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Diffusion-Influenced Reversible Trapping Problem in the Presence of an External Field

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Abstract: We investigate the field effect on the diffusion-influenced reversible trapping problem in one dimension. The exact Green function for a particle undergoing diffusive motion between two static reversible traps with a constant external field is obtained. From the Green function, we derive the various survival probabilities. Two types of trap distribution for the many-body problem are considered, the periodic and random distributions. The mean survival probability is obtained for the crossing-forbidden case for the two types of trap distribution. For the periodic distribution it decays exponentially. For the random trap distribution, similar to the irreversible case, there exists a critical field strength at which the long time asymptotic behavior undergoes a kinetic transition from the power law to exponential behaviors. The difference between equilibrium concentrations for the two types of trap distribution due to the fluctuation effect of trap concentration vanishes as the field strength increases.

Keywords: diffusion • external fields • kinetic transition • survival probability

Introduction

The diffusion-influenced trapping problem has been extensively studied theoretically and experimentally during the last few decades.[1–21] Usually, the trapping problem has been treated in the irreversible case, whether the traps are perfect or imperfect. For the irreversible perfect traps, the exact solution is known only for one dimension (1D).[1–5] However, the asymptotic behavior is known not only for 1D but also for higher dimensions. In the absence of an external field, it is known that the long-time asymptotic behavior of the survival probability follows $\exp\left[-\mathrm{const}\cdot t^{d/(d+2)}\right]$ in d dimensions.[6–13] The slower decay relative to that of the classical exponential decay results from the existence of rare but large trap-free regions, where the lifetime of the particle is extremely long. This asymptotic behavior was proved rigorously by Donsker and Varadhan.[7]

Grassberger and Procaccia[14] found that, in the presence of an external field, the survival probability decays exponentially $\exp(-\kappa t)$ (κ is an effective rate constant depending on the field strength a). Moreover, it was found that there exists a critical field strength that separates two different regimes.[14–16] For the external field strength below its critical value, κ is proportional to the square of the field strength, whereas it is proportional to the field strength above its critical value. This transition can be explained qualitatively as follows. At low field strengths, the surviving particles spend all the time in large trap-free regions resisting the drift imparted by the applied external field ("localized behavior"), whereas at high field strengths, they go with the drift ("delocalized behavior"). Eisele and Lang proved this heuristic analysis rigorously.[15]

The trapping problem has been studied intensively in 1D as the effects of field strength and many-body correlations[17] are much more conspicuous than in higher dimensions. The experimental studies of the transfer of the excitation or charge carrier in many organic and nonorganic crystals[17,18] for high anisotropy (quasi-1D behavior) is an additional source of interest to the 1D case. Movaghar et al.[3] considered the hopping motion of a charge carrier on a 1D lattice with deep traps in the presence of an external field. They obtained an expression for the survival probability, which is exact over the whole time regime and arbitrary field strength for the low concentration of traps. Studies of the relaxation of photoconductivity in polydiacetylene crystals demonstrated that the predictions of their theory are in good agreement with the photocurrent kinetics observed over a wide range of fields, temperature, and times.[17] Glasser and Agmon[19] considered the trapping problem with

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scavengers. Aldea et al.[20] found an exact expression for the effective rate constant κ, thereby determining the long-time behavior in the hopping model on a lattice. For the continuous diffusion model, Agmon[4] analyzed the low-field case in detail over the whole time regime, and, later, Makhnovskii et al.[5] obtained the exact solution for the survival probability for arbitrary field strengths.

Tachiya and co-workers investigated the effect of an external electric field for the irreversible target problem in three dimensions and applied it to the analysis of relevant experiments.[22]

For the reversible trapping problem in 1D, Kim and Shin[23] obtained the exact solutions for a particle moving between two static traps at first and applied them to the many-body case. They found an interesting result in that the equilibrium concentration itself can be changed from the classical results due to the fluctuation of trap concentration.

The purpose of this work is to investigate the effect of an external field on the reversible trapping problem in 1D for a continuous diffusion model. The exact Green function for a particle moving between two static traps is shown below. From this Green function, various probabilities are exactly derived for an initially unbound or bound state. We also investigate the reversible trapping problem in 1D, in which many static traps are distributed along the line. We consider two types of distribution: periodic and random. On the basis of the assumption that the moving particle is forbidden to cross the traps, the mean survival probabilities of the particle are obtained exactly for both distributions. The kinetic transition behavior in the long-time asymptotic region is investigated for the random trap distribution, for which the critical value of the field strength is the same as for the irreversible perfect traps.

