Exact Solution of the Reversible Diffusion-Influenced Reaction for an Isolated Pair in Three Dimensions

Hyojoon Kim and Kook Joe Shin*

Department of Chemistry and Center for Molecular Catalysis,
Seoul National University, Seoul 151-742, Korea

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An exact Green's function of the reversible diffusion-influenced reaction for an isolated pair in three dimensions with spherical symmetry for the "backreaction" boundary condition is presented. From this function, the survival probability and the rate coefficient are derived exactly in the time domain for the initially unbound pair. [S0031-9007(99)08485-9]

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Since the seminal work of Smoluchowski [1], many physicochemical processes have been studied with the diffusion-reaction theories [2]. An isolated pair recombination reaction is the simplest system and has been widely studied. If one finds the Green's function for the system, the solution for any initial distribution is also obtained and other interesting quantities can be easily derived. Exact Green's functions may sometimes be obtained in the irreversible case in the presence of a potential, e.g., linear or parabolic potentials in one dimension (1D) [3] and the Coulomb potential in three dimensions (3D) [4]. In the reversible case, the exact Green's function is known for the potential-free case only in 1D as explained below [5].

Recently, considerable interest has focused on the reversible reaction of the type $A + B \leftrightarrow C$ for both the isolated pair and the pseudo-first-order cases [5–12]. For the reversible case the "backreaction" boundary condition (BC) [5,13], which is a generalization of the well-known "radiation" BC for the irreversible case, is usually adopted and the exact Green's function for an isolated pair was obtained only in 1D [5]. An efficient Brownian dynamics simulation algorithm was developed for the reversible pseudo-first-order systems adopting the exact solution for an isolated pair in 1D [9,12]. Although the solution in 3D is more demanding than other dimensions, no result has been reported for the backreaction BC to our knowledge.

In this Letter we present an exact Green's function for the reversible diffusion-influenced reaction for an isolated pair in 3D with spherical symmetry for the backreaction BC. Using this function, the important quantities such as the survival probability and the rate coefficient are also derived.

Consider two spherical particles diffusing under the influence of an interaction potential $U(r)$. The recombination reaction occurs instantaneously when they approach within the reaction distance σ with the intrinsic reaction rate k_r. The back reaction can occur to the dissociation distance σ with the reaction rate k_d. Let $p(r,t|r_0)$ be the probability that the interparticle distance is r at time t given that it was r_0 at $t = 0$. Then the time evolution of $p(r,t|r_0)$ in 3D with spherical symmetry can be given by the following diffusion equation [2]:

$$\frac{\partial}{\partial t}\,p(r,t|r_0) = \left(\frac{\partial}{\partial r} + \frac{2}{r}\right)D(r) \times \left(\frac{\partial}{\partial r} + \frac{1}{k_B T}\,\frac{\partial U(r)}{\partial r}\right)p(r,t|r_0)\,, \quad r \geq \sigma\,, \tag{1}$$

where k_B is the Boltzmann constant, T the temperature, and $D(r)$ denotes the relative diffusion coefficient. In this work we approximate, for simplicity, $D(r)$ as a constant D and also ignore the interaction potential $[U(r) = 0]$. The initial and the BC's are given by

$$4\pi r_0^2\,p(r,0|r_0) = \delta(r - r_0)\,, \tag{2}$$

$$\lim_{r\to\infty} p(r,t|r_0) = 0\,, \tag{3}$$

$$4\pi\sigma^2 D\,\frac{\partial}{\partial r}\,p(r,t|r_0)|_{r=\sigma} = k_r\,p(\sigma,t|r_0) - k_d[1 - S(t|r_0)]\,, \tag{4}$$

where $\delta(r)$ is the Dirac delta function and $S(t|r_0)$ is the survival probability that a pair of particles initially separated by r_0 survives and does not recombine by time t given by

$$S(t|r_0) = 1 - \int_0^t dt'\,4\pi\sigma^2 D\,\frac{\partial p(r,t'|r_0)}{\partial r}\bigg|_{r=\sigma}\,. \tag{5}$$

