Theory of reversible diffusion-influenced reactions with non-Markovian dissociation in two space dimensions

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We investigate the reversible diffusion-influenced reaction of an isolated pair in the presence of a non-Markovian generalization of the backreaction boundary condition in two space dimensions. Following earlier work by Agmon and Weiss, we consider residence time probability densities that decay slower than an exponential and that are characterized by a single parameter $0 < \sigma \leq 1$. We calculate an exact expression for a Green's function of the two-dimensional diffusion equation subject to a non-Markovian backreaction boundary condition that is valid for arbitrary σ and for all times. We use the obtained expression to derive the survival probability for the initially unbound pair and we calculate an exact expression for the probability $S(t|*)$ that the initially bound particle is unbound. Finally, we obtain an approximate solution for long times. In particular, we show that the ultimate fate of the bound state is complete dissociation, as in the Markovian case. However, the limiting value is approached quite differently: Instead of a $\sim t^{-1}$ decay, we obtain $1 - S(t|*) \sim t^{-\sigma} \ln t$. The derived expressions should be relevant for a better understanding of reversible membrane-bound reactions in cell biology. [<http://dx.doi.org/10.1063/1.4794311>]

I. INTRODUCTION

It has been shown that the ultimate fate of an isolated pair for the reversible diffusion-influenced reaction is complete dissociation, independent of the dimensionality of space. In fact, the probability that the initially bound pair is unbound at time t , $S(t|*)$, is unity in one, two, and three space dimensions for $t \rightarrow \infty$.^{1–6} However, the dimensionality does have an influence on how the limiting value for $S(t|*)$ is approached: Denoting the number of dimensions by d , the decay goes as $1 - S(t|*) \sim t^{-d/2}$, which has important implications for the off-rate. This dependence from the dimension can be traced back to the return to the origin probability of the underlying random walk. In one and two dimensions (2D), Brownian motion is recurrent, i.e., the return to the origin happens with probability one, while in 3D it is transient, meaning that the non-return probability does not vanish.

It is reasonable to assume that, apart from the diffusive motion of the particles, the type of their interaction potentially influences the time-dependence of the probability $S(t|*)$ and, in particular, its long-time behavior. Indeed, in most cases the problem has been studied by tacitly assuming a Markovian residence time probability density $\psi(t)$ for the bound state, i.e., $\psi(t)$ takes an exponential form

$$\psi(t) = \kappa_d e^{-\kappa_d t}, \quad (1)$$

where κ_d denotes an intrinsic dissociation constant.³ However, Agmon and Weiss³ demonstrated that abandoning the Markovian assumption changes the time-dependence of $S(t|*)$ in a substantial way in one and three space dimensions. They

found a phase transition as a function of the parameter σ , which is a measure for the deviation from the Markovian density (where $\sigma = 1$ corresponds to the Markovian limit). In one dimension, they found a first-order phase transition in which the long-time behavior of $S(t|*)$ undergoes a discontinuous change at $\sigma = 1/2$. In contrast, in 3D they observed a second-order phase transition at $\sigma = 1$ and the ultimate fate is again complete dissociation, independent of σ .

In what follows, we will extend the analysis presented in Ref. 3 to the 2D case. We will investigate non-Markovian dissociation for an isolated pair of reversibly binding particles that move in an infinitely extended two dimensional plane. We emphasize that we will not restrict our analysis to the case of an initially bound pair and to the probability $S(t|*)$. Instead, we will derive an exact Green's function (GF) $p(r, t|r_0)$ of the diffusion equation subject to the initial condition that the pair is initially separated at a distance r_0 and subject to a generalized backreaction boundary condition (BC) that incorporates non-Markovian dissociation. This GF may be considered as the central theoretical object in the theory of diffusion-influenced reactions⁷ in the sense that it permits calculating the solution for any given initial distribution and deriving other important and observable quantities, for instance, survival probabilities.^{1,4–6} We will show that the obtained GF and all other derived quantities reduce to the corresponding known expressions that describe Markovian dissociation in 2D in the limit $\sigma \rightarrow 1$. In this sense, the present work generalizes and extends the results given in Ref. 6.

The theory of diffusion-influenced reactions facilitates an understanding of the influence of stochastic fluctuations and spatial heterogeneities on the behavior of biochemical networks. Analytical representations of two-particle GFs play a salient role in a number of particle-based stochastic

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simulation algorithms, because a reaction network may be thought of as composed of unimolecular and bimolecular reactions $A + B \rightarrow \text{products}$. In this context, GFs have been employed to enhance the efficiency of Brownian dynamics simulations.^{8–10} Furthermore, exact analytical expressions can be used to validate newly proposed stochastic simulation algorithms.¹¹ Obviously, the scope of a simulation framework is limited by the choice of the GF, and an algorithm built on GFs cannot transcend the physical assumptions on which the derivation of the GF's mathematical form is based. Therefore, any newly obtained analytical solution will potentially increase the range and power of simulation algorithms. In this context, the two dimensional case is of particular importance in cell biological applications. In particular, in view of the intricate and heterogeneous composition of biological cell membranes,¹² generalizations of the Markovian behavior could potentially be significant for more realistic descriptions of signal-induced local biochemistries.

From a theoretical point of view, the case of two dimensions is special, because it is the critical dimension with regard to recurrence and transience of random walks.¹³ In the context of non-Markovian dissociations the question arises if the observed difference between 1D and 3D (first-order vs second-order phase transition) can indeed be traced back to the recurrent and transient properties of the underlying random walk picture.

The organization of the paper is as follows. First, we will introduce the general theoretical context, especially the Smoluchowski equation and conventional backreaction BC. Note that in the following we will use the terms Smoluchowski equation and diffusion equation interchangeably. Next, we will give a non-Markovian generalization of the backreaction BC for the initially unbound state and we will derive a GF for the diffusion equation subject to that BC. In addition, we will obtain an exact expression for the GF describing the initially bound state and the corresponding survival probabilities. Furthermore, we will present an approximate solution for the long-time behavior of the probability $S(t|*)$ and we will discuss similarities and differences to the non-Markovian 1D and 3D cases. Finally, we will summarize our main results.

