

First-encounter time of two diffusing particles in confinementF. Le Vot  and S. B. Yuste *Departamento de Física and Instituto de Computación Científica Avanzada (ICCAEx) Universidad de Extremadura, E-06071 Badajoz, Spain*E. Abad *Departamento de Física Aplicada and Instituto de Computación Científica Avanzada (ICCAEx) Centro Universitario de Mérida Universidad de Extremadura, E-06800 Mérida, Spain*D. S. Grebenkov *Laboratoire de Physique de la Matière Condensée (UMR 7643), CNRS–Ecole Polytechnique, IP Paris, 91128 Palaiseau, France and Institute of Physics & Astronomy, University of Potsdam, 14476 Potsdam-Golm, Germany*

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We investigate how confinement may drastically change both the probability density of the first-encounter time and the associated survival probability in the case of two diffusing particles. To obtain analytical insights into this problem, we focus on two one-dimensional settings: a half-line and an interval. We first consider the case with equal particle diffusivities, for which exact results can be obtained for the survival probability and the associated first-encounter time density valid over the full time domain. We also evaluate the moments of the first-encounter time when they exist. We then turn to the case with unequal diffusivities and focus on the long-time behavior of the survival probability. Our results highlight the great impact of boundary effects in diffusion-controlled kinetics even for simple one-dimensional settings, as well as the difficulty of obtaining analytic results as soon as the translational invariance of such systems is broken.

DOI: [10.1103/PhysRevE.102.032118](https://doi.org/10.1103/PhysRevE.102.032118)**I. INTRODUCTION**

As most chemical reactions are encounter-controlled, the first-encounter time (FET) of the reactants is one of the central quantities characterizing diffusion-influenced reactions. The first study of the FET goes back to Smoluchowski, who reduced a many-body reaction problem for two species (i.e., a bimolecular reaction) with a vast excess of one of them, to the problem of two diffusing reactive particles [1]. By selecting a coordinate system that follows one of the diffusing particles, the original problem is reduced to the simpler problem of a single particle diffusing toward a static target (or sink). Smoluchowski solved this problem and determined the survival probability, whence the probability density of the first-passage time to the target (here equivalent to the FET) and the associated reaction rate immediately follow.

Since Smoluchowski's seminal work, first-passage times to fixed targets have been thoroughly investigated for various kinds of diffusion processes, chemical kinetics, and geometric settings [2–25]. In particular, when the fixed target is small, one deals with the so-called narrow escape problem, for which many asymptotic results have been derived [26–34] (see also a review [35]). Another well-explored research direction concerns multiple particles diffusing on infinite lattices or in Euclidean spaces. This general setting allows one to investigate elaborate chemical reactions involving various species, the effect of inter-particle interactions (e.g., excluded volume), and cooperativity effects when, for instance, several predators hunt for a prey [36–43]. In this context, one clearly identifies two types of problems, (i) those where any pair of

particles can interact with each other as long as such interactions are not precluded by geometric constraints, and (ii) those where particles of a given species (usually the majority species) do not interact with one another, but do so with a target particle or with a set of targets. The first type is well exemplified by binary reactions such as one-species and two-species coalescence/annihilation reactions [44], whereas the second type includes the so-called target problem and the trapping problem, as well as variants thereof [38–40,45–60]. In particular, the generic question on how the mobility of a target or a trap impacts the reaction rate has long been a subject of interest [38–40,45,56,61–65]. The third direction regroups numerical works, in which diffusion-reaction processes are modeled by molecular dynamics or Monte Carlo simulations [66–68]. While such approaches are admittedly the most realistic ones, they often lack analytic insights which are often of great help for the intuitive understanding and systematic characterization of diffusion-reaction processes.

Quite surprisingly, the influence of confinement on the FET distribution of two diffusing particles and on the associated chemical reactions is much less studied. The evident consequence of the presence of a confining boundary is the translational symmetry breaking that prohibits the reduction of a problem involving two diffusing particles to the problem of a single particle diffusing toward a static target. One therefore has to describe the dynamics of two particles inside a confining domain, and the solution of the relevant diffusion-reaction equations becomes much more sophisticated. We are aware of only several works dealing with such problems,

and they are concerned with the simplest possible scenario of infinite reaction rate: the reaction takes place with unit probability upon encounter. In situations when the fate of the reaction products is not of primary interest (e.g., if the reaction products are inert), one may formally consider that any two diffusing walkers annihilate irreversibly upon encounter but do not interact otherwise. Fisher coined the term “vicious walkers” for such nonintersecting walks [69,70]. Upon Fisher’s systematic study of their statistical properties, vicious walkers became an important paradigm in statistical physics. Fisher’s original formulation was in terms of lattice walks, but the diffusive limit of the latter is often considered, as it greatly simplifies the mathematical treatment. In this diffusive approximation, Bray and Winkler studied one-dimensional vicious walkers in a potential, including the case of an interval [71]. Further references on vicious walkers in finite systems are given at the end of Sec. II.

