Diffusion-influenced reversible geminate recombination in one dimension. II. Effect of a constant field

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The diffusion-influenced reversible geminate-pair recombination problem is solved exactly in one dimension, in the presence of a constant external field. As the field strength changes sign, the long time asymptotics of the components of the Green function solution show a primary kinetic transition, in which the equilibrium values are changed. At two other critical values of the external field the approach to equilibrium changes, from a $t^{-3/2}$ power-law to exponential. At the three critical fields, asymptotic $t^{-1/2}$ decay prevails.
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I. INTRODUCTION

In 1913 Smoluchowski[1,2] has extended the diffusion equation to the case of an external field of force [derived from an interaction potential, $U(x)$]. He has added to Fick's Law a drift term which is proportional to the external force. The equation has, in fact, been derived by Lord Rayleigh in 1891 for the special case of a parabolic potential.[3] Both he and Smoluchowski have obtained the fundamental solution (Green function) for it, a problem treated (and generalized) later by Ornstein and Uhlenbeck.[3] Smoluchowski has also obtained the fundamental solution for a linear potential in one dimension (even with a reflective boundary condition),[2] a problem reviewed by Chandrasekhar.[4] To-date, these are the two ''canonical'' potentials for which simple analytic solutions are known.

To describe a chemical reaction which is coupled to diffusive motion, either boundary conditions or sink terms are added to the equation.[5] The traditional theory of diffusion influenced reactions[6] deals with irreversible reactivity, which was treated by Collins and Kimball[7] via the so-called ''radiation'' boundary condition.[8] With the added complexity of an interaction potential, not much could be done to solve the Smoluchowski equation analytically in the time-domain: Agmon obtained the exact solution for diffusion in a linear potential with this boundary condition.[9] Bagchi, Fleming, and Oxtoby[10] have found an analytic solution for diffusion in a harmonic potential with a delta-function sink at its minimum, whereas Weiss has obtained it for a parabolic sink.[11]

The effect of an interaction potential on many-body reactivity has been studied predominantly at steady-state. There is on-going work concerning electric-field effect on irreversible ion recombination in solution.[12–15] From these studies it appears that the steady-state rate constant for recombination typically decreases with increasing electric field. Time-dependent solutions or reversibility were not considered.

Recently, the study of reversible diffusion-influenced reactions has attracted growing interest. Reversibility may be depicted by the so-called ''back-reaction'' boundary condition.[9,16] The simplest case (''geminate recombination'') involves a pair which evolves along a single separation coordinate. Because of its inherent complexity, closed-form analytic solutions for reversible geminate recombination have been found only in the absence of an interaction potential.[17–19] An exception is the work of Agmon,[9] who has found the Laplace transform for reversible binding of a particle diffusing under the influence of a linear one-dimensional potential. The goal of the present article is to extend this solution to the time domain. We achieve this by noting the mathematical isomorphism with a one-dimensional problem previously solved by us,[19] that involves excited-state geminate recombination with different lifetimes and quenching.

For the latter problem, Gopich and Agmon discovered an interesting kinetic transition as a function of the difference in excited-state decay rates[20,21] and even in the presence of a competing quenching process.[22] The simplest (''first order'') transition involves a change in the asymptotic decay from power-law to exponential. The mapping we establish between these rate-constants and the external force for the two isomorphic problems, implies that kinetic transitions occur also for the present problem as a function of the field strength. Thus although the one-dimensional problem can be solved numerically with relative ease,[23] the analytic solution allows us to investigate kinetic transitions which are driven by the external field.

In addition, analytic solutions (even one-dimensional ones) have a practical application for generating random-numbers for moving particles in many-body Brownian dynamics simulations of reversible reactions.[24–27] Thus far, these simulations were conducted in the absence of an inter-

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action potential. Since physical potentials are typically smooth and continuous, they could be linearized over intervals for which our analytic solution should hold. This could allow incorporation of a potential without sacrificing much of the efficiency arising from the large time steps.

Finally, one-dimensional diffusion with trapping does occur in nature for example, in charge migration along polymers[28] or DNA chains.[29,30] It is likely that some of these trapping events are actually reversible. The equations derived below could then describe the effect of an external electric field on these systems. This might have practical implications in the emerging field of molecular electronics.

II. EXACT SOLUTION

Consider a particle diffusing in one dimension under the influence of a constant external field *and* with a reversible trap at the origin. Let $p(x,t)$ be the probability density for observing the particle at a distance x by time t. Its time evolution can be described by the following diffusion equation[1,2]

$$\frac{\partial p(x,t)}{\partial t}=D\left[\frac{\partial^2 p(x,t)}{\partial x^2}+2a\frac{\partial p(x,t)}{\partial x}\right] \quad (x>0), \tag{2.1}$$

where D is the diffusion constant and a determines the magnitude of the field [i.e., the particle moves in the potential $U(x)=2k_BTax$]. When $a>0$, the particle moves toward the origin, whereas when $a<0$ it may rapidly escape to infinity. The theory is applicable also for a pair of particles moving on the line with diffusion coefficients D_1 and D_2 and field strengths a_1 and a_2 (e.g., two different ions in a constant external force field). As shown in Appendix A, Eq. (2.1) is valid for motion in the relative coordinate $x=x_2-x_1$, provided that we set $D=D_1+D_2$ and $a=(D_2a_2-D_1a_1)/D$.

