The area reactivity model of geminate recombination

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(Received 3 December 2013; accepted 4 March 2014; published online 21 March 2014)

We investigate the reversible diffusion-influenced reaction of an isolated pair in the context of the area reactivity model that describes the reversible binding of a single molecule in the presence of a binding site in terms of a generalized version of the Feynman-Kac equation in two dimensions. We compute the corresponding exact Green's function in the Laplace domain for both the initially unbound and bound molecule. We discuss convolution relations that facilitate the calculation of the binding and survival probabilities. Furthermore, we calculate an exact analytical expression for the Green's function in the time domain by inverting the Laplace transform via the Bromwich contour integral and derive expressions for the binding and survival probability in the time domain as well. We numerically confirm the accuracy of the obtained expressions by propagating the generalized Feynman-Kac equation in the time domain. Our results should be useful for comparing the area reactivity model with the contact reactivity model. [<http://dx.doi.org/10.1063/1.4868554>]

I. INTRODUCTION

The diffusion-influenced reaction of an isolated pair of molecules $A + B \rightarrow C$ may be described by a kinetic scheme^{1,2} that is comprised of two separate physical processes: First, the two molecules encounter each other through their diffusive motion at a critical distance $r = a$. Then, the actual chemical reaction may take place with a certain likelihood. This two-step picture suggests that geminate recombination can be modeled in terms of solutions of the diffusion equation that satisfy suitable boundary conditions (BC), which incorporate the physics at the critical contact distance. In his seminal paper,³ Smoluchowski considered a completely absorbing BC enforcing the reaction to take place immediately upon contact. This special case can be generalized to a radiation BC⁴ that takes into account the more generic situation where an encounter leads to an actual reaction only with a certain likelihood. The inclusion of reversible reactions in this theoretical framework requires a further generalization of the imposed BC: The so-called back-reaction BC^{5,6} permits to take into account dissociations and involves, besides an intrinsic association constant that appears already in the radiation BC, an additional intrinsic dissociation constant.

A considerable body of work has been dedicated to the study of irreversible and reversible diffusion-influenced reactions in terms of these Smoluchowski-type contact reactivity models.^{1,2,7,8} For the case of an isolated pair, exact expressions for Green's functions (GF) in the time domain, describing irreversible and reversible reactions in one, two, and three space dimensions, have been obtained.^{6,9–11} GF play a particular role in the theoretical description, because they can be used to derive other important quantities, for

instance, survival probabilities and time-dependent reaction rate coefficients. Moreover, they can be employed to calculate the time evolution for any given initial distribution. Analytical representations of GF have also been utilized as essential ingredient of particle-based stochastic simulation algorithms, where GF enhance the efficiency of Brownian dynamics simulations.^{12–14} Finally, the availability of exact expressions permits validating newly proposed stochastic simulation algorithms.¹⁵

However, despite the success and broad applicability of contact reactivity models, their underlying assumption of the existence of a sharply defined reaction radius lacks a rigorous physical justification, and the corresponding unique role of the BC in the formalism have provoked criticism.¹⁶ It was pointed out that a more realistic description may be provided by including sink terms in the diffusion equation. Under certain conditions, sink terms and BC give rise to equivalent descriptions, but sink terms allow to accommodate more general underlying models that cannot be implemented in terms of BC.

These considerations have prompted the search for alternative theoretical approaches^{17–19} that abandon a description in terms of BC imposed at an encounter distance altogether. Reference 19 discussed the so-called volume reactivity model that eliminates the particular role of the encounter radius $r = a$ and instead postulates that the reaction can happen throughout the spherical volume $r \leq a$. In this paper, we discuss the corresponding model in two dimensions (2D) and hence refer to it as the “area reactivity” model. In volume/area reactivity models, the central equations of motion are given by a generalized version of the Feynman-Kac equation (FKE) that incorporates reversible binding. The conventional FKE^{20–22} figures prominently in the theory of diffusion, because its solution provides the residence time of a particle within the reaction sphere.²³ The generalized FKE has previously been discussed in 3D.^{18,19} Here, we will study the corresponding 2D version.

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Diffusion in 2D is special from a conceptual, technical, and application point of view. Conceptually, the 2D case is special because it is the critical dimension regarding recurrence and transience of random walks.²⁴ Technically, the mathematical treatment appears to be more involved than in 1D and 3D.^{10,25–27} From an application point of view, the 2D case is of particular importance in cell biological applications, where it may help shed light on processes such as signal-induced inhomogeneities and receptor clustering on cell membranes.²⁸

Whereas the practical difference between volume and contact reactivity models may be negligible in terms of the binding probability in 3D,¹⁸ this may be different for the full GF and requires further clarification in the 2D case. GF of the 3D generalized FKE have been obtained in the Laplace domain before.¹⁹ Here, we provide exact expressions for the GF of the initially unbound and bound molecule as well for the binding and survival probability in both, the Laplace and time domain.

II. THEORY

A. Generalized Feynman-Kac equation in two dimensions

In this section, we will closely follow Ref. 19. A system of two molecules *A* and *B* with diffusion constants D_A and D_B , respectively, may also be described as the diffusion of a point-like molecule with diffusion constant $D = D_A + D_B$ around a static disk. More precisely, the area reactivity model assumes that the molecule undergoes free diffusion apart from inside the static “reaction disk” of radius $r = a$, where it may react reversibly. Without loss of generality, we assume that the disk’s center is located at the origin. A central notion is the probability density function (PDF) $p(r, t|r_0)$ that gives the probability of finding the molecule unbound at a distance equal to r at time t , given that the distance was initially r_0 at time $t = 0$. Note that in contrast to the contact reactivity model, $p(r, t|r_0)$ is also defined for $r < a$. Moreover, because the molecule may bind anywhere within the disk $r < a$, it makes sense to define another PDF $q(r, t|r_0)$, which yields the probability to find the molecule bound at a distance equal to $r < a$ at time t , given that the distance was initially r_0 at time $t = 0$. In contrast to contact reactivity models that describe one bound state, there are uncountably infinite bound states for $r < a$ in the area reactivity model. The rates for association and dissociation are $\kappa_r \Theta(a - r)p(r, t|r_0)$ and $\kappa_d q(r, t|r_0)$, respectively, where $\Theta(x)$ refers to the Heaviside step-function that vanishes for $x < 0$ and assumes unity otherwise. Furthermore, it is postulated that the dissociated molecule is released at the same point where it assumed its bound state. The equations of motion for the PDF $p(r, t|r_0)$ and $q(r, t|r_0)$ are coupled and read¹⁹

$$\frac{\partial p(r, t|r_0)}{\partial t} = \mathcal{L}_r p(r, t|r_0) - \kappa_r \Theta(a - r)p(r, t|r_0) + \kappa_d q(r, t|r_0), \quad (1)$$

$$\frac{\partial q(r, t|r_0)}{\partial t} = \kappa_r \Theta(a - r)p(r, t|r_0) - \kappa_d q(r, t|r_0), \quad (2)$$

where

$$\mathcal{L}_r = D \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} \right) \quad (3)$$

is the rotationally symmetric diffusion operator in 2D. The equations of motion have to be supplemented by BC at infinity and at the origin, respectively,

$$\lim_{r \rightarrow \infty} p(r, t|r_0) = 0, \quad (4)$$

$$\lim_{r \rightarrow 0} r \frac{\partial p(r, t|r_0)}{\partial r} = 0. \quad (5)$$

