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 (TSM) of the process which is known to be valid in the deep well limit in the absence of external force. The generalized variant of the TSM, 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 TSM, simple expressions for the well depopulation kinetics and, in particular, for the escape rate are obtained. These expressions show that the effect of a force (F) manifests itself in the escape rate dependence on only one parameter $\varphi = Fa/(2k_bT)$, where a is the Onsager radius of the attractive part of the well $U(r)$, defined by the relation $|U(a)| \approx k_bT$. 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.

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.[1−4] The active interest of scientists to this phenomenon results from its great practical importance.

One of the most important systems, in which the force effect is investigated very thoroughly, is recombining geminate ion pairs, undergoing relative diffusion in the electric field.[2,3,5,6] 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 the 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.[2,7−9] Even in this most simple formulation, the problem can, in general, be solved only numerically, though detailed analytical analysis of some simple variants of the problem has also been made,[2,7] for example, within the prescribed diffusion approximation.[10]

Recent advances in time-resolved studies of charge transfer and escaping processes in fast geminate reactions[19] and, in particular, geminate reactions involving ions and ion pairs in nonpolar and polar liquids[11−26] 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.[2] 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 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 Figure 1) with a markedly high barrier at distances r of the order of the distance of closest approach d. This effect is found, for example, in the case of ion pairs in polar liquids.[2,27,28]

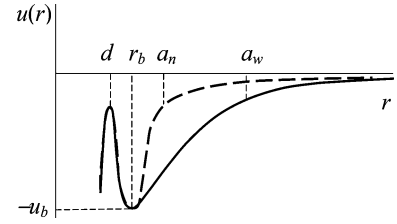

Figure 1. The picture of the interaction potential $u(r) = U(r)/(k_BT)$ for two models of its shape: narrow (dashed) and wide (full) well; a_n and a_w are the Onsager radii for these models (defined by $u(a_\nu) = 1$ (ν = n, w)), d is the distance of close approach, and r_b is the coordinate of the bottom.

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 Figure 1 is in their cusp 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 quasi-equilibrium 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.[29−32] 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 quasi-equilibrium localized state within the well and the free diffusion state outside the well.[31]

The TSM enables one to obtain the well depopulation kinetics in a relatively simple analytical form. The kinetics, determined by the monomolecular reactive crossing over the barrier at $r \sim$

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d and escaping from well (cage), appears to be nonexponential, in general. In the limit of a deep well, however, the deviation from the exponential kinetics is shown to be fairly small.[30,31]

In this paper we generalize the TSM to describe the effect of the external force on the well depopulation kinetics. We assume that effect results only from the force-induced change of the rate of escaping from the well without changing the reaction rate in the well.

Within the generalized TSM we derive simple formulas for the well depopulation (or escaping) kinetics for different models of the well shape. Moreover, taking into account that in the limit of a deep well (which is of main interest in 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 derived formulas are fairly useful for the analysis of different experiments. As examples we considered recent (time-resolved) experiments on liquid phase chemical reactions,[19−22] transient photocurrents arising from dissociation of exciplexes in solutions,[24−26,33] and the kinetics of colloidal particle trapping into and escaping from the optical force induced potential well (tweezers).[34,35]

II. Formulation of the Problem

The main purpose of the work is to analyze the kinetics of diffusion-assisted escaping of the Brownian particle from the MFP well $U(\mathbf{r})$ in the presence of the external force $-\mathbf{F}$, i.e., escaping from the well of the potential $U_\mathbf{f} = U(\mathbf{r}) + (\mathbf{F}\cdot\mathbf{r})$, where $\mathbf{r}$ is the vector of the particle position. For definiteness we assume that the force is directed along the axis z: $\mathbf{F} = (0, 0, F)$.

The well $U(\mathbf{r})$ is suggested to be spherically symmetric: $U(\mathbf{r}) \equiv U(r) = (k_\mathrm{B}T)u(r)$, and centered at $r = 0$. The dependence of $U(r)$ on the distance $r = |\mathbf{r}|$ is schematically pictured in Figure 1. The well will be characterized by three parameters: the distance a (called hereafter the Onsager radius), at which $U(a) \approx k_\mathrm{B}T$, defined as

$$a = \left(\int_{r_\mathrm{b}}^{\infty} \mathrm{d}r\, r^{-2} \mathrm{e}^{u(r)}\right)^{-1} \tag{2.1}$$

(in Figure 1 a_n and a_w denote the radii in two models of the well shape, discussed in section V), the distance of closest approach d, and the radius r_b of the well bottom whose energy is $U(r_\mathrm{b}) = -U_\mathrm{b} = -(k_\mathrm{B}T)u_\mathrm{b}$. At $r \sim d$ the MFP $U(r)$ is assumed to be of the shape of a barrier, diffusive crossing over which models the reaction in the well.

The diffusive space−time evolution of the Brownian particle is described by the PDF $\rho(\mathbf{r}, t)$, which in spherical coordinates $\mathbf{r} = (r \sin\theta \cos\phi, r \sin\theta \sin\phi, r \cos\theta)$ depends, in general, on all three variables (r, θ, ϕ). However, in the case of isotropic diffusion and initial condition $\rho(\mathbf{r}, t = 0) = \rho_i(r)$, considered in this work, the PDF $\rho(\mathbf{r}, t)$ is independent of the azimuthal angle ϕ so that $\rho(\mathbf{r}, t) \equiv \rho(r, \theta|t)$. In our analysis we will assume that particles are created within the well at initial distance $r_\mathrm{i} \sim r_\mathrm{b}$

$$\rho(\mathbf{r}, t = 0) = \rho_\mathrm{i}(r) = (4\pi r_\mathrm{i}^2)^{-1}\delta(r - r_\mathrm{i}) \tag{2.2}$$

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

$$\dot{\rho} = D\nabla_\mathbf{r}[(\nabla_\mathbf{r}\rho + \rho\nabla_\mathbf{r}u_\mathbf{f})] \tag{2.3}$$

where $\nabla_\mathbf{r}$ is the gradient operator

$$u_\mathbf{f}(\mathbf{r}) = u(r) + (\mathbf{f}\cdot\mathbf{r}) \tag{2.4}$$

with $u(r) = U(r)/(k_\mathrm{B}T)$ and $\mathbf{f} = \mathbf{F}/(k_\mathrm{B}T)$, is the dimensionless MFP, and D is the diffusion coefficient for the particle, 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 an equation similar to eq 2.3 with $\mathbf{r} = \mathbf{r}_\mathrm{a} - \mathbf{r}_\mathrm{b}$ and parameters expressed in terms of those for separate particles.[2,6]

In the absence of force, the kinetics of escaping from the potential well was analyzed earlier.[29−32] Here we extend the approach applied in these works to describe the effect of external force. The approach is based on the approximate solution of eq 2.3 in the limit of a deep well by expansion in the small parameter $\tau_\mathrm{c}/\tau_\mathrm{e} \ll 1$, where

$$\tau_\mathrm{c} \sim (a - d)^2/\mathrm{D},\ \tau_\mathrm{e} \sim (a^2/D)\mathrm{e}^{u_\mathrm{b}} \sim \tau_\mathrm{c}\mathrm{e}^{u_\mathrm{b}} \tag{2.5}$$

are the time of equilibration within the well and the time of escaping from the well, respectively.[30,31]

Analysis of this solution shows[31] that in the lowest order in $\tau_\mathrm{c}/\tau_\mathrm{e} \ll 1$ the Smoluchowski approximation 2.3 is equivalent to the TSM (see section III).