II. SMOLUCHOWSKI EQUATION AND BACKREACTION BC

To derive the GF in 2D we consider an isolated pair of two disk-like particles A and B with diffusion constants D_A and D_B , respectively. The particles may associate when their separation equals the encounter distance a to form a bound molecule AB . When bound, the molecules may dissociate again into an unbound pair $A + B$. Such a system may be described as the diffusion of a point-like particle with diffusion constant $D = D_A + D_B$ around a static disk with radius a . In this picture, reactions are introduced by imposing boundary conditions at the disk's surface. The irreversible association reaction is described by the radiation boundary condition¹⁴ that is characterized by an intrinsic association constant κ_a . To take into account reversible reactions, i.e., to allow for dissociations, the radiation BC has to be generalized to the

backreaction BC^{1–5,15–18} that involves an additional intrinsic dissociation constant κ_d . We consider the probability density function (PDF) $p(r, t|r_0)$ that gives the probability to find the particles at a distance r at time t , given that the distance initially was r_0 at time $t = 0$. The time evolution of $p(r, t|r_0)$ is governed by the 2D diffusion equation⁴

$$\frac{\partial}{\partial t} p(r, t|r_0) = -\frac{1}{2\pi r} \frac{\partial}{\partial r} J(r, t|r_0) \quad (2)$$

$$= D \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} \right) p(r, t|r_0), \quad r \geq a. \quad (3)$$

Here, $J(r, t|r_0)$ denotes the total diffusional flux

$$J(r, t|r_0) = -2\pi r D \frac{\partial}{\partial r} p(r, t|r_0). \quad (4)$$

The diffusion equation has to be completed by specifying boundary conditions. Together with the following initial

$$2\pi r_0 p(r, 0|r_0) = \delta(r - r_0) \quad (5)$$

and boundary condition

$$\lim_{r \rightarrow \infty} p(r, t|r_0) = 0, \quad (6)$$

Eq. (3) is equivalent to the free-space diffusion equation in 2D (if $a = 0$, $r > 0$) with the solution (Eq. (1), Chap. 14.8 of Ref. 19)

$$p_{\text{free}}(r, t|r_0) = \frac{1}{4\pi D t} e^{-(r^2+r_0^2)/4Dt} I_0\left(\frac{rr_0}{2Dt}\right), \quad (7)$$

which is also known as the free-space GF. $I_0(x)$ denotes the modified Bessel function of first kind and zero order (Sec. 9.6 of Ref. 20). The PDF we are interested in is only defined for $r \geq a > 0$ and one has to impose a BC for $r = a$ specifying the behavior at the encounter distance. To incorporate association and dissociation on the surface of the “interaction disk” one requires^{1–5,15–18}

$$-J(a, t|r_0) = \kappa_a p(a, t|r_0) - \kappa_d [1 - S(t|r_0)]. \quad (8)$$

$S(t|r_0)$ is the “survival probability” that a pair of molecules with initial distance r_0 is separated at time t

$$S(t|r_0) := 2\pi \int_a^\infty p(r, t|r_0) r dr \quad (9)$$

$$= 1 - 2\pi a D \int_0^t \frac{\partial}{\partial r} p(r, \tau|r_0)|_{r=a} d\tau. \quad (10)$$

Hence, we obtain for the Laplace transform

$$1 - s\tilde{S}(s|r_0) = 2\pi a D \frac{\partial}{\partial r} \tilde{p}(r, s|r_0)|_{r=a}. \quad (11)$$

We point out that, assuming that the flux at infinity vanishes, Eq. (10) results from the diffusion equation (Eq. (2)), the definitions (Eqs. (4) and (9)) and from the initial condition

$$S(t = 0|r_0) = 1, \quad (12)$$

which immediately follows from Eqs. (5) and (9).

So far the theory was formulated for the initially unbound state, but quite analogously one can treat the case of an initially bound state.³ The corresponding PDF is denoted by

$p(r, t|*)$ and it satisfies the same diffusion equation, Eq. (3). However, the initial condition is

$$p(r, t = 0|*) = 0 \quad (13)$$

and the backreaction BC becomes

$$-J(a, t|*) = \kappa_a p(a, t|*) - \kappa_d [1 - S(t|*)]. \quad (14)$$

The “survival probability” $S(t|*)$ is the probability that an initially bound pair of molecules is found unbound at a distance r at time t

$$S(t|*) := 2\pi \int_a^\infty p(r, t|*) r dr \quad (15)$$

$$= -2\pi a D \int_0^t \frac{\partial}{\partial r} p(r, \tau|*)|_{r=a} d\tau. \quad (16)$$

The second identity Eq. (16) may be obtained in an analogous way as Eq. (10) and by observing that

$$S(t = 0|*) = 0, \quad (17)$$

as a consequence of the initial condition, Eq. (13). In the Laplace domain we have

$$-s\tilde{S}(s|*) = 2\pi a D \frac{\partial}{\partial r} \tilde{p}(r, s|*)|_{r=a}. \quad (18)$$

We would like to point out that the notion of a “survival probability” is somewhat misleading in the case we are considering here. For the irreversible reaction, a non-vanishing likelihood to find a separated isolated pair at a time t necessarily implies that no association has occurred before. For the reversible reaction, association and subsequent dissociation events occur possibly many times before t and also contribute to the probability of finding an isolated pair unbound at a time t . Therefore, more precisely, one could refer to the quantities $S(t|r_0)$, $S(t|*)$ as a separation probability of the initially unbound and bound pair, respectively.⁴ Nevertheless, the term “survival probability” has been used in the literature⁵ also in the context considered here and in the following, we will use survival probability interchangeably with separation probability.