As far as other works are concerned, Agliari *et al.* investigated the first-encounter problem on branched and comblike structures, with special emphasis on the encounter probability [72–74]. Amitai *et al.* estimated the mean FET between two ends of a polymer chain by computing the mean time for a Brownian particle to reach a narrow domain in the polymer configuration space [75]. Tejedor *et al.* investigated diffusion of two particles with equal diffusivities on an interval with either absorbing or reflecting boundary conditions and computed two quantities: the probability that the random walkers meet before one of them is removed at the boundaries of an absorbing interval, and the typical encounter time of the two walkers in the presence of reflecting boundaries [76]. The related epidemic spreading problem has been discussed in Ref. [77]. Tzou *et al.* studied the mean FET for two particles diffusing on a one-dimensional interval by solving numerically the underlying diffusion equations and by deriving some asymptotic relations [78]. In particular, they studied under which conditions a mobile trap can capture a diffusing particle more efficiently than a fixed trap. Even for such a simple geometric setting, an analytical solution of the problem was not provided. More recently, Lawley and Miles computed the mean FET for a very general diffusion model with many *small* targets that can diffuse either inside a three-dimensional domain, or on its two-dimensional boundary, their diffusivities are subject to random fluctuations, while their reactivity can be stochastically gated [79]. However, a systematic study of the FET *distribution* for diffusing particles in confinement is still missing.

In this paper, we consider two Brownian particles A and B diffusing inside a bounded Euclidean domain with reflecting boundary, and investigate the probability of both particles not having met up to a given time t . This quantity is the survival probability for a pair of two molecules with infinite reactivity so that their first collision leads to a chemical reaction: $A + B \rightarrow C$. In chemical kinetics, the survival probability can be interpreted as the fraction of particles still reactive at time t with respect to the initial number of particles. The survival probability determines other important quantities: the probability density of the FET, its mean value and higher-order moments, as well as the reaction rate.

For two diffusing spherical particles without confinement (i.e., in \mathbb{R}^d), the survival probability and related quantities

are functions only of the initial distance between the centers of the particles, of the sum of their radii, and of the sum of their diffusion constants. In contrast, confinement induces new length scales involving distances between the particles and the reflecting boundary, and changes chemical kinetics, particularly at long times at which the typical distance traveled by particles is comparable with the system size. Even though most chemical reactions occur under confinement, its impact on the survival probability and related quantities remains poorly understood. In view of these shortcomings, our work aims to shed further light on the role of confinement in diffusion-limited bimolecular reactions. To this end, we will use both analytical tools and numerical simulations. In contrast with some previous works, our analysis will extend beyond the long-time asymptotic regime whenever possible, since the influence of the domain boundaries may already become apparent for comparatively short times. As it turns out, the interaction with the reflecting boundaries does not only alter the value of the mean FET, but also affects higher order moments, which assess the impact of trajectory-to-trajectory fluctuations and the statistical significance of the mean FET.

The paper is organized as follows. In Sec. II, we formulate diffusion-reaction problem and summarize the main known theoretical results that are relevant for our study. In Sec. III, we consider the most studied case of two particles diffusing on a half-line \mathbb{R}_+ with reflecting endpoint at 0. We provide the exact solutions for the survival probability, the FET probability density, as well as the moments of the FET. In Sec. IV, we explore the FET problem for diffusion on an interval $(0, L)$ with reflecting endpoints. In spite of the apparent simplicity of this geometric setting, much fewer analytical results are known, especially for unequal diffusivities. First, we consider in Sec. IV A the problem with equal diffusivities, for which an exact solution for the survival probability, the FET density and moments are obtained in the form of spectral expansions. Next, we discuss in Sec. IV B the case of unequal diffusivities; even though the exact solution is unknown, we assess the accuracy of a previously obtained asymptotic formula for the mean FET [78] and investigate the long-time decay of the survival probability in the general case by studying the behavior of the smallest eigenvalue of the Laplace operator in this setting. In particular, we show that the associated decay time depends on both D_1 and D_2 in a complex way. Finally, our main conclusions are summarized in Sec. V. In summary, our results for the survival probability and related quantities reveal the intricate dependence on both diffusivities as soon as the interaction with the boundaries comes into play, and highlight the difficulties of obtaining analytical results for diffusive systems under confinement due to the lack of translational invariance in space. While some aspects of this first encounter problem have been analyzed in earlier works, many of the reported properties are new, to our knowledge.