III. Two-State Model

Originally, the TSM was proposed to treat the kinetics of diffusion-assisted escaping from the well in the absence of force, when eq 2.3 is spherically symmetric. In this case the TSM is shown to be equivalent to the Smoluchowski approach[30,31] in the lowest order in $\tau_\mathrm{c}/\tau_\mathrm{e} \sim \mathrm{e}^{-u_\mathrm{a}} \ll 1$.

In the presence of force [$\mathbf{f} = \mathbf{F}/(k_\mathrm{B}T) \neq 0$], however, the potential $u_\mathbf{f}(r) = u(r) + (\mathbf{f}\cdot\mathbf{r})$ in eq 2.3, is anisotropic, which results in the dependence of $\rho(\mathbf{r}, t)$ on polar angle θ: $\rho(\mathbf{r}, t) \equiv \rho(r, \theta|t)$. In this case the TSM turns out to be valid for a variety of shapes of the well $u(r)$ (though some additional remarks on validity are needed (see section IV))].

A. General Kinetic Equations. In general, the TSM describes the process as the evolution of two kinetically coupled states: the state localized within the well, whose population is given by

$$n(\theta|t) = 4\pi \int_d^a \mathrm{d}r\, r^2 \rho(r, \theta|t) \tag{3.1}$$

and the free diffusion state outside the well ($r > a$) described by the PDF $c(r, \theta|t)$. Within the TSM the effect of the force $\mathbf{f}$ shows itself in the dependence of kinetic parameters on θ. The form of this dependence is determined by the particular variant of the model (see below).

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[30,31]

$$\dot{n} = S_\mathrm{a}K_+(\theta)c(a|t) + [\hat{L}_\mathrm{c} - (K_-(\theta) + w_\mathrm{r})]n \tag{3.2}$$

$$\dot{c} = \hat{L}_f c + [S_a^{-1} K_-(\theta) n - K_+(\theta) c]\delta(r - a) \quad (3.3)$$

where $S_a = 4\pi a^2$, $\hat{L}_f = D\nabla_{\mathbf{r}}(\nabla_{\mathbf{r}} + \mathbf{f})$ 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, and

$$w_r = (Dl_r/Z_w),\ Z_w = \int_d^a \mathrm{d}r\, r^2 \mathrm{e}^{-u(r)} \quad (3.4)$$

is the rate of reaction in the potential well, in which $l_r = (\int_0^a \mathrm{d}r\, r^{-2} e^{u(r)})^{-1}$ and Z_w is the partition function for the well $u(r) = U(r)/(k_B T)$ (in the absence of force ($f = 0$)).[30,31] The parameters $K_+(\theta)$ and $K_-(\theta)$ are the rates of transitions between the two states. Expression 3.4 corresponds to the simplest model of reaction in the well treated as a reactive flux over a barrier at $r \sim d$. Equations 3.2 and 3.3, however, remain valid for any other model of reactivity in the well as long as it predicts first-order kinetics of reaction.

The essential difference of anisotropic equations from isotropic ones consists in the orientation dependence of the 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[31]

$$K_\pm \to \infty \quad \text{and} \quad K_-(\theta)/K_+(\theta) = K_e(\theta) \quad (3.5)$$

Therefore in this limit θ-dependence of rates $K_\pm(\theta)$ show itself in that of the equilibrium constant: $K_e(\theta)$.[29−31] The form of the function $K_e(\theta)$ is determined by the shape of the well. Some model well shapes and corresponding $K_e(\theta)$ dependences, as well as applicability of the corresponding TSMs, are discussed below.

Equations 3.2 and 3.3 should be solved with boundary conditions

$$(\nabla_r + f\cos\theta)c\Big|_{r=a} = 0 \qquad \text{and} \qquad c\Big|_{r\to\infty} \to 0 \quad (3.6)$$

the 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 $|\mathbf{n}(t)\rangle$ and $|\mathbf{c}(r, t)\rangle$, whose components are obtained by expansion of these functions in the orthonornmal basis of properly normalized Legendre polynomials (spherical functions)[36]

$$|l\rangle = \left(l + \frac{1}{2}\right)P_l(\cos\theta), \quad \langle l| = \int_0^\pi \mathrm{d}\theta \sin\theta P_l(\cos\theta) \ldots \quad (3.7)$$

with $l = 0, 1, \ldots$,

$$|\mathbf{n}\rangle = \sum_{l=0}^{\infty} n_l |l\rangle \quad \text{and} \quad |\mathbf{c}\rangle = \sum_{l=0}^{\infty} c_l |l\rangle \quad (3.8)$$

where for any vector $|\chi(\theta)\rangle$, ($\chi = n, c$), its components χ_l are defined by $\chi_l = \langle l|\chi\rangle = \int_0^\pi \mathrm{d}\theta \sin\theta\, P_l(\cos\theta)\chi(\theta)$.

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

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

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 3.2 and 3.3 can be solved by the method used 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 $|\mathbf{n}(t)\rangle$ and $|\mathbf{c}(r|t)\rangle$ (see eq 3.8]. The solution yields for the Laplace transform

$$|\tilde{n}(\epsilon)\rangle = \int_0^\infty \mathrm{d}t \mathrm{e}^{-\epsilon t}|\mathbf{n}(t)\rangle \quad (3.10)$$

$$|\tilde{\mathbf{n}}(\epsilon)\rangle = [\epsilon + w_r - \hat{L}_c + \hat{W}_e(\epsilon)]^{-1}|\mathbf{n}_i\rangle \quad (3.11)$$

where $|\mathbf{n}_i\rangle = (1/2\pi)|0\rangle$. The operator

$$\hat{W}_e(\epsilon) = \hat{G}^{-1}(a, a|\epsilon)\hat{K}_e \quad (3.12)$$

determines the generalized ϵ-dependent escape rate (see below). In eq 3.12 $\hat{K}_e$ is the equilibrium constant in the operator form (this operator representation results from $\hat{K}_e$ dependence on the angle θ) and $\hat{G}(a,a|\epsilon)$ is the evolution operator for diffusive motion outside the well (evaluated at $r = r_i = a$)

$$\hat{G}(a, a|\epsilon) = \langle a|(\epsilon - \hat{L}_f)^{-1}|a\rangle \quad (3.13)$$
$$= \mathrm{e}^{-\varphi\cos\theta}\langle a|(\epsilon - \hat{\Lambda}_f)^{-1}|a\rangle \mathrm{e}^{\varphi\cos\theta}$$

where $\varphi = fa/2$ and $\hat{\Lambda}_f = D(\hat{L}_r + r^{-2}\hat{L}_\theta - f^2)$ is the auxiliary operator in which

$$\hat{L}_\theta = (\sin\theta)^{-1}\nabla_\theta(\sin\theta\nabla_\theta) = -\sum_{l=0}^{\infty} l(l+1)|l\rangle\langle l| \quad (3.14)$$

and $\hat{L}_r = Dr^{-2}\nabla_r(r^2\nabla_r)$ are the operators of free orientational and radial diffusion, respectively.