For the Markovian case considered so far exact expressions for the GFs $p(r, t|r_0)$, $p(r, t|*)$ are known.⁶ For later use we give the result for the GF corresponding to an initially unbound state

$$p(r, t|r_0) = \frac{1}{2\pi} \int_0^\infty e^{-Dx^2 t} T(x, r) T(x, r_0) x dx, \quad (19)$$

where

$$T(x, r) := \frac{J_0(rx)\beta(x) - Y_0(rx)\alpha(x)}{[\alpha(x)^2 + \beta(x)^2]^{1/2}} \quad (20)$$

and

$$\alpha(x) := (x^2 - \kappa_D)J_1(xa) + hxJ_0(xa), \quad (21)$$

$$\beta(x) := (x^2 - \kappa_D)Y_1(xa) + hxY_0(xa), \quad (22)$$

where we introduced

$$h = \frac{\kappa_a}{2\pi a D}, \quad \kappa_D = \frac{\kappa_d}{D}, \quad (23)$$

and $J_n(x)$, $Y_n(x)$ denote the Bessel functions of first and second kinds, respectively (Sec. 9.1 of Ref. 20).

III. NON-MARKOVIAN THEORY

In its conventional form, the backreaction BC (Eq. (8)) assumes a Markovian probability density for the residence time,³ given by Eq. (1) or, equivalently, by

$$\tilde{\psi}(s) = \frac{\kappa_d}{\kappa_d + s} \quad (24)$$

in the Laplace domain. Equation (1) corresponds to the situation where the bound molecule can be sufficiently well described by a single, discrete state. However, the bound state is typically comprised of a large number of different internal states. It follows that the associated probability density $\psi(t)$ for residence time in the set of all possible bound states is given by a superposition of exponentials that correspond to the individual states³

$$\psi(t) = \sum_{n=0}^{\infty} \varphi_n e^{-\lambda_n t}. \quad (25)$$

Only if the time scales set by the λ_n parameters are sufficiently separated, i.e., the decay of the ground state (= dissociation) is much slower than the decay of all other internal states, Eq. (25) can be replaced by Eq. (1) and the Markovian description is justified. However, if there is no sufficient separation of the involved time scales, the effective description of all internal states as one single state cannot be Markovian any more, cf. the discussion given in Ref. 3. Furthermore, as already mentioned in the introduction, a non-Markovian deviation could be caused by a complex environment, for instance in biological cellular systems. In Ref. 3, the following choice of densities was employed:

$$\tilde{\psi}(s) = \frac{1}{1 + (s\kappa^{-1})^\sigma}, \quad 0 < \sigma \leq 1. \quad (26)$$

For a discussion and motivation for this particular form, we refer to Ref. 3. Here, we only note that for $\sigma = 1$ and by identifying κ with κ_d , one recovers Eq. (24). However, for $\sigma < 1$, $\psi(t)$ decays slower than an exponential.³

Next, we will derive a non-Markovian generalization of the backreaction BC, Eq. (8). Following Ref. 3, we retain the assumption that association is described by first order kinetics. Hence, we only have to consider the term $\kappa_d[1 - S(t|r_0)]$. Clearly, $1 - S(t|r_0)$ gives the probability to find the pair in the bound state at time t , provided it was separated at a distance r_0 at time $t = 0$. This probability can alternatively be obtained in the following way. The probability that the particles associated at an earlier time between τ and $\tau + d\tau$ is $\kappa_a p(a, \tau|r_0) d\tau$. Then, the subsequent residence time in the bound state is given by $t - \tau$ and, therefore, the generalized backreaction BC can be rewritten in terms of the residence time probability density as follows:

$$\begin{aligned} -J(a, t|r_0) &= \kappa_a p(a, t|r_0) \\ &\quad - \kappa_a \int_0^t p(a, \tau|r_0) \psi(t - \tau) d\tau \end{aligned} \quad (27)$$

and the Laplace transformed BC is

$$-\tilde{J}(a, s|r_0) = \kappa_a[1 - \tilde{\psi}(s)]\tilde{p}(a, s|r_0). \quad (28)$$

Note that in the Markovian case where $\psi(t)$ is given by Eq. (1), one has

$$\kappa_d[1 - S(t|r_0)] = \kappa_a \int_0^t p(a, \tau|r_0)\psi(t - \tau)d\tau. \quad (29)$$

This can be shown as follows. Starting from the Laplace transformed version of the BC, Eq. (8),

$$-\tilde{J}(a, s|r_0) = \kappa_a\tilde{p}(a, s|r_0) - \kappa_d[s^{-1} - \tilde{S}(s|r_0)], \quad (30)$$

and using Eq. (11) we arrive at

$$s^{-1} - \tilde{S}(s|r_0) = \frac{\kappa_a}{s + \kappa_d}\tilde{p}(a, s|r_0) \quad (31)$$

and Eq. (29) follows.

To calculate the GF we closely follow Ref. 6 and make an ansatz for the Laplace transform of the Green's function that satisfies the generalized backreaction BC

$$\tilde{p}(r, q|r_0) = \tilde{p}_{\text{free}}(r, q|r_0) + \tilde{p}_{\text{br}}(r, q|r_0). \quad (32)$$

Here

$$\tilde{p}_{\text{free}}(r, q|r_0) = \frac{1}{2\pi D} \begin{cases} I_0(qr_0)K_0(qr), & r > r_0 \\ I_0(qr)K_0(qr_0), & r < r_0 \end{cases} \quad (33)$$

is the Laplace transform of the free-space GF Eq. (7) (Eq. (2), Chap. 14.8 of Ref. 19). $K_0(x)$ refers to the modified Bessel function of second kind and zero order (Sec. 9.6 of Ref. 20). The variable q is defined by $q := \sqrt{s/D}$. The part $\tilde{p}_{\text{br}}$ that takes into account the BC is a solution of the Laplace transformed 2D diffusion equation

$$\frac{d^2 \tilde{p}_{\text{br}}}{dr^2} + \frac{1}{r} \frac{d\tilde{p}_{\text{br}}}{dr} - q^2 \tilde{p}_{\text{br}} = 0. \quad (34)$$

