Survival probabilities and rates derived from an exact Green’s function of the reversible diffusion-influenced reaction for an isolated pair in 2D

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Abstract

Recently, an exact Green’s function of the diffusion equation for a pair of spherical interacting particles in two dimensions subject to a backreaction boundary condition was derived. Here, we use the obtained Green’s function to calculate exact expressions for the survival probability, the time-dependent reaction rate coefficient for the initially unbound pair and the survival probability of the bound state in the time domain. Moreover, we derive an exact expression for the off-rate.

1 Introduction

In [1], an exact Green’s function (GF) \( g(r,t|r_0) \) of the two dimensional (2D) diffusion equation for a pair of spherical interacting particles was derived. The GF satisfies the backreaction boundary condition [2, 3, 4, 1]

\[
2\pi aD \frac{\partial}{\partial r} g(r, t|r_0)|_{r=a} = \kappa_a g(a, t|r_0) - \kappa_d [1 - S(t|r_0)]. \tag{1.1}
\]

Here, \( D \) is the sum of the particles’ diffusion constants, \( r \) is the inter-particle distance and \( a \) is the encounter radius. Furthermore, \( \kappa_a \) and \( \kappa_d \) denote the intrinsic association and dissociation rate constants, respectively. Finally, \( S(t|r_0) \) refers to the probability that a pair of molecules with initial distance \( r_0 \) survives until time \( t \),

\[
S(t|r_0) = 2\pi \int_a^\infty g(r, t|r_0)r dr \tag{1.2}
\]

\[
= 1 - 2\pi aD \int_0^{t'} \frac{\partial}{\partial r} g(r, t'|r_0)|_{r=a} dt'. \tag{1.3}
\]

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It was shown that the associated GF takes the form

\[ g(r, t | r_0) = \frac{1}{2\pi} \int_0^\infty e^{-Dx^2} T(x, r) T(x, r_0) \, dx, \]  

(1.4)

where we introduced the functions

\[ T(x, r) = \frac{J_0(rx) \beta(x) - Y_0(rx) \alpha(x)}{[\alpha(x)^2 + \beta(x)^2]^{1/2}}, \]  

(1.5)

and

\[
\begin{align*}
\alpha(x) & := (x^2 - \kappa_D) J_1(xa) + hx J_0(xa), \\
\beta(x) & := (x^2 - \kappa_D) Y_1(xa) + hx Y_0(xa).
\end{align*}
\]

(1.6, 1.7)

\( J_0, J_1, Y_0, Y_1 \) denote the Bessel functions of first and second kind and of zeroth and first order, respectively \([5]\). Furthermore, by definition we have

\[
\begin{align*}
h & := \frac{\kappa_a}{2\pi a D} \quad \text{(1.8)} \\
\kappa_D & := \frac{\kappa_d}{D} \quad \text{(1.9)}
\end{align*}
\]

Knowing the GF allows us to derive further important quantities, notably, the survival probability. For the following calculations, it turns out to be convenient to introduce the function

\[ P(x, r) := -\frac{1}{x} \frac{\partial}{\partial r} T(x, r) = \frac{J_1(rx) \beta(x) - Y_1(xr) \alpha(x)}{[\alpha(x)^2 + \beta(x)^2]^{1/2}}, \]  

(1.10)

where we used \([5]\)

\[
\begin{align*}
J'_0(x) & := \frac{d}{dx} J_0(x) = -J_1(x) \quad \text{(1.11)} \\
Y'_0(x) & := \frac{d}{dx} Y_0(x) = -Y_1(x). \quad \text{(1.12)}
\end{align*}
\]

The survival probability may be calculated according to (1.2) or, alternatively, using (1.3). Either way, we find

\[
S(t | r_0) = 1 - a \int_0^\infty e^{-Dtx^2} P(x, a) T(x, r_0) \, dx.
\]

(1.13)

To obtain (1.13) via (1.3) we used the integral identity

\[
\int_0^\infty P(x, a) T(x, r_0) \, dx = 0. \quad \text{(1.14)}
\]