The solution $p(r,t|r_0)$ is known as Green's function. If one finds this Green's function, the solution for an arbitrary initial distribution $p^0(r)$ is also found by its integral [5]

$$p(r,t|p^0) = \int_\sigma^\infty p(r,t|r_0)\,p^0(r_0)\,dr_0\,. \tag{6}$$

Now we seek a solution of the type

$$p(r,t|r_0) = f(r,t|r_0) + g(r,t)\,, \tag{7}$$

where $f(r,t|r_0)$ is the solution for the reflecting BC ($k_r = k_d = 0$) given by [3]

$$f(r,t|r_0)4\pi r r_0\sqrt{D} = \frac{1}{\sqrt{4\pi t}}\left\{\exp\left[-\frac{(r-r_0)^2}{4Dt}\right] + \exp\left[-\frac{(r+r_0-2\sigma)^2}{4Dt}\right]\right\} - \frac{\sqrt{D}}{\sigma}W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}}, \frac{\sqrt{Dt}}{\sigma}\right), \tag{8}$$

where $W(a,b) \equiv \exp(2ab + b^2)\,\mathrm{erfc}(a+b)$ and $\mathrm{erfc}(x)$ denotes the complementary error function.

The reactive part of $p(r,t|r_0)$ is represented by $g(r,t)$ which is the solution for the backreaction BC given by Eq. (4). Since $f(r,t|r_0)$ accounts for the whole initial distribution, $g(r,t=0)=0$. If we use the Laplace transform, $\hat{g}(r,s) = \int_0^\infty g(r,t)\exp(-st)\,dt$, $\hat{g}(r,s)$ can be readily obtained as

$$r\hat{g}(r,s) = A(s)\exp[-(r-\sigma)\sqrt{s/D}\,]. \tag{9}$$

In order to determine the coefficient $A(s)$, we first transform Eq. (4) with the help of Eq. (7) to obtain

$$4\pi\sigma^2 D\frac{\partial}{\partial r}\hat{g}(r,s)|_{r=\sigma} = k_r[\hat{f}(\sigma,s|r_0) + \hat{g}(\sigma,s)] - \frac{k_d}{s}4\pi\sigma^2 D\frac{\partial}{\partial r}\hat{g}(r,s)|_{r=\sigma}. \tag{10}$$

We used the fact that $\partial\hat{f}(r,s)/\partial r|_{r=\sigma} = 0$ to obtain the above equation. Substitution of Eq. (9) into Eq. (10) leads to

$$A(s) = -\frac{\sigma\hat{f}(\sigma,s|r_0)}{1 + (1+\sigma\sqrt{s/D}\,)(1+k_d/s)k_D/k_r}, \tag{11}$$

where $k_D \equiv 4\pi\sigma D$. Therefore, combining Eqs. (8), (9), and (11), we get

$$\begin{aligned}\hat{p}(r,s|r_0)4\pi r_0 r\sqrt{D} = {} & \{\exp[-|r-r_0|\sqrt{s/D}\,] + \exp[-(r+r_0-2\sigma)\sqrt{s/D}\,]\}/2\sqrt{s} \\ & - \frac{(1+k_r/k_D)\sqrt{sD} + k_d\sqrt{D/s}}{s\sqrt{s}\,\sigma + (1+k_r/k_D)s\sqrt{D} + k_d\sqrt{s}\,\sigma + k_d\sqrt{D}} \times \exp[-(r+r_0-2\sigma)\sqrt{s/D}\,].\end{aligned} \tag{12}$$

Finally, Green's function, $p(r,t|r_0)$, is obtained as follows by the inverse Laplace transformation:

$$\begin{aligned}p(r,t|r_0)4\pi r r_0\sqrt{D} = {} & \frac{1}{\sqrt{4\pi t}}\left\{\exp\left[-\frac{(r-r_0)^2}{4Dt}\right] + \exp\left[-\frac{(r+r_0-2\sigma)^2}{4Dt}\right]\right\} \\ & + \frac{\alpha(\gamma+\alpha)(\alpha+\beta)}{(\gamma-\alpha)(\alpha-\beta)}W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}}, \alpha\sqrt{t}\right) \\ & + \frac{\beta(\alpha+\beta)(\beta+\gamma)}{(\alpha-\beta)(\beta-\gamma)}W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}}, \beta\sqrt{t}\right) \\ & + \frac{\gamma(\beta+\gamma)(\gamma+\alpha)}{(\beta-\gamma)(\gamma-\alpha)}W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}}, \gamma\sqrt{t}\right).\end{aligned} \tag{13}$$

The denominator of the third term on the right-hand side (rhs) of Eq. (12) can be regarded as a cubic equation in $\sqrt{s}$ and its three roots ($-\alpha$, $-\beta$, and $-\gamma$) satisfy the following relations:

$$\alpha + \beta + \gamma = (1 + k_r/k_D)\sqrt{D}/\sigma, \tag{14}$$

$$\alpha\beta + \beta\gamma + \gamma\alpha = k_d, \tag{15}$$

$$\alpha\beta\gamma = k_d\sqrt{D}/\sigma. \tag{16}$$

These roots may be complex numbers. Then the complex exponential function and the complex complementary error function should be used. However, the sum of the last three terms on the rhs in Eq. (13) is a real number. An alternative derivation of Eq. (13) can be done by combining $f(r,t|r_0)$ given by Eq. (8) with $g(r,t)$ which can be obtained by inverting $\hat{g}(r,s)$. The explicit expression of $\hat{g}(r,s)$, in turn, can be derived from Eqs. (9) and (11) with the Laplace transformed expression of Eq. (8).