II. SUMMARY OF KNOWN RESULTS

In this section, we summarize some theoretical results on the first-encounter time in the one-dimensional case. Even though these results are known, they are dispersed in the literature and not easily accessible. The problem of the FET of two diffusing particles in the one-dimensional case is very

specific and different from higher-dimensional settings: (i) the particles can be pointlike and still meet with probability one; (ii) the particle cannot overpass each other without meeting, i.e., their initial order is always preserved. These two properties allow one to derive some analytical solutions which are not available in higher dimensions. Nevertheless, the one-dimensional setting provides a solid theoretical background and some intuition on the FET and related properties in higher dimensions. Beyond this immediate justification, the considered setting is also directly related to several fundamental problems in statistical physics concerning fibrous structures [80], polymer networks [81], wetting transitions, dislocations, and melting [69,82].

We consider the problem of finding the FET for two independent pointlike particles diffusing with diffusion coefficients D_1 and D_2 on a domain $\Omega \subset \mathbb{R}$ with reflections on its boundary $\partial\Omega$. Let us, respectively, denote by x_1 and x_2 the starting positions of the particles and assume that $x_1 \geq x_2$ without loss of generality. The FET \mathcal{T} of these particles is a random variable characterized by a cumulative probability distribution, $\mathbb{P}\{\mathcal{T} < t\}$, or, equivalently, by the survival probability $S(t|x_1, x_2) = \mathbb{P}\{\mathcal{T} > t\}$. As the encounter depends on the positions of both particles, it is natural to consider their joint dynamics in the phase space $\Omega \times \Omega$. In particular, the survival probability satisfies the backward diffusion equation (which in the present homogeneous setting with constant diffusivities is formally equivalent to the usual diffusion equation),

$$\frac{\partial S}{\partial t} = \left(D_1 \frac{\partial^2}{\partial x_1^2} + D_2 \frac{\partial^2}{\partial x_2^2} \right) S \quad (x_1, x_2) \in \Omega \times \Omega, \quad (1)$$

subject to the initial condition $S(t = 0|x_1, x_2) = 1$ for $x_1 \neq x_2$, the Neumann boundary condition on the reflecting boundary $\partial\Omega$ (there is no net diffusive flux across the boundary), and the Dirichlet boundary condition $S(t|x_1, x_2 = x_1) = 0$, meaning an immediate reaction upon the first encounter. Once the survival probability is found, one easily gets the FET probability density,

$$H(t|x_1, x_2) = -\frac{\partial}{\partial t} S(t|x_1, x_2), \quad (2)$$

and the associated moments,

$$\langle \mathcal{T}^k \rangle = k \int_0^\infty dt t^{k-1} S(t|x_1, x_2) \quad (3)$$

(note that, depending on the problem at hand, such integrals may not converge, i.e., some moments or even all of them can be infinite). Alternatively, integrating Eq. (1) over time from 0 to ∞ and taking into account Eq. (3) for $k = 1$, one finds that the mean FET $\langle \mathcal{T} \rangle$ satisfies

$$-1 = \left(D_1 \frac{\partial^2}{\partial x_1^2} + D_2 \frac{\partial^2}{\partial x_2^2} \right) \langle \mathcal{T} \rangle \quad (x_1, x_2) \in \Omega \times \Omega, \quad (4)$$

the Neumann boundary condition $\partial \langle \mathcal{T} \rangle / \partial n = 0$ on the reflecting boundary $\partial\Omega$, and the annihilation reaction condition $\langle \mathcal{T} \rangle(x_1, x_2) = 0$ when $x_1 = x_2$. Similar equations are available for higher-order integer moments.

