Exact evaluation of diffusion dynamics in a potential well with a general delocalized sink

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We derive an exact solution of the Smoluchowski equation for a Brownian particle moving in an arbitrary potential well with a general delocalized sink. The average rate constant for the general sink is expressed explicitly in terms of the corresponding rate constants for localized sinks with different initial conditions and sink positions. Simple analytical expressions are provided for diffusion in a harmonic potential well.

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The study of dynamics of diffusive motion in a potential well in the presence of a sink has long been of interest [1] due to its applications to a wide variety of dynamical processes [2,3] in different branches of physics and chemistry. The modified Smoluchowski equation governing the probability distribution $f(x,t)$ corresponding to diffusion in a potential $V(x)$ in the presence of a sink function $S(x)$ and also a position-independent radiative decay rate k_r is given by

$$\frac{\partial f}{\partial t}=D\left[\frac{\partial^2 f}{\partial x^2}+(k_BT)^{-1}\frac{\partial}{\partial x}\left[f\frac{dV}{dx}\right]\right]-S(x)f-k_rf\ , \qquad (1)$$

where D is the diffusion constant at temperature T and k_B is the Boltzmann constant. Although Eq. (1) corresponds to diffusive motion along a one-dimensional reaction coordinate x, its generalization to higher dimensions is straightforward. The one-dimensional model itself is used in a variety of problems of interest, viz. proton [4] or electron-transfer processes [5] involving an activated barrier crossing or barrierless processes such as relaxation from an excited state [6,7], etc. The purpose of the present work is to provide an exact solution for the rate constant corresponding to $f(x,t)$ of Eq. (1) for a general delocalized sink function. As will be shown, the rate constant for the general sink problem in the absence of radiative decay can be evaluated in terms of the corresponding rate constants for localized sinks, with suitable sink positions and initial conditions.

To solve Eq. (1), we first use the transformation

$$f(x,t)=P(x,t)\exp(-k_rt) \qquad (2)$$

and obtain the simplified equation

$$\frac{\partial P}{\partial t}=D\left[\frac{\partial^2 P}{\partial x^2}+(k_BT)^{-1}\frac{\partial}{\partial x}\left[P\frac{dV}{dx}\right]\right]-S(x)P\ . \qquad (3)$$

The solution of Eq. (3) can be written as

$$P(x,t|x_0,0)=P_0(x,t|x_0,0)-\int_{-\infty}^{\infty}dx'\int_0^t dt'P_0(x,t-t'|x',0)\times S(x')P_0(x',t'|x_0,0)\ , \qquad (4)$$

where the function $P_0(x,t|x_0,0)$ is the solution of Eq. (3) in the absence of any sink term, i.e., $S(x)=0$. Both $P(x,t|x_0,0)$ and $P_0(x,t|x_0,0)$ correspond to the same initial condition, which we consider here to be $P(x,t)=P_0(x,t)=\delta(x-x_0)$ at $t=0$, although other initial conditions discussed later are also of interest.

The forms of the potential $V(x)$ and the sink function $S(x)$ depend on the physical problem of interest. In many cases, the potential is chosen to be parabolic and the simplest sink function is the localized sink at a suitable location x_i given by $S(x)=k_i\delta(x-x_i)$, where k_i is the sink strength. The majority of the problems of interest, however, do not correspond to a localized sink and one requires a delocalized sink function $S(x)$ for a proper description of the dynamics in such situations. Recently Szabo, Lamm, and Weiss [8] provided an exact Green's-function solution of Eq. (3) for an arbitrary potential and a sink function expressed in terms of a linear combination of δ functions. The results of Szabo, Lamm, and Weiss [8] is, however, quite general since an arbitrary sink function $S(x)$ can be written as $S(x)=\int_{-\infty}^{\infty}dx'S(x')\delta(x-x')$ and the integral can be discretized as

$$S(x)=\sum_{i=1}^{N}k_i\delta(x-x_i)\ , \qquad (5)$$

where k_i $[=w_iS(x_i)]$ denotes the sink strengths, with weight factors w_i depending on the scheme of discretization used. For this sink function, Eq. (4) becomes

$$P(x,t|x_0,0)=P_0(x,t|x_0,0)-\sum_{i=1}^{N}k_i\int_0^t dt'P_0(x,t-t'|x_i,0)\times P(x_i,t'|x_0,0)\ . \qquad (6)$$