In what follows we will restrict ourselves to the analysis of the well depopulation kinetics $\bar{n}(t)$, whose Laplace transform is given by

$$\tilde{\bar{n}}(\epsilon) = 2\pi\int_0^\pi \mathrm{d}\theta \sin\theta\tilde{n}(\theta,\epsilon) \equiv 2\pi\langle 0|\tilde{\mathbf{n}}(\epsilon)\rangle \quad (3.15)$$
$$= \langle 0|[\epsilon + w_r - \hat{L}_c + \hat{W}_e(\epsilon)]^{-1}|0\rangle$$

Thus the problem of the analysis of the kinetics consists in the evaluation of the matrix $\hat{W}_e(\epsilon)$ which reduces, in fact, to the calculation of the operator $\hat{G}^{-1}(a,a|\epsilon)$. Mathematical details of the evaluation are given in the Appendix. The final expression is written as

$$\hat{G}^{-1}(a,a|\epsilon) = D[\hat{q} + \mathrm{e}^{-\varphi\cos\theta}\hat{q}_K(\epsilon)\mathrm{e}^{\varphi\cos\theta}] \quad (3.16)$$

Here

$$\hat{q} = a^{-1}(1 - \varphi\cos\theta) \quad \text{with} \quad \varphi = fa/2 \quad (3.17)$$

and the operator $\hat{q}_K(\epsilon)$ is defined by fomula

$$\hat{q}_K(\epsilon) = \sum_{l=0}^{\infty} |l\rangle q_{K_l}(\epsilon)\langle l| \quad (3.18)$$

in which $q_{K_l}(\epsilon) = a^{-1}[l + \varphi_\epsilon K_{l-1/2}(\varphi_\epsilon)/K_{l+1/2}(\varphi_\epsilon)]$ (see Appendix) with

$$\varphi_\epsilon = \varphi(1 + \epsilon/\epsilon_f)^{1/2}, \quad \epsilon_f = \frac{1}{4}Df^2 = (D/a^2)\varphi^2 \quad (3.19)$$

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

$$\hat{L}_c = D_c(\sin\theta)^{-1}\nabla_\theta[\sin\theta(\nabla_\theta + \nabla_\theta\bar{u})] \quad (3.20)$$

where $D_c \sim D/r_b^2$ is the orientational diffusion coefficient $\bar{u}(\theta)$ 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.

C. Fast Reorientation in the Well. The fast orientational relaxation limit implies that $D_c \gg \tau_e^{-1}$. This relation means that after some time $\sim\tau_c \sim D_c^{-1}$ of orientational relaxation (of the initial population in the well) the vector of well population $|\mathbf{n}(t)\rangle$ remains close to the equilibrium one $|\Psi_e\rangle$ during the process

$$|\mathbf{n}(t)\rangle \approx \bar{n}(t)|\Psi_e\rangle \quad (3.21)$$

where

$$|\Psi_e\rangle = Z_\theta^{-1}\mathrm{e}^{-\bar{u}_b(\theta)}, \quad Z_\theta = \int_0^\pi \mathrm{d}\theta\,\sin\theta\mathrm{e}^{-\bar{u}_b(\theta)} \quad (3.22)$$

Note that within bra-ket notation the adjoint vector $\langle\psi_e|$ coincides with $\langle 0|$: $\langle\Psi_e| = \langle 0| = \int_0^\pi \mathrm{d}\theta\,\sin\theta$, ..., which can be confirmed by the relation $\langle\Psi_e|\hat{L}_c = 0$ directly following from the definition of $\hat{L}_c$ (see eq 3.20). 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 δL_c of eigenvalues of the operator $\hat{L}_c$ ($\delta L_c \sim D_c$) is much larger than $||\hat{W}_e|| \sim w_e^0$. In such a case in the lowest order in the parameter $w_e^0/D_c \ll 1$ we can significantly simplify the general expression for $\tilde{n}_0(\epsilon)$ (eq 3.15) and thus for the inverse average lifetime $\bar{w}_0 = \bar{\tau}_0^{-1} = [\int_0^\infty \mathrm{d}t\, n(t)]^{-1} = \tilde{n}_0^{-1}(0)$ as follows

$$\tilde{\bar{n}}(\epsilon) = [\epsilon + w_r + w_e(\epsilon)]^{-1} \quad (3.23)$$

and

$$\bar{w}_0 = w_r + \bar{w}_e$$

where

$$w_e(\epsilon) = \langle\Psi_e|\hat{W}_e(\epsilon)|\Psi_e\rangle \quad (3.24)$$

and

$$\bar{w}_e = w_e(0)$$

Equation 3.23 presents the main result of the work for the kinetics of the well depopulation in the limit of fast orientational relaxation.

It is interesting to note that formula 3.23 predicts simple expressions for the total probabilities (or yields) $P_r = w_r\int_0^\infty \mathrm{d}t\, n(t)$ and $P_e = 1 - P_r$ of geminate reaction and escaping, respectively

$$P_r = w_r\tilde{\bar{n}}(0) = w_r/\bar{w}_0 \quad \text{and} \quad P_e = \bar{w}_e/\bar{w}_0 \quad (3.25)$$

The depopulation kinetics predicted by formulas 3.23 and 3.24 essentially depends on the well shape, determining the orientational potential $\bar{u}(\theta)$ in the Smoluchowski-type operator $\hat{L}_c$ (eq 3.20) and, therefore, the equilibrium state $|\Psi_e\rangle$. In our work we will consider two realistic models of the well shape in which simple expressions for well depopulation kinetics can be obtained.

IV. Two Types of Well Shapes

In this section we will analyze the specific features of mean escape rate w_e for two variants of the well shape: (1) The narrow well shape (shown in Figure 1 by dashed line with $a = a_n$), for which $a - d \ll d$ and the time of equilibration in the well $\tau_c \sim (a - d)^2/D \ll a^2/D \ll \tau_e$, where τ_e is the escaping time (see eq 2.5); (2) The wide well shape (full line in Figure 1 with $a = a_w$), corresponding to a small distance of closest approach $d \ll a$ (for which one gets $fd \ll 1$ even at $fa \geq 1$).

The analysis will be made in the limit of fast orientational relaxation in the well with the use of eq 3.23 for the well depopulation kinetics.

A. Narrow Well Shape. In the case of a narrow well, when $a - d \ll d$, the well is of the shape of an 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 $\bar{u}_(\theta)$ on the orientation angle θ

$$\bar{u}_b(\theta) \approx u_f(r_b,\theta) \approx u_b + fa\cos\theta \quad (4.1)$$

with $f = |\mathbf{f}| > 0$, and the force effect on free diffusion in the state outside the well. In eq 4.1 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 $fr_b \approx fa$.