It is natural to assume that the domain Ω is connected (otherwise, the particles could not move from one component to another, and the problem would be trivially reduced to

that with a single component). As a consequence, there are only three possible settings: (i) $\Omega = \mathbb{R}$, (ii) Ω is a half-line, and (iii) Ω is a finite interval. The first case, also known as “the diffusing cliff” in the literature on first-passage processes [4], is well studied; as already anticipated, Smoluchowski’s argument reduces the original problem to that of a single effective particle diffusing with diffusivity $D_1 + D_2$ toward a fixed target. The related survival probability is retrieved by solving the simple diffusion equation on a half-line,

$$S_{\text{free}}(t|x_1, x_2) = \text{erf} \left[\frac{\delta}{\sqrt{4(D_1 + D_2)t}} \right], \quad (5)$$

where $\text{erf}(z)$ is the error function and $\delta \equiv x_1 - x_2$ is the initial separation distance between the particles. Thus, the statistics of the FET depends only on the sum of diffusion coefficients and on the initial interparticle distance. In particular, the long-time decay of Eq. (5) is obtained from the asymptotic behavior of the error function:

$$S_{\text{free}}(t|x_1, x_2) \sim \frac{\delta}{\sqrt{\pi(D_1 + D_2)t}}, \quad t \gg \frac{\delta^2}{D_1 + D_2}. \quad (6)$$

The FET probability density follows upon differentiating Eq. (5) with respect to time,

$$H_{\text{free}}(t|x_1, x_2) = \frac{\delta \exp(-\frac{\delta^2}{4(D_1 + D_2)t})}{\sqrt{4\pi(D_1 + D_2)t^3}}, \quad (7)$$

implying the long-time behavior

$$H_{\text{free}}(t|x_1, x_2) = \frac{\delta t^{-3/2}}{\sqrt{4\pi(D_1 + D_2)}}, \quad t \gg \frac{\delta^2}{D_1 + D_2}. \quad (8)$$

The mean FET, as well as higher-order moments, are infinite. In fact, even though the particles meet with probability 1, long trajectories before encounter provide dominant contributions to these moments. In the following, these results for the infinite system will be used as a reference for the half-line and for the finite interval.

The solutions for both a half-line ($\Omega = \mathbb{R}_+$) and an interval [$\Omega = (0, L)$] are obtained by stretching one of the coordinates to reduce Eq. (1) to a diffusion equation with equal diffusivities on a planar domain (see below). The half-line case has been extensively studied by Redner *et al.* (see Refs. [4,37] and references therein). In particular, the long-time asymptotic behavior of the survival probability was provided in Ref. [4]. Despite such extensive studies, the main focus so far was clearly on the long-time asymptotics, to the extent that we have not been able to directly find the exact solution of this problem, but rather the solution of an equivalent problem with a single particle diffusing in a wedge with absorbing boundaries. For this reason, not only do we provide this solution in Sec. III, but we also analyze some interesting features characterizing the moments of the FET and the transient behavior of the survival probability.

Apart from the above results, problems of vicious walkers under geometric constraints remain widely unexplored. In Ref. [69], Fisher considered the effect of an absorbing wall on the reunion statistics of identical or dissimilar walkers; the reunion of dissimilar walkers was subsequently studied by Fisher and Gelfand [83]. Forrester [84] investigated finite size effects introduced by periodic boundaries.

The problem of diffusion on an interval has been studied much less extensively. Bray and Winkler considered the problem of N vicious walkers in different settings, including an interval with reflecting endpoints [71], thereby generalizing previous results by Krattenthaler [85]. However, they restricted their analysis to the case of identical particles and focused on the asymptotic long-time behavior of the survival probability. More recently, Forrester *et al.* [86] considered from another viewpoint the reunion statistics of nonintersecting Brownian motions (i.e., surviving vicious walks) on an interval with periodic, reflecting and absorbing boundary conditions. In the absorbing case, they showed that the normalized reunion probability is related to the statistics of the outermost Brownian path on the half line. These results were further explored by Liechty [87]. We will revisit the problem of diffusion on an interval in Sec. IV.

III. HALF-LINE

A. Survival probability

We consider the problem of the first-encounter time for two particles started from points $x_1 > x_2$ and diffusing with diffusion coefficients D_1 and D_2 on the positive half-line \mathbb{R}_+ with reflections at 0. As mentioned in Sec. II, this problem is equivalent to two-dimensional diffusion in the half-quadrant (or wedge of angle $\pi/4$) with reflecting horizontal axis and the absorbing diagonal. Rescaling the coordinate of the second particle by $\sqrt{D_1/D_2}$, i.e., setting new coordinates $y_1 = x_1$ and $y_2 = x_2\sqrt{D_1/D_2}$, one maps the original problem onto the problem of isotropic diffusion (with diffusion coefficient D_1) in a wedge $\Omega_0 = \{0 < r < \infty, 0 < \theta < \Theta\}$, with reflecting ray at $\theta = 0$ and absorbing ray at $\theta = \Theta$, and with the wedge angle