Thus the solution $P(x,t|x_0,0)$ depends on a time integral involving its values at the special points $x=\{x_i\}$ and also the function $P_0(x,t|x',0)$. Substituting Eq. (6) into Eq. (2) and taking a Laplace transform, we obtain

$$\tilde{P}(x,k_r+s|x_0,0)=\tilde{P}_0(x,k_r+s|x_0,0)-\sum_{j=1}^{N}k_j\tilde{P}_0(x,k_r+s|x_j,0)\times\tilde{P}(x_j,k_r+s|x_0,0)\ , \qquad (7)$$

where

$$\tilde{P}(x,k_r+s|x_0,0)=\int_0^{\infty}dt\exp[-(k_r+s)t]P(x,t|x_0,0)\ , \qquad (8)$$

with a similar expression for $\tilde{P}_0(x,k_r+s|x',0)$.

Considering Eq. (7) at the discrete points $x=x_1,x_2,\ldots,x_N$, we obtain a set of linear equations, which can be written as

$$AP=Q\ , \tag{9}$$

where the elements of the matrices $A\equiv\{a_{ij}\}$, $P\equiv\{p_i\}$, and $Q\equiv\{q_i\}$ are given by

$$a_{ij}=k_j\tilde{P}_0(x_i,k_r+s|x_j,0)+\delta_{ij}\ , \tag{10a}$$

$$p_i=\tilde{P}(x_i,k_r+s|x_0,0)\ , \tag{10b}$$

$$q_i=\tilde{P}_0(x_i,k_r+s|x_0,0)\ . \tag{10c}$$

One can solve the matrix equation (9) easily and obtain $\tilde{P}(x_i,k_r+s|x_0,0)$ for all x_i. Equation (7) then yields the Laplace transforms of $f(x,t)$ and $P(x,t|x_0,0)$.

An important quantity of interest is the survival probability $F(t)$ defined as

$$F(t)=\int_{-\infty}^{\infty}f(x,t)dx$$
$$=\exp(-k_rt)\left[1-\sum_{i=1}^{N}k_i\int_0^t P(x_i,t'|x_0,0)dt'\right]\ , \tag{11}$$

in terms of which one defines an average rate constant k_I as

$$k_I^{-1}=\int_0^{\infty}F(t)dt\ , \tag{12}$$

and also a long-time rate constant k_L as

$$k_L=-\lim_{t\to\infty}(d/dt)\ln F(t)\ . \tag{13}$$

Clearly $k_I^{-1}=\tilde{F}(0)$ and k_L is the negative pole of $\tilde{F}(s)$ closest to the origin. Therefore, the Laplace transform of $F(t)$ is sufficient to evaluate the two rate constants k_I and k_L.

The average rate constant k_I is thus given by

$$k_I^{-1}=\lim_{s\to0}(k_r+s)^{-1}\left[1-\sum_{i=1}^{N}k_i\tilde{P}(x_i,k_r+s|x_0,0)\right]\ , \tag{14}$$

where $\tilde{P}(x_i,k_r+s|x_0,0)$ is to be obtained by solving Eq. (9), which is straightforward if the Laplace transformed quantities $\tilde{P}_0(x_i,k_r+s|x_j,0)$ and $\tilde{P}_0(x_i,k_r+s|x_0,0)$ appearing in the matrices A and Q, respectively, can be evaluated analytically. In general, however, this analytical evaluation may not always be possible and one may have to take recourse to numerical evaluation of the integral

$$\tilde{P}_0(x_i,k_r+s|x',0)=\int_0^{\infty}dt\exp[-(k_r+s)t]P_0(x_i,t|x',0)\ . \tag{15}$$