Applying the Laplace transform

$$\tilde{p}(r, s|r_0) = \int_0^\infty p(r, t|r_0) e^{-st} dt, \quad (6)$$

Eqs. (1) and (2) take the form

$$s \tilde{p}(r, s|r_0) - p(r, 0|r_0) = \mathcal{L}_r \tilde{p}(r, s|r_0) - \kappa_r \Theta(a - r) \tilde{p}(r, s|r_0) + \kappa_d \tilde{q}(r, s|r_0), \quad (7)$$

$$s \tilde{q}(r, s|r_0) - q(r, 0|r_0) = \kappa_r \Theta(a - r) \tilde{p}(r, s|r_0) - \kappa_d \tilde{q}(r, s|r_0). \quad (8)$$

Equation (8) gives the relation between the PDF $\tilde{q}(r, s|r_0)$ and $\tilde{p}(r, s|r_0)$ in the Laplace domain¹⁹

$$\tilde{q}(r, s|r_0) = \frac{1}{s + \kappa_d} [\kappa_r \Theta(a - r) \tilde{p}(r, s|r_0) + q(r, 0|r_0)], \quad (9)$$

which, upon applying the convolution theorem of the Laplace transform, immediately gives the following expression in the time domain:

$$q(r, t|r_0) = \kappa_r \Theta(a - r) \int_0^t e^{-\kappa_d(t-\tau)} p(r, \tau|r_0) d\tau + e^{-\kappa_d t} q(r, 0|r_0). \quad (10)$$

Clearly, relation (9) permits to eliminate $\tilde{q}(r, s|r_0)$ from Eq. (7), which then becomes an ordinary differential equation for $\tilde{p}(r, s|r_0)$ alone, as soon as we specify initial conditions for the GF $q(r, t|r_0)$ and $p(r, t|r_0)$.

Knowledge of the GF enables one to calculate further important quantities. For instance, the survival probability $S(t|r_0)$ that gives the probability to find the particle unbound at time t is defined by

$$S(t|r_0) = 2\pi \int_0^\infty p(r, t|r_0) r dr. \quad (11)$$

The binding probability $Q(t|r_0)$, providing the likelihood that the particle is bound at time t , can be calculated via

$$Q(t|r_0) = 2\pi \int_0^\infty q(r, t|r_0) r dr = 2\pi \int_0^a q(r, t|r_0) r dr, \quad (12)$$

where the last equality follows from $q(r, t|r_0) = 0$ for $r > a$. The equations of motion subject to the BC at the origin and at infinity guarantee that the total probability $S(t|r_0) + Q(t|r_0)$ is a constant of motion, as must be the case. In fact, adding Eqs. (1) and (2), integrating the resulting equation over the

whole space and taking into account the definitions (11) and (12) as well as the BC Eqs. (4) and (5) gives

$$\frac{\partial}{\partial t}[S(t|r_0) + Q(t|r_0)] = j(r=0, t|r_0) - \lim_{r \rightarrow \infty} j(r, t|r_0) = 0, \quad (13)$$

where $j(r, t|r_0)$ refers to the total diffusional flux

$$j(r, t|r_0) = -2\pi r D \frac{\partial}{\partial r} p(r, t|r_0). \quad (14)$$

Because necessarily $S(t=0) = 1$, $Q(t=0) = 0$, and $S(t=0) = 0$, $Q(t=0) = 1$ for the initially unbound and bound state, respectively, it follows that for all times,

$$S(t) + Q(t) = 1, \quad (15)$$

independent of the initial state. For the sake of convenience, we henceforth adopt the following notation. The PDF describing the unbound molecule within ($r < a$) and outside of ($r > a$) the reactive disk is referred to as $p^<(r, t|r_0)$ and $p^>(r, t|r_0)$, respectively. Furthermore, the initially bound state is denoted by $*$ and the PDF for the initially bound state is referred to as $p^<(r, t|r_0, *)$ and $p^>(r, t|r_0, *)$, and we define $p^<(r, t|r_0) = 0 = p^<(r, t|r_0, *)$ for $r > a$ and $p^>(r, t|r_0) = 0 = p^>(r, t|r_0, *)$ for $r < a$. Similarly, we make use of the notation $q(r, t|r_0)$, $q(r, t|r_0, *)$ as well as $S(t|r_0)$ and $S(t|r_0, *)$ and analogously for the binding probability. In the following, we will compute for all these quantities exact expressions in both, the Laplace and time domain.

B. Initial conditions and convolution relations

As discussed previously, one has to specify initial conditions to arrive at an ordinary differential equation for $\tilde{p}(r, s|r_0)$. The solution of this equation allows us to calculate all other quantities of interest, in particular the PDF $\tilde{q}(r, s|r_0)$, $q(r, t|r_0)$ via Eqs. (9) and (10), respectively, and the survival and binding probability according to Eqs. (11) and (12). However, the calculations can be greatly facilitated by first deriving a few convolution equations that relate some of the central quantities.

1. Initially unbound molecule

We first consider an initially unbound molecule at r_0 . In this case, the initial conditions are given by¹⁹

$$2\pi r_0 p(r, 0|r_0) = \delta(r - r_0), \quad (16)$$

$$q(r, 0|r_0) = 0. \quad (17)$$

Then, the relation between $\tilde{q}(r, s|r_0)$ and $\tilde{p}(r, s|r_0)$ (Eq. (9)) reads¹⁹

$$\tilde{q}(r, s|r_0) = \frac{\kappa_r \Theta(a-r)}{s + \kappa_d} \tilde{p}(r, s|r_0) = \frac{\kappa_r}{s + \kappa_d} \tilde{p}^<(r, s|r_0). \quad (18)$$

Integrating over the entire space and using Eqs. (11), (12), (15), and to¹⁹

$$\tilde{Q}(s|r_0) = \frac{2\pi \kappa_r}{s + \kappa_d} \int_0^a \tilde{p}^<(r, s|r_0) r dr, \quad (19)$$

$$s \tilde{S}(s|r_0) = 1 - \frac{2\pi \kappa_r s}{s + \kappa_d} \int_0^a \tilde{p}^<(r, s|r_0) r dr, \quad (20)$$

which tells us that both the binding and survival probability can be obtained from $\tilde{p}^<(r, s|r_0)$ alone and knowledge of $\tilde{p}^>(r, s|r_0)$ is not necessary for this purpose.

The relation between $\tilde{q}(r, s|r_0)$ and $\tilde{p}(r, s|r_0)$ (Eq. (18)) and the initial conditions (Eqs. (16) and (17)) can be used to decouple the equations of motion (Eqs. (7) and (8))¹⁹

$$\left[\mathcal{L}_r - s - \frac{s \kappa_r}{s + \kappa_d} \Theta(a-r) \right] \tilde{p}(r, s|r_0) = -\frac{\delta(r-r_0)}{2\pi r_0}. \quad (21)$$

Note that in terms of $\tilde{p}^<(r, s|r_0)$ and $\tilde{p}^>(r, s|r_0)$, Eq. (21) implies two separate differential equations,

$$\left[\mathcal{L}_r - s - \frac{s \kappa_r}{s + \kappa_d} \right] \tilde{p}^<(r, s|r_0) = 0, \quad (22)$$

$$[\mathcal{L}_r - s] \tilde{p}^>(r, s|r_0) = -\frac{\delta(r-r_0)}{2\pi r_0}, \quad (23)$$

for $r_0 > a$ and

$$\left[\mathcal{L}_r - s - \frac{s \kappa_r}{s + \kappa_d} \right] \tilde{p}^<(r, s|r_0) = -\frac{\delta(r-r_0)}{2\pi r_0}, \quad (24)$$

$$[\mathcal{L}_r - s] \tilde{p}^>(r, s|r_0) = 0, \quad (25)$$

for $r_0 < a$, respectively. We will exploit the differences between these equations, in particular, the shift of the δ -function term, to make a convenient ansatz for the GF in Sec. III. Finally, we would like to point out that under the transformation $r \leftrightarrow r_0$ the solutions of Eq. (22) should become solutions of Eq. (25), i.e., $\tilde{p}^<(r, s|r_0) = \tilde{p}^>(r_0, s|r)$ (where $r < a$, $r_0 > a$). We will later confirm this by explicit computation.