$$\Theta = \text{atan}(\sqrt{D_1/D_2}). \tag{9}$$

The latter ray accounts for the encounter condition $y_1 = x_1 = x_2 = y_2\sqrt{D_2/D_1}$ when two particles meet. The initial position in the wedge is determined by polar coordinates (r_0, θ_0) with $r_0 = \sqrt{y_1^2 + y_2^2} = \sqrt{x_1^2 + x_2^2 D_1/D_2}$ and $\theta_0 = \text{atan}(y_2/y_1) = \text{atan}(x_2\sqrt{D_1/D_2}/x_1)$. Note that the assumed condition $x_1 > x_2$ implies $\theta_0 < \Theta$.

In polar coordinates, the survival probability reads $S(t|x_1, x_2) = U(t|r_0, \theta_0)$, where the function $U(t|r_0, \theta_0)$ satisfies the diffusion equation,

$$\frac{\partial}{\partial t} U = D_1 \Delta U, \tag{10}$$

subject to two boundary conditions:

$$\left(\frac{\partial U}{\partial \theta}\right)_{\theta=0} = 0, \quad U_{\theta=\Theta} = 0. \tag{11}$$

Due to the symmetry, one can replace Ω_0 by a twice larger wedge $\Omega = \{0 < r < \infty, -\Theta < \theta < \Theta\}$, with Dirichlet condition $U = 0$ on its boundary. Note that a similar problem but with different boundary conditions was studied by Ben-Naim and Krapivsky to investigate the slow kinetics of Brownian maxima [88].

The radial Green's function for a wedge domain Ω was provided in Ref. [89] (see p. 379)

$$G(r, \theta, t|r_0, \theta_0) = \sum_{n=1}^{\infty} \frac{e^{-(r^2+r_0^2)/(4D_1t)}}{D_1t} I_{\nu_n}[rr_0/(2D_1t)] \times \frac{1}{2\Theta} \sin[\nu_n(\theta + \Theta)] \sin[\nu_n(\theta_0 + \Theta)], \tag{12}$$

where $\nu_n = \pi n/(2\Theta)$, and $I_{\nu}(\cdot)$ is the modified Bessel function of the first kind. To use the result of Ref. [89], here we have considered the wedge of angle 2Θ and we have then shifted the angular coordinate by Θ . The integral of this formula over the arrival point (r, θ) yields the survival probability

$$S(t|r_0, \theta_0) = \int_{-\Theta}^{\Theta} d\theta \int_0^{\infty} dr r G(r, \theta, t|r_0, \theta_0) = 4 \sum_{n=1}^{\infty} \frac{1 - (-1)^n}{\pi n} \sin(\nu_n(\theta_0 + \Theta)) R_{\nu_n}(r_0/\sqrt{D_1t}), \tag{13}$$

where

$$R_{\nu}(z) = e^{-z^2/4} \int_0^{\infty} dx x e^{-x^2} I_{\nu}(xz) = \frac{\sqrt{\pi}}{8} z e^{-z^2/8} [I_{\nu-1/2}(z^2/8) + I_{\nu+1/2}(z^2/8)]. \tag{14}$$

Note that this function approaches 1/2 in the limit $z \rightarrow \infty$ and behaves as $R_{\nu}(z) \propto z^{\nu}$ as $z \rightarrow 0$. The probability density of the FET then reads

$$H(t|r_0, \theta_0) = \frac{2r_0}{\sqrt{D_1} t^{3/2}} \sum_{n=1}^{\infty} \frac{1 - (-1)^n}{\pi n} \sin[\nu_n(\theta_0 + \Theta)] \times R'_{\nu_n}(r_0/\sqrt{D_1t}), \tag{15}$$

where

$$R'_{\nu}(z) = \frac{\sqrt{\pi} \nu}{8} e^{-z^2/8} [I_{\nu-1/2}(z^2/8) - I_{\nu+1/2}(z^2/8)]. \tag{16}$$

Note that if one sets $x_1 = x_2 + \delta$ in Eqs. (13) and (15) and takes the limit $x_2 \rightarrow \infty$, one recovers Eqs. (5) and (7) for an infinite system.

As discussed by Redner [4], the survival probability decays asymptotically as

$$S \propto (r_0/\sqrt{D_1t})^{\pi/(2\Theta)} \propto t^{-\pi/(4\Theta)} \quad (t \rightarrow \infty), \tag{17}$$

so that the probability density decays as $H \propto t^{-\pi/(4\Theta)-1}$. Note that, since one always has $\pi/(4\Theta) > 1/2$, the long-time decay of both S and H is faster than in the free case [cf. Eqs. (6) and (8)]. This simply reflects the fact that the boundary favors a faster reaction.