The boundary condition at infinity is simply

$$p(\infty,t)=0, \tag{2.2}$$

whereas the boundary condition at the origin depicts reversible binding[9]

$$D\left[\frac{\partial p(x,t)}{\partial x}+2ap(x,t)\right]_{x=0}=k_ap(0,t)-k_dp(*,t). \tag{2.3a}$$

Here k_a and k_d are the association and dissociation rate constants, respectively, and $p(*,t)$ denotes the binding probability (an asterisk stands for a trapped particle). Its time evolution is given by a simple kinetic equation

$$\frac{\partial p(*,t)}{\partial t}=k_ap(0,t)-k_dp(*,t), \tag{2.3b}$$

which is an ordinary differential equation. If $k_d=0$ one obtains the radiation boundary condition applied by Collins and Kimball,[7,9] whereas if also $k_a=0$ one regains the reflective boundary condition as used by Smoluchowski and Chandrasekhar.[2,4] Our solution will reduce to these special cases in the appropriate limits.

We are interested in the ''fundamental solution'' or Green function for the problem, $p(\cdots|x_0)$ and $p(\cdots|*)$, which correspond to the particle initially in the unbound state at $x=x_0$ or in the bound state, respectively. These correspond to one of the two following initial conditions:

$$p(x,0|x_0)=\delta(x-x_0), \quad p(*,0|x_0)=0, \tag{2.4a}$$

$$p(x,0|*)=0, \quad p(*,0|*)=1. \tag{2.4b}$$

Smoluchowski noted[2,4] that the transformation

$$q(x,t|x_0)=\exp[a(x-x_0+aDt)]\,p(x,t|x_0) \tag{2.5}$$

reduces Eq. (2.1) to the field-free diffusion equation,

$$\frac{\partial q(x,t)}{\partial t}=D\frac{\partial^2 q(x,t)}{\partial x^2}. \tag{2.6}$$

In order to extend his method to the bound state, we supplement Eq. (2.5) by

$$q(*,t|x_0)=\exp[a(-x_0+aDt)]\,p(*,t|x_0), \tag{2.7a}$$

$$q(x,t|*)=\exp[a(x+aDt)]\,p(x,t|*), \tag{2.7b}$$

$$q(*,t|*)=\exp[a^2Dt]\,p(*,t|*). \tag{2.7c}$$

These may formally be obtained from Eq. (2.5) by setting x or x_0 in the exponent to zero whenever they correspond to the bound state,$*$. With the aid of Eqs. (2.7), Eqs. (2.3) become

$$D\frac{\partial q(x,t)}{\partial x}\bigg|_{x=0}=(k_a-aD)q(0,t)-k_dq(*,t), \tag{2.8a}$$

$$\frac{\partial q(*,t)}{\partial t}=k_aq(0,t)-(k_d-a^2D)q(*,t). \tag{2.8b}$$

In Part I we have treated the one-dimensional problem of reversible geminate recombination in the excited-state,[19] with two different excited-state decay rate constants, k_0 for the bound state and k_0' for the unbound state, and a competing quenching reaction (rate coefficient k_q). Specifically, we have solved

$$\frac{\partial q(x,t)}{\partial t}=D\frac{\partial^2 q(x,t)}{\partial x^2}-k_0'\,q(x,t), \tag{2.9}$$

supplemented by the conditions that

$$D\frac{\partial q(x,t)}{\partial x}\bigg|_{x=0}=(k_a+k_q)q(0,t)-k_dq(*,t), \tag{2.10a}$$

$$\frac{\partial q(*,t)}{\partial t}=k_aq(0,t)-(k_d+k_0)q(*,t). \tag{2.10b}$$

It is immediately evident that the two problems are mathematically isomorphic, provided that we identify $k_q=-aD$, $k_0=-a^2D$, and $k_0'=0$. We can use the solution from Part I, but its behavior will differ due to the possibility of negative values for the ''rate constants'' k_q and k_0.

The solution in Part I was obtained in terms of three roots of a cubic polynomial, denoted by $-\alpha$, $-\beta$, and $-\gamma$, which obey [cf. Eq. (2.14) in Ref. 19]

$$\alpha+\beta+\gamma=(k_a+k_q)/D, \tag{2.11a}$$

$$\alpha\beta+\beta\gamma+\gamma\alpha=(k_0-k_0'+k_d)/D, \tag{2.11b}$$

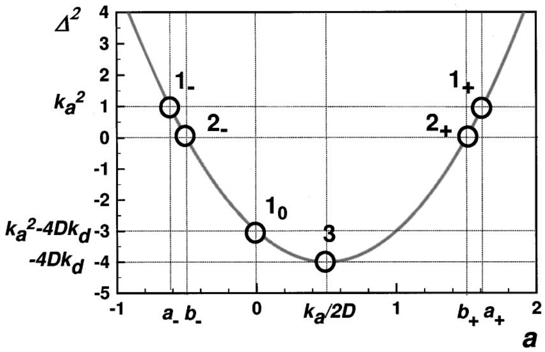

FIG. 1. The field dependence of the discriminant in Eq. (2.14b) for $k_a=1$, $k_d=1$, and $D=1$ (all subsequent figures use this parameter set). The various transitions are denoted by circles, with their values appearing on the axes.