The general solution to Eq. (34) is $AK_0(qr) + BI_0(qr)$. Because we require $\lim_{r \rightarrow \infty} \tilde{p}_{\text{br}} \rightarrow 0$, and $\lim_{x \rightarrow \infty} I_0(x) \rightarrow \infty$, the coefficient B has to vanish and hence,

$$\tilde{p}_{\text{br}}(r, q|r_0) = A(q, r_0)K_0(qr). \quad (35)$$

$A(q, r_0)$ is determined by the requirement that the complete GF (Eq. (32)) satisfies the Laplace transformed backreaction BC (Eq. (28)), which we now write in the form

$$\frac{\partial}{\partial r} \tilde{p}(r, q|r_0)|_{r=a} = h[1 - \tilde{\psi}(s)]\tilde{p}(a, q|r_0). \quad (36)$$

Using Eqs. (32), (33), (35), (36), and $I'_0(x) = I_1(x)$, $K'_0(x) = -K_1(x)$, (Eq. (9.6.27) of Ref. 20) we obtain

$$\begin{aligned} \tilde{p}_{\text{br}}(r, q|r_0) &= \frac{1}{2\pi D} K_0(qr)K_0(qr_0) \\ &\times \frac{qI_1(qa) - h[1 - \tilde{\psi}]I_0(qa)}{qK_1(qa) + h[1 - \tilde{\psi}]K_0(qa)}. \end{aligned} \quad (37)$$

We now assume that the residence time PDF is indeed given by Eq. (26). Then we have, defining $\kappa_D^\sigma := \kappa^\sigma / D^\sigma$,

$$\begin{aligned} \tilde{p}_{\text{br}}(r, q|r_0) &= \frac{1}{2\pi D} K_0(qr)K_0(qr_0) \\ &\times \frac{(q^{2\sigma} + \kappa_D^\sigma)I_1(qa) - hq^{2\sigma-1}I_0(qa)}{(q^{2\sigma} + \kappa_D^\sigma)K_1(qa) + hq^{2\sigma-1}K_0(qa)}. \end{aligned} \quad (38)$$

We point out that, alternatively, one can obtain Eqs. (37) and (38) in the following way. First, it has been shown that for both the irreversible and reversible cases the GF that takes into account the reaction by satisfying the radiation/background BC can be rewritten in terms of the GF p_{ref} that corresponds to nonreactive diffusion and satisfies a reflective BC.^{21,22} For the reversible case one finds²² in the Laplace domain

$$\begin{aligned} \tilde{p}(r, q|r_0) &= \tilde{p}_{\text{ref}}(r, q|r_0) \\ &- \kappa_a q^2 \frac{\tilde{p}_{\text{ref}}(r, q|a)\tilde{p}_{\text{ref}}(a, q|r_0)}{q^2 + \kappa_D + \kappa_a q^2 \tilde{p}_{\text{ref}}(a, q|a)}. \end{aligned} \quad (39)$$

Note that there is also an analogue formula for $\tilde{S}(s|*)$.³ Clearly, the form of $\tilde{p}_{\text{ref}}$ is not affected by a generalization to non-Markovian dissociation. Hence, the non-Markovian case Eq. (37) can be heuristically derived from Eq. (39) upon substituting κ_d by $s\tilde{\psi}/[1 - \tilde{\psi}]$.^{3,4} Although we will not make use of it, we point out that all following generalized expressions in the Laplace domain are consistent with this “correspondence rule.”

The inversion theorem for the Laplace transformation can be applied to find the expression for p_{br} in the time domain

$$p_{\text{br}}(r, t|r_0) = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} e^{st} \tilde{p}_{\text{br}}(r, q|r_0) ds. \quad (40)$$

To calculate the Bromwich contour integral we first note that $\tilde{p}_{\text{br}}$ has a branch point at $s = 0$. Therefore, we use the contour of Fig. 1 with a branch cut along the negative real axis, cf. Fig. 40, Chap. 12.3 of Ref. 19. Furthermore, we note that the integrand has no poles within and on the contour²³ and that the contribution from the small circle around the origin vanishes, which can be seen by the limiting forms of the modified Bessel functions for small arguments (Eqs. (9.6.7)–(9.6.9) of

FIG. 1. Integration contour used in Eq. (41).

Ref. 20). Therefore, we obtain

$$\begin{aligned} & \int_{\gamma-i\infty}^{\gamma+i\infty} e^{st} \tilde{p}_{\text{br}}(r, q|r_0) ds \\ &= - \int_{\mathcal{C}_2} e^{st} \tilde{p}_{\text{br}}(r, q|r_0) ds - \int_{\mathcal{C}_4} e^{st} \tilde{p}_{\text{br}}(r, q|r_0) ds. \end{aligned} \quad (41)$$

Thus, it remains to calculate the integrals $\int_{\mathcal{C}_2}, \int_{\mathcal{C}_4}$. To this end, we choose $s = Dx^2 e^{i\pi}$ and use (Eqs. (25) and (26), Appendix 3 of Ref. 19)

$$I_n(xe^{\pm\pi i/2}) = e^{\pm n\pi i/2} J_n(x), \quad (42)$$

$$K_n(xe^{\pm\pi i/2}) = \pm \frac{1}{2} \pi i e^{\mp n\pi i/2} [-J_n(x) \pm i Y_n(x)]. \quad (43)$$

It follows that

$$\begin{aligned} & \int_{\mathcal{C}_2} e^{st} \tilde{p}_{\text{br}}(r, q|r_0) ds \\ &= \frac{1}{2} \int_0^\infty e^{-Dx^2 t} [\Omega(x) - i\Pi(x)] \\ & \quad \times \frac{[\beta_\sigma^-(x) + i\alpha_\sigma^+(x)][\alpha_\sigma(x) + i\beta_\sigma(x)]}{\alpha_\sigma^2(x) + \beta_\sigma^2(x)} x dx. \end{aligned} \quad (44)$$