2. Initially bound molecule

The initial conditions that describe the initially bound molecule located at $r_0 \leq a$ are¹⁹

$$p(r, 0|r_0, *) = 0, \quad (26)$$

$$2\pi r_0 q(r, 0|r_0, *) = \delta(r - r_0). \quad (27)$$

As a consequence, the relation between $\tilde{q}(r, s|r_0, *)$ and $\tilde{p}(r, s|r_0, *)$ (Eq. (9)) now reads

$$\tilde{q}(r, s|r_0, *) = \frac{1}{s + \kappa_d} \left[\kappa_r \Theta(a-r) \tilde{p}(r, s|r_0, *) + \frac{\delta(r-r_0)}{2\pi r_0} \right], \quad (28)$$

and therefore one can again eliminate $\tilde{q}(r, s|r_0, *)$ from the equation of motion (Eq. (7))¹⁹

$$\left[\mathcal{L}_r - s - \frac{s \kappa_r}{s + \kappa_d} \Theta(a-r) \right] \tilde{p}(r, s|r_0, *) = -\frac{\kappa_d}{s + \kappa_d} \frac{\delta(r-r_0)}{2\pi r_0}. \quad (29)$$

A comparison with the equation of motion in the case of the initially unbound molecule (Eq. (21)) shows that¹⁹

$$\tilde{p}(r, s|r_0, *) = \frac{\kappa_d}{s + \kappa_d} \tilde{p}(r, s|r_0). \quad (30)$$

We can combine this equation with Eq. (18) to obtain

$$\kappa_r \tilde{p}(r, s|r_0, *) = \kappa_d \tilde{q}(r, s|r_0), \quad \text{for } r \leq a. \quad (31)$$

This equation is the detailed balance condition in the context of the area reactivity model. Note that this relation is a consequence of the equations of motion and has not to be introduced in the theory as an extra postulate.

In addition, we note that because of the relation between the PDF for the initially bound and unbound molecule (Eq. (30)) we have

$$\begin{aligned} \tilde{q}(r, s|r_0, *) &= \frac{\kappa_r \kappa_d}{(s + \kappa_d)^2} \Theta(a - r) \tilde{p}^<(r, s|r_0) \\ &+ \frac{1}{s + \kappa_d} \frac{\delta(r - r_0)}{2\pi r_0}. \end{aligned} \quad (32)$$

We can now again conclude that the knowledge of $\tilde{p}^<(r, s|r_0)$ alone is sufficient for the calculation of the binding and survival probability. Indeed, integrating over space and taking into account Eqs. (11), (12), (15), and yields

$$\tilde{Q}(s|r_0, *) = \frac{2\pi\kappa_r\kappa_d}{(s + \kappa_d)^2} \int_0^a \tilde{p}^<(r, s|r_0) r dr + \frac{1}{s + \kappa_d}, \quad (33)$$

$$s\tilde{S}(s|r_0, *) = 1 - \frac{2\pi\kappa_r\kappa_d s}{(s + \kappa_d)^2} \int_0^a \tilde{p}^<(r, s|r_0) r dr - \frac{s}{s + \kappa_d}. \quad (34)$$

III. EXACT GREEN'S FUNCTION IN THE LAPLACE DOMAIN

A. The initially unbound state with $r_0 > a$

To compute the GF we adopt the following strategy. We calculate the GF separately on the two different domains defined by $r > a$ and $r < a$, i.e., $p^>(r, t|r_0)$ and $p^<(r, t|r_0)$, respectively. The two obtained solutions will still contain unknown constants. The GF can then be completely determined by matching both expressions implementing continuity requirements at $r = a$.

Alternatively, we could proceed as in Ref. 19 and consider the three regions, $r < a$, $a < r < r_0$, and $r > r_0$. In this case, one would have to use extra conditions at $r = r_0$ to match the corresponding three solutions. However, this strategy implies in the present case extra computational burden. Therefore, we make instead the following ansatz for the Laplace transform of the PDF $p^>(r, t|r_0)$ outside the disk $r > a$,

$$\tilde{p}^>(r, s|r_0) = \tilde{p}_0(r, s|r_0) + \tilde{f}(r, s|r_0), \quad (35)$$

where

$$\tilde{p}_0(r, s|r_0) = \frac{1}{2\pi D} \begin{cases} I_0(vr_0)K_0(vr), & r > r_0, \\ I_0(vr)K_0(vr_0), & r < r_0, \end{cases} \quad (36)$$

is the Laplace transform of the free-space GF of the diffusion equation, cf. Chap. 14.8 and Eq. (2) in Ref. 9. $I_0(x)$, $K_0(x)$ denote the modified Bessel functions of first and second kind, respectively, and zero order (Sec. 9.6 in Ref. 29). The variable v is defined by

$$v \equiv \sqrt{\frac{s}{D}}. \quad (37)$$

The free-space GF takes into account the δ -function term in Eq. (23) and therefore, the function $\tilde{f}(r, s|r_0)$ in Eq. (35) satisfies the Laplace transformed 2D diffusion equation (Chap. 14.8 and Eq. (3) in Ref. 9)

$$\frac{d^2 \tilde{f}}{dr^2} + \frac{1}{r} \frac{d\tilde{f}}{dr} - v^2 \tilde{f} = 0. \quad (38)$$

The general solution to Eq. (38) is given by

$$\tilde{f}(r, s|r_0) = B(s, r_0)I_0(vr) + C(s, r_0)K_0(vr), \quad (39)$$

where $B(s, r_0)$, $C(s, r_0)$ are “constants” that may depend on s and r_0 . Because we require the BC Eq. (4) and $\lim_{x \rightarrow \infty} I_0(x) \rightarrow \infty$, the coefficient $B(s, r_0)$ has to vanish and the solution becomes

$$\tilde{f}(r, s|r_0) = C(s, r_0)K_0(vr). \quad (40)$$

Next, turning to the case $r < a$, the Laplace transformed PDF $\tilde{p}^<(r, s|r_0)$ satisfies Eq. (22), which may be rewritten as

$$\frac{d^2 \tilde{p}^<}{dr^2} + \frac{1}{r} \frac{d\tilde{p}^<}{dr} - w^2 \tilde{p}^< = 0, \quad (41)$$

where w is defined by

$$w \equiv v \sqrt{\frac{s + \kappa_r + \kappa_d}{s + \kappa_d}}. \quad (42)$$

Therefore, the general solution that takes into account the BC Eq. (5) is

$$\tilde{p}^<(r, s|r_0) = A(s, r_0)I_0(wr), \quad (43)$$

because $\lim_{x \rightarrow 0} xK_1(x) \neq 0$.