When the backreaction is turned off ($k_d = 0$), the irreversible roots satisfying Eqs. (14)–(16) can be readily found: $\alpha_{\mathrm{irr}} = (1 + k_r/k_D)\sqrt{D}/\sigma$ and $\beta_{\mathrm{irr}} = \gamma_{\mathrm{irr}} = 0$. Therefore, Eq. (13) reduces to the well-known Green's function of the irreversible reaction [3]:

$$p_{\mathrm{irr}}(r,t|r_0)4\pi r r_0\sqrt{D} = \frac{1}{\sqrt{4\pi t}}\left\{\exp\left(-\frac{(r-r_0)^2}{4Dt}\right) + \exp\left(-\frac{(r+r_0-2\sigma)^2}{4Dt}\right)\right\} - \alpha_{\mathrm{irr}}W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}}, \alpha_{\mathrm{irr}}\sqrt{t}\right). \tag{17}$$

The subscript irr denotes the irreversible case.

Once the Green's function is found, other quantities of interest can be easily obtained utilizing the known relations. The survival probability can be obtained by the direct integral of Green's function as

$$S(t|r_0) = 1 - \frac{k_r}{4\pi r_0 \sigma \sqrt{D}} \left\{ \frac{\alpha}{(\gamma - \alpha)(\alpha - \beta)} W\left(\frac{r_0 - \sigma}{\sqrt{4Dt}}, \alpha\sqrt{t}\right) + \frac{\beta}{(\alpha - \beta)(\beta - \gamma)} W\left(\frac{r_0 - \sigma}{\sqrt{4Dt}}, \beta\sqrt{t}\right) + \frac{\gamma}{(\beta - \gamma)(\gamma - \alpha)} W\left(\frac{r_0 - \sigma}{\sqrt{4Dt}}, \gamma\sqrt{t}\right)\right\}, \quad (18)$$

which becomes unity at long times ($t \to \infty$). This means that the ultimate fate of an isolated pair for the reversible reaction is always dissociation [5]. Equation (18) can be reduced, when $k_d = 0$, to the well-known irreversible survival probability [2]:

$$S_{\mathrm{irr}}(t|r_0) = 1 - \left(\frac{\sigma}{r_0}\right) \frac{k_r}{k_r + k_D} \left[\mathrm{erfc}\left(\frac{r_0 - \sigma}{\sqrt{4Dt}}\right) - W\left(\frac{r_0 - \sigma}{\sqrt{4Dt}}, \alpha_{\mathrm{irr}}\sqrt{t}\right)\right]. \quad (19)$$

Agmon and Szabo obtained earlier the expression of $\hat{S}(s|r_0)$ in terms of the irreversible survival probability and the irreversible rate coefficient for the absorbing BC [8].

If we define the deviation function from the equilibrium as $\xi(t|r_0) \equiv S(\infty|r_0) - S(t|r_0)$, its long-time behavior shows $t^{-3/2}$ power law in the leading term as follows:

$$\lim_{t\to\infty} \xi(t|r_0) \sim \frac{K_{\mathrm{eq}}}{(4\pi D t)^{3/2}}, \quad (20)$$

where $K_{\mathrm{eq}} = k_r/k_d$ and this expression is exact. For the irreversible reaction the deviation function shows the well-known $t^{-1/2}$ long-time behavior,

$$\lim_{t\to\infty} \xi_{\mathrm{irr}}(t|r_0) \sim \frac{\sigma}{r_0} \frac{k_r k_D}{(k_r + k_D)^2} \frac{\sigma}{(\pi D t)^{1/2}}. \quad (21)$$

Notice that, comparing with the irreversible result, the distance dependence (σ or r_0) disappears in the reversible case due to the backreaction.