A Particle Moving Between Two Static Traps

Consider a particle diffusing between the two reversible static traps located at the origin $x=0$ and at $x=L$ under the influence of a constant external field of strength $2a$, that is, the particle moves in the potential $V(x)=2k_{\mathrm{B}}Tax$ ($k_{\mathrm{B}}T$ is the Boltzmann factor). When $a>0$, the particle moves toward the origin, whereas it moves to the trap located at L when $a<0$. The particle is trapped instantaneously with the intrinsic rate k_{a} and dissociates with the rate k_{d}. The Green function $p(x,t|x_0)$ is the probability density that the diffusing particle is located at x at time t, given that it is initially located at x_0. The Green function $p(x,t|x_0)$ evolves in time according to the diffusion Equation (1) (D is the diffusion constant of the particle).

$$\frac{\partial}{\partial t}p(x,t|x_0)=D\left(\frac{\partial^2}{\partial x^2}+2a\frac{\partial}{\partial x}\right)p(x,t|x_0) \tag{1}$$

The initial and boundary conditions are given by [Eq. (2)], [Eq. (3a)], [Eq. (3b)],

$$p(x,0|x_0)=\delta(x-x_0) \tag{2}$$

$$D\left(\frac{\partial}{\partial x}+2a\right)p(x,t|x_0)\bigg|_{x=0}=k_a p(0,t|x_0)-k_d p(*_0,t|x_0) \tag{3a}$$

$$D\left(\frac{\partial}{\partial x}+2a\right)p(x,t|x_0)\bigg|_{x=L}=-k_a p(L,t|x_0)+k_d p(*_L,t|x_0) \tag{3b}$$

where $\delta(x)$ is the Dirac delta function and $p(*,t|x_0)$ is the binding probability that the particle is in the bound state $(*)$ at time t, given that its initial location is x_0 in the unbound state. The evolution Equations (4a) and (4b) of the bound states are:

$$\frac{\partial}{\partial t}p(*_0,t|x_0)=k_a p(0,t|x_0)-k_d p(*_0,t|x_0) \tag{4a}$$

$$\frac{\partial}{\partial t}p(*_L,t|x_0)=k_a p(L,t|x_0)-k_d p(*_L,t|x_0) \tag{4b}$$

It is well-known that, after the transformation[24] $q(x,t|x_0)=e^{a(x-x_0+aDt)}p(x,t|x_0)$, [Eq. (1)] reduces to the simple diffusion Equation (5).

Abstract in Korean:

본 연구에서는 1차원에서 확산에 지배되는 가역적 함정문제에 미치는 외부 힘의 영향을 고찰하였다. 먼저 두 개의 고정된 가역적 함정 사이에 있는 한 입자의 확산운동에 대하여 정확한 그린함수를 구하고 이로부터 각종 생존 확률을 구하였다. 다체문제에 대하여는 주기적 또는 무질서한 두 가지 형태의 함정분포를 고려하였으며 입자가 함정을 뚫고 지나갈 수 없는 경우에 대하여 평균생존확률을 구하였다. 주기적 함정분포에 대한 평균생존확률은 시간에 대하여 지수함수적으로 감소하는 것을 보였다. 무질서한 함정분포의 경우 비가역적인 경우와 마찬가지로 외부 힘의 세기에 어떤 임계값이 존재하여 이 값을 중심으로 장시간 점근 양상이 지수법칙으로부터 지수함수로 전환되는 동역학적 전이현상이 나타나는 것을 발견하였다. 두 형태의 함정 분포에 대한 평형농도는 함정농도의 요동에 의하여 차이를 보이고 있으나 외부 힘의 세기가 증가함에 따라 그 차이가 사라지는 것을 발견하였다.

International Advisory Board Member

Kook Joe Shin *was born in 1946 in Seoul, Korea. He obtained his BSc at Seoul National Univ. (1970) and his PhD (1978) at McGill Univ. (Canada). After postdoctoral studies at the Univ. of Toronto (1977–1979), he joined the faculty at Seoul National Univ., where he is currently Professor. His research interests lie in theoretical chemistry (molecular and reaction dynamics in solution, diffusion of molecules on solid surfaces) and in their computer simulation. He has served on many committees and societies, most recently as President of the Korean Chemical Society.*

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$$\frac{\partial}{\partial t} q(x,t|x_0) = D\frac{\partial^2}{\partial x^2} q(x,t|x_0) \tag{5}$$

For the bound states, we introduce the supplementary transformations [Eq. (6a–d)].[25]

$$q(*_0,t|x_0) = \exp[a(-x_0 + aDt)]\,p(*_0,t|x_0) \tag{6a}$$

$$q(*_L,t|x_0) = \exp[a(L - x_0 + aDt)]\,p(*_L,t|x_0) \tag{6b}$$

$$q(x,t|*_0) = \exp[a(x + aDt)]\,p(x,t|*_0) \tag{6c}$$

$$q(x,t|*_L) = \exp[a(x - L + aDt)]\,p(x,t|*_L) \tag{6d}$$

With the aid of [Eq. (6a–d)], [Eq. (2)] and [Eq. (3a,b)] become [Eq. (7)] and [Eq. (8a,b)], respectively,

$$q(x,0|x_0) = \delta(x - x_0) \tag{7}$$

$$D\frac{\partial}{\partial x} q(x,t|x_0)\bigg|_{x=0} = (k_a - aD)\,q(0,t|x_0) - k_d q(*_0,t|x_0) \tag{8a}$$

$$D\frac{\partial}{\partial x} q(x,t|x_L)\bigg|_{x=L} = -(k_a + aD)\,q(L,t|x_0) + k_d q(*_L,t|x_0) \tag{8b}$$

and [Eq. (4a,b)] become [Eq. (9a,b)], respectively.

$$\frac{\partial}{\partial t} q(*_0,t|x_0) = k_a q(0,t|x_0) - \left(k_d - a^2D\right) q(*_0,t|x_0) \tag{9a}$$

$$\frac{\partial}{\partial t} q(*_L,t|x_0) = k_a q(L,t|x_0) - \left(k_d - a^2D\right) q(*_L,t|x_0) \tag{9b}$$