It remains to determine the two “constants” $A(s, r_0)$ and $C(s, r_0)$. To this end, we require that the PDF and its derivative have to be continuous at $r = a$,

$$\tilde{p}^<(r = a, s|r_0) = \tilde{p}^>(r = a, s|r_0), \quad (44)$$

$$\left. \frac{\partial \tilde{p}^<(r, s|r_0)}{\partial r} \right|_{r=a} = \left. \frac{\partial \tilde{p}^>(r, s|r_0)}{\partial r} \right|_{r=a}. \quad (45)$$

Using Eqs. (35), (36), (40), and (43) as well as

$$I'_0(x) = I_1(x), \quad (46)$$

$$K'_0(x) = -K_1(x), \quad (47)$$

$$I_0(x)K_1(x) + I_1(x)K_0(x) = x^{-1}, \quad (48)$$

(Eqs. (9.6.27) and (9.6.15) in Ref. 29), we arrive at

$$A(s, r_0) = \frac{K_0(vr_0)}{2\pi a D \mathcal{N}}, \quad (49)$$

$$C(s, r_0) = \frac{K_0(vr_0)}{2\pi a D K_0(va)} \left[\frac{I_0(wa)}{\mathcal{N}} - a I_0(va) \right], \quad (50)$$

where we introduced

$$\mathcal{N} = v I_0(wa) K_1(va) + w I_1(wa) K_0(va). \quad (51)$$

From the obtained expression for $\tilde{p}^<(r, s|r_0)$, we immediately arrive at exact expressions for $\tilde{q}(r, s|r_0)$ and $\tilde{Q}(s|r_0)$, $\tilde{S}(s|r_0)$ via Eqs. (18)–(20).

B. The initially unbound state with $r_0 < a$

In the case $r_0 < a$, we seek solutions to Eqs. (24) and (25). Using the same line of reasoning as above, it is now natural to make the ansatz

$$\tilde{p}^<(r, s|r_0) = \tilde{p}_0(r, w|r_0) + \tilde{f}(r, s|r_0), \quad (52)$$

where $\tilde{p}_0(r, w|r_0)$ is given by Eq. (36) with v replaced by w . By virtue of the chosen ansatz (Eq. (52)), $\tilde{f}(r, s|r_0)$ is now a solution of Eq. (41). Employing again the BC Eq. (5), we therefore obtain

$$\tilde{f}(r, s|r_0) = B(s, r_0)I_0(wr). \quad (53)$$

The Laplace transformed $\tilde{p}^>(r, s|r_0)$ now satisfies Eq. (38) subject to the BC Eq. (4) and thus we find

$$\tilde{p}^>(r, s|r_0) = G(s, r_0)K_0(vr). \quad (54)$$

We again determine the coefficients $B(s, r_0)$, $G(s, r_0)$ via the matching conditions and arrive at

$$B(s, r_0) = \frac{1}{2\pi D} \frac{I_0(wr_0)}{\mathcal{N}} [wK_1(wa)K_0(va) - vK_0(wa)K_1(va)], \quad (55)$$

$$G(s, r_0) = \frac{1}{2\pi Da} \frac{I_0(wr_0)}{\mathcal{N}}. \quad (56)$$

Equations (43), (49), (54), and (56) verify that indeed $\tilde{p}^>(r, s|r_0) = \tilde{p}^<(r_0, s|r)$ for $r > a$, $r_0 < a$, as discussed before.

C. The initially bound state

We have already seen that $\tilde{p}(r, s|r_0, *)$ and $\tilde{p}(r, s|r_0)$ are related by Eq. (30) and in this way we immediately obtain from Eqs. (52)–(56) the exact expression for $\tilde{p}(r, s|r_0, *)$. Similarly, we arrive at the corresponding expressions for $\tilde{q}(r, s|r_0, *)$, $\tilde{Q}(s|r_0, *)$, and $\tilde{S}(s|r_0, *)$ by making use of Eqs. (32)–(34), respectively.

IV. EXACT GREEN'S FUNCTION IN THE TIME DOMAIN

In the following, we will derive analytical expressions for the GF in the time domain. Alternatively, one could use the obtained GF solution in the Laplace domain (Eqs. (35), (43), (52), and (54)) as a starting point for a numerical inversion. However, the numerical computation of the inverse Laplace transform is not entirely straightforward and, depending on the task at hand, researchers typically have to employ several different methods concurrently to achieve reliable results.³⁰ In this situation, exact analytical results provide a valuable and robust way to verify the correctness of a chosen numerical inversion algorithm. We believe that this advantage outweighs the difficulties associated with the evidently somewhat complicated expressions of the analytical results.

FIG. 1. Integration contour used for calculating the GF in the time domain, Eq. (58). $C_{c-i\infty}^{c+i\infty}$ refers to the Bromwich contour from $c - i\infty$ to $c + i\infty$.

A. Initially unbound state with $r_0 > a$

We first consider the case of the initially unbound molecule with $r_0 > a$. To find the corresponding expressions for $p^<(r, t|r_0)$, $p^>(r, t|r_0)$ in the time domain, we apply the inversion theorem for the Laplace transformation

$$p^<(r, t|r_0) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} e^{st} \tilde{p}^<(r, s|r_0) ds, \quad (57)$$

where, as usual, c has to be taken to the right of any singularities, cf. Chap. 12.3 and p. 302 in Ref. 9. We note that the $\tilde{p}^<(r, s|r_0)$ has three branch points at $s = 0$, $s = -\kappa_d$ and $s = -\kappa_r - \kappa_d$. Therefore, to calculate the Bromwich integral, we use the contour of Fig. 1 with a branch cut along the negative real axis, cf. Chap. 12.3 and Fig. 40 in Ref. 9. It follows that

$$\begin{aligned} \int_{c-i\infty}^{c+i\infty} e^{st} \tilde{p}^<(r, s|r_0) ds &= - \int_{C_2} e^{st} \tilde{p}^<(r, s|r_0) ds \\ &\quad - \int_{C_4} e^{st} \tilde{p}^<(r, s|r_0) ds. \end{aligned} \quad (58)$$

Note that, more precisely, the contour $\mathcal{C}_2$ (and similarly $\mathcal{C}_4$) consists of the contours

$$\mathcal{C}_{-\infty}^{-\epsilon-\kappa_r-\kappa_d}, \mathcal{C}_{-\kappa_r-\kappa_d, \epsilon}^{-\epsilon-\kappa_d}, \mathcal{C}_{\epsilon-\kappa_r-\kappa_d}^{-\epsilon-\kappa_d}, \mathcal{C}_{-\kappa_d, \epsilon}^{-\epsilon}, \mathcal{C}_{\epsilon-\kappa_d}^{-\epsilon}, \mathcal{C}_{0, \epsilon},$$

where $\epsilon \rightarrow 0$ and $\mathcal{C}_{z_1}^{z_2}$ denotes the contour with endpoints from z_1 to z_2 and $\mathcal{C}_{z, \epsilon}$ refers to the contour $s = z + \epsilon e^{i\vartheta}$, $\pi \geq \vartheta \geq 0$.