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 θ. In such a case $K_e(\theta)$ is given by the relation[30,31]

$$K_e(\theta) = K_e^{\,0} = a^2/Z_w \tag{4.2}$$

in which the effective partition function Z_w is given in eq 3.4, i.e., is controlled by the shape of the potential $u(r)$ without external force, despite a possible strong force effect on the energy of the bottom predicted by eq 4.1. This is because the external force leads to the identical change of both the bottom energy $\bar{u}_b(\theta) \approx u_b + fa\cos\theta$ and the energy of the free diffusion state at $r = a$: $u_f(a, \theta) \approx fa\cos\theta$.

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 (3.20) with

$$\bar{u}(\theta) = \bar{u}_b(\theta) - u_b = 2\varphi\cos\theta \tag{4.3}$$

where

$$\varphi = fa/2$$

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

$$|\Psi_e\rangle = \frac{e^{-2\varphi\cos\theta}}{Z_0(\varphi)} \tag{4.4}$$

with

$$Z_0(\varphi) = \frac{\sinh(2\varphi)}{\varphi}$$

Substituting formula 4.4 into the expression 3.24 and taking into account the relation[37] $e^{\pm\varphi\cos\theta} = (2\pi/\varphi)^{1/2}\sum_{l=0}^{\infty}(\pm 1)^l(l + (1/2))I_{l+(1/2)}(\varphi)P_l(\cos\theta)$, we get

$$w_e(\varepsilon)/w_e^{\,0} = \frac{1}{2} + \varphi\coth(2\varphi) + S_\varphi(\epsilon) \tag{4.5}$$

In this formula[30,31]

$$w_e^{\,0} = w_e(\varphi = 0, \epsilon = 0) = Da/Z_w \tag{4.6}$$

is the escape rate in the absence of a force[30,31] and

$$S_\varphi(\epsilon) = \frac{2\pi}{\varphi Z_0(\varphi)}\sum_{l=0}^{\infty}\left(l + \frac{1}{2}\right)I_{l+1/2}^{\,2}(\varphi)q_l(\varphi_\epsilon) \tag{4.7}$$

where

$$q_l(\varphi_\epsilon) = aq_{K_l}(\epsilon) = l + \varphi_\epsilon K_{l-1/2}(\varphi_\epsilon)/K_{l+1/2}(\varphi_\epsilon) \tag{4.8}$$

with $\varphi_\epsilon = \varphi(1 + \epsilon/\epsilon_f)^{1/2}$ (eq 3.19) and $I_\nu(x)$ and $K_\nu(x)$ being the modified Bessel functions.[37]

The function $w_e(\epsilon)$ is fairly complicated so that, in general, the well depopulation kinetics $n(t)$ can hardly be obtained in analytical form. In the considered limit of a deep well, however, the main ϵ dependent contribution $\sim\varphi_\epsilon$ comes from the term with $l = 0$ of the sum in eq 4.7. The ϵ-dependence of other terms with $l \geq 1$, which are of higher order in φ_ϵ ($\sim\varphi_\epsilon^{\,2}$), can be neglected by taking $\varphi_\epsilon \approx \varphi_{\epsilon=0} = \varphi$. In so doing one gets

$$S_\varphi(\epsilon) \approx \bar{S}_\varphi + \sigma_\varphi(\epsilon) \quad \text{and} \quad w_e(\epsilon) \approx \bar{w}_e + w_e^{\,0}\sigma_\varphi(\epsilon) \tag{4.9}$$

where $\sigma_\varphi(\epsilon) = (\varphi_\epsilon/\varphi - 1)\tanh\varphi = ((1 + \epsilon/\epsilon_f)^{1/2} - 1)\tanh\varphi$

$$\bar{S}_\varphi = S_\varphi(0) = \frac{2\pi}{\varphi Z_0(\varphi)}\sum_{l=0}^{\infty}\left(l + \frac{1}{2}\right)I_{l+1/2}^{\,2}(\varphi)q_l(\varphi) \tag{4.10}$$

$\bar{w}_e = w_e(\epsilon = 0)$ (see eq 3.24) and $\epsilon_f = (D/a^2)\varphi^2$.

The inverse Laplace transformation of thus obtained $\tilde{\bar{n}}(\epsilon)$ yields[32]

$$\bar{n}(t) = \frac{1}{2\pi i}\int_{-i\infty+0}^{i\infty+0} d\varepsilon \frac{\exp[\varepsilon(w_\varphi t)]}{1 + \varepsilon + \bar{\gamma}(\varepsilon_f + \varepsilon)^{1/2}} \tag{4.11}$$

where $\varepsilon_f = \epsilon_f/w_\varphi$, $w_\varphi = w_r + \bar{w}_e - w_e^{\,0}\tanh\varphi$, and

$$\bar{\gamma} = \sqrt{\frac{w_e^{\,0}}{w_\varphi}}\frac{\tanh\varphi}{\varphi}\gamma_e \tag{4.12}$$

with

$$\gamma_e = \sqrt{\frac{a^2 w_e^{\,0}}{D}}$$

The dependence 4.11 can be expressed in terms of the error function.[32] In the absence of force formula 4.11, naturally, reduces to that derived earlier for $\varphi = 0$:[30,31]

$$\bar{n}_{\varphi=0}(t) = \frac{1}{2\pi i}\int_{-i\infty+0}^{i\infty+0} \mathrm{d}\varepsilon \frac{\exp[\varepsilon(w_0 t)]}{1 + \varepsilon + \gamma_0\varepsilon^{1/2}} \tag{4.13}$$

where $w_0 = w_r + w_e^{\,0}$ and $\gamma_0 = (w_e^{\,0}/w_0)^{1/2}\gamma_e$.

Here we are not going to discuss general properties of the 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 a deep potential well, and in the most realistic case of relatively weak force, in which $\epsilon_f < 1$, i.e., $D/\bar{w}_0 < 4/f^2$. For $\gamma_e \ll 1$ at relatively short times $t < \bar{w}_0^{-1}\ln(1/\gamma_\varphi) \sim \bar{w}_0^{-1}\ln(1/\gamma_0)$ the kinetics is exponential,[30,31] $\bar{n}(t) \approx e^{-\bar{w}_0 t}$ ($\bar{w}_0 = w_r + \bar{w}_e$). In the opposite case $t \gg \bar{w}_0^{-1}\ln(1/\gamma_\varphi)$ the dependence $\bar{n}(t)$ is nonexponential:[30,31] $\bar{n}(t) \sim t^{-3/2}e^{-\epsilon_f t}$. In the absence of force ($\epsilon_f = 0$) the kinetics at long times becomes of inverse type power,[30,31] as expected. Note that for weak force $\varphi \ll 1$ the parameter ϵ_f is small: $\epsilon_f \sim \varphi^2$, and can be neglected. This means that in the weak force limit with

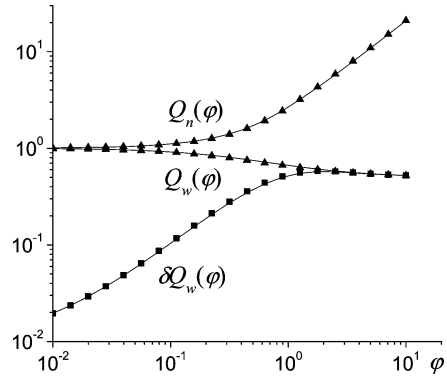

Figure 2. The force ($\varphi = fa/2$) dependence of dimensionless escape rates $Q_\nu(\varphi)$ for narrow (ν = n) and wide (ν = w) wells, calculated with exact eqs 4.14 and 4.18 (full lines) and interpolation formulas (4.16) and (4.20) (triangles). Shown also is the dependence of the dimensionless difference of rates $\delta Q_w(\varphi)$ (see eq 5.2_ calculated with the exact formula (full line) and the interpolation expression 4.20 (squares).

high accuracy the kinetics $\bar{n}(t)$ coincides with that for $\varphi = 0$ in which $w = w_0$. Detailed analysis of specific features of the kinetics predicted by formulas 4.11 and 4.12 is made in ref 32.