Here we introduced the following notation:

$$\Omega = \Omega(x, r, r_0) = J_0(xr)J_0(xr_0) - Y_0(xr)Y_0(xr_0),$$

$$\Pi = \Pi(x, r, r_0) = Y_0(xr)J_0(xr_0) + J_0(xr)Y_0(xr_0),$$

and

$$\alpha_\sigma(x) = \alpha_\sigma^+(x) + \alpha_\sigma^-(x), \quad (45)$$

$$\beta_\sigma(x) = \beta_\sigma^+(x) + \beta_\sigma^-(x), \quad (46)$$

where

$$\alpha_\sigma^+(x) = -\omega_J \cos(\pi\sigma) - \kappa_D^\sigma J_1(xa), \quad (47)$$

$$\alpha_\sigma^-(x) = -\omega_Y \sin(\pi\sigma), \quad (48)$$

$$\beta_\sigma^+(x) = -\omega_Y \cos(\pi\sigma) - \kappa_D^\sigma Y_1(xa), \quad (49)$$

$$\beta_\sigma^-(x) = \omega_J \sin(\pi\sigma), \quad (50)$$

and

$$\omega_J = x^{2\sigma} J_1(xa) + h x^{2\sigma-1} J_0(xa), \quad (51)$$

$$\omega_Y = x^{2\sigma} Y_1(xa) + h x^{2\sigma-1} Y_0(xa). \quad (52)$$

We note that under the formal transformation $\sigma \rightarrow -\sigma$, the functions $\alpha_\sigma^+(x)$, $\beta_\sigma^+(x)$ and $\alpha_\sigma^-(x)$, $\beta_\sigma^-(x)$ are even and odd, respectively. Therefore, one also has

$$\alpha_\sigma^+(x) = \frac{1}{2} [\alpha_\sigma(x) + \alpha_{-\sigma}(x)], \quad (53)$$

$$\alpha_\sigma^-(x) = \frac{1}{2} [\alpha_\sigma(x) - \alpha_{-\sigma}(x)], \quad (54)$$

and corresponding formulas hold for $\beta_\sigma^+(x)$, $\beta_\sigma^-(x)$. Furthermore, we note that for the Markovian limit $\sigma = 1$ one obtains

$$\alpha_{\sigma=1}^+(x) = \alpha(x), \quad (55)$$

$$\beta_{\sigma=1}^+(x) = \beta(x), \quad (56)$$

$$\alpha_{\sigma=1}^-(x) = 0 = \beta_{\sigma=1}^-(x). \quad (57)$$

Hence, the functions α_σ , β_σ may be considered as non-Markovian generalizations of the functions α , β that appear in the Markovian GF, cf. Eqs. (19)–(22).

Next, we turn to the computation of the integral along the contour $\mathcal{C}_4$. We choose $s = Dx^2 e^{-i\pi}$ and after an analogous calculation one finds that $\int_{\mathcal{C}_2} e^{st} \tilde{p}_{\text{br}}(r, q|r_0) ds = -(\int_{\mathcal{C}_4} e^{st} \tilde{p}_{\text{br}}(r, q|r_0) ds)^*$, where $*$ means complex conjugation. Thus, one arrives at

$$p_{\text{br}}(r, t|r_0) = -\frac{1}{\pi} \Im \left(\int_{\mathcal{C}_2} e^{st} \tilde{p}_{\text{br}}(r, q|r_0) ds \right) \quad (58)$$

and making use of the fact that the free-space Green's function may be written as

$$p_{\text{free}}(r, t|r_0) = \frac{1}{2\pi} \int_0^\infty e^{-Dx^2 t} J_0(xr) J_0(xr_0) x dx$$

one arrives at the exact Green's function in the time domain

$$\begin{aligned} p(r, t|r_0) &= \frac{1}{2\pi} \int_0^\infty e^{-Dx^2 t} [T_\sigma^+(x, r) T_\sigma(x, r_0) \\ & \quad + C_\sigma^-(x, r) C_\sigma(x, r_0)] x dx, \end{aligned} \quad (59)$$

where

$$T_\sigma(x, r) = \frac{J_0(rx)\beta_\sigma(x) - Y_0(rx)\alpha_\sigma(x)}{[\alpha_\sigma(x)^2 + \beta_\sigma(x)^2]^{1/2}}, \quad (60)$$

$$T_\sigma^\pm(x, r) = \frac{J_0(rx)\beta_\sigma^\pm(x) - Y_0(rx)\alpha_\sigma^\pm(x)}{[\alpha_\sigma(x)^2 + \beta_\sigma(x)^2]^{1/2}}, \quad (61)$$

$$C_\sigma(x, r) = \frac{Y_0(rx)\beta_\sigma(x) + J_0(rx)\alpha_\sigma(x)}{[\alpha_\sigma(x)^2 + \beta_\sigma(x)^2]^{1/2}}, \quad (62)$$

$$C_\sigma^\pm(x, r) = \frac{Y_0(rx)\beta_\sigma^\pm(x) + J_0(rx)\alpha_\sigma^\pm(x)}{[\alpha_\sigma(x)^2 + \beta_\sigma(x)^2]^{1/2}}. \quad (63)$$

From Eqs. (55)–(57) one can immediately see that in the Markovian limit Eq. (59) reduces to the known result Eq. (19), as it should. Furthermore, using the definitions (Eqs. (60)–(63)), we note that the GF satisfies $p(r, t|r_0) = p(r_0, t|r)$. In Fig. 2 the GF is plotted for several values of the parameter σ and compared to its Markovian limit.