$$\alpha\beta\gamma=[(k_0-k_0')(k_a+k_q)+k_dk_q]/D^2. \tag{2.11c}$$

For the present values of the rate parameters, these relations simplify to

$$\alpha=-a, \tag{2.12a}$$

$$D(\beta+\gamma)=k_a, \tag{2.12b}$$

$$D\beta\gamma=ak_a+k_d-a^2D. \tag{2.12c}$$

Thus if we denote $\beta=\lambda_+$, and $\gamma=\lambda_-$, it becomes clear from the last two equations that $\lambda_\pm$ are the roots of the following quadratic equation:

$$D\lambda^2-k_a\lambda+(ak_a+k_d-a^2D)=0. \tag{2.13}$$

These roots can be readily obtained as

$$\lambda_\pm=(k_a\pm\Delta)/2D, \tag{2.14a}$$

$$\Delta\equiv[k_a^2+4D^2(a-a_+)(a-a_-)]^{1/2}$$
$$=[4D^2(a-b_+)(a-b_-)]^{1/2}, \tag{2.14b}$$

where the ''transition fields'' (see below), $a_\pm$ and $b_\pm$, are given by

$$2D\,a_\pm\equiv k_a\pm\sqrt{k_a^2+4Dk_d}, \tag{2.15a}$$

$$2D\,b_\pm\equiv k_a\pm\sqrt{4Dk_d}. \tag{2.15b}$$

The $a_\pm$ are the solutions of the quadratic equation $\lambda_+\lambda_-=0$, see Eq. (2.12c). Thus whereas $\alpha\beta\gamma=0$ has a single solution for positive rate constants, for the present problem Eq. (2.11c) has *three* such roots, occurring at $a=0$ and $a=a_\pm$, all of which are real ($a_+>0$, $a_-<0$, and both correspond to $\lambda_-=0$). This results in a qualitative change in the behavior of the solution for the problem at hand.

By direct substitution in Eqs. (2.16), (2.20), and (2.25) of Part I,[19] the exact Green function for the present problem is finally found to be

$$\begin{aligned}
&e^{a(x-x_0+aDt)}\,p(x,t|x_0)\\
&=f(x,t|x_0)+\frac{k_da}{2k_aa+k_d}W\left(\frac{x+x_0}{\sqrt{4Dt}},-a\sqrt{Dt}\right)\\
&+\frac{k_a}{\Delta}\left[\frac{\lambda_-(\lambda_--a)}{\lambda_-+a}W\left(\frac{x+x_0}{\sqrt{4Dt}},\lambda_-\sqrt{Dt}\right)\right.\\
&\left.-\frac{\lambda_+(\lambda_+-a)}{\lambda_++a}W\left(\frac{x+x_0}{\sqrt{4Dt}},\lambda_+\sqrt{Dt}\right)\right],
\end{aligned} \tag{2.16a}$$

$$\begin{aligned}
&e^{ax+a^2Dt}\,p(x,t|*)/k_d\\
&=\frac{a}{2k_aa+k_d}W\left(\frac{x}{\sqrt{4Dt}},-a\sqrt{Dt}\right)\\
&+\frac{\lambda_-}{\Delta(a+\lambda_-)}W\left(\frac{x}{\sqrt{4Dt}},\lambda_-\sqrt{Dt}\right)\\
&-\frac{\lambda_+}{\Delta(a+\lambda_+)}W\left(\frac{x}{\sqrt{4Dt}},\lambda_+\sqrt{Dt}\right),
\end{aligned} \tag{2.16b}$$

$$p(*,t|x_0)=k_ae^{2ax_0}\,p(x_0,t|*)/k_d, \tag{2.16c}$$

$$\begin{aligned}
e^{a^2Dt}\,p(*,t|*)=&\frac{ak_a}{2k_aa+k_d}\ \Omega(-a\sqrt{Dt})\\
&+\frac{k_d\lambda_+}{\Delta(a^2-\lambda_+^2)}\ \Omega(\lambda_+\sqrt{Dt})\\
&-\frac{k_d\lambda_-}{\Delta(a^2-\lambda_-^2)}\ \Omega(\lambda_-\sqrt{Dt}),
\end{aligned} \tag{2.16d}$$

where $f(x,t|x_0)$ is the solution of the diffusion equation with a reflective boundary condition

$$f(x,t|x_0)=\frac{1}{\sqrt{4\pi Dt}}\left\{\exp\left[-\frac{(x+x_0)^2}{4Dt}\right]+\exp\left[-\frac{(x-x_0)^2}{4Dt}\right]\right\}, \tag{2.17}$$

the functions $W(y,z)$ and $\Omega(z)$ are defined by

$$W(y,z)\equiv\exp(2yz+z^2)\,\mathrm{erfc}(y+z), \tag{2.18a}$$

TABLE I. Transition values for the three roots, $-a$, λ_+, and λ_-, as a function of external field, a.

