit \( |\Psi_e| = 0 \) and \( K_{\theta}(\theta) \sim e^{-2\varphi \cos \theta} \). This means (as it is mentioned in Sec. III.E.2) that both limits the average \( \bar{w}_e(e) = (|\Psi_e|W_e(e)|\Psi_e|) \) is similar from mathematical point of view and differ only of the normalization factor \( I_0^{-1}(2\varphi) \)

\[ \bar{w}_e(\varphi \gg 1)/w_{e\infty}^* = \tilde{Q}_w(\varphi) = \bar{Q}_n(\varphi) I_0(2\varphi) e^{-2\varphi}, \tag{4.10} \]

where

\[ w_{e\infty}^* = w_{e\infty}^* e^{2\varphi}. \tag{4.11} \]

The dependence \( \bar{w}_e(\varphi) \) is shown in Fig. 3. In agreement with the above statement in the limit of weak force \( \bar{w}_e(\varphi \to 0) \to 0 \). In the opposite limit of strong force \( \varphi \gg 1 \), however, one gets \( \bar{w}_e(\varphi) \sim \sqrt{\varphi} \) as it follows from the analysis of the numerically calculated function \( \bar{w}_e(\varphi) \) presented in Fig. 3. The dependence \( \bar{w}_e(\varphi \gg 1) \sim \sqrt{\varphi} \) can easily be understood by estimations similar to those, clarifying the \( \bar{w}_e(\varphi) \)-dependence of \( \varphi \) at \( \varphi \gg 1 \) (see Sec. III.E.2). The fact is that for \( \varphi \gg 1 \) the density escaping flux \( J_\varphi \sim \varphi \) is localized in the small sector of size \( \delta \theta \sim 1/\sqrt{\varphi} \) around the most favorable direction \( \theta = \pi \). Therefore the total escaping flux \( Q_w \sim J_\varphi \delta \theta \sim \sqrt{\varphi} \). Asymptotic dependence \( \bar{w}_e(\varphi \gg 1) \) can be obtained with eq. (4.10) and formula (4.9):

\[ \bar{w}_e(\varphi \gg 1)/w_{e\infty}^* \sim \sqrt{\varphi}/\pi. \tag{4.12} \]

High accuracy of this expression at \( \varphi \gg 1 \) is demonstrated in Fig. 3.

### V. DISCUSSION AND APPLICATIONS

#### A. General remarks

This work concerns detailed theoretical study of the effect of the external force \( f = F/(k_B T) \) on the kinetics of diffusion-assisted depopulation of a deep isotropic potential well in 2D and 3D processes. Fairly simple matrix expressions for the depopulation kinetics are obtained and thoroughly analyzed.

In our work we have concentrated on the analysis in the most physically reasonable limit of fast orientational relaxation of the population 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 in the wide region of parameters of the model both for 2D and 3D processes. The total depopulation rate in this case is shown 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 \( a - d \ll d \)) and wide wells with large effective Onsager radius \( a \gg d \).

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 (or small distance \( d \)) 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 of our analysis with majority of those obtained earlier, since these 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 \( fa \ll 1 \) the force effect on the probability \( P_e(f) \) of escape from the Coulomb potential, found in ref. [5], is independent of the initial distance between ions and is represented in the form \( P_e(f) \approx P_e(f = 0)/(1 + fa/2) \), which is in apparent agreement with the field dependence of the escape rate obtained in our work [see eqs. (3.60) and (3.69)].

Noteworthy is also that in the strong force limit the escaping process becomes nearly one-dimensional in both cases of well shape considered in both for 2D and 3D...
processes. In this limit the escape rate is determined by the 1D flux in the small region of favorite orientations corresponding to θ ~ π. This fact allows one to easily improve the considered TSM, 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 TSM is actually assumed to be of cusp shape.

Concluding this short discussion of results 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 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 \( L_e = 0 \), i.e. the absence of orientational relaxation. In this case the angular dependence of the equilibrium rate \( |K_e(θ)| \), 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 \( θ \)-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.

In our further discussion possible applications of formulas obtained we will consider some types of processes recently actively analyzed experimentally.