(1.14) can be derived by substituting the GF (1.4) into the boundary condition (1.1). Then, using (1.10), (1.11) and (1.12), as well as \([5]\)

\[ Y'_0(x) J_0(x) - J'_0(x) Y_0(x) = \frac{2}{\pi x}, \]

(1.15)

we are directly led to (1.14). From (1.13) we can easily conclude that the reversible survival probability approaches unity for large times

\[
\lim_{t \to \infty} S(t | r_0) = 1, \quad \text{(1.16)}
\]

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implying that in 2D the ultimate fate of an isolated pair for the reversible reaction is always dissociation, as in the 1D and 3D case [2, 3, 4].

Turning now our attention to the initially bound pair, we use the notation * to indicate the bound state and we let \( g(r, t|\ast) \) denote the Green’s function describing an initially bound pair that is found separated by a distance \( r \) at a later time \( t \), cp [3, 4]. Knowledge of this GF is desirable, because it enables us to compute the average lifetime of the bound state and, hence, the off-rate, as we shall see later.

We note that \( g(r, t|\ast) \) is related to the GF \( g(\ast, t|r_0) \), which describes an initially unbound pair that is bound at a later time \( t \), by the detailed balance condition [3, 4]

\[
\kappa_d g(\ast, t|r) = \kappa_a g(r, t|\ast). \tag{1.17}
\]

Furthermore, we have

\[
g(\ast, t|r_0) + S(t|r_0) = 1. \tag{1.18}
\]

(1.18) makes it evident that, technically speaking, the GF \( g(\ast, t|r_0) \) represents a probability rather than a probability density.

From (1.13), (1.17) and (1.18) it follows that

\[
g(r, t|\ast) = \frac{\kappa_d}{\kappa_a} \int_0^\infty e^{-Dtx^2} P(x, a) T(x, r) dx. \tag{1.19}
\]

Upon direct integration we arrive at the probability \( S(t|\ast) \) that an initially bound pair is unbound at time \( t > 0 \) [3, 4]

\[
S(t|\ast) = 2\pi \int_0^\infty r g(r, t|\ast) dr = 1 - 2\pi \frac{\kappa_d}{\kappa_a} a^2 \int_0^\infty e^{-Dtx^2} P^2(x, a) \frac{1}{x} dx. \tag{1.20}
\]

Note that \( S(0|\ast) = 0 \), due to (3.8).

In [3] it was demonstrated that \( S(t|\ast) \) relates to \( S(t|r_0) \) in the time domain in the following way:

\[
S(t|\ast) = \kappa_d \int_0^t e^{-\kappa_a t'} S(t - t'|a) dt'. \tag{1.21}
\]

Using (1.5), (1.10), (1.13), (1.15), and (1.20), we can now explicitly show that (1.21) is indeed satisfied in 2D.

2 Rates

In the Smoluchowski approach, steady-state rate constants can be calculated in two related ways. One method employs the irreversible time-dependent solution of the diffusion equation to calculate the time-dependent rate coefficient \( k_{irr}(t) \). The steady-state rate constant \( k_{irr}^{\ast} \) is then given by the long time limit of \( k_{irr}(t) \)

\[
k_{irr}^{\ast} := \lim_{t\to\infty} k_{irr}(t) \tag{2.1}
\]

While in 3D this procedure yields the classic result \( k_{irr}^{\ast} = 4\pi aD \) (for purely absorbing boundary conditions), in 2D one obtains the result that \( k_{irr}^{\ast} \) actually vanishes. This issue is also reflected in the second approach, which is based on
steady-state solutions of the diffusion equation. In 2D, however, the steady-state solutions are logarithmic, and hence, no boundary condition can be imposed at infinity. As a remedy, several procedures have been proposed [6, 7, 8, 9]. All of them give rise to another length scale \( b > a \) in addition to the encounter radius. Furthermore, they lead, up to a constant, to the same expression for the on-rate constant

\[
\frac{1}{k_{\text{on}}} = \frac{1}{\kappa_a} + \frac{\ln(b/a) + \delta}{2\pi D}.
\]  