Surprisingly, the early time behavior of the solution seems to have received much less attention in the literature in comparison with the long-time asymptotics. In fact, at short times, subleading corrections characterize the departure of Eq. (13) from the free solution Eq. (5) arising from the perturbation introduced by the reflecting boundary. In a recent work addressing the diffusion of a random walker in a two-dimensional wedge with absorbing boundaries [90], Chupeau

et al. noted that the series representation in Eq. (13) does not allow one to extract the short-time behavior because the use of the asymptotic expansion of the modified Bessel functions would yield a divergent series. Instead, Chupeau *et al.* suggested to resort to the integral representation of the modified Bessel functions to derive an alternative form of $S(t|r_0, \theta_0)$. This yields an exact expression in terms of complementary error functions and an integral remainder, but for some specific values of Θ the latter disappears [91]. For example, when $\Theta = \pi/4$ (which corresponds to $D_1 = D_2$), one finds

$$S(t|r_0, \theta_0, \Theta = \pi/4) = \operatorname{erf}(\sqrt{2y} \sin \varphi_0) \operatorname{erf}(\sqrt{2y} \cos \varphi_0), \quad (18)$$

where $\varphi_0 = \theta_0 + \Theta$ and $y = r_0^2/(8D_1t)$. In terms of x_1 and x_2 , this gives

$$S(t|x_1, x_2, D_2 = D_1) = \operatorname{erf}\left(\frac{x_1 - x_2}{\sqrt{8D_1t}}\right) \operatorname{erf}\left(\frac{x_1 + x_2}{\sqrt{8D_1t}}\right) \quad (19a)$$

$$\begin{aligned} &= S_{\text{free}}(t|x_1, x_2, D_2 = D_1) \operatorname{erf}\left(\frac{x_1 + x_2}{\sqrt{8D_1t}}\right) \\ &= S_{\text{free}}(t|x_1, x_2, D_2 = D_1) \\ &\quad - S_{\text{free}}(t|x_1, x_2, D_2 = D_1) \operatorname{erfc}\left(\frac{x_1 + x_2}{\sqrt{8D_1t}}\right). \end{aligned} \quad (19b)$$

The last term in Eq. (19b) quantifies the effect of the boundary on the survival probability.

Another case in which a closed-form expression in terms of error functions is available is $\Theta = \pi/6$ corresponds to $D_2 = 3D_1$:

$$\begin{aligned} S(t|x_1, x_2, D_2 = 3D_1) &= \operatorname{erf}\left(\frac{x_1 - x_2}{\sqrt{16D_1t}}\right) \\ &\quad + \operatorname{erf}\left(\frac{x_1 + x_2}{\sqrt{16D_1t}}\right) - \operatorname{erf}\left(\frac{x_1}{\sqrt{4D_1t}}\right), \end{aligned} \quad (20)$$

where the first term on the rhs corresponds yet again to the free solution with diffusion coefficient $D_1 + D_2 = 4D_1$. Equations (19a) and (20), as well as the alternative general representation of the survival probability obtained in Ref. [90], provide a good starting point to study the role of the boundary by comparing the early-time behavior of the solution with that of Eq. (5), as discussed in Sec. III B.

B. Comparison with the free case

It is instructive to compare the behavior of S and H with their counterparts for the free case. Clearly, $\delta S \equiv S_{\text{free}}(t|x_1, x_2) - S(t|x_1, x_2) \geq 0$ at all times. As time goes by, δS first increases from its initial value $\delta S(t=0) = 0$, then attains a maximum value at a time t_* , and finally decreases until it eventually vanishes in the limit $t \rightarrow \infty$. One has $\partial \delta S / \partial t|_{t=t_*} = 0$, implying $H(t_*, x_1, x_2) = H_{\text{free}}(t_*, x_1, x_2)$. Thus, the value of t_* can be obtained by solving this equation numerically.

Figure 1 illustrates the typical behavior of the FET density. In an infinite system, the FET density reaches a maximum at $t_{\text{free}} = \delta^2/[6(D_1 + D_2)]$. In the half-line system, the density peaks at a time t_{HL} . Finally, both curves cross at t_* .