B. Condensed phase reaction kinetics.

The obtained formulas are quite suitable for the analysis of diffusion-assisted condensed phase geminate reactions. The effect of external force on escaping and reaction yields is of special interest in the particular case of reaction ion-pair recombination reactions in polar solids and liquids, in which the external force can be realized by applying electric field. There are a number of experimental time resolved spectroscopic studies of reactions with the participation of ions. 11, 12, 13, 14, 15

Traditionally the results of such investigations are analyzed with the use of model calculations in which interaction is assumed to be pure Coulomb [..]. It is worth noting, however, that in polar media the medium affected interaction, which can be described by the MFP, strongly deviates from the from the Coulomb one [..]: unlike the Coulomb potential the MFP oscillates at short distances of order of molecular size [..]. At distances close to that of the first coordinate shell the MFP has a most deep well, whose depth can be much larger than \( k_BT \) for dielectric constants \( ε \gg 20 \). In this case the proposed approximation of the realistic interaction with the use of well-type potential is much more accurate than pure Coulomb potential approach.

Some of earlier results of the proposed TSM, concerning the kinetics of processes in the absence of external force \( f = 0 \), have already been successfully applied to the analysis of kinetics of some liquid-phase reactions 27, 8, 9. Concerning the results obtained above for the case \( f ≠ 0 \), note that the most convenient for experimental analysis is not the force dependent inverse mean lifetime \( \bar{ν}_0(φ) \) [see eq. (3.22)], but the difference \( \bar{ν}_0(φ) - 1 = \bar{ν}_0(φ) - \bar{ν}_0(0) \), which is independent of the rate \( \bar{ν}_0 \) of reaction within the well (assumed to be independent of \( φ \)). The corresponding dimensionless parameters

\[
δQ_ν(φ) = |w_0(φ) - w_0(0)| / w_ν(0)(φ), \quad (ν = n, w),
\]

are directly related to \( Q_ν(φ) \):

\[
δQ_n(φ) = Q_n(φ) - 1, \quad δQ_w(φ) = Q_w(φ) - e^{-2φ}.
\]

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

It is of great interest to compare these theoretical predictions with experimental results of type of those given in refs. [9-13] but in the presence of electric field.

C. Transient photocurrents.

Recently considerable interest has been attracted to experimental investigations of the recombination kinetics of ion pairs in non-polar and moderately polar liquids with time resolved measurements of transient photocurrents 16, 17, 18, 25. The photocurrent is found to be fairly sensitive to the spatial evolution of photoinduced ion pairs and, in particular, to the recombination kinetics.

The proposed theory can be very fruitful for the interpretation and description of experiments on transient photocurrents. The fact is that the TSM considered above enables one to quite accurately describe the spatial evolution of ion pairs without solving the Smoluchowski equations which are rather complicated even for restrictive models of the interparticle interaction. In this short discussion we will outline and illustrate the possibilities of the proposed method.

Recall that the TSM is valid in the limit of the time \( τ_c \) of the PDF relaxation in the well much shorter than the average lifetime \( \bar{τ}_0 = \bar{w}_0^{-1} \) in the well [according to eq. (3.11) \( \bar{w}_0^{-1} \approx \bar{w}_e^{-1}, \bar{w}_r^{-1} \)]. Noteworthy is also that the TSM describes the kinetics at relatively long times \( t > τ_c \). In reality, however, the method can straightforwardly be extended to also treat the PDF relaxation at short times \( t ≲ τ_c \) (i.e. relaxation within the well) just because of assumed essential difference between thermalization time \( τ_c \) and \( τ_0 \). This difference leads, in fact, to the independence of the processes of intrawell relaxation and well depopulation, which can be described separately.
The initial stage of relaxation of the ion-pair PDF within the well results in the transient photocurrent \(J_r(t)\) at times \(t \lesssim \tau_r\). The relaxation kinetics depends on the well shape. Below, for simplicity we will consider the case of narrow well and assume that the initial PDF in the well is isotropic. For narrow wells the intrawell PDF relaxation can, in turn, be separated into two stages: radial and orientational relaxation. The first stage is the radial relaxation whose characteristic time is \(\tau_w = \Delta_w^2 / D\), where \(\Delta_w = a - d < d\), is shorter than the time \(\tau_c = Dc^{-1} \approx r_b^2 / D\) of the second stage of orientational relaxation to the anisotropic quasi-equilibrium ion-pair PDF in the well of the potential \(u(r)\) (2.4).