To calculate the integral $\int_{\mathcal{C}_2}$, we choose $s = Dx^2 e^{i\pi}$. Then,

$$v = ix, \quad \text{for } s \in (-\infty, 0), \quad (59)$$

$$w = ix \sqrt{\frac{Dx^2 - \kappa_r - \kappa_d}{Dx^2 - \kappa_d}} \equiv ix\xi_1 \quad \text{for } s \in (-\infty, -\kappa_r - \kappa_d), \quad (60)$$

$$w = x \sqrt{\frac{\kappa_r + \kappa_d - Dx^2}{Dx^2 - \kappa_d}} \equiv x\xi_2 \quad \text{for } s \in (-\kappa_r - \kappa_d, -\kappa_d), \quad (61)$$

$$w = ix \sqrt{\frac{\kappa_r + \kappa_d - Dx^2}{\kappa_d - Dx^2}} \equiv ix\xi_1 \quad \text{for } s \in (-\kappa_d, 0), \quad (62)$$

where (z_1, z_2) denotes the open interval. We now make use of Appendix 3, Eqs. (25) and (26) in Ref. 9,

$$I_n(xe^{\pm\pi i/2}) = e^{\pm n\pi i/2} J_n(x), \quad (63)$$

$$K_n(xe^{\pm\pi i/2}) = \pm \frac{1}{2} \pi i e^{\mp n\pi i/2} [-J_n(x) \pm iY_n(x)]. \quad (64)$$

Here, $J_n(x)$, $Y_n(x)$ refer to the Bessel functions of first and second kind, respectively (Sec. 9.1 in Ref. 29). We obtain

$$\begin{aligned} & \int_{\mathcal{C}_2} e^{st} \tilde{p}^<(r, s|r_0) ds \\ &= \frac{1}{\pi a} \left[\int_{\sqrt{\kappa}}^{\sqrt{\varphi}} e^{-Dx^2 t} I_0(x\xi_2 r) \frac{\eta(x, xr_0) + i\lambda(x, xr_0)}{\alpha^2(x) + \beta^2(x)} dx \right. \\ & \quad \left. - \int_{0, \sqrt{\varphi}}^{\sqrt{\kappa}, \infty} e^{-Dx^2 t} J_0(x\xi_1 r) \frac{\omega(x, xr_0) + i\kappa(x, xr_0)}{\gamma^2(x) + \delta^2(x)} dx \right], \end{aligned} \quad (65)$$

where we introduced

$$\eta(x, z) = \alpha(x)Y_0(z) + \beta(x)J_0(z), \quad (66)$$

$$\lambda(x, z) = \alpha(x)J_0(z) - \beta(x)Y_0(z), \quad (67)$$

$$\alpha(x) = \xi_2 I_1(\xi_2 xa) Y_0(xa) + I_0(\xi_2 xa) Y_1(xa), \quad (68)$$

$$\beta(x) = \xi_2 I_1(\xi_2 xa) J_0(xa) + I_0(\xi_2 xa) J_1(xa), \quad (69)$$

$$\omega(x, z) = \gamma(x)Y_0(z) + \delta(x)J_0(z), \quad (70)$$

$$\kappa(x, z) = \gamma(x)J_0(z) - \delta(x)Y_0(z), \quad (71)$$

$$\gamma(x) = \xi_1 J_1(\xi_1 xa) Y_0(xa) - J_0(\xi_1 xa) Y_1(xa), \quad (72)$$

$$\delta(x) = \xi_1 J_1(\xi_1 xa) J_0(xa) - J_0(\xi_1 xa) J_1(xa). \quad (73)$$

Furthermore, we defined

$$\varphi \equiv \frac{\kappa_r + \kappa_d}{D}, \quad (74)$$

$$\kappa \equiv \frac{\kappa_d}{D}, \quad (75)$$

and, for the sake of convenience, we introduced the notation

$$\int_{0, \sqrt{\varphi}}^{\sqrt{\kappa}, \infty} \dots \equiv \int_0^{\sqrt{\kappa}} \dots + \int_{\sqrt{\varphi}}^{\infty} \dots \quad (76)$$

Now, to calculate the integral along the contour $\mathcal{C}_4$, we choose $s = Dx^2 e^{-i\pi}$ and after an analogous calculation one finds that

$$\int_{\mathcal{C}_2} e^{st} \tilde{p}^<(r, s|r_0) ds = - \left(\int_{\mathcal{C}_4} e^{st} \tilde{p}^<(r, s|r_0) ds \right)^*, \quad (77)$$

where $*$ denotes complex conjugation. Thus, one obtains for the PDF $p^<(r, t|r_0)$ on the domain $r < a$,

$$\begin{aligned} p^<(r, t|r_0) &= -\frac{1}{\pi} \Im \left(\int_{\mathcal{C}_2} e^{st} \tilde{p}^<(r, s|r_0) ds \right) \\ &= -\frac{1}{\pi^2 a} \left[\int_{\sqrt{\kappa}}^{\sqrt{\varphi}} e^{-Dx^2 t} T^{(2)}(x, r) U^{(2)}(x, r_0) dx \right. \\ & \quad \left. - \int_{0, \sqrt{\varphi}}^{\sqrt{\kappa}, \infty} e^{-Dx^2 t} T^{(1)}(x, r) U^{(1)}(x, r_0) dx \right]. \end{aligned} \quad (78)$$

Here, we introduced

$$T^{(1)}(x, r) = \frac{J_0(x\xi_1 r)}{\sqrt{\gamma^2(x) + \delta^2(x)}}, \quad T^{(2)}(x, r) = \frac{I_0(x\xi_2 r)}{\sqrt{\alpha^2(x) + \beta^2(x)}}, \quad (79)$$

$$U^{(1)}(x, r) = \frac{\kappa(x, xr)}{\sqrt{\gamma^2(x) + \delta^2(x)}}, \quad U^{(2)}(x, r) = \frac{\lambda(x, xr)}{\sqrt{\alpha^2(x) + \beta^2(x)}}. \quad (80)$$

Analogously, we can proceed to compute the PDF $p^>(r, t|r_0)$ for the region $r > a$. Therefore, we only give the result

$$\begin{aligned} p^>(r, t|r_0) &= \frac{1}{4\pi Dt} e^{-(r^2+r_0^2)/4Dt} I_0\left(\frac{rr_0}{2Dt}\right) \\ & \quad - \frac{1}{2\pi} \int_0^{\infty} e^{-Dx^2 t} h^{(3)}(r, r_0, x) x dx \\ & \quad + \frac{1}{\pi^2 a} \left[\int_{0, \sqrt{\varphi}}^{\sqrt{\kappa}, \infty} e^{-Dx^2 t} h^{(1)}(r, r_0, x) dx \right. \\ & \quad \left. - \int_{\sqrt{\kappa}}^{\sqrt{\varphi}} e^{-Dx^2 t} h^{(2)}(r, r_0, x) dx \right], \end{aligned} \quad (81)$$

where we defined

$$\begin{aligned} & h^{(1)}(r, r_0, x) \\ &= J_0(x\xi_1 a) \frac{\rho(x, xr)\omega(x, xr_0) + \psi(x, xr)\kappa(x, xr_0)}{[\gamma^2(x) + \delta^2(x)][J_0^2(xa) + Y_0^2(xa)]}, \end{aligned} \quad (82)$$

$$h^{(2)}(r, r_0, x) = I_0(x\xi_2 a) \frac{\rho(x, xr)\eta(x, xr_0) + \psi(x, xr)\lambda(x, xr_0)}{[\alpha^2(x) + \beta^2(x)][J_0^2(xa) + Y_0^2(xa)]}, \quad (83)$$

$$h^{(3)}(r, r_0, x) = J_0(xa) \frac{\chi(xr, xr_0)Y_0(xa) + \sigma(xr, xr_0)J_0(xa)}{J_0^2(xa) + Y_0^2(xa)}, \quad (84)$$