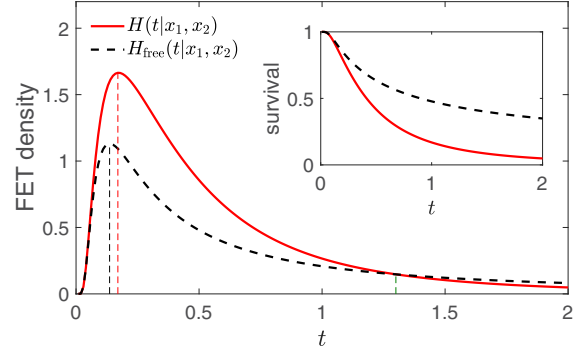


FIG. 1. FET density for the free case (dashed line) and for the half-line (solid line). The chosen parameter values are $x_2 = 0.5$, $\delta = 3$, $D_1 = 1$, and $D_2 = 10$. Vertical dashed lines indicate the times t_{free} and t_{HL} when peaks of the FET density are attained in both cases, as well as the crossing time t_* .

Finally, we note that, for $x_2 > 0$ and a fixed D_2 , one has $S(t|x_1, x_2) \rightarrow S_{\text{free}}(t|x_1, x_2)$ as $D_1 \rightarrow \infty$; however, this is not the case if one fixes D_1 and then takes the limit $D_2 \rightarrow \infty$.

In some special cases, the obtained analytic expressions are more transparent and therefore easier to interpret. For instance, for $D_1 = D_2$ and $x_2 = 0$, Eq. (19a) becomes

$$\begin{aligned} S(t|x_1 = \delta, x_2 = 0, D_2 = D_1) &= \left[\operatorname{erf}\left(\frac{\delta}{\sqrt{8D_1t}}\right) \right]^2 \\ &= S_{\text{free}}^2(t|x_1 = \delta, x_2 = 0, D_2 = D_1). \end{aligned} \quad (21)$$

Thus, the time t_ζ after which the survival probability is just a fraction $0 < \zeta < 1$ of the free solution is simply

$$t_\zeta = \frac{\delta^2}{8D_1 [\operatorname{erf}^{-1}(\zeta)]^2}. \quad (22)$$

From this equation, one immediately obtains $t_* = t_{1/2} \approx 0.55 \delta^2/D_1$, which is roughly 6.6 larger than $t_{\text{free}} = \frac{1}{12} \delta^2/D_1 \gtrsim t_{\text{HL}}$.

In most considered settings, we observed $t_{\text{free}} < t_{\text{HL}}$. However, it is also possible to get $t_{\text{free}} > t_{\text{HL}}$ when the particle 2 starts very close to the boundary. In this situation, the difference $t_{\text{free}} - t_{\text{HL}}$ can be nonnegligible when D_1 and D_2 are comparable. For instance, in the aforementioned case $x_2 = 0$ and $D_2 = D_1$, one always has $t_{\text{HL}} < t_{\text{free}}$ regardless of the initial separation δ and of the diffusivity D_1 . This can be easily seen by differentiating Eq. (21) with respect to time and by subsequently requiring that the derivative of the resulting expression for the FET density, $H(t) = 2S_{\text{free}}H_{\text{free}}$, vanishes at $t = t_{\text{HL}}$. This condition yields

$$\left. \frac{dH_{\text{free}}}{dt} \right|_{t=t_{\text{HL}}} = \frac{H_{\text{free}}^2(t_{\text{HL}})}{S_{\text{free}}(t_{\text{HL}})}. \quad (23)$$

Since the right-hand side is always a positive quantity, the solution t_{HL} of the above equation must correspond to a time when H_{free} is still increasing and has not yet reached the maximum at $t = t_{\text{free}}$, implying $t_{\text{HL}} < t_{\text{free}}$.

We close this subsection with a short general discussion on how the early-time behavior is affected by the boundary. In the case of an obtuse wedge $2\Theta > \pi/2$ (i.e., $D_1 > D_2$), the free solution is a good approximation up to relatively long times.

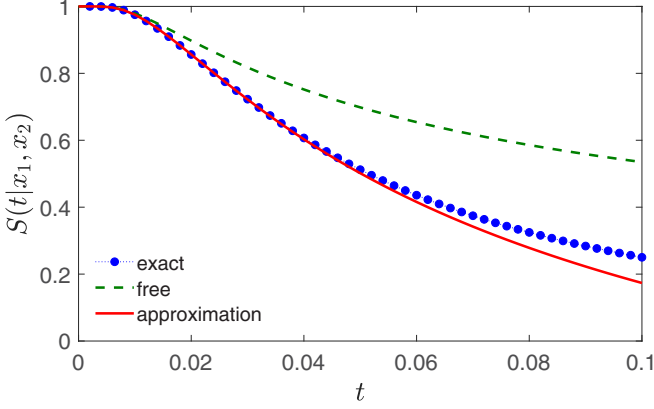


FIG. 2. Time evolution of the survival probability as given by the exact solution in Eq. (13), the free solution in Eq. (5) and the approximation Eq. (24). The chosen parameter values are $x_1 = 0.9$, $x_2 = 0.1$, $D_1 = 1$, and $D_2 = 5$, leading to $r_0 \approx 0.901$, $\Theta \approx 0.421$, and $\theta_0 \approx 0.05$.