It is easily seen that in the considered limit of a deep well the nonexponential tail of the kinetics $\bar{n}(t)$ is small tending to zero as the force strength is increased. In such a case the effect of force φ on the escaping kinetics reduces to that on the mean escape rate $\bar{w}_e(\varphi) = w_e(\epsilon = 0, \varphi)$

$$\bar{w}_e(\varphi)/w_e^{\,0} = Q_n(\varphi) = \frac{1}{2} + \varphi \coth(2\varphi) + \bar{S}_\varphi \tag{4.14}$$

Formula 4.14 shows that the force effect on the rate is characterized by only one parameter $\varphi = fa/2$. The numerically calculated universal function $Q_n(\varphi)$ is displayed in Figure 2. Important specific features of $Q_n(\varphi)$ dependence are demonstrated by limiting behavior at the weak ($\varphi \ll 1$) and strong ($\varphi \gg 1$) forces.

For the weak force $Q_n(\varphi)$ can be obtained by the analysis of the first term (with $l = 0$) of the sum $\bar{S}(\varphi)$ in eq 4.14. In the opposite strong force limit, one can derive the expression for $Q_n(\varphi \gg 1)$ by taking into account that at $\varphi \gg 1$ the escaping process is, actually, one-dimensional, for which the $Q(\varphi)$ factor is given by the expression[32] $w_1 = Df/Z_w^{(1)}$, in which $Z_w^{(1)} = \int_d^a dr\, e^{-u(r)} \approx Z_w/a^2$ is the one-dimensional partition function. Calculation in both limits yields

$$Q_n(\varphi \ll 1) \approx 1 + \varphi \quad \text{and} \quad Q_n(\varphi \gg 1) \approx 2\varphi \tag{4.15}$$

These limiting results can be combined into a simple interpolation formula

$$Q_n(\varphi) \approx Q_n^{(i)}(\varphi) = 1 + \varphi(2 - e^{-\varphi}) \tag{4.16}$$

reproducing function $Q_n(\varphi)$, numerically evaluated with eqs 4.10 and 4.14, within accuracy ~1% (see Figure 2).

B. Wide Well Shape. Another form of the well shape, in which analysis of the force affected well depopulation kinetics and, in particular, the escape rate $\bar{w}_e(\varphi)$ 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 (3.3).

It is important to note that the inequality $fr_b < 1$ 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 quasi-equilibrium population distribution within the well is isotropic: $|\Psi_e\rangle = |0\rangle$. This, in turn, means that the partition function Z_w is independent of the angle θ and is given in eq 3.4.

In the wide well case the force effect manifests itself in the anisotropy of the activation energy of escaping from the well $u_a(\theta) \approx u_f(\theta, a)$: $u_a(\theta) \approx u_b + 2\varphi \cos\theta$, which leads to the anisotropy of the detailed balance relation, i.e., the anisotropy of the equilibrium constant

$$K_e(\theta) = K_e^{\,0} e^{-2\varphi \cos\theta} \tag{4.17}$$

where $K_e^{\,0}$ is the isotropic equilibrium constant in the absence of force. The relation is based on the reasonable assumption on approximate local equilibrium of the population outside and inside the well in the region $r \approx a$ at each θ. The accuracy of this approximation becomes especially high in the strong force limit: $\varphi > 1$, so that the model (4.17) will give a quite accurate interpolation formula for the kinetics $n(t)$.

The TSM with θ-dependent equilibrium constant $K_e(\theta)$ is a quite reasonable approach for the analysis of the kinetics of the escaping process, which enables one to relatively easily describe the specific features of the force dependence of this kinetics, in particular, in the limits of weak and strong external force (see below).

The expression for the escaping kinetics can straightforwardly be derived with the use of general formulas 3.23 and 3.24 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 an angular-dependent equilibrium constant (4.17) (of type of eq 3.24) over the isotropic equilibrium state $|\Psi_e\rangle = |0\rangle$ is similar to the average over the equilibrium distribution (4.4), except for the partition function $Z_0(\varphi)$ (eq 4.4), which should be replaced by $Z_0(\varphi \to 0) = 2$ corresponding to the isotropic distribution. These simple algebraic manipulations result in the same kinetics $\bar{n}(t)$ (4.11) with a simple change of the value of $\bar{w}_e$. In particular, for $\bar{w}_e(\varphi)$ we get

$$\bar{w}_e(\varphi)/(w_e^{\,0} e^{2\varphi}) = Q_w(\varphi) = \frac{1}{2} Z_0(\varphi) e^{-2\varphi} Q_n(\varphi) \tag{4.18}$$

where $Z_0(\varphi)$ and $Q_n(\varphi)$ are determined in eqs 4.4 and 4.14, respectively. Here the auxiliary rate parameter $w_e^{\,0} e^{2\varphi}$ is the escape rate in the absence of the force but with the activation energy u_a^*, corresponding to the orientation $\theta = \pi$ (most favorable for escaping): $u_a^* \equiv u_a(\theta = \pi) = u_b - 2\varphi$.

As in the case of a narrow well the force effect on $\bar{w}_e$ is characterized by only one parameter φ. The function $Q_w(\varphi)$, which determines the pre-exponential factor in the activation type dependence of $\bar{w}_e(\varphi)$, is displayed in Figure 2. The numerical results show that $Q_w(\varphi)$ monotonically decreases (with increasing φ) with

$$Q_w(\varphi \ll 1) \approx 1 - \varphi \quad \text{and} \quad Q_w(\varphi \gg 1) \to \frac{1}{2} \tag{4.19}$$

This limiting behavior of the function $Q_w(\varphi)$, looking unexpected at first sight, can easily be understood.

In the weak force limit ($\varphi \ll 1$) the behavior of $Q_w(\varphi)$ differs from that of $Q_n(\varphi)$ ($Q_w(\varphi)$ decreases with increasing φ) due to the use of φ-dependent normalizing rate $w_e^0 e^{2\varphi}$ (instead of w_e^0) in the definition of $Q_w(\varphi)$.