(2.2)

Using \( K_{\text{eq}} := \frac{\kappa_a}{\kappa_d} = K_{\text{eq}}k_{\text{on}}^{-1} \) one arrives at an expression for the off-rate

\[
\frac{1}{k_{\text{off}}} = \frac{1}{\kappa_d} + K_{\text{eq}} \frac{\ln(b/a) + \delta}{2\pi D}.
\]  

(2.3)

Here \( \delta \) denotes the above mentioned constant that assumes a varying value depending on the chosen method.

In the following we will use the reversible GF \((1.4)\) to address these issues. The time-dependent reaction rate coefficient can be obtained from the survival probability \( S(t|r_0) \) [3, 4]

\[
k(t) = 2\pi a D \frac{\partial}{\partial r_0} S(t|r_0)|_{r_0=a}.
\]  

(2.4)

Using \((1.13)\), we obtain the exact expression in the time domain

\[
k(t) = 2\pi a^2 D \int_0^\infty e^{-Dtx^2} P^2(x, a) dx.
\]  

(2.5)

It follows immediately from (2.5) that the long time limit of \( k(t) \) vanishes.

As shown in the appendix, the integral \( \int_0^\infty P^2(x, a) dx \) can be computed analytically and we find

\[
\int_0^\infty P^2(x, a) \frac{dx}{x} = \frac{\kappa_a}{\kappa_d 2\pi a^2}.
\]  

(2.6)

With the help of this equation and (2.5) we recover the correct expression for the equilibrium constant \( K_{\text{eq}} \)

\[
\int_0^\infty k(t) dt = \frac{\kappa_a}{\kappa_d} = K_{\text{eq}}.
\]  

(2.7)

Alternatively, identity (2.7) may be deduced in the following way. According to reference [3] the time-dependent reaction rate can also be calculated by using the survival probability \( S(t|\ast) \), cp (2.4)

\[
k(t) = K_{\text{eq}} \frac{\partial S(t|\ast)}{\partial t}.
\]  

(2.8)

Now, given \((1.13)\) and \((1.20)\), one can explicitly show that (2.4) and (2.8) yield the same result. Then, taking into account that \( S(\infty|\ast) = 1 \) and \( S(0|\ast) = 0 \), (2.7) is immediately implied by (2.8).

The steady-state dissociation rate constant, or off-rate, is defined by [3, 4]

\[
k_{\text{off}} = \tau^{-1},
\]  

(2.9)
where $\tau$ refers to the average lifetime of the bound state. $\tau$ can be calculated according to \([3, 4]\)

$$\tau = \int_0^\infty [1 - S(t^*)] dt. \quad (2.10)$$

Using (1.20) and after transforming from the dummy integration variable $x$ to the dimensionless integration variable $\xi := ax$ we arrive at

$$\tau = 2\pi \frac{\kappa_d a^4}{D} \int_0^\infty \frac{f(\xi)}{\xi} d\xi, \quad (2.11)$$

where we have introduced the function

$$f(\xi) := \frac{P^2(\xi, 1)}{\xi^2} \quad (2.12)$$

for notational convenience. We note that the integrand in (2.11) depends on the dimensionless constants $\tilde{h} = ha, \tilde{\kappa}_D := \kappa_D a^2$ only, due to the transformation $x \to \xi = xa$. Since

$$\lim_{\xi \to 0} f(\xi) = \frac{\tilde{h}^2}{\tilde{\kappa}_D^2} \neq 0, \quad (2.13)$$

it follows that the integrand is singular at the lower endpoint $\xi = 0$ of the integration interval, which implies that the integral does not exist. However, one can still assign a well-defined value to integrals of that type upon regularizing them in the sense of Hadamard’s one-sided finite-part integrals \([10]\)

$$\int_0^c \frac{f(\xi)}{\xi} d\xi := \int_c^\infty \frac{f(\xi)}{\xi} d\xi + \int_0^c \frac{f(\xi) - f(0)}{\xi} d\xi + f(0) \int_0^c \frac{d\xi}{\xi}. \quad (2.14)$$