and

$$\rho(x, z) = J_0(z)Y_0(xa) - Y_0(z)J_0(xa), \quad (85)$$

$$\psi(x, z) = J_0(z)J_0(xa) + Y_0(z)Y_0(xa), \quad (86)$$

$$\sigma(z, z_0) = J_0(z)J_0(z_0) - Y_0(z)Y_0(z_0), \quad (87)$$

$$\chi(z, z_0) = Y_0(z)J_0(z_0) + J_0(z)Y_0(z_0). \quad (88)$$

Note that the first term appearing on the rhs of Eq. (81) is the inverse Laplace transform of Eq. (36), cf. Chap. 14.8 and Eq. (2) in Ref. 9. Furthermore, using the fact that the first term may also be written as

$$\begin{aligned} & \frac{1}{4\pi Dt} e^{-(r^2+r_0^2)/4Dt} I_0\left(\frac{rr_0}{2Dt}\right) \\ &= \frac{1}{2\pi} \int_0^\infty e^{-Dx^2 t} J_0(xr)J_0(xr_0)xdx, \end{aligned} \quad (89)$$

it turns out that the two first terms on the rhs of Eq. (81) give the GF subject to an absorbing (“Smoluchowski”) BC,

$$\begin{aligned} p_{\text{abs}}(r, t|r_0) &= \frac{1}{4\pi Dt} e^{-(r^2+r_0^2)/4Dt} I_0\left(\frac{rr_0}{2Dt}\right) \\ &\quad - \frac{1}{2\pi} \int_0^\infty e^{-Dx^2 t} h^{(3)}(r, r_0, x)xdx \\ &= \frac{1}{2\pi} \int_0^\infty e^{-Dx^2 t} C_{\text{abs}}(x, r)C_{\text{abs}}(x, r_0)xdx, \end{aligned} \quad (90)$$

where

$$C_{\text{abs}}(x, r) = \frac{J_0(rx)Y_0(ax) - Y_0(rx)J_0(ax)}{\sqrt{J_0^2(ax) + Y_0^2(ax)}}. \quad (91)$$

Now, we can compute an exact expression for $q(r, t|r_0)$ by virtue of Eq. (10). We find

$$\begin{aligned} q(r, t|r_0) &= -\frac{\kappa_r \Theta(a-r)}{\pi^2 a} \left[\int_{\sqrt{\kappa}}^{\sqrt{\varphi}} e^{-Dx^2 t} \frac{T^{(2)}(x, r)U^{(2)}(x, r_0)}{\kappa_d - Dx^2} dx \right. \\ &\quad \left. - \int_{0, \sqrt{\varphi}}^{\sqrt{\kappa}, \infty} e^{-Dx^2 t} \frac{T^{(1)}(x, r)U^{(1)}(x, r_0)}{\kappa_d - Dx^2} dx \right]. \end{aligned} \quad (92)$$

Finally, using Eq. (19), we can compute the survival and binding probability. For this purpose, we introduce the functions

$$P^{(1)}(x, r) = \frac{J_1(x\xi_1 r)}{\sqrt{\gamma^2(x) + \delta^2(x)}}, \quad (93)$$

$$P^{(2)}(x, r) = \frac{I_1(x\xi_2 r)}{\sqrt{\alpha^2(x) + \beta^2(x)}}. \quad (94)$$

Then, we obtain

$$\begin{aligned} S(t|r_0) - 1 &= -Q(t|r_0) \\ &= \frac{2\kappa_r}{\pi} \left[\int_{\sqrt{\kappa}}^{\sqrt{\varphi}} e^{-Dx^2 t} \frac{P^{(2)}(x, a)U^{(2)}(x, r_0)}{\kappa_d - Dx^2} \frac{dx}{x\xi_2} \right. \\ &\quad \left. - \int_{0, \sqrt{\varphi}}^{\sqrt{\kappa}, \infty} e^{-Dx^2 t} \frac{P^{(1)}(x, a)U^{(1)}(x, r_0)}{\kappa_d - Dx^2} \frac{dx}{x\xi_1} \right]. \end{aligned} \quad (95)$$

To perform the integral, we employed $d/dx[x^\nu J_\nu(x)] = x^\nu J_{\nu-1}$ and $d/dx[x^\nu I_\nu(x)] = x^\nu I_{\nu-1}$ cf. Eqs. (9.1.30) and (9.6.28) in Ref. 29.

B. Initially unbound state with $r_0 < a$

Turning to the case $r_0 < a$, we note that the expressions for the Laplace transformed PDF $\tilde{p}(r, s|r_0)$ Eqs. (52)–(56) possess the same analytical structure as the corresponding expressions for $r_0 > a$ and hence we can proceed in the same way as presented in more detail in Sec. IV A, in particular, we again employ the integration contour depicted in Fig. 1. Hence, we give here only the results. The PDF $p^<(r, t|r_0)$ takes the form

$$\begin{aligned} p^<(r, t|r_0) &= \frac{2}{\pi^3 a^2} \left[\int_{0, \sqrt{\varphi}}^{\sqrt{\kappa}, \infty} e^{-Dx^2 t} T^{(1)}(x, r)T^{(1)}(x, r_0) \frac{dx}{x} \right. \\ &\quad \left. + \int_{\sqrt{\kappa}}^{\sqrt{\varphi}} e^{-Dx^2 t} T^{(2)}(x, r)T^{(2)}(x, r_0) \frac{dx}{x} \right]. \end{aligned} \quad (96)$$

As previously discussed, we should have $\tilde{p}^>(r, s|r_0) = \tilde{p}^<(r_0, s|r)$ for $r > a, r_0 < a$ and this was explicitly verified by the corresponding expressions in the Laplace domain (Eqs. (43), (49), (54), and (56)). Therefore, we easily obtain $p^>(r, t|r_0)$ from Eq. (78),

$$\begin{aligned} p^>(r, t|r_0) &= \frac{1}{\pi^2 a} \left[\int_{0, \sqrt{\varphi}}^{\sqrt{\kappa}, \infty} e^{-Dx^2 t} U^{(1)}(x, r)T^{(1)}(x, r_0)dx \right. \\ &\quad \left. - \int_{\sqrt{\kappa}}^{\sqrt{\varphi}} e^{-Dx^2 t} U^{(2)}(x, r)T^{(2)}(x, r_0)dx \right]. \end{aligned} \quad (97)$$

We employ again the relation between $p^<(r, t|r_0)$ and $q(r, t|r_0)$ (Eq. (18)) to find

$$\begin{aligned} q(r, t|r_0) &= \frac{2\kappa_r \Theta(a-r)}{\pi^3 a^2} \left[\int_{0, \sqrt{\varphi}}^{\sqrt{\kappa}, \infty} e^{-Dx^2 t} \frac{T^{(1)}(x, r)T^{(1)}(x, r_0)}{\kappa_d - Dx^2} \frac{dx}{x} \right. \\ &\quad \left. + \int_{\sqrt{\kappa}}^{\sqrt{\varphi}} e^{-Dx^2 t} \frac{T^{(2)}(x, r)T^{(2)}(x, r_0)}{\kappa_d - Dx^2} \frac{dx}{x} \right]. \end{aligned} \quad (98)$$

We compared the obtained analytical expression for the GF describing the initially unbound state, located at three different initial positions $r_0 = 1.5a, a, 0.5a$ (Eqs. (78), (81), and (92), (96)–(98)), respectively, to numerical solutions that were obtained using the SSDP software, version 2.66.³¹ The results

FIG. 2. The GF for an initially unbound molecule located at $r_0 = 1.5a$. The other parameters are: $a = 1$, $D = 1$, $\kappa_r = 2$, $\kappa_d = 0.5$. The figure shows the r dependence of the GF at times $t_1 = 0.05$, $t_2 = 0.2$, $t_3 = 0.4$. The solid lines are obtained from the analytical expression for $p(r, t|r_0)$ (Eqs. (78) and (81)). The dashed lines refer to the PDF $q(r, t|r_0)$ that describes the bound state (Eq. (92)). The various markers indicate the corresponding numerical solutions that were generated using the SSDP software, ver. 2.66.³¹

are shown in Figs. 2–4. We find excellent agreement. The GF qualitatively resembles the GF solutions obtained earlier for the 3D case,¹⁹ hence, basically the same remarks made in Ref. 19 apply to the case considered here. Notably, while the $p(r, t|r_0)$ -part of the GF is given by a smooth density that spreads and decreases in amplitude over time, the $q(r, t|r_0)$ -part describing the bound state features a cusp that is either located on the boundary of the reaction area or at the initial position r_0 , depending on if the initial position is located

FIG. 3. The GF for an initially unbound molecule located at the boundary of the reaction area $r_0 = a$. The other parameters are the same as in Fig. 2.