For $\varphi \gg 1$ the force strongly affects $\bar{w}_e$, first of all, by significant change of the activation energy of the process. The obtained $Q_w(\varphi \gg 1)$ independence can easily be understood by taking into account that, according to formula 4.17, in the case of wide well for strong external forces the flux of escaping particles is highly localized in a small region of orientations (small patch) of radius $\delta\theta = \pi - \theta \leq 1/\varphi^{1/2} \ll 1$. The escape rate is determined by the total flux J_w through this region of size $s_w \sim (\delta\theta)^2 \sim \varphi^{-1}$. In the strong force limit $\varphi \gg 1$ the flux $J_w \sim \varphi$, as it follows from eq 4.15, so that $Q_w(\varphi) \sim s_w J_w \sim$ constant. The exact estimation $Q_w(\varphi \rightarrow \infty) = 1/2$ can be obtained by substituting the limiting expression 4.15 into eq 4.18.

Note that in both cases of narrow and wide wells for $\varphi \gg 1$ the escape rate is determined by the quasi-one-dimensional flux of escaping particles. The mechanism of formation of this flux is, however, different in these cases: for narrow wells the one-dimensional regime results from high localization of the well population in the small region at $\theta \sim \pi$, while for wide wells it is caused by strong localization of favorable transition rates in this region.

A simple interpolation expression for $Q_w^{(i)}(\varphi)$ can be derived, for example, with the use of similar formula for $Q_n(\varphi)$ presented in eq 4.16:

$$Q_w(\varphi) \approx Q_w^{(i)}(\varphi) = \frac{1}{2} Z_0(\varphi) e^{-2\varphi} Q_n^{(i)}(\varphi) \qquad (4.20)$$

High accuracy of this formula is demonstrated in Figure 2.

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. 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 is valid in the wide region of parameters of the model. The total average 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 $\bar{w}_e$ whose value appears to strongly depend on the well shape. Analytical expressions for $\bar{w}_e(f)$ are obtained for two limiting types of well shapes: narrow wells for which $a - d < d$ and wide wells with large effective Onsager radius $a > d$.

In the case of a 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 without strong effect on the activation energy. In the case of a wide well, however, the force affects not only the preexponential factor but the activation energy as well.

It is worth noting that the force effect on the diffusion-assisted processes in the presence of interaction between particles is studied in a number of works (see, for example, refs 2 and 3). Especially comprehensively this effect (electric field effect) is analyzed in the case of an ion pair recombination reaction.

Unfortunately it is difficult to compare the results of earlier studies with results obtained above because of essential difference in models of interparticle interaction applied. In particular, in these studies ion pair recombination was usually treated as diffusion in pure Coulomb potential with high reactivity at a contact, which does not result in a well.[2,5,6] It is, nevertheless, interesting to note that in the weak force limit $fa \ll 1$ the force affected probability of escape from the Coulomb potential was found to be represented as $P_e(f) \approx P_e(f = 0)(1 + fa/2)$.[6] This dependence is in apparent agreement with the field dependence of the escaping probability P_e obtained in our work, which in the appropriate limit $\bar{w}_e/w_r \ll 1$ is represented as $P_e = \bar{w}_e/\bar{w}_0 \approx \bar{w}_e/w_r$ (see eqs 3.25 and 4.15).

Noteworthy is also that in the strong force limit the escaping process becomes nearly one-dimensional for both well shapes considered. In this limit the escape rate is determined by the flux in the small region of favorite orientations with $\theta \sim \pi$. This fact allows one to improve the TSM, in which the force effect on the location of the barrier top (at $r = a$) is originally 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 assumed to be of cusp shape.

In our work we restricted ourselves to the analysis of the most realistic limit of fast orientational relaxation within the well. In reality, however, general formula 3.15 also describes the manifestation of finite relaxation time. The effect is, of course, largest in the absence of relaxation ($\hat{L}_c = 0$). In this case the angular dependent equilibrium rate $K_e(\theta)$ results in the nonexponential kinetics $n(t)$, represented as a sum of exponential contributions with θ-dependent rates, coming from different orientations.

Concluding this discussion, note that this work considered the force effect on three-dimensional diffusion assisted escaping. The proposed TSM, however, can be applied to the analysis of two-dimensional processes as well. The corresponding results will be published elsewhere.[38]

Our further discussion concerns applications of obtained results to the analysis of some processes recently actively studied experimentally.

B. Condensed Phase Reaction Kinetics. ***1. Time-Dependent Reaction Yield.*** The obtained formulas are very 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 ion-pair recombination reactions in polar solids and liquids, in which the external force can be realized by applying an electric field. There are a number of experimental time-resolved spectroscopic studies of reactions with the participation of ions.[1−4,11,13,19−23]

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 Coulomb one:[27,28] unlike the Coulomb potential the MFP oscillates at short distances of order of molecular size.[27,28] At distances close to that of the first coordinate shell the MFP has a most deep well, whose depth can be much larger than $k_B T$ for dielectric constants $\varepsilon > 15$. In this case the proposed approximation of the MFP by the well-type potential is much closer to reality than the pure Coulomb potential approach.

Some of earlier results of the discussed TSM, concerning the kinetics of processes in the absence of external force ($f = 0$),

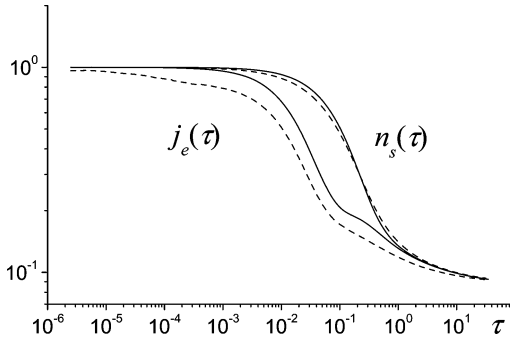

Figure 3. The comparison of time ($\tau = tD/a^2$) dependences of the ion-pair survival probability $n_s(\tau)$ and the normalized transient current $j_e(\tau) = J_e(\tau)/J_0$, calculated analytically with eqs 5.6 and 5.7 (full lines) and numerically[33] (dashed lines). The parameters used are presented in section V.C.

have already been successfully applied to the analysis of the kinetics of some liquid-phase reactions.[2,7−9] As for the results obtained above for the case $f \neq 0$, note that the most convenient for experimental analysis is not the force dependent inverse mean lifetime $\bar{w}_0(\varphi)$ (see eq 3.24) but the difference $\bar{w}_0(\varphi) - \bar{w}_0(0) = \bar{w}_e(\varphi) - w_e^0$, which is independent of the rate w_r of reaction in the well (assumed to be independent of φ). In the proposed dimensionless representation the parameters $\delta\bar{w}_0 = \bar{w}_0(\varphi) - \bar{w}_0(0)$ are written as

$$\delta Q_n(\varphi) = \delta\bar{w}_0/w_e^0(\varphi) = Q_n(\varphi) - 1 \qquad (5.1)$$

$$\delta Q_w(\varphi) = \delta\bar{w}_0/(w_e^0 e^{2\varphi}) = Q_w(\varphi) - e^{-2\varphi} \qquad (5.2)$$

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

It is of great interest to compare these theoretical predictions with experimental results of the type given in refs 12−15 but in the presence of an electric field.