By definition, the following finite part integral yields \([10]\)

$$\int_0^c \frac{d\xi}{\xi} := \ln c \quad (2.15)$$

We would like to point out that one has to split the integral at $\infty > \xi = c > 0$ in (2.14), because otherwise the regularization would introduce another singularity due to the occurrence of $\ln \infty$ terms. It is instructive to compare the resulting expression for $\tau$ with (2.3). Clearly, the third term on the rhs of (2.14) gives rise to precisely the logarithmic contribution if one set $c = b/a$. Moreover, one can show numerically that the other two integrals in (2.14) yield

$$\int_c^\infty \frac{f(\xi)}{\xi} d\xi = \frac{\tilde{h}}{\tilde{\kappa}_D} + C(c) \frac{\tilde{h}^2}{\tilde{\kappa}_D^2}, \quad (2.16)$$

where $C(c)$ depends on the choice of $c$ only. Taken together this means that one seemingly recovers the result (2.3). However, it is easily demonstrated that the regularized integral is actually independent of the choice of $c$. Thus, in particular, one can choose $c = 1$, which shows that the logarithmic contribution actually vanishes and one obtains

$$\tau = \frac{1}{\kappa_d} = \frac{1}{\kappa_d} + K_{\text{co}} \frac{C}{2\pi D}, \quad (2.17)$$

where $C := C(1) \approx 0.11593...$. We find the result that the off-rate does not depend on the encounter radius.
3 Appendix

In this appendix we will compute the integrals that are needed in the main text.

The GF has to satisfy the initial condition [1]

\[ g(r, t = 0 | r_0) = \frac{\delta(r - r_0)}{2\pi r_0}, \quad (3.1) \]

i.e. in the case considered here we have

\[ \frac{1}{2\pi} \int_0^\infty T(x, r) T(x, r_0) dx = \frac{\delta(r - r_0)}{2\pi r_0} \quad (3.2) \]

From (3.2) it follows by direct integration over \( \int_a^r dx' r' \)

\[ \int_0^\infty P(x, r) T(x, r_0) dx = \begin{cases} 0, & r < r_0, \\ r^{-1}, & r > r_0, \end{cases} \quad (3.3) \]

where we have used [1,14]. Furthermore, to perform the integral we used [3]

\[ \frac{d}{dx} [x^\nu J_\nu(x)] = x^\nu J_{\nu-1} \quad (3.4) \]

and

\[ \frac{d}{dx} [x^\nu Y_\nu(x)] = x^\nu Y_{\nu-1}. \quad (3.5) \]

Next, we apply the derivative \( \frac{\partial}{\partial r_0} \) to the boundary condition [1] and subsequently integrate from 0 to \( t \). Taking the limit \( t \to \infty \) leads to

\[ \int_0^\infty P(x, a) P(x, r_0) dx = -\frac{\kappa_a}{2\pi a D} \int_0^\infty T(x, a) P(x, r_0) dx + \frac{\kappa_d}{D} \int_0^\infty P(x, a) P(x, r_0) \frac{dx}{x} \quad (3.6) \]

The integral on the lhs has to vanish, as can be seen by taking into account [1,14] and

\[ \int_0^\infty P(x, a) P(x, r_0) dx = -\frac{\partial}{\partial r_0} \int_0^\infty P(x, a) T(x, r_0) dx. \quad (3.7) \]

Furthermore, we just calculated the first integral on the rhs, cp Eq. (3.3). Hence, we arrive at

\[ \int_0^\infty P(x, a) P(x, r_0) \frac{dx}{x} = \frac{\kappa_a}{\kappa_d} \frac{1}{2\pi a r_0}. \quad (3.8) \]

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