FIG. 4. The GF for an initially unbound molecule located inside the reaction area at $r_0 = 0.5a$. The figure shows the r dependence of the GF at times $t_1 = 0.025$, $t_2 = 0.035$, $t_3 = 0.075$. The other parameters are $a = 1$, $D = 1$, $\kappa_r = 2$, $\kappa_d = 0.5$. The solid lines are obtained from the analytical expression for $p(r, t|r_0)$ (Eqs. (96) and (97)). The dashed lines refer to the PDF $q(r, t|r_0)$ that describes the bound state (Eq. (98)). The various markers refer to the numerical solutions obtained by using the SSDP software.³¹

outside $r_0 \geq a$ or inside $r_0 < a$ of the reaction area, respectively. The observed derivative discontinuity can be traced back to the fact that the initial δ -function density of the unbound state induces via recombination a δ -function density of the bound state that cannot be altered by diffusion, but only by dissociation.¹⁹

FIG. 5. The survival probability for an initially unbound molecule. The parameters are: $a = 1$, $D = 1$, $\kappa_r = 3$, $\kappa_d = 0.5$. The figure shows the time dependence of the survival probability $S(t|r_0)$ for different values of the initial position $r_0 = 1.5a$, a , $0.5a$, obtained from the analytical expressions Eqs. (95) and (99). The markers indicate the SSDP³¹ results.

FIG. 6. The GF for an initially bound molecule located at $r_0 = 0.5a$. The other parameters are $a = 1$, $D = 1$, $\kappa_d = 0.5$, $\kappa_r = 2.5$. The left panel shows the r dependence of the PDF for the unbound state $p(r, t|r_0, *)$ at various times $t_i = 1 \dots 8 \in [0.05, 0.1, 0.5, 1, 2, 4.5, 6.5, 11.5]$, corresponding to Eqs. (100) and (101). The right panel shows the r dependence of the PDF for the bound state $q(r, t|r_0, *) - e^{-\kappa_d t} \delta(r - r_0) / (2\pi r_0)$ at the same times (Eq. (102)). The markers refer to the corresponding SSDP³¹ results.

The corresponding survival probability takes the form

$$S(t|r_0) - 1 = \frac{4\kappa_r}{\pi^2 a} \left[\int_{0, \sqrt{\varphi}}^{\sqrt{\kappa}, \infty} e^{-Dx^2 t} \frac{P^{(1)}(x, a) T^{(1)}(x, r_0)}{[Dx^2 - \kappa_d] \xi_1} \frac{dx}{x^2} + \int_{\sqrt{\kappa}}^{\sqrt{\varphi}} e^{-Dx^2 t} \frac{P^{(2)}(x, a) T^{(2)}(x, r_0)}{[Dx^2 - \kappa_d] \xi_2} \frac{dx}{x^2} \right]. \quad (99)$$

A comparison between the analytical and numerical solution is shown in Fig. 5.

C. Initially bound state

As we discussed before, the PDF $p(r, t|r_0, *)$ for the initially bound state can be derived from the PDF $p(r, t|r_0)$ for the initially unbound state by virtue of the relation (30). Because of Eq. (31) and the already known expression for $q(r, t|r_0)$ (Eq. (98)), we can immediately write

$$p^<(r, t|r_0, *) = \frac{2\kappa_d}{\pi^3 a^2} \left[\int_{0, \sqrt{\varphi}}^{\sqrt{\kappa}, \infty} e^{-Dx^2 t} \frac{T^{(1)}(x, r) T^{(1)}(x, r_0)}{\kappa_d - Dx^2} \frac{dx}{x} + \int_{\sqrt{\kappa}}^{\sqrt{\varphi}} e^{-Dx^2 t} \frac{T^{(2)}(x, r) T^{(2)}(x, r_0)}{\kappa_d - Dx^2} \frac{dx}{x} \right]. \quad (100)$$

The expression for $p^>(r, t|r_0, *)$ follows from Eqs. (30) and (97):

$$p^>(r, t|r_0, *) = \frac{\kappa_d}{\pi^2 a} \left[\int_{0, \sqrt{\varphi}}^{\sqrt{\kappa}, \infty} e^{-Dx^2 t} \frac{U^{(1)}(x, r) T^{(1)}(x, r_0)}{\kappa_d - Dx^2} dx - \int_{\sqrt{\kappa}}^{\sqrt{\varphi}} e^{-Dx^2 t} \frac{U^{(2)}(x, r) T^{(2)}(x, r_0)}{\kappa_d - Dx^2} dx \right]. \quad (101)$$

Next, we can compute $q(r, t|r_0, *)$ from the convolution relation (28) and the just obtained expression for $p^<(r, t|r_0, *)$

$$\begin{aligned} q(r, t|r_0, *) &= \frac{2\kappa_r \kappa_d \Theta(a - r)}{\pi^3 a^2} \left[\int_{0, \sqrt{\varphi}}^{\sqrt{\kappa}, \infty} [e^{-Dx^2 t} - e^{-\kappa_d t}] \times \frac{T^{(1)}(x, r) T^{(1)}(x, r_0)}{[\kappa_d - Dx^2]^2} \frac{dx}{x} + \int_{\sqrt{\kappa}}^{\sqrt{\varphi}} [e^{-Dx^2 t} - e^{-\kappa_d t}] \frac{T^{(2)}(x, r) T^{(2)}(x, r_0)}{[\kappa_d - Dx^2]^2} \frac{dx}{x} \right] + e^{-\kappa_d t} \frac{\delta(r - r_0)}{2\pi r}. \end{aligned} \quad (102)$$

FIG. 7. The survival probability for an initially bound molecule. The parameters are: $a = 1$, $D = 1$, $\kappa_d = 0.5$, $r_0 = 0.5a$. The figure shows the time dependence of the survival probability $S(t|r_0, *)$ for different values of association rate κ_r corresponding to the analytical expression Eq. (103). The markers indicate the SSDP³¹ results.

FIG. 8. The time dependence of the survival probability $S(t|r_0)$ according to the area (solid lines, (Eq. (95))) and contact reactivity model¹⁰ (dashed lines). The parameters are $r_0 = a = 1$. Furthermore, the other parameters are for the top left panel: $\kappa_r = \kappa_d = 10$, $D = 0.25$, top right panel: $\kappa_r = \kappa_d = 1$, $D = 0.25$, bottom left panel: $\kappa_r = \kappa_d = 10$, $D = 2.5$, bottom right panel: $\kappa_r = \kappa_d = 1$, $D = 2.5$.