2. Transient Photocurrents. Recently, considerable interest has been attracted to experimental investigations of the recombination kinetics of ion pairs by time-resolved measurements of transient photocurrent.[24−26,33] The photocurrent is found to be fairly sensitive to the spatial evolution of photoinduced ion pairs and to the recombination kinetics.

The proposed theory is very helpful in the interpretation of experiments on transient photocurrents. The fact is that the TSM considered above enables one to quite accurately and easily 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 TSM approach.

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 $\bar{\tau}_0 = \bar{w}_0^{-1}$ in the well (according to eq 3.23 $\bar{w}_0^{-1} \sim (w_e^0)^{-1}, w_r^{-1}$). Noteworthy is also that the TSM describes the kinetics at relatively long times $t > \tau_c$. In reality, however, the method can straightforwardly be extended to also treat the PDF relaxation at short times $t \leq \tau_c$ (i.e., relaxation within the well) just because of assumed essential difference between thermalization time τ_c and $\bar{\tau}_0$. This difference enables one to describe intrawell relaxation and well depopulation separately.

The initial stage of relaxation of the ion-pair PDF within the well results in the transient photocurrent $J_e(t)$ at times $t \leq \tau_c$. The relaxation kinetics depends on the well shape. Below, for simplicity, we will consider the case of a narrow well and assume that the initial PDF in the well is isotropic. For narrow wells the intrawell PDF relaxation can be separated into two stages: radial and orientational relaxation, which differ in the characteristic time. For the first stage (radial relaxation) this time $\tau_w = (a - d)^2/D < d^2/D$ is shorter than that $\tau_c = D_c^{-1} \approx r_b^2/D$ of the second stage (of orientational relaxation to the ion-pair PDF in the well of the potential $u_f(\mathbf{r})$ (2.4)).

Together with the final stage, described by the TSM, the current relaxation kinetics 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

$$J_e(t) \approx \bar{J}_0 + (J_0 - \bar{J}_0)e^{-t/\tau_w} \qquad (5.3)$$

where $J_0 = eDf$ is the current produced by freely diffusing the ion pair and $\bar{J}_0 = (2/3)J_0$ is the final current after radial relaxation (see eq 5.4).

2. At $t \sim \tau_c$ (the stage of orientational relaxation in the well) the current $J_e(t)$ can be evaluated using the relation $\bar{J}_e = \dot{\bar{p}}(t)$, where $\bar{p}(t) = e\langle r_f(t)\rangle$ is the average electric dipole moment of ion pairs within the well, where r_f is the projection of the interion radius vector on the direction of the field: $r_f = (\mathbf{r}\cdot\mathbf{f})/f$. For the case of a narrow well, $\dot{\bar{p}}(t)$ can be calculated in the limit of weak external force f in the lowest order in f (in the linear response approach)

$$J_e(t) \approx \bar{J}_0 e^{-2D_c t} \quad \text{with} \quad \bar{J}_0 = \frac{2}{3}J_0 \qquad (5.4)$$

where $D_c \approx D/r_b^2$.

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

$$J_e(t) \approx J_0 n_e(t) \quad \text{with} \quad n_e(t) = n_s(t) - n(t) \qquad (5.5)$$

Here

$$n_s(t) = 1 - w_r \int_0^t d\tau\, n(\tau) \qquad (5.6)$$

is the ion-pair survival probability.

Taking into account the difference of time scales of these three kinetic stages, one can represent the current relaxation kinetics by the combined expression

$$j_e(t) = J_e(t)/J_0 \approx \frac{1}{3}(2 + e^{-t/\tau_w})e^{-2D_c t}n(t) + n_e(t) \qquad (5.7)$$

This simple expression allows one to describe fairly accurately the specific features of $J_e(t)$ behavior in a wide time period. In deriving eq 5.7, we have assumed the well to be narrow. As already noted, this assumption (as applied to ion pair recombination) is quite appropriate in the limit of a relatively polar solvent with dielectric constant $\epsilon_s > 15$, in which the ion-pair

MFP $u(r)$ is known to be of the shape of deep narrow well at short distances $r \sim d$.[27,28] We have also neglected the contribution to the second stage of $J_c(t)$-relaxation caused by the (small) decrease of the well population at $t < 1/D_c$ [$\sim \dot{n}(t)$], which in the limit of a deep well is small.

Formula 5.7, however, turns out to be of quite reasonable accuracy even in the case of pure Coulomb potential $u(r) = a/r$ with a 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 $a \gg d$. Reasonably good accuracy of eq 5.7 in this case results from the cusplike shape of the well at $r \sim d$, where the major part 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.[33] These calculations have been made for $u(r) = a/r$, with $a = 63.3$ A, and small force $\varphi = 0.05$, which only weakly affects the escaping rate $\bar{w}_e$. Other parameters of the model are[33] the coefficient $D = 3.1 \times 10^{-5}$ cm^2/s of relative diffusion of ions, the contact distance $d = 9$ Å, and the reactivity σ_r at a contact distance $r = d$, defined by $D[\nabla_r \rho + (\nabla_r u + f \cos\theta)\rho]|_{r=d} = \rho(\sigma_r/4\pi d^2)|_{r=d}$, whose value $\sigma_r = 0.01(4\pi D a)$ corresponds to weak reactivity.

Recall that the discussed TSM is applicable in the limit $\gamma_e = (a^2 w_e^0/D)^{1/2} \ll 1$ (see eq 4.12). For parameters of the model chosen above, however, $\gamma_e \approx 0.9$; i.e., the TSM is not expected to reproduce the exact numerical results very accurately. Nevertheless, even in this case the accuracy of the TSM appears to be quite good (see below).

Noteworthy is also that in the considered model assuming a not very deep well of cusplike shape the quasi-equilibrium PDF in the well is somewhat displaced to $r > d$. In this case, with reasonable accuracy one can put $r_b = \bar{r} = \int_d^\infty dr\, r e^{-u(r)}/Z_w \approx 20$ Å so that $D_c \approx 8 \times 10^8$ s^{-1} (eq 5.4). For this value of r_b one can also approximately estimate τ_w^{-1}: $\tau_w^{-1} \approx D/(r_b - d)^2 \approx 3.1 \times 10^9$ s^{-1}.

For the chosen parameters of the model the survival probability $n_s^\infty = n_s(t \to \infty) \approx 0.085$.[33] Taking into account that the TSM exactly predicts the asymptotic (at $t \to \infty$) behavior of the well depopulation kinetics, we can write the relation $n_s^\infty = \bar{w}_e/\bar{w}_0 = \bar{w}_e/(w_r + \bar{w}_e) = 0.085$.

Figure 3 displays the comparison of the analytically evaluated time-dependent survival probability $n_s(t)$ and transient current $J_e(t)$ with those calculated by numerical solution of the Smoluchowski equation.[33] For convenience of the comparison in Figure 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 $\tau > 0.1$. As for the time-dependent transient current $J_e(\tau)$, it is also quite accurately reproduced by the TSM at long times, when it is controlled by $n_s(t)$ kinetics. Some 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.