By introducing the Laplace transform, $\hat{f}(s) = \int_0^\infty f(t)e^{-st}\,dt$, [Eq. (5)] becomes [Eq. (10)].

$$s\hat{q}(x,s|x_0) - \delta(x - x_0) = D\frac{\partial^2}{\partial x^2}\hat{q}(x,s|x_0) \tag{10}$$

The boundary conditions in the Laplace space can be rewritten, with the help of [Eq. (9a,b)] as [Eq. (11a,b)],

$$D\frac{\partial}{\partial x}\hat{q}(x,s|x_0)\bigg|_{x=0} = D\left[\left(z^2 - a^2\right)U(z) - a\right]\hat{q}(0,s|x_0) \tag{11a}$$

$$D\frac{\partial}{\partial x}\hat{q}(x,s|x_0)\bigg|_{x=L} = -D\left[\left(z^2 - a^2\right)U(z) + a\right]\hat{q}(L,s|x_0) \tag{11b}$$

where $z \equiv \sqrt{s/D}$ and $U(z) = k_a/\left[k_d + D\left(z^2 - a^2\right)\right]$.

We start with the trial solution of the form [Eq. (12)].[26]

$$\hat{q}(x,s|x_0) = \frac{1}{2Dz}e^{-z|x-x_0|} + Ae^{zx} + Be^{-zx} \tag{12}$$

In this case, the unknown coefficients A and B are to be determined so that the trial solution satisfies the initial and boundary conditions. One readily obtains the coefficients as [Eq. (13a,b)],

$$A = \frac{1 - (z+a)U(z)}{2Dz(z+a)Y(z,L)} \times\left\{z\cosh zx_0 + \left[\left(z^2 - a^2\right)U(z) - a\right]\sinh zx_0\right\}\exp(-zL) \tag{13a}$$

$$B = \frac{1 - (z-a)\,U(z)}{2Dz(z-a)Y(z,L)} \times\left\{z\cosh z(L - x_0) + \left[\left(z^2 - a^2\right)U(z) + a\right]\sinh z(L - x_0)\right\} \tag{13b}$$

where $Y(z,L) \equiv \left[1 + \left(z^2 - a^2\right)U^2(z)\right]\sinh zL + 2zU(z)\cosh zL$. By substituting [Eq. (13a,b)] into [Eq. (12)], after some rearrangements, we obtain [Eq. (14)],

$$\hat{q}(x,s|x_0) = \frac{W_+(z, L - x_>)\,W_-(z, x_<)}{Dz(z^2 - a^2)Y(z,L)} \tag{14}$$

where $x_> = \max\{x, x_0\}$, $x_< = \min\{x, x_0\}$, and [Eq. (15)].

$$W_\pm(z,x) = z\cosh zx + \left[\left(z^2 - a^2\right)U(z) \pm a\right]\sinh zx \tag{15}$$

From the theory of inverse Laplace transform,[26] the inversion of $\hat{q}(x,s|x_0)$ into the time domain is given by $q(x,t|x_0) = \sum_{\text{residues}} \lim_{s\to s^*}(s - s^*)\hat{q}(x,s|x_0)e^{st}$, where s^* is one of the roots of the denominator in [Eq. (14)]. Thus the exact solution in the time domain can be obtained by summing up an infinite number of residues to find [Eq. (16a–c)],

$$q(x,t|x_0) = \frac{a\exp\{a[L - (x + x_0) + aDt]\}}{\sinh aL + 2aK\cosh aL} + 2\sum_{n=1}^{\infty}\frac{F_-(\beta_n)W_-(\beta_n,x)\,W_-(\beta_n,x_0)}{\left(\beta_n^2 - a^2\right)X(\beta_n,L)}\exp\left(-D\alpha_n^2 t/L^2\right) \tag{16a}$$

$$X(\beta,L) = L\,N(\beta) + 2U(\beta)\left[1 - \left(\beta^2 + a^2\right)U^2(\beta)\right] + 2\beta\frac{dU(\beta)}{d\beta}\left[1 - \left(\beta^2 - a^2\right)U^2(\beta)\right] \tag{16b}$$

$$Y[\beta(\neq 0), L] = 0 \tag{16c}$$

where $K = k_a/k_d$, $\beta_n = i\alpha_n/L$, $F_\pm(\beta) = [1 \pm aU(\beta)]^2 - \beta^2U^2(\beta)$, and $N(\beta) \equiv F_+(\beta)\,F_-(\beta)$ with $i = \sqrt{-1}$. β_n and α_n can be obtained by finding the roots of Equation (16c). One can easily find that as n increases α_n becomes closer to the integral multiple of π. The solution is not in a closed form. However, its value can be easily calculated, as the exponential factor $\exp\left(-D\alpha_n^2 t/L^2\right)$ decays rapidly as α_n becomes large. Notably, the Green function given by Equation (16a) reduces correctly to the solutions of the reflecting boundary, perfect traps, and zero-field case,[23,26] respectively. It can be shown that Equation (16a) reduces to the solution of the reversible geminate reaction when $L \to \infty$.[25]