Together with the final stage, described by the TSM, the kinetics of the transient current relaxation can be represented as follows:

1. At \(t \sim \tau_w\) (the stage of radial relaxation in the well) the transient current can approximately be described by the simple expression

\[
J_w(t) \approx J_0 + (J_0 - J_0)e^{-t / \tau_w},
\]

where \(J_0 = DF/\delta f\) is the current produced by freely diffusing ion pair [initial current for the isotropic initial PDF (2.2)] and \(\hat{J}_0 = J_0\) is the final current after radial relaxation [see eq. (5.4)].

2. At \(t \sim \tau_r\) (the stage of orientational relaxation in the well) the current \(J_w(t)\) can be evaluated using the relation \(\hat{J}_w = \hat{p}(t)\), where \(\hat{p}(t) = c(r_f(t))\) is the the average electric dipole moment of ion pairs within the well, in which \(r_f\) is the projection of radius vector of the ion pair on the direction of the field: \(r_f = (r \cdot f) / f\). For the case of narrow well the derivative of the average dipole moment \(\hat{p}(t)\) is easily evaluated in the limit of weak external force in the lowest order in \(f\) (in the linear response approach):

\[
J_w(t) \approx J_0 e^{-2Dr_c t} \quad \text{with} \quad \hat{J}_w = \frac{2}{3} J_0,
\]

where \(J_0\) is defined in eq. (5.4), and \(Dc \approx D / r_b^2\) (\(r_b\) is the radius of the well bottom).

3. At \(t > \tau_c\) (the stage escaping from the well) the TSM predicts the following expression for the current:

\[
J_w(t) \approx J_0 n_w(t) \quad \text{with} \quad n_w(t) = n_s(t) - n(t).
\]

Here

\[
n_s(t) = 1 - w_r \int_0^t d\tau \ n(\tau)
\]

is the ion-pair survival probability.

Taking into account different time scales of these three kinetic stages one can describe the current relaxation kinetics by the combined expression

\[
j_w(t) = J_w(t) / J_0 \approx \frac{1}{3} (2 + e^{-t / \tau_w}) e^{-2Dt / r_b} + n_w(t).
\]

This simple expression enables one to quantitatively describe the specific features of the current relaxation kinetics in a wide region of times. In deriving eq. (5.7) we have assumed the well to be narrow. As applied to the ion pair recombination and transient current relaxation this assumption is quite appropriate in the limit of relatively polar solvent with dielectric constant \(\epsilon_s \gtrsim 15\), in which the ion-pair MFP \(\bar{u}(r)\) is known to be of the shape of deep narrow well at short distances \(r \sim d\).

Formula (5.7), however, turns out to be of quite reasonable accuracy even in the case of diffusion-assisted processes in the pure Coulomb potential \(u(r) = a/r\) with nearly reflective (low reactivity) boundary condition at \(r = d\), whose well (at \(r \geq d\)), at first sight, can hardly be treated as narrow for \(a \gg d\). The fairly good accuracy of eq. (5.7) in this case results from the cusp-like shape of the well at \(r \sim d\), where the major of the well population is localized (see below).

To demonstrate the accuracy of eq. (5.7) we will compare its predictions with recent calculations of the current relaxation kinetics based on numerical solution of the Smoluchowski equation. These calculations have been made for \(u(r) = a/r\), with \(a = 63.3\) A, and for small force \(\varphi = 0.05\), which only very weakly affects the escaping rate \(\bar{w}_r\). The other parameters of the model are \(D = 3.1 \times 10^{-5}\) cm²/s of relative diffusion of ions, the contact distance \(d = 9\) A, and the reactivity \(\sigma_r\), which determines the reactive flux at a contact distance \(r = d\): \(D[(\nabla r \rho + (\nabla r u + f \cos \theta)\rho)]_{r=d} = (\rho / 4\pi D^2)(\bar{r})_{r=d}\), and whose value \(\sigma_r = 0.01 \cdot (4\pi Da)\) corresponds to the weak reactivity limit.

Recall that the discussed TSM is applicable in the limit of small \(\gamma_e = (a^2 w_0 / D)^{1/2} \ll 1\) [see eq. (5.7)]. However, for the parameters of the model chosen above \(\gamma_e \approx 0.9\), i.e. the TSM is not expected to reproduce the exact numerical results very accurately. Nevertheless, even in this case the accuracy of this model appears to be quite good (see below).