Knowledge of the GF permits to derive further important quantities. We employ Eq. (10) to obtain the survival probability of the initially unbound state

$$\begin{aligned} S(t|r_0) &= 1 - a \int_0^\infty e^{-Dx^2 t} [P_\sigma^+(x, a) T_\sigma(x, r_0) \\ & \quad + D_\sigma^-(x, a) C_\sigma(x, r_0)] dx, \end{aligned} \quad (64)$$

where we defined the functions

$$P_\sigma(x, r) = -\frac{1}{x} \frac{\partial}{\partial r} T_\sigma(x, r), \quad (65)$$

FIG. 2. The Green's function of the reversible non-Markovian dissociation reaction for an initially unbound isolated pair in 2D. The parameters are: $a = 1$, $D = 2$, $r_0 = 1.1$, $\kappa_a = 2\pi D$, $\kappa = 0.5 \eta^{-1}$, where $\eta = a^2 D^{-1}$ denotes the natural time scale of the system. The figure shows the r dependence of the generalized reversible GF $2\pi p(r, t|r_0)$ at time $t = 10 \eta$ for various values of the parameter σ , corresponding to the analytical expression (Eq. (59)) or, equivalently, Eq. (73).

$$P_\sigma^\pm(x, r) = -\frac{1}{x} \frac{\partial}{\partial r} T_\sigma^\pm(x, r), \quad (66)$$

$$D_\sigma(x, r) = -\frac{1}{x} \frac{\partial}{\partial r} C_\sigma(x, r), \quad (67)$$

$$D_\sigma^\pm(x, r) = -\frac{1}{x} \frac{\partial}{\partial r} C_\sigma^\pm(x, r). \quad (68)$$

Again, due to the properties of α_σ , β_σ Eqs. (55)–(57) one recovers from Eq. (64) the known expression for the Markovian survival probability in the case $\sigma = 1$, cf. Ref. 6.

Alternatively, in order to obtain an expression for $S(t|r_0)$, one may first calculate the Laplace transform $\tilde{S}(s|r_0)$ upon Eqs. (11) and (38) and then perform the Bromwich integral.

We point out that the functions (Eqs. (45)–(52) and (60)–(63)) permit a geometric interpretation that motivates the introduction of an alternative set of functions. This new set of functions will turn out to be convenient to express further derived quantities in a form that makes the correspondence to the Markovian limit manifest. To this end, we first note that the functions α_σ , β_σ may be viewed as the components of an abstract 2D vector. Then, we see from Eqs. (45)–(52) that they can be re-expressed as a matrix equation

$$\begin{pmatrix} \alpha_\sigma \\ \beta_\sigma \end{pmatrix} = -D(\sigma) \begin{pmatrix} \omega_J \\ \omega_Y \end{pmatrix} - \mathbf{1} \begin{pmatrix} \kappa_D^\sigma J_1 \\ \kappa_D^\sigma Y_1 \end{pmatrix}, \quad (69)$$

where we introduced a rotation matrix in an abstract space

$$D(\sigma) = \begin{pmatrix} \cos(\pi\sigma) & \sin(\pi\sigma) \\ -\sin(\pi\sigma) & \cos(\pi\sigma) \end{pmatrix}. \quad (70)$$

Now, we may define a rotated vector comprised of $\tilde{\alpha}_\sigma$, $\tilde{\beta}_\sigma$ functions by

$$\begin{pmatrix} \tilde{\alpha}_\sigma \\ \tilde{\beta}_\sigma \end{pmatrix} = -D(-\sigma) \begin{pmatrix} \alpha_\sigma \\ \beta_\sigma \end{pmatrix}. \quad (71)$$

Because the matrix $D(\sigma)$ is orthogonal, i.e., it satisfies $D(-\sigma) = D^{-1}(\sigma) = D^T(\sigma)$, it immediately follows from Eq. (71) that the denominator of the functions (Eqs. (60)–(63) and (65)–(68)) can also be written in terms of the functions $\tilde{\alpha}_\sigma$, $\tilde{\beta}_\sigma$, more precisely, one has $\alpha_\sigma^2 + \beta_\sigma^2 = \tilde{\alpha}_\sigma^2 + \tilde{\beta}_\sigma^2$. We also note that in a way analogue to Eqs. (53) and (54) we may define functions $\tilde{\alpha}_\sigma^\pm$, $\tilde{\beta}_\sigma^\pm$ that also satisfy Eqs. (55)–(57). With these new functions at our disposal, it is natural to introduce functions $\tilde{T}_\sigma$, $\tilde{T}_\sigma^\pm$, $\tilde{P}_\sigma$, $\tilde{P}_\sigma^\pm$, etc., which are defined in a completely analogue fashion to their counterparts Eqs. (60)–(63) and (65)–(68). Then the survival probability, for instance, can more neatly be re-written as

$$S(t|r_0) = 1 - a \int_0^\infty e^{-Dx^2t} \tilde{P}_\sigma^+(x, a) \tilde{T}_\sigma(x, r_0) dx, \quad (72)$$

making the correspondence to the Markovian limiting case as $\sigma \rightarrow 1$ manifest. Furthermore, the GF (Eq. (59)) now takes the form

$$p(r, t|r_0) = \frac{1}{2\pi} \int_0^\infty e^{-Dx^2t} \times [\tilde{T}_\sigma^+(x, r) \tilde{T}_\sigma(x, r_0) + \tilde{C}_\sigma^-(x, r) \tilde{C}_\sigma(x, r_0)] x dx. \quad (73)$$

Finally, we note in this context that the functions T_σ , $\tilde{T}_\sigma$, C_σ , $\tilde{C}_\sigma$, etc., can also be written in a more geometric form as a symplectic and inner form, respectively. For instance, one has

$$T(x, r) = \frac{1}{[\alpha_\sigma^2 + \beta_\sigma^2]^{1/2}} \begin{pmatrix} J_0(xr) \\ Y_0(xr) \end{pmatrix}^T \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} \alpha_\sigma \\ \beta_\sigma \end{pmatrix}, \quad (74)$$

$$C(x, r) = \frac{1}{[\alpha_\sigma^2 + \beta_\sigma^2]^{1/2}} \begin{pmatrix} J_0(xr) \\ Y_0(xr) \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \alpha_\sigma \\ \beta_\sigma \end{pmatrix}, \quad (75)$$

and analogue expressions for the other functions. The appearance of an inner form is a result of the non-Markovian generalization. We now turn our focus to the case of the initially bound state that may be treated quite analogously to the case of the unbound state, i.e., first one seeks a solution of the diffusion equation subject to the initial condition (Eq. (13)) and to the generalized form of the backreaction BC³ and, making use of that solution, one can calculate other quantities of interest. Here, we will follow another route, relating the solutions of the initially unbound and bound state. Conventionally, i.e., in the Markovian case, this relationship is established via detailed balance