Using the SSDP software,³¹ we numerically confirmed the analytical expressions of the GF solutions for the initially bound state, located at $r_0 = 0.5a$ (Eqs. (100)–(102)). The results are presented in Fig. 6, which shows the time evolution of the $p(r, t|r_0, *)$ -part (left panel) and of the $q(r, t|r_0, *)$ -part (right panel) of the GF as a sequence of density profiles at different times. Again, we find excellent agreement between analytical and numerical results and again, qualitatively, the GF exhibits a behavior that is quite similar to the dynamics of its 3D counterpart.¹⁹ The initial δ -function density of the bound state leads via dissociation to a non-vanishing density of the unbound molecule, whose form resembles a δ -function at early times (t_1). Diffusion and ongoing dissociation cause the density to spread and its amplitude to increase, respectively (t_2 , t_3). Finally, at later times, the amplitude starts decreasing (t_4), due to an increasing fraction of the unbound state that escapes to infinity. Due to recombination, the $p(r, t|r_0, *)$ density gives rise to a non- δ -function part of $q(r, t|r_0, *)$, and its time evolution mirrors that of $p(r, t|r_0, *)$ with a delay, as can be seen from the ongoing increase of the amplitude of $q(r, t|r_0, *)$ at times t_5 and t_6 , while at the same times the amplitude of $p(r, t|r_0, *)$ is decreasing.¹⁹ Furthermore, in contrast to the

case of the initially unbound state, both solutions, $p(r, t|r_0, *)$ and $q(r, t|r_0, *)$, have a derivative discontinuity at the initial position r_0 .¹⁹

Finally, we can now calculate the associated binding probability according to Eq. (33),

$$Q(t|r_0, *) = \frac{4\kappa_r\kappa_d}{\pi^2 a} \left[\int_{0, \sqrt{\varphi}}^{\sqrt{\kappa}, \infty} e^{-Dx^2 t} \frac{P^{(1)}(x, a)T^{(1)}(x, r_0)}{[\kappa_d - Dx^2]^2} \frac{dx}{\xi_1 x^2} + \int_{\sqrt{\kappa}}^{\sqrt{\varphi}} e^{-Dx^2 t} \frac{P^{(2)}(x, a)T^{(2)}(x, r_0)}{[\kappa_d - Dx^2]^2} \frac{dx}{\xi_2 x^2} \right]. \quad (103)$$

Fig. 7 shows the corresponding survival probability, again the numerical solutions confirm our obtained analytical results.

V. DISCUSSION

In this paper, we derived exact analytical expressions (in the Laplace and time domain) for the GF of the generalized FKE in two space dimensions. The GF solution describes the reversible diffusion influenced reaction of an isolated pair in

the context of the area reactivity model that, in contrast to the contact reactivity model, avoids a particular role for the encounter radius. Instead, reactions can occur throughout the area of a reactive disk. Furthermore, we calculated exact analytical expressions for the survival (and binding) probabilities. In addition, we confirmed the obtained expressions in the time domain by constructing numerical solutions via the SSDP software.³¹

An interesting question is obviously whether, or to what extent, the conceptual differences between the two models result in different predictions. To explore this, we consider the initially unbound state located at $r_0 = a$. We are interested in the time evolution of its survival probability according to the area reactivity model (Eq. (95)) and the contact reactivity model.¹⁰ We set $\kappa_a = \pi a^2 \kappa_r$, where κ_a refers to the intrinsic association constant that appears in the formulation of the contact reactivity model.¹⁰ We keep $K_{eq} = \kappa_a / \kappa_d = \pi a^2$ constant, while we vary the recombination κ_a (hence κ_r) and dissociation rate κ_d , as well as the diffusion constant D . The results are shown in Fig. 8. Evidently, the extent of the difference between the models strongly depends on the chosen parameters. While the case of slow diffusion and fast recombination/dissociation rates (top left panel) gives the strongest deviations, the combination of fast diffusion and slow recombination/dissociation rates (right bottom panel) leads to a small difference only. These results are hardly surprising: Slow diffusion and fast recombination/dissociation mean that the particle, before escaping to infinity, interacts with the reaction area/encounter radius many times, hence, the differences between the two models should become most visible in this case. In conclusion, while far from comprehensive, these considerations point to the possibility that the area reactivity model may give a significantly different description of biological/chemical reality than contact reactivity models. Much more work, including taking into account many-particle systems and simulation studies, has to be done to elucidate this more thoroughly.

ACKNOWLEDGMENTS

This research was supported by the Intramural Research Program of the National Institutes of Health (NIH), National Institute of Allergy and Infectious Diseases (NIAID).

APPENDIX: TIME-DEPENDENT RATE COEFFICIENT

In contact reactivity theories, the time-dependent rate coefficient is defined as the reactive flux at the encounter distance⁸

$$k(t) = 2\pi a D \frac{\partial}{\partial r} p(r, t|eq)|_{r=a}, \quad (\text{A1})$$

where $p(r, t|eq)$ denotes the radial distribution function of the reactants at time t , provided that the initial distribution takes the (equilibrium) form $p(r, 0|eq) = 1$ for $r > a$ and $p(r, 0|eq) = 0$ for $r < a$. However, the definition (A1) does not appear to be appropriate for theories, where the special role of the encounter radius is eliminated. To address this

issue, we employ an alternative expression for $k(t)$,⁸

$$k(t) = 2\pi \int_a^\infty R(t|r_0) r_0 dr_0, \quad (\text{A2})$$

where $R(t|r_0)$ refers to the reaction rate given by⁸

$$R(t|r_0) = -\frac{\partial}{\partial t} S(t|r_0). \quad (\text{A3})$$

The relations provided by Eqs. (A2) and (A3) are more general than the definition (A1), in particular we can use them to find the time-dependent rate coefficient in the context of the area reactivity model. Integrating the FKE Eq. (1) over the entire space, we obtain

$$R(t|r_0) = 2\pi \kappa_r \int_0^a p^<(r, t|r_0) r dr - \kappa_d [1 - S(t|r_0)], \quad (\text{A4})$$

in analogy to the corresponding expression in the context of the contact reactivity model⁸

$$R(t|r_0) = \kappa_a p(r = a, t|r_0) - \kappa_d [1 - S(t|r_0)]. \quad (\text{A5})$$

Next, using Eqs. (A2)–(A4) and switching to the Laplace domain we arrive at

$$\tilde{k}(s) = (2\pi)^2 \frac{\kappa_r s}{s + \kappa_d} \int_a^\infty \int_0^a \tilde{p}^<(r, s|r_0) r dr r_0 dr_0, \quad (\text{A6})$$

$$= \frac{2\pi a}{D} \frac{\kappa_r s}{s + \kappa_d} \frac{K_1(va) I_1(wa)}{\mathcal{N}}, \quad (\text{A7})$$

where Eq. (A7) follows from Eqs. (43), (49), and $d/dx[x^\nu I_\nu(x)] = x^\nu I_{\nu-1}$, $d/dx[x^\nu K_\nu(x)] = -x^\nu K_{\nu-1}$, see Eq. (9.6.28) in Ref. 29.

Finally, to check consistency, we calculate $\int_0^\infty k(t) dt$. Making use of the small argument expansions of the modified Bessel functions (Appendix 3, Eqs. (7) and (10) in Ref. 9), we obtain

$$\int_0^\infty k(t) dt = \lim_{s \rightarrow 0} \tilde{k}(s) = \frac{\pi a^2 \kappa_r}{\kappa_d} \equiv K_{eq}. \quad (\text{A8})$$

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