Transition	Da	$D\lambda_+$	$D\lambda_-$
1_-	$\frac{1}{2}(k_a-\sqrt{k_a^2+4Dk_d})$	k_a	0
2_-	$\frac{1}{2}(k_a-\sqrt{4Dk_d})$	$k_a/2$	$k_a/2$
1_0	0	$\frac{1}{2}(k_a+\sqrt{k_a^2-4Dk_d})$	$\frac{1}{2}(k_a-\sqrt{k_a^2-4Dk_d})$
3	$k_a/2$	$k_a/2+i\sqrt{Dk_d}$	$k_a/2-i\sqrt{Dk_d}$
2_+	$\frac{1}{2}(k_a+\sqrt{4Dk_d})$	$k_a/2$	$k_a/2$
1_+	$\frac{1}{2}(k_a+\sqrt{k_a^2+4Dk_d})$	k_a	0

$$\Omega(z)\equiv W(0,z)=\exp(z^2)\,\mathrm{erfc}(z), \tag{2.18b}$$

and erfc(z) denotes the complementary error function of the (possibly complex) argument z. As discussed in Appendix B, the above solution reduces correctly to the one for irreversible reaction, when either $k_d=0$ (irreversible recombination) or $k_a=0$ (irreversible dissociation).

III. ROOTS AND TRANSITIONS

The solution in Eq. (2.16) is determined by the three roots of the cubic polynomial, $-a$, λ_+, and λ_-. Gopich and Agmon[18] have identified three types of transitions for the three roots in the complex plane. First order transitions occur when one root vanishes, second order transitions are when two roots coincide and a third order transition is when the real part of all three roots coincide. Thus for the root $-a$, a first order transition (1_0) occurs at zero field. We proceed to analyze the dependence of the remaining two roots, $\lambda_\pm$.

A convenient starting point is the discriminant in Eq. (2.14b), which is plotted in Fig. 1. The four transition fields, $a_\pm$ and $b_\pm$ [see Eq. (2.15)] are depicted as circles. When $a=a_\pm$, $\Delta=k_a$ and thus λ_- vanishes [see Eq. (2.14a)]. These first order transitions are denoted by $1_\pm$, respectively. In contrast to λ_-, λ_+ does not undergo such a transition, as it is always positive. When $a=b_\pm$, Δ vanishes and then $\lambda_+=\lambda_-=k_a/2D$. We denote these second-order transitions by $2_\pm$, respectively. The minimum of Δ^2 occurs at $a=k_a/2D$. At this point the absolute value of the real part of all three roots coincide, which we term a third-order transition (this is a slight modification of the original definition). The various transitions are summarized in Table I.

The real and imaginary parts of $\lambda_\pm$ are depicted in Fig. 2. The significance of the second order transition is clear: Outside the interval $[b_-,b_+]$, the two roots are real. They coincide when $a=b_-$ or $a=b_+$. Inside the interval $[b_-,b_+]$, the two roots are complex: Their real part is $k_a/2D$, whereas the absolute value of their imaginary parts reaches a maximum ($\sqrt{k_d/D}$) at the third order transition, where also $a=k_a/2D$.

With the aid of Fig. 2, it is easy to envision the trajectories of $\lambda_\pm$ in the complex plane. As a increases from $-\infty$, λ_- moves right along the real axis until it hits the origin. This first order transition, denoted 1_-, occurs when $a=a_-$. In parallel, λ_+ moves left on the real axis, from $+\infty$ to k_a/D. As the field further increases, these two roots collide ($\Delta=0$) at the point $k_a/2D$ on the real axis. This second order transition is denoted 2_-. The field at this transition may have a negative or a positive value. For the latter case, the transition 1_0 appears first. Upon further increase in a, the

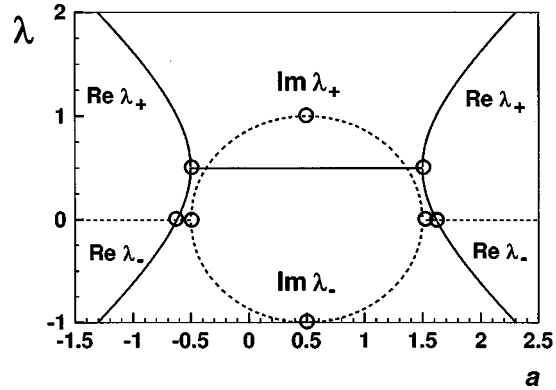

FIG. 2. The real (full line) and imaginary (dashed line) parts of the two roots from Eq. (2.14a), for the same parameters as in Fig. 1. The various transitions (except 1_0) are denoted by circles, corresponding to those in Fig. 1. The values of $\lambda_\pm$ at these transitions are summarized in Table I.

roots move into the complex plane, perpendicular to the real axis. They are now complex-conjugate: Their real part remains at $k_a/2D$, whereas their imaginary parts increase (in absolute value) to a maximum, $\sqrt{k_d/D}$, occurring when $a=k_a/2D$. Upon further increase in a, $\lambda_\pm$ retrace their trajectories: They collide again on the real axis (transition 2_+), then λ_- vanishes (transition 1_+), and finally they retreat to $\pm\infty$, respectively.

The case of $k_d=0$ is seen to be singular in the sense that the two second order transitions coincide, $b_+=b_-$. This occurs at the third order transition, $a=k_a/2D$.