$$\kappa_a p(r, t|*) = \kappa_d p(*, t|r). \quad (76)$$

Because

$$p(*, t|r) = 1 - S(t|r), \quad (77)$$

Eq. (76) can be used to calculate the GF of the initially bound state $p(r, t|*)$ once $S(t|r)$ is known. However, in the non-Markovian case, one has to find an appropriate substitute for Eq. (76), because the rhs is exactly the Markovian backreaction term that we had to replace in the BC. Hence, we already know how to substitute this expression and we can write,

generalizing Eq. (76),

$$p(r, t|*) = \int_0^t p(a, t - \tau|r)\psi(\tau)d\tau, \quad (78)$$

which becomes in the Laplace domain

$$\tilde{p}(r, s|*) = \tilde{p}(a, s|r)\tilde{\psi}(s). \quad (79)$$

Combining the generalized detailed balance condition with Eqs. (26) and (37) one arrives at

$$\tilde{p}(r, s|*) = \frac{\kappa_D^\sigma K_0(qr)}{2\pi a D q} \times \frac{1}{(q^{2\sigma} + \kappa_D^\sigma) K_1(qa) + h q^{2\sigma-1} K_0(qa)}. \quad (80)$$

To find the expression for the GF in the time domain we can proceed analogously to the calculation of the GF for the initially unbound pair, in particular we can use the same integration contour. Because the actual calculation is quite similar to the one we did before for the GF $p(r, t|r_0)$, we only give the result

$$p(r, t|*) = D^{1-\sigma} \frac{\kappa^\sigma}{\kappa_a} a \int_0^\infty e^{-Dtx^2} \tilde{P}_\sigma^+(x, a) T_\sigma(x, r) \frac{dx}{x^{2\sigma-2}}. \quad (81)$$

Note that the form of Eq. (81) makes it manifest that we recover the Markovian version of the GF $p(r, t|*)^6$ as $\sigma \rightarrow 1$. The survival probability of the initially bound state can now be calculated using Eq. (16). We obtain

$$S(t|*) = 1 - 2\pi a^2 \frac{\kappa^\sigma}{\kappa_a} D^{1-\sigma} \times \int_0^\infty e^{-Dtx^2} \tilde{P}_\sigma^+(x, a) P_\sigma(x, a) \frac{dx}{x^{2\sigma-1}}. \quad (82)$$

Again, it is clear that we recover the Markovian limiting case of the separation probability⁶ as $\sigma \rightarrow 1$. Furthermore, using the definitions of $\tilde{P}_\sigma^+$, P_σ one can see that Eq. (82) is equal to the more explicit expression for $S(t|*)$ given in Ref. 24. Moreover, it follows that the separation probability approaches unity for large times, $\lim_{t \rightarrow \infty} S(t|*) = 1$. Therefore, it can explicitly be shown that, independent of the value of the parameter σ , the ultimate fate of an isolated pair for the reversible reaction with non-Markovian backreaction is always complete dissociation in 2D, in contrast to the non-Markovian 1D case.³ In Fig. 3, we plot $\ln[1 - S(t|*)]$ vs $\log t$ for several values of the parameter σ and compare the exact expression (Eq. (82)) to the approximate solution (Eq. (91)).

Alternatively, one may choose to obtain the expression for the separation probability in the Laplace domain first and then to perform the Bromwich integral to arrive at Eq. (82). For later use we give here the corresponding expression²⁴

$$\tilde{S}(s|*) = \frac{1}{s} \frac{\kappa^\sigma q K_1(qa)}{q K_1(qa)(s^\sigma + \kappa^\sigma) + h s^\sigma K_0(qa)}. \quad (83)$$

The generalized detailed balance condition can also be employed to establish a relationship between the survival probability of the initially unbound and bound state. From Eqs. (28) and (79) and the non-Markovian backreaction BC

FIG. 3. The survival probability for an initially bound isolated pair in 2D. The parameters are: $a = 1$, $D = 2$, $\kappa_a = 2\pi D$, $\kappa = 2\eta^{-1}$, where $\eta = a^2 D^{-1}$ denotes the natural time scale of the system. The figure shows the time dependence of the survival probability $S(t|*)$ for various values of the parameter σ . The solid lines are obtained from the analytical expression, Eq. (82). The dashed lines refer to the approximate solution (Eq. (91)) and, for $\sigma = 1$, Eq. (88).

for the bound state³

$$-\tilde{J}(a, s|*) = \kappa_a [1 - \tilde{\psi}(s)] \tilde{p}(a, s|*) - \tilde{\psi}(s), \quad (84)$$

it follows that

$$\tilde{S}(s|*) = \tilde{\psi}(s) \tilde{S}(s|a), \quad (85)$$

which yields a convolution integral in the time domain

$$S(t|*) = \int_0^t \psi(\tau) S(t - \tau|a) d\tau. \quad (86)$$

Again, Eqs. (85) and (86) are completely analogous to the Markovian case.^{4,6}

Finally, we are interested in how the limiting value is approached. To this end, we derive the asymptotic behavior for $t \rightarrow \infty$. The starting point is the expression for $\tilde{S}(s|*)$, Eq. (83). Using the series expansions of the modified Bessel functions for small arguments (Eqs. (9.6.10)–(9.6.13) of Ref. 20), we obtain

$$\tilde{S}(s|*) = \frac{1}{s} + \frac{ha}{\kappa^\sigma} s^{\sigma-1} \ln\left(\frac{1}{2} e^{\gamma_E} qa\right) - \frac{s^{\sigma-1}}{\kappa^\sigma} + \dots, \quad (87)$$

where γ_E denotes Euler's number $\gamma_E = 0.5772156649\dots$ (Eq. (6.1.3) of Ref. 20). For $\sigma = 1$ we obtain in the time domain