Although for nonzero values of k_r, there is no problem as such in the numerical evaluation of this integral, for $k_r=0$, i.e., in the absence of radiative decay, divergences appear in the evaluation of Eq. (15) in the limit $s\to0$ if the distribution function $P_0(x,t)$ attains a nonzero stationary value at $t\to\infty$. To overcome this problem, we propose a simple method, discussed below.

The set of linear equations represented by Eq. (9) can be solved by Cramer's method, and the solution for $P_j\equiv\tilde{P}(x_j,k_r+s|x_0,0)$ is given by

$$P_j=\det A^{(j)}/\det A\ , \tag{16}$$

where $\det A$ represents the determinant of matrix A and $A^{(j)}$ is a matrix obtained by replacing the jth column of the matrix A by the column vector Q [see Eq. (10c)]. Substituting this solution into Eq. (14) one has the result

$$k_I^{-1}=\lim_{s\to0}\left[\det A-\sum_{j=1}^{N}k_j\det A^{(j)}\right]\Big/\{(k_r+s)\det A\}\ . \tag{17}$$

The problem is that for $k_r=0$, although the ratio on the right-hand side of Eq. (17) is finite in the limit $s\to0$, the elements in the matrices A and $A^{(j)}$ appearing in the expression are divergent in this limit if the stationary limit ($t\to\infty$) of $P_0(x,t)$ does not vanish. The divergence problem, however, does not arise if one considers the Laplace transform in Eq. (15) after subtracting the stationary value $P_0^{\rm st}(x)\equiv P_0(x,t=\infty)$ from the expression of $P_0(x,t)$, i.e., one defines the quantity

$$\Delta\tilde{P}_0(x,k_r+s|x',0)=\int_0^{\infty}dt\exp[-(k_r+s)t]\times[P_0(x,t|x',0)-P_0^{\rm st}(x)]\ , \tag{18}$$

which is uniformly convergent and can easily be evaluated numerically even in the limit $s\to0$ for $k_r=0$. Therefore, if it is possible to express the rate constant in terms of this new quantity, the evaluation would face no divergence problem.

Using simple algebraic manipulations, it is straightforward to show that the numerator of Eq. (17) remains unchanged if in all the elements of the matrices, the quantities $\tilde{P}_0(x_i,k_r+s|x_j,0)$ and $\tilde{P}_0(x_i,k_r+s|x_0,0)$ are replaced, respectively, by $\Delta\tilde{P}_0(x_i,k_r+s|x_j,0)$ and $\Delta\tilde{P}_0(x_i,k_r+s|x_0,0)$, defined by Eq. (18). Denoting the modified A matrix as matrix B with elements $b_{ij}\equiv k_j\Delta\tilde{P}_0(x_i,k_r+s|x_j,0)+\delta_{ij}$, the numerator of Eq. (17) becomes $(\det B-\sum_{j=1}^{N}k_j\det B^{(j)})$, where in the matrix $B^{(j)}$ the jth column of matrix B has been replaced by the column vector $Q'\equiv\{q_i'\}$ with $q_i'=\Delta\tilde{P}_0(x_i,k_r+s|x_0,0)$.

From Eq. (18), one has $\Delta\tilde{P}_0(x_i,k_r+s|x_j,0)=\tilde{P}_0(x_i,k_r+s|x_j,0)-(k_r+s)^{-1}P_0^{\rm st}(x_i)$, and hence the denominator of Eq. (17) can be rewritten as

$$(k_r+s)\det A=\left[(k_r+s)\det B+\sum_{j=1}^{N}k_j\det B^{(j)'}\right]\ , \tag{19}$$

where the matrix $B^{(j)'}$ is obtained from matrix B by replacing the elements b_{ij} of its jth column by the stationary values $p_0^{\rm st}(x_i)$ for all the rows, i.e., $i=1,\ldots,N$.