IV. ASYMPTOTIC BEHAVIOR

The property of the three roots that affects most the solution in Eq. (2.16) is their sign. Whereas λ_+ is always positive, a and λ_- may be either positive or negative. The sign changes involved in the first order transitions (1_0 and $1_\pm$) induce corresponding transitions in the transient kinetics. Interestingly, sign changes in a and λ_- affect different portions of the asymptotic behavior. The first determines the $t=\infty$ equilibrium solution, that exists only when $a>0$ (''primary transition''). The sign of λ_- determines the approach to the $t=\infty$ limit (''secondary transition''). It is a $t^{-3/2}$ power-law in the ''inner region'' $[a_-,a_+]$, and exponential in the complementary ''outer region.'' At the transitions ($a=0$ or $\lambda_\pm=0$) a different, $t^{-1/2}$ power-law holds. To demonstrate this, we shall obtain the asymptotic behavior for some of the relevant functions, evaluated for $k_d>0$.

The long time behavior stems directly from that of the error-functions appearing in Eq. (2.16). The kinetic transition arises from the different behavior of erfc(z) as $|\arg z|$ goes through the value $3\pi/4$, see Ref. 31. As a result, we find that

$$W\left(\frac{x}{\sqrt{4Dt}},y\sqrt{Dt}\right)\sim\begin{cases}\dfrac{1}{y\sqrt{\pi Dt}}-\dfrac{1}{2Dt\sqrt{\pi Dt}}\left(\dfrac{x^2}{2y}+\dfrac{x}{y^2}+\dfrac{1}{y^3}\right), & \text{when } |\arg y|<3\pi/4,\\[2ex] 2e^{(y^2Dt+xy)}-W\left(\dfrac{-x}{\sqrt{4Dt}},-y\sqrt{Dt}\right), & \text{when } |\arg y|>3\pi/4.\end{cases} \tag{4.1}$$

The asymptotics of $\Omega(y\sqrt{Dt})$ are obtained by setting $x=0$ in the above equation. Thus, in our case, when a root is in the positive half of the complex plane the power-law asymptotics holds, whereas when it is negative an exponential term is added.

Consider first the possibility that a nonzero equilibrium solution is approached as $t\to\infty$. This cannot arise from the W-term with $y=\lambda_+$, since λ_+ is always positive. It cannot arise from the W-term with $y=\lambda_-$, although λ_- may be negative. This follows from the inequality

$$\lambda_-^2-a^2<0, \tag{4.2}$$

which we prove in Appendix C. Thus the factor $\exp[(\lambda_-^2-a^2)Dt]$, produced by the exponential factors in Eqs. (2.16) and (4.1), decays to zero with time. It remains to consider the root $y=-a$. When $a<0$, the argument of the W-function is positive so it decays to zero. However, when a is positive, the exponential factors in Eqs. (2.16) and (4.1) cancel identically, and the solution approaches its equilibrium limit

$$p(x,\infty)=\frac{2ak_d}{2k_aa+k_d}\exp(-2ax), \tag{4.3a}$$

$$p(*,\infty)=2ak_a/(2k_aa+k_d). \tag{4.3b}$$

Note that these two solutions are valid for *any* initial condition, and obey detailed balancing in the form $k_dp(*,\infty)=k_a\exp[U(x)/k_BT]p(x,\infty)$. Physically, it is expected to have an equilibrium solution only when diffusion is biased toward the (reversible) trap. The behavior for $k_d=0$ should be obtained separately, see Appendix B.

For brevity, let us introduce the notation

$$p_{\mathrm{eq}}=\begin{cases}2ak_a/(2k_aa+k_d), & \text{when } a>0,\\ 0, & \text{when } a\leqslant 0.\end{cases} \tag{4.4}$$

We can now obtain the long time asymptotic behavior for $p(*,t|*)-p_{\mathrm{eq}}$ and $p_{\mathrm{eq}}-p(*,t|x_0)$, which may correspond to experimentally observable populations. Since the transition in a has already been taken into account, the asymptotic behavior of these functions depends on λ_-. Thus we expect three different asymptotic behaviors according to the sign of λ_-, which is positive in the ''inner region'' $[a_-,a_+]$, negative in the ''outer region'' and zero for $a=a_\pm$.

(a) In the inner region, when $a_-<a<a_+$,

$$\lim_{t\to\infty}[p_{\mathrm{eq}}-p(*,t|x_0)]\sim\frac{k_a(-x_0\lambda_+\lambda_-aD+k_d-a^2D)}{(\lambda_+\lambda_-aD)^2}\,\frac{\exp(ax_0-a^2Dt)}{2Dt\sqrt{\pi Dt}}, \tag{4.5a}$$

$$\lim_{t\to\infty}[p(*,t|*)-p_{\mathrm{eq}}]\sim\frac{k_ak_d}{(\lambda_+\lambda_-aD)^2}\,\frac{\exp(-a^2Dt)}{2Dt\sqrt{\pi Dt}}. \tag{4.5b}$$

Note that $\lambda_+\lambda_-=(a_+-a)(a-a_-)$ is positive in this regime. Also, when $x_0=(k_d-a^2D)/(\lambda_+\lambda_-aD)$, the $t^{-3/2}$ term in Eq. (4.5a) vanishes so that the asymptotic behavior is determined by the next order term, which decays as $t^{-5/2}\exp(-a^2Dt)$.