C. Optical Tweezers. The important problem, which has recently attracted much attention, and in the study of which the TSM can be very fruitful, is the kinetics of trapping of colloidal particles by optical tweezers, i.e., by the optical force induced potential wells.[34,35] Detailed experimental investigations show that the tweezers potential well $u(r)$ is highly localized (the size is about a micrometer).[39] Of course, in general the well is not quite spherically symmetric, but to a good accuracy, for description of trapping and escaping kinetics one can neglect this anisotropy.

Application of the TSM can significantly simplify the problem of description of the kinetics of trapping into and escaping from tweezers potential well thus allowing for the analysis of more complicated effects of a large number of potential wells.[40]

Of special interest is the effect of well motion on the trapping/escaping kinetics.[41] This effect is known to reduce to that of the external force discussed above. The fact is that the well motion induces the force $\mathbf{F}_v$ acting on a particle. In the frame of reference, moving with the well, the force is proportional to the well velocity $\mathbf{v}$: $\mathbf{F}_v = \mu^{-1}\mathbf{v}$, where $\mu = D/(k_B T)$ is the mobility of the particle, i.e., $\mathbf{f}_v = D^{-1}\mathbf{v}$. Note that this relation holds in the case of time-dependent velocity $\mathbf{v}(t)$ as well.

Thus the problem of the analysis of the effect of the well motion is equivalent to that of the external force $\mathbf{f} = \mathbf{f}_v$. In our consideration we have assumed that $\mathbf{f}$ is independent of time. The case of time-dependent $\mathbf{f}$ (for example, because of time-dependent velocity $\mathbf{v}(t)$) 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 $\bar{w}_e(\varphi)$ is replaced by the corresponding time-dependent expression $\bar{w}_e(\varphi(t))$.

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Appendix

Formulas 3.13−3.14 allow us to evaluate the operator $\hat{G}^{-1}(a, a|\epsilon)$ in analytical form. In the evaluation it is worth taking into account the useful relation which simplifies the differential operator in the radial space

$$\langle a|(\epsilon - \hat{\Lambda}_f)^{-1}|a\rangle = \langle a|(\epsilon - \hat{\lambda}_f)^{-1}|a\rangle \qquad (6.1)$$

where $\hat{\lambda}_f = D(\nabla_r^2 + r^{-2}\hat{L}_\theta - 1/4\, f^2)$.

The evolution operator $\langle a|(\epsilon - \hat{\lambda}_f)^{-1}|a\rangle$ can be obtained[42] with the use of two linearly independent operator solutions $\hat{\psi}_-(r)$ and $\hat{\psi}_+(r)$ of equation

$$(\epsilon - \hat{\lambda}_f)\hat{\psi}_\pm = 0 \qquad (6.2)$$

in which the operator $\hat{L}_\theta$ is treated as a parameter. These solutions satisfy two boundary conditions corresponding to those given in eq 3.6 (after change of variable $c(r) = e^{-(fr\cos\theta)/2}\psi(r)$)

$$\left(\nabla_r + \frac{1}{2}f\hat{\omega}\right)\hat{\psi}_-\Big|_{r=a} = 0 \quad \text{and} \quad \hat{\psi}_+\Big|_{r\to\infty} \to 0 \qquad (6.3)$$

where $\hat{\omega} = \sum_{l,l'=0}^{\infty} |l\rangle\langle l|\cos\theta|l'\rangle\langle l'|$ is the matrix representation of the function $\cos\theta$. The matrix elements $\langle l|\cos\theta|l'\rangle = \langle l|P_1(\cos\theta)|l'\rangle$ are evaluated analytically[36] 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 $K_{l+(1/2)}(x)$ and $I_{l+(1/2)}(x)$[37]

$$\hat{X}(r) = \sqrt{r}\sum_{l=0}^{\infty} |l\rangle X_{l+(1/2)}(\varphi_\epsilon r/a)\langle l| \qquad (6.4)$$

$$X = I, K:$$

$$\hat{\psi}_+(r) = \hat{K}(r), \quad \hat{\psi}_-(r) = \hat{I}(r) + \hat{K}(r)\hat{\kappa} \qquad (6.5)$$

where $\varphi = fa/2$, $\varphi_\varepsilon = \varphi(1 + \epsilon/\epsilon_f)^{1/2}$, $\epsilon_f = Df^2/4 = (D/a^2)\varphi^2$, and $\hat{\kappa}$ is the matrix determined by the boundary condition at $r = a$ (see eq 6.3)

$$\hat{\kappa} = [\nabla_r \hat{K}(r) - \hat{q}\hat{K}(r)]^{-1}[\hat{q}\hat{I}(r) - \nabla_r \hat{I}(r)]\Big|_{r=a} \qquad (6.6)$$

in which

$$\hat{q} = a^{-1}(1 - \varphi\hat{\omega}) \equiv a^{-1}(1 - \varphi\cos\theta) \qquad (6.7)$$

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 6.5 and 6.6 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.

Representation of the operator $\langle r|(\epsilon - \hat{\lambda}_f)^{-1}|r_i\rangle$ in terms of noncommuting solutions $\hat{\psi}_+(r)$ and $\hat{\psi}_-(r)$ is proposed in ref 42. It 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 6.4, however, it reduces to a more simple one

$$\langle r|(\epsilon - \hat{\lambda}_f)^{-1}|r_i\rangle = \hat{g}(r, r_i) + \hat{K}(r)\hat{\kappa}\hat{K}(r_i)\hat{W}_{\hat{I}\hat{K}}^{-1} \qquad (6.8)$$

Here $\hat{W}_{\hat{I}\hat{K}} = D[\nabla_r \hat{I}(r)\hat{K}(r) - \nabla_r \hat{K}(r)\hat{I}(r)] = D$ is the Wronskian of two solutions and

$$\hat{g}(r, r_i) = [\hat{K}(r)\hat{I}(r_i)\theta(r - r_i) + \hat{I}(r)\hat{K}(r_i)\theta(r_i - r)]W_{\hat{I}\hat{K}}^{-1} \qquad (6.9)$$

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

The validity of the expression 6.8 can be verified by direct substitution to the inhomogeneous variant of eq 6.2 with the delta-function in the right-hand side.

For the particular case $r = r_i = a$ formula 6.8 yields

$$\langle a|(\epsilon - \hat{\lambda}_f)^{-1}|a\rangle = D^{-1}[\hat{q} + \hat{q}_K(\epsilon)]^{-1} \qquad (6.10)$$

where $\hat{q}_K(\epsilon) = -\nabla_r \hat{K}(r)/\hat{K}(r)|_{r=a} = \sum_{l=0}^{\infty}|l\rangle q_{K_l}(\epsilon)\langle l|$ with $q\kappa_l(\epsilon) = a^{-1}[l + \varphi_\epsilon K_{l-(1/2)}(\varphi_\epsilon)/K_{l+(1/2)}(\varphi_\epsilon)]$.

Substituting the expression 6.10 into eq 6.1 and then into eqs 3.13 and 3.12, we obtain formula 3.16.

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