Thus, on taking the limit $s\to0$, the final expression for the rate constant k_I is given by

$$k_I^{-1}=\left[\det B-\sum_{j=1}^{N}k_j\det B^{(j)}\right]\Big/\left[k_r\det B+\sum_{j=1}^{N}k_j\det B^{(j)'}\right]\ , \tag{20}$$

where $\Delta\tilde{P}_0$ appearing in the matrices here correspond to $s=0$. Therefore if the solution for the potential in the absence of sink is known, the evaluation of $\Delta\tilde{P}_0$ is straightforward at least numerically using Eq. (18) since there are no divergences in the matrix B and the rate constant can be evaluated easily using Eq. (20).

While Eq. (20) denotes the rate constant for a delocalized sink, for the special case of a localized sink at a point x_1, i.e., $S(x)=k_1\delta(x-x_1)$, it can be expressed in a simple form given by

$$k_I=\{k_1P_0^{\rm st}(x_1)+k_r[1+k_1\Delta\tilde{P}_0(x_1,k_r|x_1,0)]\}/\{1+k_1[\Delta\tilde{P}_0(x_1,k_r|x_1,0)-\Delta\tilde{P}_0(x_1,k_r|x_0,0)]\}\ . \tag{21}$$

For problems with no radiative decay, i.e., $k_r=0$, the rate constant k_I for the general delocalized sink given by Eq. (20) can be reexpressed in terms of the rate constant of Eq. (21). The quantities that will appear in the final expression are denoted here as $k_0(x_i,x')$, which is the rate constant (in case of $k_r=0$) for the δ-function sink $S(x)=k_i\delta(x-x_i)$ if the particle is initially fed at $x=x'$ and is given by

$$k_0^{-1}(x_i,x')=[k_iP_0^{\rm st}(x_i)]^{-1}+k_d^{-1}(x_i,x')\ , \tag{22}$$

where $k_d(x_i,x')$ represents the well dynamics rate constant (also equal to the overall rate constant for a pinhole sink, i.e., in the limit $k_i\to\infty$), defined as

$$k_d^{-1}(x_i,x')=[1/P_0^{\rm st}(x_i)]\times[\Delta\tilde{P}_0(x_i,0|x_i,0)-\Delta\tilde{P}_0(x_i,0|x',0)]\ , \tag{23a}$$

which can also be written as

$$k_d^{-1}(x_i,x')=[1/P_0^{\rm st}(x_i)]\times\int_0^\infty dt[P_0(x_i,t|x_i,0)-P_0(x_i,t|x',0)]\ . \tag{23b}$$

Substituting $\Delta\tilde{P}_0(x_i,0|x',0)$ from Eq. (22) and (23a) into Eq. (20), and using somewhat lengthy algebra to eliminate $P_0^{\rm st}(x_i)$ and $\Delta\tilde{P}_0(x_i,0|x_i,0)$, one finally obtains the general rate constant given by

$$k_I^{-1}=\left[-\det C+\sum_{j=1}^{N}\det C^{(j)}\right]\Bigg/\left[\sum_{j=1}^{N}\det C^{(j)'}\right]\ , \tag{24}$$

where the elements of the matrix $C\equiv\{c_{ij}\}$ are given by

$$c_{ij}=\begin{cases}k_0^{-1}(x_i,x_j)\ \text{for}\ i\neq j & (25a)\\ 0\ \text{for}\ i=j\ . & (25b)\end{cases}$$

The matrix $C^{(j)}$ is obtained from the matrix C by replacing only its jth column by the column vector $D=\{d_i\}$, where

$$d_i=k_0^{-1}(x_i,x_0)\ . \tag{25c}$$

Similarly, the matrix $C^{(j)'}$ is same as matrix C, but for the elements of the jth column all of which are replaced by unity.