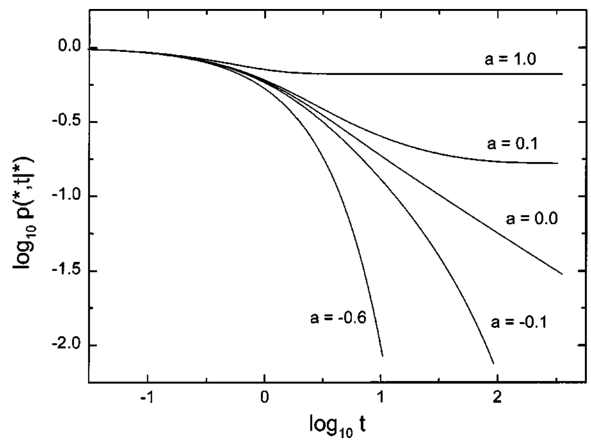

FIG. 3. The primary kinetic transition behavior in the long time asymptotic relaxation of the binding probability $p(*,t|*)$ for several values of a with the same parameters as in Fig. 1.

(b) In the outer region, when $a<a_-$ or $a>a_+$,

$$\lim_{t\to\infty}[p_{\mathrm{eq}}-p(*,t|x_0)]\sim-\frac{2k_a\lambda_-}{\Delta(\lambda_-+a)}\exp[(\lambda_-+a)x_0+(\lambda_-^2-a^2)Dt], \tag{4.6a}$$

$$\lim_{t\to\infty}[p(*,t|*)-p_{\mathrm{eq}}]\sim-\frac{2k_d\lambda_-}{\Delta(a^2-\lambda_-^2)}\exp[(\lambda_-^2-a^2)Dt]. \tag{4.6b}$$

Note that $\Delta>0$, whereas λ_- and $\lambda_-^2-a^2$ are negative in this regime.

(c) At the transitions $a=a_\pm$,

$$\lim_{t\to\infty}[p_{\mathrm{eq}}-p(*,t|x_0)]\sim\frac{1}{a}\,\frac{\exp(ax_0-a^2Dt)}{\sqrt{\pi Dt}}, \tag{4.7a}$$

$$\lim_{t\to\infty}[p(*,t|*)-p_{\mathrm{eq}}]\sim\frac{k_d}{k_aa^2}\,\frac{\exp(-a^2Dt)}{\sqrt{\pi Dt}}. \tag{4.7b}$$

Finally, when $a=0$, the results reduce to those of the field-free system,

$$\lim_{t\to\infty}p(*,t|x_0)=\lim_{t\to\infty}p(*,t|*)\sim\frac{k_a}{k_d}\,\frac{1}{\sqrt{\pi Dt}}. \tag{4.8}$$

In order to illustrate the primary transition behavior, we plot in Fig. 3 the binding probability $p(*,t|*)$ for several values of a in a log–log scale. When $a<0$, the decay curves decrease exponentially. On the other hand, when $a>0$, the binding probability approaches the constant $p(*,\infty)$ as given by Eq. (4.3b). These two regimes are separated by the transition region at $a=0$, for which the asymptotic behavior is the $t^{-1/2}$ power law decay.

In Fig. 4, the secondary transition behavior in $p'(*,t|*)\equiv p(*,t|*)\exp(a^2Dt)$ is demonstrated around $a_-=(1-\sqrt{5})/2=-0.618\,034\ldots$ on a log–log scale. Again a small difference around the transition value changes the fate of the probability drastically. When $a<a_-$, the relaxation curve increases exponentially. On the other hand, an

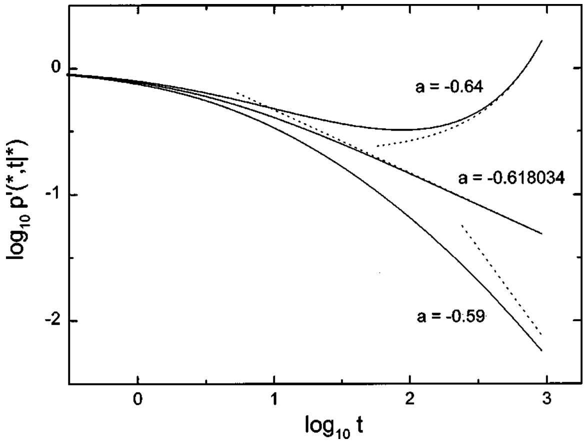

FIG. 4. The secondary kinetic transition in the long time asymptotic relaxation of the effective binding probability $p'(*,t|*)\equiv p(*,t|*)\exp(a^2Dt)$ near $a=a_-$ for several values of a with the same parameters as in Fig. 1. Dashed lines are the asymptotic expressions from Sec. IV.

asymptotic $t^{-3/2}$ decay appears when $a>a_-$. At the transition, $a=a_-$, the $t^{-1/2}$ asymptotics prevails. We observe a similar behavior also near $a=a_+$.

V. CONCLUSION

We have obtained the exact Green function solution for a reversible diffusion-influenced geminate reaction in the presence of a constant external field. Furthermore, we have analyzed the analytic solution, particularly at asymptotically long times, observing different kinds of kinetic transitions as a function of the field strength, a. A primary transition occurs when a changes sign, and then the ultimate ($t=\infty$) limits of the various probabilities change discontinuously. Secondary transitions occur at $a_\pm$, involving a discontinuous change in the approach to the $t=\infty$ limit, from a $t^{-3/2}$ power-law in the ''inner region'' $[a_-,a_+]$, to exponential in the region external to this interval. In the outer region, the absolute field strength $|a|$ is large and the effect of diffusion is rather suppressed to give exponential asymptotic behavior whereas $|a|$ is small in the inner region and the power law behavior typical of the diffusion process appears. Exactly at the three critical fields ($a=0$, a_+ and a_-) a $t^{-1/2}$ asymptotics sets in. Yet another transition occurs when $k_d=0$ namely, in the limit of irreversible recombination. To our knowledge, such intricate field-dependence of diffusion-influenced reactions has not been reported before.