The reversible reaction rate coefficient can be defined, in analogy to the irreversible case, as $k(t) \equiv 4\pi\sigma^2 D \partial S \times (t|r_0)/\partial r_0|_{r_0=\sigma}$ [8], and the calculation gives

$$k(t) = -K_{\mathrm{eq}} \left[\frac{\alpha^3(\beta + \gamma)}{(\gamma - \alpha)(\alpha - \beta)} \Omega(\alpha\sqrt{t}) + \frac{\beta^3(\gamma + \alpha)}{(\alpha - \beta)(\beta - \gamma)} \Omega(\beta\sqrt{t}) + \frac{\gamma^3(\alpha + \beta)}{(\beta - \gamma)(\gamma - \alpha)} \Omega(\gamma\sqrt{t})\right], \quad (22)$$

where $\Omega(a) \equiv \exp(a^2)\,\mathrm{erfc}(a)$. Equation (22) can be reduced in the irreversible limit to the well-known expression [2]:

$$k_{\mathrm{irr}}(t) = \frac{k_r}{k_r + k_D} [k_D + k_r \Omega(\alpha_{\mathrm{irr}}\sqrt{t})]. \quad (23)$$

The expression of $\hat{k}(s)$ in terms of $\hat{k}_{\mathrm{irr}}(s)$ and $\hat{S}_{\mathrm{irr}}(s|r_0)$ was also obtained earlier by Agmon and Szabo [8].

Let $S(t|*)$ be the survival probability of a pair which is initially bound. We use the asterisk to denote the bound state. Similarly, $p(r,t|*)$ and $p(*,t|r_0)$ are defined as Green's functions for the initial and final bound states, respectively. Note that $1 - p(*,t|r_0) = S(t|r_0)$. Then the detailed balance condition becomes $k_r p(r,t|*) = k_d p(*,t|r)$. Therefore, one can easily obtain that

$$p(r,t|*) = \frac{k_d}{4\pi r \sigma \sqrt{D}} \left\{ \frac{\alpha}{(\gamma - \alpha)(\alpha - \beta)} W\left(\frac{r - \sigma}{\sqrt{4Dt}}, \alpha\sqrt{t}\right) + \frac{\beta}{(\alpha - \beta)(\beta - \gamma)} W\left(\frac{r - \sigma}{\sqrt{4Dt}}, \beta\sqrt{t}\right) + \frac{\gamma}{(\beta - \gamma)(\gamma - \alpha)} W\left(\frac{r - \sigma}{\sqrt{4Dt}}, \gamma\sqrt{t}\right)\right\}. \quad (24)$$

The direct integration of the above equation gives

$$S(t|*) = 1 - \frac{\alpha(\beta + \gamma)}{(\gamma - \alpha)(\alpha - \beta)} \Omega(\alpha\sqrt{t}) - \frac{\beta(\gamma + \alpha)}{(\alpha - \beta)(\beta - \gamma)} \Omega(\beta\sqrt{t}) - \frac{\gamma(\alpha + \beta)}{(\beta - \gamma)(\gamma - \alpha)} \Omega(\gamma\sqrt{t}), \quad (25)$$

which vanishes in the irreversible limit. This expression was obtained earlier by Agmon and Weiss [14] using the fact that the survival probability can be expressed by Green's function for the reflecting boundary condition.

Another interesting quantity is the average lifetime of the bound particle defined as $\tau \equiv \int_0^\infty dt\,[1 - S(t|*)]$ which can be calculated from Eq. (25):

$$\tau^{-1} = \frac{k_d k_D}{k_r + k_D}, \tag{26}$$

which is in agreement with the previous works [6–8] of Agmon *et al.* Note that Eq. (26) is the exact result for the case of $U(r) = 0$.

The long-time behavior of the deviation function for the initially bound pair is

$$\lim_{t\to\infty} \xi(t|*) \sim \frac{K_{\mathrm{eq}}}{(4\pi Dt)^{3/2}}, \tag{27}$$

which is again in agreement with Eq. (23) of Ref. [7]. An interesting relation can be found from Eqs. (20) and (27), that

$$\lim_{t\to\infty} \xi(t|r_0) \sim \lim_{t\to\infty} \xi(t|*), \tag{28}$$

which shows that the effect of the difference in the initial separation distances fades away at long times.

More complex systems, for instance, the pseudo-first-order system, can be studied by the present results. Especially, the efficient Brownian dynamics simulation algorithm [9] which adopts the exact solution for an isolated pair can now be applied to the 3D system with spherical symmetry. The results will be reported elsewhere.

In summary, we have presented an exact Green's function for the reversible diffusion-influenced reaction for an isolated pair in 3D with spherical symmetry for the back-reaction BC. From this function, the survival probability and the rate coefficient are derived exactly in the time domain for the initially unbound pair.

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*To whom correspondence should be addressed.
Email address: statchem@plaza.snu.ac.kr

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