Equations (24) and (25) imply that for $k_r=0$, the rate constant k_I for diffusion in a potential $V(x)$ with a generalized sink, described as a set of N localized sinks, can be obtained if the corresponding localized sink rate constant $k_0(x_i,x')$ defined in Eq. (22) can be evaluated for arbitrary values of initial feeding position (x'), sink position (x_i), and sink strength (k_i). For potentials for which analytical solution for $P_0(x,t|x',0)$ is available, $k_0(x_i,x')$ can be obtained from Eq. (22) by evaluating the integral for k_d in Eq. (23b).

As an illustrative example, we consider the case of a particle of effective mass m diffusing in a parabolic potential $V(x)=\frac{1}{2}m\omega^2x^2$, for which

$$P_0(x,t|x',0)=[(\gamma/2\pi)(1-e^{-2\gamma Dt})]^{1/2}\times\exp\left[\frac{-(\gamma/2)(x-x'e^{-\gamma t})^2}{(1-e^{-2\gamma Dt})}\right] \tag{26a}$$

and therefore

$$P_0^{\rm st}(x_i)=(\gamma/2\pi)^{1/2}\exp[-(\gamma/2)x_i^2]\ , \tag{26b}$$

with $\gamma=m\omega^2/(k_BT)$. Using Eq. (26a), the integral in Eq. (23b) can be rewritten so as to obtain an explicit dependence of k_d on the diffusion constant D, viz.

$$k_d^{-1}(x_i,x')=(\gamma D)^{-1}\int_0^\infty dy[1-\exp(-2y)]^{-1/2}[\exp[\gamma x_i^2e^{-y}/(1+e^{-y})]-\exp(\gamma\{x_ix'e^{-y}-(e^{-2y}/2)[x_i^2+(x')^2]\}/(1-e^{-2y}))]\ . \tag{27}$$

Equation (27) shows that the rate constant k_d depends linearly on the diffusion constant D. Although in general, it might be difficult to evaluate the integration in Eq. (27) analytically, simplified expressions result for special cases. Thus we first rewrite Eq. (27) as

$$k_d^{-1}(x_i,x')=\frac{1}{D}\int_{x'}^{x_i}dx\int_0^\infty dy[1-\exp(-2y)]^{-3/2}\times[2xe^{-y}(1-e^{-y})\exp[\gamma x^2e^{-y}/(1+e^{-y})]-e^{-y}(x'-xe^{-y})\times\exp(\gamma\{xx'e^{-y}-(e^{-2y}/2)[x^2+(x')^2]\}/(1-e^{-2y}))]\ , \tag{28}$$

in which the inner integration can be evaluated for the special cases of $x_i=0$ or $x'=0$. When the sink position is at the origin ($x_i=0$), i.e., the minimum of the potential well, corresponding to a barrierless process, encountered in the case of relaxation from an excited state, the expression for $k_d(x_i,x')$ of Eq. (28) simplifies to

$$k_d^{-1}(0,x')=(\pi/2\gamma)^{1/2}D^{-1} \times \int_0^{|x'|} dx \exp(\gamma x^2/2) \times\{1-\mathrm{erf}[(\gamma/2)^{1/2}x]\} , \quad (29)$$

where erf(z) denotes the error function. The case of initial feeding position of the particle at the origin ($x'=0$) is of importance in most of the activated barrier-crossing-type processes such as the one encountered in the case of electron-transfer reactions. For this case, Eq. (28) becomes

$$k_d^{-1}(x_i,0)=(\pi/2\gamma)^{1/2}D^{-1} \times \int_0^{|x_i|} dx \exp(\gamma x^2/2) \times[1+\mathrm{erf}\{(\gamma/2)^{1/2}x\}] . \quad (30)$$