$$S(t|*) = 1 - \frac{\kappa_a}{\kappa_d} \frac{1}{4\pi D t} + \dots, \quad (88)$$

which is the known Markovian result. If $0 < \sigma < 1$, we use (Eqs. (29.3.99) and (29.3.7) of Ref. 20)

$$\mathcal{L}^{-1}\left[\frac{1}{s^k} \ln s\right] = \frac{t^{k-1}}{\Gamma(k)} [\Psi(k) - \ln t], \quad k > 0, \quad (89)$$

$$\mathcal{L}^{-1}\left[\frac{1}{s^k}\right] = \frac{t^{k-1}}{\Gamma(k)}, \quad k > 0, \quad (90)$$

where $\mathcal{L}^{-1}$, Γ , Ψ denote the inverse Laplace transform, the gamma function and the digamma function (Eqs. (6.1.1) and (6.3.1) of Ref. 20), respectively. Hence, we arrive at²⁴

$$S(t|*) = 1 - \frac{\kappa_a}{\kappa^\sigma} \frac{1}{4\pi D} \frac{t^{-\sigma}}{\Gamma(1-\sigma)} \ln(\varrho t) + \varkappa \frac{t^{-\sigma}}{\Gamma(1-\sigma)} + \dots, \quad (91)$$

where we introduced the constants

$$\varkappa = \frac{\kappa_a}{\kappa^\sigma} \frac{1}{4\pi D} \Psi(1-\sigma) - \frac{1}{\kappa^\sigma}, \quad (92)$$

$$\varrho = 4e^{-2\gamma_E} D a^{-2}. \quad (93)$$

We find again that, independent of the parameter σ , the ultimate fate is complete dissociation, although the underlying random walk is recurrent. In contrast, in 1D, the parameter σ determines if the particles escape or remain bound at long times.³ In this regard, the 2D case is more similar to the (non-Markovian) 3D case. However, it is very different to the 3D case with respect to how the limiting value is approached. In 3D, it was shown³ that the decay goes as $t^{-\sigma}$ at $\sigma < 1$, but as $t^{-3/2}$ at $\sigma = 1$, which means there is a second-order phase transition. However, in 2D, even the functional form is different: While we observe a $t^{-\sigma} \ln t$ decay at $\sigma < 1$, we find t^{-1} at $\sigma = 1$. Still, the limit $\sigma \rightarrow 1$ is smooth in the following sense. For small arguments $1 - \sigma = \epsilon \rightarrow 0$ the reciprocal gamma function has the expansion (Eq. (6.1.34) of Ref. 20)

$$\frac{1}{\Gamma(\epsilon)} = \epsilon + \mathcal{O}(\epsilon^2), \quad (94)$$

while the digamma function has a simple pole at the point zero with residue -1 , cf. Eqs. (6.3.5) and (6.3.16) of Ref. 20

$$\Psi(\epsilon) = -\frac{1}{\epsilon} - \gamma_E + \mathcal{O}(\epsilon). \quad (95)$$

Equations (94) and (95) imply that, as $\sigma \rightarrow 1$, the $t^{-\sigma} \ln t$ term vanishes in Eq. (91) and only the $t^{-\sigma}$ term that is multiplied by the digamma function (cf. Eq. (92)) does not vanish. Thus, one recovers the Markovian result (Eq. (88)) in a smooth way from the non-Markovian generalization as $\sigma \rightarrow 1$. In conclusion, one finds that there is neither a first- nor second-order phase transition in the 2D case, although the approximative solution's functional form is quite different from its Markovian counterpart.

IV. SUMMARY OF MAIN RESULTS

We studied the reversible diffusion-influenced reaction of an isolated pair in 2D in the presence of a generalized back-reaction BC (Eq. (27)) that incorporates non-Markovian dissociation, i.e., the residence time probability density takes a non-exponential form Eq. (26). We obtained an exact expression (Eq. (59)) for the corresponding GF

$$p(r, t|r_0) = \frac{1}{2\pi} \int_0^\infty e^{-Dx^2 t} \times [T_\sigma^+(x, r) T_\sigma(x, r_0) + C_\sigma^-(x, r) C_\sigma(x, r_0)] x dx$$

that is valid for arbitrary $0 < \sigma \leq 1$ and for all times. The second term $C_\sigma^-(x, r) C_\sigma(x, r_0)$ is foreign to the Markovian lim-

iting case. In the limit $\sigma \rightarrow 1$ it vanishes and one recovers the known GF (Eq. (19)) that describes Markovian dissociation in 2D. Knowledge of the GF permitted deriving the survival probability for the initially unbound pair (Eq. (72))

$$S(t|r_0) = 1 - a \int_0^\infty e^{-Dx^2 t} \tilde{P}_\sigma^+(x, a) \tilde{T}_\sigma(x, r_0) dx,$$

that makes the correspondence to the Markovian limiting case manifest.⁶ Using a generalized detailed balance condition (Eq. (78)), we obtained an exact expression (Eq. (82)) for the probability $S(t|*)$ that the initially bound particle is unbound at time t

$$S(t|*) = 1 - 2\pi a^2 \frac{\kappa^\sigma}{\kappa_a} D^{1-\sigma} \times \int_0^\infty e^{-Dtx^2} \tilde{P}_\sigma^+(x, a) P_\sigma(x, a) \frac{dx}{x^{2\sigma-1}}.$$

Our results demonstrate that the 2D case is quite different from both the non-Markovian 1D and 3D cases.³ In particular, the obtained expressions for $S(t|r_0)$, $S(t|*)$ show that the ultimate fate of an isolated pair is, independent of σ , always dissociation, as in the one, two- and three-dimensional Markovian case $\sigma = 1$. To see how the limiting value of $S(t|*)$ is approached, we derived an asymptotic expansion for long times (Eq. (91)) and found that there is neither a first nor second-order phase transition: Although the expansion contains a $t^{-\sigma} \ln t$ term, one recovers the Markovian result $1 - S(t|*) \sim t^{-1}$ in the limit $\sigma \rightarrow 1$ in a smooth way.

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