The survival probability of the particle that is initially in the unbound state located at x_0 to remain in the unbound state at time t, $S(t|x_0)$, is defined as $S(t|x_0) = int_0^L dx\, p(x,t|x_0) = \exp[\,a\,(x_0 - aDt)\,] \int_0^L dx\, e^{-ax} q(x,t|x_0)$. Thus we need to integrate $e^{-ax}q(x,t|x_0)$ over x. The survival probability can be obtained as [Eq. (17)],

$$S(t|x_0) = \frac{\tanh aL}{\tanh aL + 2aK} - 2\sum_{n=1}^{\infty} \frac{\beta_n U(\beta_n)\, W_-(\beta_n, L)}{\left(\beta_n^2 - a^2\right) X(\beta_n, L)} \times \left[\, F_-(\beta_n) + M(\beta_n, L)\, e^{-aL}\,\right] \exp\left[\, a\,(x_0 - aDt) - D\alpha_n^2 t/L^2\,\right] \tag{17}$$

where $M(\beta,\, L)$ is given by [Eq. (18)].

$$M(\beta, L) \equiv \frac{F_\pm(\beta)\, W_\pm(\beta, L)}{\beta} = \frac{N(\beta)\, \cosh\beta L}{\left[\,1 + (\beta^2 - a^2)\, U^2(\beta)\,\right]} \tag{2.18}$$

The value of $M(\beta, L)$ is either $\sqrt{N(\beta)}$ or $-\sqrt{N(\beta)}$ as $Y(\beta, L) = 0$. Furthermore, $M(\beta, L)$ satisfies the following relation [Eq. (19)].

$$M(\beta, L)\, W_\pm(\beta, L) \equiv F_\pm(\beta)\, W_\mp(\beta, L) \tag{19}$$

In the absence of an external field, Equation (17) reduces correctly to the previous results, Equation (11) of reference [23]. However, the expression for $H(\beta)$ in reference [23] should be corrected to $H(\beta, L) = \left\{\,\left[\,1 - X^2(\beta)\,\right] / \left[\,1 + X^2(\beta)\,\right]\,\right\} \cosh\beta L$.

The binding probabilities for the initially unbound states can be obtained from the Laplace-transformed Equation (9) through Equation (14) as [Eq. (20 a, b)].

$$p(*_0, t|x_0) = \frac{aK \exp(aL)}{\sinh aL + 2aK \cosh aL} + 2\sum_{n=1}^{\infty} \frac{\beta_n U(\beta_n)\, W_-(\beta_n, x_0)}{\left(\beta_n^2 - a^2\right) X(\beta_n, L)} F_-(\beta_n) \times \exp\left[\, a\,(x_0 - aDt) - D\alpha_n^2 t/L^2\,\right] \tag{20a}$$

$$p(*_L, t|x_0) = \frac{aK \exp(-aL)}{\sinh aL + 2aK \cosh aL} + 2\sum_{n=1}^{\infty} \frac{\beta_n U(\beta_n)\, W_-(\beta_n, x_0)}{\left(\beta_n^2 - a^2\right) X(\beta_n, L)} M(\beta_n, L) e^{-aL} \times \exp\left[\, a\,(x_0 - aDt) - D\alpha_n^2 t/L^2\,\right] \tag{20b}$$

The normalization condition, $S(t|x_0) + p(*_0, t|x_0) + p(*_L, t|x_0) = 1$, can be easily verified by summing Equation (17) and Equation (20).

One can show the symmetry relations with respect to the direction of the applied field $[S(t|x_0)]_a = [S(t|L - x_0)]_{-a}$ and $[p(*_0, t|x)]_a = [p(*_L, t|L - x)]_{-a}$ by using Equation (19). On the other hand, the symmetry of the binding probabilities between the left and right traps averaged over the initial position is now broken in the presence of the applied field.

The probabilities of finding the unbound particle at x at time t for the initially bound states can be obtained by using the detailed balance conditions [Eq. (21 a, b)].[27]

$$k_a p(x, t|*_0) = k_d \exp(-2ax) p(*_0, t|x) \tag{21a}$$

$$k_a p(x, t|*_L) = k_d \exp[2a(L - x)] p(*_L, t|x) \tag{21b}$$

Notably, Equation (21 a, b) can be simplified to $k_a q(x, t|*) = k_d q(*, t|x)$ for the transformed quantity, where $*$ represents the bound state (either $*_0$ or $*_L$). Equation (21 a, b) and Equation (20) can then be used to determine the probabilities of finding the unbound particle at x at time t for the initially bound states [Eq. (22 a, b)].

$$p(x, t|*_0) = \frac{a \exp[\, a\,(L - 2x)\,]}{\sinh aL + 2aK \cosh aL} + \frac{2}{K}\sum_{n=1}^{\infty} \frac{\beta_n U(\beta_n)\, W_-(\beta_n, x_0)}{\left(\beta_n^2 - a^2\right) X(\beta_n, L)} F_-(\beta_n) \times \exp\left[\, -a\,(x + aDt) - D\alpha_n^2 t/L^2\,\right] \tag{22a}$$

$$p(x, t|*_L) = \frac{a \exp[\, a\,(L - 2x)\,]}{\sinh aL + 2aK \cosh aL} + \frac{2}{K}\sum_{n=1}^{\infty} \frac{\beta_n U(\beta_n)\, W_-(\beta_n, x_0)}{\left(\beta_n^2 - a^2\right) X(\beta_n, L)} M(\beta_n, L) e^{aL} \times \exp\left[\, -a\,(x + aDt) - D\alpha_n^2 t/L^2\,\right] \tag{22b}$$