It is important to note that an analogus simplified general expression for $k_d^{-1}(x_i,x')$ has recently been derived by Sebastian [9] using a different approach and is given by

$$k_d^{-1}(x_i,x')=(\pi/2\gamma)^{1/2}D^{-1} \times \int_{x'}^{x_i} dx \exp(\gamma x^2/2) \times\{1+\mathrm{erf}[(\gamma/2)^{1/2}x]\} , \quad (31)$$

which is valid for $x_i > x'$. Results for $x_i < x'$ can be generated using the relation $k_d^{-1}(x_i,x')=k_d^{-1}(-x_i,-x')$, since the potential is symmetric.

It is interesting to note that $k_d^{-1}(x_i,x')$, which depends on both x_i and x', is decoupled and is expressed in Eq. (31) as a combination of two terms depending on x_i and x', respectively. This leads to a tremendous simplification in evaluating k_I for a general sink using Eq. (24), since $k_d^{-1}(x_i,x_j)$ can be obtained from $k_d^{-1}(x_{i\pm1},x_{j\pm1})$ by adding or subtracting the value of the integrand of Eq. (31) at $x=x_i$ or x_j in a simple scheme of numerical integration.

While so far we have considered only the initial condition $P(x,0)=\delta(x-x_0)$, also of interest is the case where initial condition is the stationary distribution, i.e., $P(x,0)=P_0^{\mathrm{st}}(x)$. In this case, the rate constant k_I for the general sink is again given by Eqs. (24) and (25), but the expression for d_i given by Eq. (25c) is to be replaced by

$$d_i=[k_i P_0^{\mathrm{st}}(x_i)]^{-1}+[k_d^{\mathrm{st}}(x_i)]^{-1} , \quad (32a)$$

where

$$[k_d^{\mathrm{st}}(x_i)]^{-1}=\Delta\tilde{P}_0(x_i,0|x_i,0)/P_0^{\mathrm{st}}(x_i) , \quad (32b)$$

which for the parabolic potential is given by

$$k_d^{\mathrm{st}}(x_i)=(\gamma D)[(\gamma/2\pi)x_i^2]^{1/2}\exp[-(\gamma/2)x_i^2]/\phi(x_i) , \quad (33)$$

with

$$\phi(x_i)=\mathrm{erf}\{[(\gamma/2)x_i^2]^{1/2}\}+[(\gamma/2)x_i^2]^{1/2}\exp[-(\gamma/2)x_i^2] \times\left[-2+\ln 2+(\gamma/2)x_i^2\sum_{k=0}^{\infty}\sum_{m=0}^{\infty}(-1)^k[(\gamma/2)x_i^2]^{k+m}\Big/[(k!m!(m+\tfrac{1}{2})(k+m+1)]\right] . \quad (34)$$

The quantity $k_d^{\mathrm{st}}(x_i)$ is of considerable importance in the discussion of diffusion for a localized sink at x_i, for which an alternative expression has been derived by Hynes [10] earlier. For the special case of high barrier limit ($|x_i|\gg 0$) in Eq. (34), $\phi(x_i)$ becomes unity, while for a barrierless process ($x_i=0$), $k_d^{\mathrm{st}}(0)=(\gamma D/\ln 2)$.

The central result of this work is Eq. (24), where the overall rate constant for a generalized sink is expressed in terms of localized sink rate constants with different values for the sink position and initial positions. For a parabolic potential, the localized sink rate constants can be calculated easily from Eq. (31) and the form of this equation leads to tremendous simplification in the evaluation of the general sink rate constant, as already mentioned. The present results on the rate constants for a general sink would be of much importance to a number of studies such as activated-barrier-crossing processes used in the study of chemical reactions in condensed phase, electron-transfer reactions [5], as well as barrierless processes such as relaxation [6,7] from an excited state in solution, etc., where the diffusive motion in a one-dimensional parabolic potential is a tractable but still realistic model.

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