Our analytic solution is based on mapping the problem solved in Part I, namely, excited-state reversible geminate-recombination without a field,[19] on the present problem. It follows that the analytic solution may be further extended, if desired, to the excited-state problem *with* a field. From a numerical point of view, the new Green function has an important role in allowing one to extend the many-body Brownian dynamics algorithms[24–27] to include an interaction potential in the simulation of reversible chemical reactions in solution. From a physical point of view, we have unraveled the possible field effects on one dimensional conductors[28,29] in the presence of a reversible trap. It would be interesting to search for the predicted behavior experimentally. This may not be a far-fetched aspiration, given that the corresponding transition in excited-state kinetics[20–22] has just been observed experimentally.[32]

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APPENDIX A: TRANSFORMATION TO RELATIVE COORDINATES

It is well known that two diffusing particles obey a diffusion equation in their relative separation coordinate, with a diffusion constant which equals the sum of their individual diffusion constants. In this appendix we extend the derivation to a constant force (e.g., ions between the plates of an infinite capacitor), showing that in the relative coordinate there will be an effective constant force. The starting equation in the laboratory coordinate system is the diffusion equation for the joint probability density of the two particles

$$\frac{\partial p(x_1,x_2,t)}{\partial t}=D_1\left[\frac{\partial^2 p(x_1,x_2,t)}{\partial x_1^2}+2a_1\frac{\partial p(x_1,x_2,t)}{\partial x_1}\right]+D_2\left[\frac{\partial^2 p(x_1,x_2,t)}{\partial x_2^2}+2a_2\frac{\partial p(x_1,x_2,t)}{\partial x_2}\right], \tag{A1}$$

where a_i is the field strength acting on the particle i and D_i its diffusion constant. Let us transform into the two variables

$$X=(D_2x_1+D_1x_2)/D, \quad x=(x_2-x_1), \tag{A2}$$

where $D\equiv D_1+D_2$ is an ''effective'' diffusion constant. X and x correspond to the ''center-of-mass'' and the relative interparticle separation, respectively. From the chain-rule for differentiation one obtains

$$\frac{\partial p}{\partial x_i}=\frac{\partial p}{\partial X}\frac{\partial X}{\partial x_i}+\frac{\partial p}{\partial x}\frac{\partial x}{\partial x_i}=\frac{D_j}{D}\frac{\partial p}{\partial X}+(-1)^i\frac{\partial p}{\partial x}, \tag{A3a}$$

$$\frac{\partial^2 p}{\partial x_i^2}=\left(\frac{D_j}{D}\right)^2\frac{\partial^2 p}{\partial X^2}+\frac{\partial^2 p}{\partial x^2}+2(-1)^i\frac{D_j}{D}\frac{\partial p}{\partial X}\frac{\partial p}{\partial x}, \tag{A3b}$$

where $i\neq j=1,2$. Substituting, we can rewrite Eq. (A1) as

$$\frac{\partial p(X,x,t)}{\partial t}=D'\frac{\partial^2 p(X,x,t)}{\partial X^2}+D\frac{\partial^2 p(X,x,t)}{\partial x^2}+2D'(a_1+a_2)\frac{\partial p(X,x,t)}{\partial X}+2(D_2a_2-D_1a_1)\frac{\partial p(X,x,t)}{\partial x}, \tag{A4}$$

where $D'=D_1D_2/D$. Using separation of variables

$$p(X,x,t)\equiv q(X,t)p(x,t), \tag{A5}$$

we get the following set of equations:

$$\frac{\partial q(X,t)}{\partial t} = D' \left[\frac{\partial^2 q(X,t)}{\partial X^2} + 2(a_1+a_2) \frac{\partial q(X,t)}{\partial X} \right], \quad \text{(A6a)}$$

$$\frac{\partial p(x,t)}{\partial t} = D \left[\frac{\partial^2 p(x,t)}{\partial x^2} + 2a \frac{\partial p(x,t)}{\partial x} \right], \quad \text{(A6b)}$$

where the effective field in the second equation is $a = (D_2 a_2 - D_1 a_1)/D$. For a pair of geminate particles, Eq. (A6b) is the one treated in the sequel.

APPENDIX B: IRREVERSIBLE LIMITS

The solutions given by Eqs. (2.16) comprise the limiting cases of both irreversible recombination ($k_d = 0$) and irreversible dissociation ($k_a = 0$), which we discuss herein.