The survival probabilities of finding the particle in the unbound state at time t for the initially bound states, $S(t|*) = \int_0^L dx\, p(x, t|*)$, are obtained by the direct integration of [Eq. (22 a, b)] to give [Eq. (23 a, b)].

$$S(t|*_0) = \frac{\tanh aL}{\tanh aL + 2aK} - \frac{2}{K}\sum_{n=1}^{\infty} \frac{\beta_n^2 U^2(\beta_n) \exp\left[\, -D\,\left(\alpha_n^2/L^2 + a^2\right) t\,\right]}{\left(\beta_n^2 - a^2\right) X(\beta_n, L)} \times \left[\, F_-(\beta_n) + M(\beta_n, L)\, e^{-aL}\,\right] \tag{23a}$$

$$S(t|*_L) = \frac{\tanh aL}{\tanh aL + 2aK} - \frac{2}{K}\sum_{n=1}^{\infty} \frac{\beta_n^2 U^2(\beta_n) \exp\left[\, -D\,\left(\alpha_n^2/L^2 + a^2\right) t\,\right]}{\left(\beta_n^2 - a^2\right) X(\beta_n, L)} \times \left[\, F_+(\beta_n) + M(\beta_n, L)\, e^{aL}\,\right] \tag{23b}$$

The probabilities of the particle that is initially in the bound state and remains bound at time t can be obtained from Equations (5), (8), and (9), which hold also for the initially bound state. These are obtained as [Eq. (24 a–d)].

$$p(*_0, t|*_0) = \frac{aK \exp(aL)}{\sinh aL + 2aK \cosh aL} + \frac{2}{K}\sum_{n=1}^{\infty} \frac{\beta_n^2 U^2(\beta_n) \exp\left[\, -D\,\left(\alpha_n^2/L^2 + a^2\right) t\,\right]}{\left(\beta_n^2 - a^2\right) X(\beta_n, L)} F_-(\beta_n) \tag{24a}$$

$$p(*_L, t|*_0) = \frac{aK\exp(-aL)}{\sinh aL + 2aK\cosh aL} + \frac{2}{K}\sum_{n=1}^{\infty}\frac{\beta_n^2 U^2(\beta_n)\exp\left[-D\left(\alpha_n^2/L^2 + a^2\right)t\right]}{\left(\beta_n^2 - a^2\right)X(\beta_n, L)} M(\beta_n, L)e^{-aL} \tag{24b}$$

$$p(*_0, t|*_L) = \frac{aK\exp(aL)}{\sinh aL + 2aK\cosh aL} + \frac{2}{K}\sum_{n=1}^{\infty}\frac{\beta_n^2 U^2(\beta_n)\exp\left[-D\left(\alpha_n^2/L^2 + a^2\right)t\right]}{\left(\beta_n^2 - a^2\right)X(\beta_n, L)} M(\beta_n, L)e^{aL} \tag{24c}$$

$$p(*_L, t|*_L) = \frac{aK\exp(-aL)}{\sinh aL + 2aK\cosh aL} + \frac{2}{K}\sum_{n=1}^{\infty}\frac{\beta_n^2 U^2(\beta_n)\exp\left[-D\left(\alpha_n^2/L^2 + a^2\right)t\right]}{\left(\beta_n^2 - a^2\right)X(\beta_n, L)} F_+(\beta_n) \tag{24d}$$

The normalization condition and the symmetry relations, $[S(t|*_0)]_a = [S(t|*_L)]_{-a}$, $[p(*_0,t|*_0)]_a = [p(*_L,t|*_L)]_{-a}$, and $[p(*_L,t|*_0)]_a = [p(*_0,t|*_L)]_{-a}$ hold also for the initially bound states.

The equilibrium expression of the probabilities in the weak-field and strong-field limits are summarized in Table 1. For the weak-field limit, the equilibrium expressions are the same as in the previous work.[23] On the other hand, for the strong-field limit, the probabilities vanish, except for the final bound state at the origin for which it becomes unity: $p(x,\infty) = S(\infty) \approx 0$, $p(*_L,\infty) \approx 0$, and $p(*_0,\infty) \approx 1$ when $a > 0$, that is, the particle is pushed to the trap at the origin. When the field is reversed, it is forced to move toward the opposite trap, that is, $p(*_0,\infty) \approx 0$ and $p(*_L,\infty) \approx 1$.

Table 1. Equilibrium expressions of the binding and survival probabilities.