Noteworthy is also that in the considered model assuming not very deep well of cusp-like shape the quasi-equilibrium PDF in the well is somewhat displaced to \(r > d\). In this case, with reasonable accuracy one can put \(r_0 = \bar{r} = \int_0^d dr e^{-u(r)} / Z_w \approx 19\) A so that \(Dc \approx 8 \times 10^8\) s⁻¹ [eq. (5.3)]. For this value of \(r_0\) one can also approximately estimate \(\tau_w^{-1} / \tau_r^{-1} \approx D / (r_b - d)^2 \approx 3.1 \times 10^9\) s⁻¹.

For the chosen parameters of the model the survival probability \(n_s(\infty) = n_s(t \to \infty) \approx 0.085\). Taking into account that the TSM exactly predicts the asymptotic (at \(t \to \infty\)) behavior of the escaping kinetics we can write the relation \(n_s(\infty) = \bar{w}_r / \bar{w}_0 = \bar{w}_r / (\bar{w}_r + \bar{w}_e) = 0.085\).

Figure 3 displays the comparison of the time dependent survival probability \(n_s(t)\) and the transient current \(J_w(t)\) with those calculated by numerical solution of the Smoluchowski equation. For convenience of the comparison with numerical results in Fig. 3 we use the dimensionless time \(\tau = Dt / a^2\). The comparison shows good accuracy of the TSM prediction for the kinetics \(n_s(t)\), which is determined by the evolution of the system at long times \(\tau > 0.1\). As for the time dependence of the transient current \(J_w(\tau)\), it is also quite accurately reproduced at
long times, when the contribution of \( n_s(t) \)-kinetics [represented by the last term in eq. (5.7)] is dominated. Some (not very strong) difference between analytical and numerical behavior at shorter times \( \tau < 0.1 \) is a result of above-mentioned approximations applied in deriving eq. (5.7) for \( J_e(t) \) at first two short time stages of the current relaxation.

D. Optical tweezers.

The important problem which have recently attracted much attention, and in study of which the TSM can be very suitable is the kinetics of trapping of colloidal particles by optical tweezers, i.e. by the optical force induced potential wells (arising due to gradients of laser beam intensity). Detailed experimental investigations show that the tweezers potential well \( u(r) \) is highly localized (the size is about \( \mu \text{m} \)) and is expected to be highly localized\(^{21}\). Of course, in general the well is not spherically symmetric. Moreover, recently the axial (non-potential) component of the trapping force is found\(^{22}\). However, to a good accuracy, for description of trapping and escaping kinetics one can neglect these non-trivial contributions to the trapping force and use the isotropic approximation for the tweezers well.

The proposed theory based on the TSM is very useful for the analysis of the kinetics of trapping into and escaping from tweezers potential well. Application of the TSM significantly simplifies the problem of description of the kinetics thus allowing for the analysis of more complicated effects of a large number potential wells\(^{23}\).

Of special interest is the effect of well motion on the trapping/escaping kinetics discussed in a number of papers concerning possible applications of tweezers\(^{24}\). This effect is known to reduce to that of the external force discussed above. The fact is that the well motion induces the force \( F \) acting on a particle. In the frame of reference, moving with the well, the force is proportional to the well velocity \( v_c = \mu^{-1}v \), where \( \mu = D/(k_B T) \) is the mobility of the particle, i.e. \( F_c = D^2 \). Note that this relation holds in the case of time dependent velocity \( v(t) \) as well.

Thus the problem of the analysis of the effect of well motion is equivalent to that thoroughly discussed above with the external force \( F = F_c \) (and without reactivity, i.e. \( w_r = 0 \)). In our consideration we have assumed that \( F \) is independent of time. The case of time dependent \( F \) [for example, because of time dependent velocity \( v(t) \)] is, in general, much more complicated and can hardly be analyzed analytically. However, in a quite realistic case of relatively slowly changing force, for which the characteristic changing time \( \tau_f > 1/\bar{w}_0 \), one can treat the force effect adiabatically evaluating the nearly exponential escaping kinetics with the use of formulas derived above for static \( f \), in which the escaping rate \( \bar{w}_e(\psi) \) is replaced by the corresponding time dependent expression \( \bar{w}_e(\psi(t)) \).

Acknowledgements. The author is grateful to Dr. V. P. Sakun for valuable discussions. The work was supported by the Russian Foundation for Basic Research.

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