When $k_d = 0$, we have $a_+ = k_a/D$, $a_- = 0$. Allowing $\Delta = k_a - 2Da$ to be both positive and negative, the two roots $\lambda_\pm$ are replaced by one which equals a, and a second one which we denote simply by $\lambda = k_a/D - a$. Subsequently, in Eq. (2.16a) only the last W-function survives, and we obtain

$$e^{a(x-x_0+aDt)}\, p(x,t|x_0) = f(x,t|x_0) - \lambda\; W\left(\frac{x+x_0}{\sqrt{4Dt}}, \lambda\sqrt{Dt} \right). \quad \text{(B1a)}$$

In contrast, all three W-functions survive in Eqs. (2.16b) and (2.16c), which reduce to

$$e^{-ax_0+a^2Dt}\, p(*,t|x_0) = \frac{1}{2} W\left(\frac{x_0}{\sqrt{4Dt}}, -a\sqrt{Dt} \right) + \frac{k_a}{2\Delta} W\left(\frac{x_0}{\sqrt{4Dt}}, a\sqrt{Dt} \right) - \frac{D\lambda}{\Delta}\; W\left(\frac{x_0}{\sqrt{4Dt}}, \lambda\sqrt{Dt} \right). \quad \text{(B1b)}$$

These solutions for irreversible recombination are equivalent to Eqs. (48) and (49) as reported by Agmon.[9]

The fact that now *two* roots change sign at $a = 0$, implies that two W-terms may contribute to the $t = \infty$ limit. The first one contributes, as in the reversible case, for $a > 0$, to give $p(*,\infty|x_0) = 1$. This agrees with the $k_d = 0$ limit of Eq. (4.4). Physically, it reflects the known property that in one dimension the probability of returning to the origin is unity. Unlike the reversible case, when $a < 0$ (motion away from the origin) the second W-term contributes to the limiting value of the binding probability. It becomes [cf. Eq. (51) of Ref. 9]

$$p(*,\infty|x_0) = \frac{k_a e^{2ax_0}}{k_a - 2Da}, \quad \text{(B2)}$$

instead of 0 in the reversible case. Indeed, reversibility provides repeated escape opportunities down the potential gradient, whereas in the irreversible case the fate is determined after a single binding event (if it occurs).

The approach to these limits can be obtained by setting $k_d = 0$ in the asymptotic expressions in Sec. IV, except in the case $a = 0$, where Eq. (4.8) does not hold. Indeed, when both $k_d = 0$ and $a = 0$ (therefore also one of the $\lambda_\pm$ vanishes), two of the W prefactors in (each of) Eqs. (2.16) assumes the form 0/0, which should be treated separately. Also note that since $a_- = 0$, there is no secondary first-order transition for $a < 0$, resulting in a $t^{-3/2}$ decay throughout this region.

When $k_a = 0$ (irreversible dissociation), $a_\pm = b_\pm = \pm\sqrt{k_d/D}$, $\Delta^2 = D(Da^2 - k_d)$, and $\lambda_\pm = \pm\Delta/2$. In Eq. (2.16a), only the first W-function contributes, and we obtain

$$e^{a(x-x_0+aDt)} p(x,t|x_0) = f(x,t|x_0) + aW\left(\frac{x+x_0}{\sqrt{4Dt}}, -a\sqrt{Dt} \right), \quad \text{(B3a)}$$

which is the solution for a reflective boundary. In the initially bound state, all three W-terms contribute, giving

$$e^{ax+a^2Dt} p(x,t|*) = a\; W\left(\frac{x}{\sqrt{4Dt}}, -a\sqrt{Dt} \right) - \frac{k_d}{2D(a+\lambda_-)} W\left(\frac{x}{\sqrt{4Dt}}, \lambda_-\sqrt{Dt} \right) - \frac{k_d}{2D(a+\lambda_+)} W\left(\frac{x}{\sqrt{4Dt}}, \lambda_+\sqrt{Dt} \right). \quad \text{(B3b)}$$

The binding probabilities clearly obey $p(*,t|x_0) = 0$ and $p(*,t|*) = \exp(-k_d t)$. The $t = \infty$ behavior in this case does follow Eq. (4.3) with $k_a = 0$. Whereas $p(x,\infty)$ shows a transition from 0 (for $a < 0$) to $2a\exp(-2ax)$ (for $a > 0$), $p(*,t) = 0$ in both cases so it does not undergo a transition at all.

APPENDIX C: IDENTITIES AND INEQUALITIES

To show that in the outer region $\lambda_-^2 - a^2 < 0$ when $k_d > 0$, consider the following identities:

$$D(\lambda_+ + a)(\lambda_- + a) = 2ak_a + k_d, \quad \text{(C1a)}$$

$$D(\lambda_+ - a)(\lambda_- - a) = k_d, \quad \text{(C1b)}$$

which follow directly from Eq. (2.12). Therefore, for $a > 0$, since $\lambda_+ + a > 0$ and also $2ak_a + k_d > 0$, one concludes that $\lambda_- + a > 0$. For $a < 0$, since $\lambda_+ - a > 0$ one has that $\lambda_- - a > 0$. Summarizing, we have

$$\begin{cases} \lambda_- + a > 0 & \text{when } a > 0, \\ \lambda_- - a > 0 & \text{when } a < 0. \end{cases} \quad \text{(C2)}$$

Now, in the outer region, either $a > a_+ > 0$ or $a < a_- < 0$. In both cases $\lambda_- < 0$. In the first case, $\lambda_- - a < 0$, therefore $\lambda_-^2 - a^2 = (\lambda_- - a)(\lambda_- + a) < 0$. In the second case, $\lambda_- + a < 0$, and we arrive at the same conclusion.

When $k_d = 0$, however, $\lambda_-^2 - a^2 = 0$ and thus the factor $\exp[(\lambda_-^2 - a^2)Dt]$ becomes unity for all times.

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