Probabilities	$t \to \infty$	Weak field[23]	Strong field
$p(x,t)$	$\frac{a\exp[a(L-2x)]}{\sinh aL + 2aK\cosh aL}$	$\frac{1}{L+2K}$	$\frac{2a\exp(-2ax)}{1+2aK} \approx 0$
$p(*_0,t)$	$\frac{aK\exp(aL)}{\sinh aL + 2aK\cosh aL}$	$\frac{K}{L+2K}$	$\frac{2aK}{1+2aK} \approx 1$
$p(*_L,t)$	$\frac{aK\exp(-aL)}{\sinh aL + 2aK\cosh aL}$	$\frac{K}{L+2K}$	$\frac{2aK\exp(-aL)}{1+2aK} \approx 0$
$S(t)$	$\frac{\sinh aL}{\sinh aL + 2aK\cosh aL}$	$\frac{L}{L+2K}$	$\frac{1}{1+2aK} \approx 0$

The Reversible Trapping Problem

In this section, we consider the reversible trapping problem in 1D in which many traps are distributed along a straight line. For the reversible systems, unlike the irreversible perfect trapping problem, we have two cases to consider. We exclude the possibility that the particle jumps over a trap. When the dissociation occurs, a particle bound to a trap can be released either in the same or in the opposite direction relative to the previous location of its unbound state. For a usual chemical reaction, the particle remembers its history, that is, it tends to dissociate toward the past location unless the rotational diffusion of the bound pair is so fast that the particle can forget its history while it is in the bound state. Another case would be the recombination of charge carriers for which the particle can be released from the trap randomly. In the previous work,[23] we defined the two cases as a) the crossing-forbidden trapping problem (CFTP) and b) the crossing-allowed trapping problem (CATP), respectively. Notably, the crossing takes place only when the bound particle dissociates. The CFTP can be reduced effectively to the problem of a particle between two static traps considered in the previous section. The CATP does not exist for the irreversible perfect traps.

Let us consider the survival probability $Q(t)$ for an unbound particle between two traps when the initial distribution of the particle is uniform [Eq. (25a)]:

$$Q(t) = \frac{1}{L}\int_0^L dx_0\, S(t|x_0) = \frac{\tanh aL}{\tanh aL + 2aK} + \frac{4}{L}\sum_{n=1}^{\infty}\frac{\beta_n^2 U(\beta_n)\left[R(\beta_n) + T(\beta_n, L)M(\beta_n, L)\right]}{\left(\beta_n^2 - a^2\right)^2 X(\beta_n, L)} \times \exp\left[-D\left(\alpha_n^2/L^2 + a^2\right)t\right], \tag{25a}$$

where $R(\beta)$ and $T(\beta,L)$ are given by [Eq. (25b,c)].

$$R(\beta) = U(\beta)\left\{\left(\beta^2 - a^2\right)\left[1 - \left(\beta^2 - a^2\right)U^2(\beta)\right] + 4a^2\right\} \tag{25b}$$

$$T(\beta, L) = \left(\beta^2 - a^2\right)U(\beta)\cosh aL + 2a\sinh aL \tag{25c}$$

As $Q(t)$ does not depend on the initial position, it shows the same long-time asymptotic behavior as $S(t|x_0)$. Notably, [Eq. (25a)] is symmetrical under inversion of the applied field. The mean survival probability $\langle S(t)\rangle$ for an initially unbound particle averaged over all intertrap intervals for the CFTP is given by[2,4] $\langle S(t)\rangle = \int_0^\infty dL\, Q(t)w(L)$ where $w(L)$ is the weight function for an interval L. We now consider two types of trap distribution: periodic and random.

Periodic Trap Distribution

For the periodic trap distribution, the weight function is given by $w(L) = \delta(L - c^{-1})$ (c is the concentration of traps). Thus the mean survival probability for the periodic trap distribution, $\langle S_p(t)\rangle$, for the CFTP is easily obtained as [Eq. (26)].

$$\langle S_p(t)\rangle = \left\langle S_p^{\mathrm{eq}}\right\rangle - 4c^3 \sum_{n=1}^{\infty}\frac{\alpha_n^2 U(ic\alpha_n)\left[R(ic\alpha_n) + T\left(ic\alpha_n, c^{-1}\right)M\left(ic\alpha_n, c^{-1}\right)\right]}{\left(c^2\alpha_n^2 + a^2\right)^2 X(ic\alpha_n, c^{-1})} \times \exp\left[-D\left(\alpha_n^2 c^2 + a^2\right)t\right] \tag{26}$$

In this equation, $\left\langle S_p^{\rm eq}\right\rangle = \tanh(a/c)\left[\tanh(a/c)+2aK\right]^{-1}$. As the symmetry between the left and right traps for a given interval is now broken, as noted earlier for [Eq. (20)], the CATP is not equivalent to the CFTP when the field is applied, in contrast to the reversible traps without the field.[23]

For the CFTP, one can verify that the equilibrium constant is given by [Eq. (27)].

$$K_{\rm eq} \equiv \frac{1-\left\langle S_p^{\rm eq}\right\rangle}{C\langle S_p^{\rm eq}\rangle} = 2K\frac{a/c}{\tanh(a/c)} \tag{27}$$

Interestingly, the equilibrium ratio of the bound and unbound particles is an even function of the ratio of the applied field strength and the concentration, a/c. The meaning of the above equation is that a) for a given concentration, more bound product is created as the field strength increases and, b) for a given field strength, an increase in the concentration lowers the field effect. The weak and strong field approximations of [Eq. (27)] can be obtained as [Eq. (28a, b)], respectively.

$$K_{\rm eq}/2K \approx 1+(a/c)^2/3 \qquad \text{(weak field)} \tag{28a}$$

$$K_{\rm eq}/2K \approx a/c \qquad \text{(strong field)} \tag{28b}$$

The constant $2K$ in [Eq. (28 a, b)] can be explained by the fact that we have to count the incoming fluxes of the particle from both sides of a trap for the many-trap problem, which is equivalent to replacing $k_{\rm a}$ by $2k_{\rm a}$.[23]

For the irreversible perfect traps ($k_{\rm a}\to\infty$ and $k_{\rm d}=0$), [Eq. (26)] correctly reduces to the expression [Eq. (29)] obtained earlier.[3,4]

$$\begin{aligned}\left\langle S_p(t)\right\rangle = 4c^4\pi^2 \sum_{n=1}^{\infty}\frac{n^2\left[1-(-1)^n\cosh(a/c)\right]}{(c^2\pi^2n^2+a^2)^2}\\ \times\exp\left[-D\left(c^2n^2\pi^2+a^2\right)t\right]\end{aligned} \tag{29}$$

For the periodic traps, the mean survival probability shows exponential decay for both reversible and irreversible cases at long times, namely, the same decay law as in the classical kinetics. This can be explained by the lack of the fluctuation effect for the periodic traps.

Random Trap Distribution

The mean survival probability for the random trap distribution, $\langle S_r(t)\rangle$, for the CFTP can be evaluated again from [Eq. (25 a–c)] with the well known weight function[2,4] $w(L)=c^2L\exp(-cL)$ to give [Eq. (30)],

$$\begin{aligned}\langle S_r(t)\rangle = \left\langle S_r^{\rm eq}\right\rangle\\ +4c^2\int_0^\infty dL\sum_{n=1}^{\infty}\frac{\beta_n^2U(\beta_n)\left[R(\beta_n)+T(\beta_n,L)\,M(\beta_n,L)\right]}{\left(\beta_n^2-a^2\right)^2X(\beta_n,L)}\\ \times\exp\left[-\left(cL+D\alpha_n^2t/L^2\right)-Da^2\,t\right],\end{aligned} \tag{30}$$

where $\left\langle S_r^{\rm eq}\right\rangle$ is given by [Eq. (31)].

$$\left\langle S_r^{\rm eq}\right\rangle = \int_0^\infty dL\,c^2L\exp(-cL)\,\frac{\tanh aL}{\tanh aL+2aK} \tag{31}$$

For the irreversible perfect traps, [Eq. (30)] reduces correctly to Equation (51) of reference [4].

The weak- and strong-field approximations for $\left\langle S_r^{\rm eq}\right\rangle$ can be obtained, respectively, as [Eq. (32 a, b)].

$$\left\langle S_r^{\rm eq}\right\rangle \approx \left\langle S_r^{\rm eq}\right\rangle_0-(2cK/3)g(2cK)(a/c)^2 \qquad \text{(weak field)} \tag{32a}$$

$$\left\langle S_r^{\rm eq}\right\rangle \approx \left(1+2|a|K\right)^{-1} \qquad \text{(strong field)} \tag{32b}$$

$\left\langle S_r^{\rm eq}\right\rangle_0 \equiv 1-2cK+(2cK)^2\exp(2cK)E_1(2cK)$ is the equilibrium mean survival probability in the absence of the field and $g(x)\equiv 2-2x+3x^2+x^3-x^3(4+x)\exp(x)E_1(x)$ with $E_1(x)\equiv\int_x^\infty dt\,e^{-t}/t$ the exponential integral. Notably, when $2aK=\pm1$, $\left\langle S_r^{\rm eq}\right\rangle = (1+2cK)\left[2\left(1+cK\right)^2\right]^{-1}$.

For the irreversible perfect traps with no external field ($a=0$), the asymptotic behavior of the decay kinetics follows the $\exp\left(-\text{const}\cdot t^{1/3}\right)$ law,[1,6–13] which is quite different to the classical one owing to the fact that contribution to the survival probability from the large trap-free region makes the kinetics become slower than the classical version. Similarly, for the reversible CFTP without the field, it is easy to show that the asymptotic behavior is qualitatively the same as that for the irreversible perfect traps. However, for the irreversible perfect traps in the presence of an external field, the asymptotic behavior of the survival probability is always exponential, $\exp(-\kappa t)$, in contrast to the case without the field. Moreover, it was found that there exists a critical field strength that separates two different regimes.[2–5,14–16] If the field strength is below the critical value, κ depends only on the field strength and diffusion constant. On the other hand, above the critical value, it depends also on the concentration of the traps. It can be explained qualitatively as follows. When the field is applied, the drift is caused by the field and competes with the diffusion. The drift accelerates the trapping while the diffusion resists the trapping by spreading the particle throughout the free region. Thus, as the field increases, there exists a kinetic transition from one which is governed by the diffusion to the other which is dominated by the drift. This transition in kinetics was proved rigorously by Eisele and Lang[15] for the continuum model.

For the reversible traps with an external field, we also expect the kinetic transition of the long-time asymptotic behavior of the second term of [Eq. (30)], $\langle S_r(t)\rangle-\left\langle S_r^{\rm eq}\right\rangle$, which corresponds to the concentration deviation, in the CFTP. In Figure 1, $\log_{10}\left[-\ln\left(\langle S_r(t)\rangle-\left\langle S_r^{\rm eq}\right\rangle\right)-Da^2t\right]$ is plotted against $\log_{10}t$. For $a<c$, its slope approaches $1/3$ which means that the deviation of the mean survival probability follows asymptotically as $\exp\left(-\text{const}\cdot t^{1/3}\right)\exp\left(-Da^2t\right)$. As the field strength increases, the approach to the asymptotic slope $1/3$ occurs later in time. For $a>c$, it first increases and then decreases exponentially as $\exp(-\kappa t)$. Apparently, the transition region occurs at $a=c$.

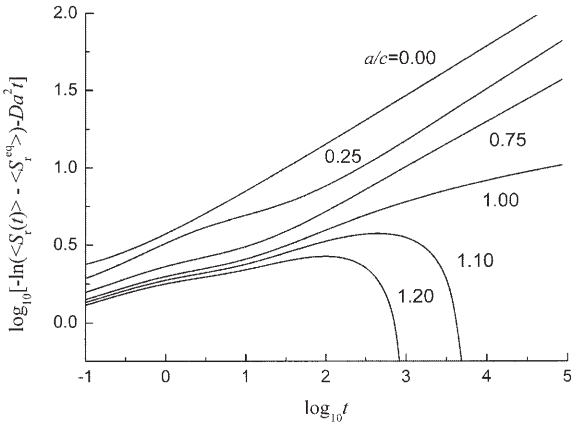

Figure 1. Time dependence of $-\ln\left(\langle S_r(t)\rangle - \langle S_r^{\rm eq}\rangle\right) - Da^2t$ in log scale for various field strengths a/c for the CFTP. Parameter values are $k_a = 100$ Å ns^{-1}, $k_d = 10$ Å ns^{-1}, $D = 200$ Å^{2}ns^{-1}, and $c = 2.0 \times 10^{-2}$ Å^{-1}. Notably, the slope is 1/3 at long times when $a < c$, whereas $\langle S_r(t)\rangle - \langle S_r^{\rm eq}\rangle \sim \exp(-\kappa t)$ with $\kappa = Dc(2a - c)$ when $a > c$.

As the particles cannot cross the traps in the CFTP, the competition between the drift caused by the applied field and the diffusion is the same as that for the irreversible perfect traps. Therefore, it is not surprising to find that κ should have the same value, $Dc(2a - c)$, as for the irreversible perfect traps.[5]

For finite field strengths, the equilibrium concentration is given by the first term in [Eq. (26)] for the periodic trap distribution and [Eq. (31)] for the random distribution, respectively. As the field strength increases the difference between equilibrium concentrations, owing to the fluctuation effect of the trap concentration, for the two types of trap distributions vanishes near the transition region and eventually the equilibrium concentration vanishes as shown in Figure 2.

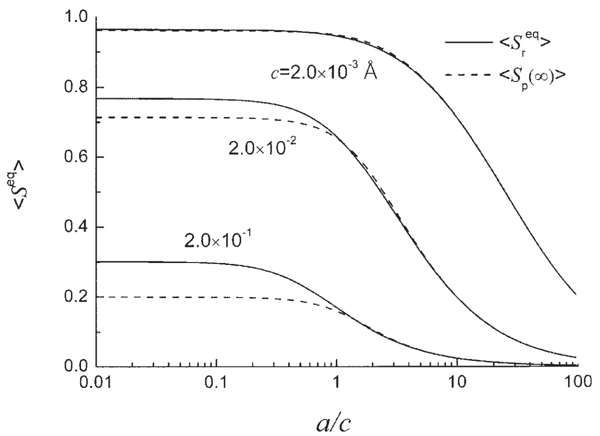

Figure 2. Plot of the equilibrium survival probabilities as functions of a/c for several values of c for the CFTP: $\langle S_r^{\rm eq}\rangle$ (solid lines) for the random trap distribution and $\langle S_p^{\rm eq}\rangle$ (dashed lines) for the periodic distributions. Other parameter values are the same as in Figure 1. The fluctuation effect on the equilibrium survival probabilities vanishes as the external field strength increases.

Concluding Remarks

We investigate the field effect on the diffusion-influenced reversible trapping problem in 1D. The exact Green function for a particle undergoing diffusive motion between two static reversible traps with a constant external field is obtained. We also obtained the analytical expressions of the mean survival probabilities for the periodic and random distributions of traps for the CFTP.

For the periodic trap distribution, the deviation of the mean survival probability from its equilibrium value decays exponentially owing to the lack of the fluctuation effect. However, for the random distribution, the asymptotic behavior of the deviation of the mean survival probability, $\langle S_r(t)\rangle - \langle S_r^{\rm eq}\rangle$, undergoes the kinetic transition from $\exp(-\kappa t)$, in which $\kappa = Dc(2a - c)$, when $a > c$ to $\exp(-{\rm const}\cdot t^{1/3})\exp(-Da^2t)$ when $a < c$.

The difference between equilibrium concentrations for both trap distributions due to the fluctuation effect of trap concentration vanishes as the field strength increases. On the other hand, in the case without field, the ratio of both equilibrium concentrations reaches a plateau value as the concentration is increased.[23]

Previously, the *irreversible* trapping problem had been studied by the Monte Carlo simulation which is rather inefficient for the *reversible* problem to study the long-time behavior since it requires too much computing time. A very efficient Brownian dynamics simulation algorithm was developed by Edelstein and Agmon[28] for the diffusion-influenced reversible reactions which utilizes the exact geminate solutions. Their algorithm, which enabled us to extend the time regime long enough to investigate the long-time asymptotic behavior of the system, is being extended to be applied to the reversible trapping problem.

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