This holds even if the particle starts close to the boundary, provided that δ is not too small and D_2 is not too large. In the case of an acute wedge $2\Theta < \pi/2$ (i.e., $D_1 < D_2$), the time up to which the free solution is a good approximation, can be significantly shorter. The free solution is still an acceptable approximation as long as $\Theta > \pi/6$ but it progressively deteriorates as D_2 increases for a fixed D_1 . If D_2 is not too large (such that $\pi/10 < \Theta \leq \pi/6$), a better early-time approximation can be obtained from Eq. (39) in Ref. [90] by retaining the first two complementary error functions,¹

$$S(t|x_1, x_2, D_2, D_1) \approx \underbrace{1 - \psi_- - \psi_+}_{S_{\text{free}}(t)}, \quad (24)$$

with

$$\psi_{\pm} = \text{erfc}\left(\frac{x_1 \pm x_2}{2\sqrt{(D_1 + D_2)t}}\right) \quad (25)$$

(since the complementary error function is a monotonically decreasing function, for fixed x_2 the correction ψ_+ to the free solution becomes increasingly important with decreasing interparticle distance δ). The good accuracy of the approximation Eq. (24) in comparison with the free solution is illustrated in Fig. 2.

C. Moments of the FET

We now provide exact expressions for the moments of the FET density. They can be computed from the survival probability by applying Eq. (3). Different behaviors are observed

¹We note that, in the language of Ref. [90], the free solution corresponds to the asymptotic behavior $S(y) \simeq 1 - \text{erfc}[\sqrt{2y} \sin(2\Theta - \varphi_0)]$ of the survival probability, which holds in the limit $y \equiv r_0^2/(8D_1t) \rightarrow \infty$ in the parameter range of our problem ($\varphi_0 > \Theta$). This is different from their prediction $S(y) \simeq 1 - \text{erfc}[\sqrt{2y} \sin(\varphi_0)]$, which is not valid in this range. The difference arises because, in our case, $\psi_+ = o(\psi_-)$, rather than $\psi_- = o(\psi_+)$ (note that $-\psi_+$ and $-\psi_-$ were respectively termed ψ_1 and ψ_2 in Ref. [90]).

depending on the parameter Θ . If $\Theta \geq \pi/4$ or, equivalently, $D_1 \geq D_2$, then one sees from Eq. (17) that the mean FET is still infinite, as in the free case. In turn, if $D_1 < D_2$, the mean FET becomes finite and can be computed from Eq. (3) as

$$\langle \mathcal{T} \rangle = 4 \sum_{n=1}^{\infty} \frac{1 - (-1)^n}{\pi n} \sin[v_n(\theta_0 + \Theta)] \int_0^{\infty} dt R_{v_n} \left(\frac{r_0}{\sqrt{D_1 t}} \right),$$

and the last integral reads

$$\begin{aligned} & \frac{\sqrt{2\pi}}{32} \frac{r_0^2}{D_1} \int_0^{\infty} \frac{dz}{z^{3/2}} e^{-z} [I_{\frac{v_n-1}{2}}(z) + I_{\frac{v_n+1}{2}}(z)] \\ & = \frac{r_0^2}{2D_1(v_n^2 - 4)}. \end{aligned}$$

The last equality holds for $v_n > 2$, which is valid for all $n = 1, 2, 3, \dots$ since $\Theta < \pi/4$. We thus get the mean FET as

$$\langle \mathcal{T} \rangle = \frac{2r_0^2}{D_1} \sum_{n=1}^{\infty} \frac{1 - (-1)^n}{\pi n(v_n^2 - 4)} \sin[v_n(\theta_0 + \Theta)]. \quad (26)$$

Using the identity [92]

$$\begin{aligned} & \sum_{n=1}^{\infty} \frac{[1 - (-1)^n] \sin(\pi n x)}{\pi n(z^2 - \pi^2 n^2)} \\ & = \frac{\sin(z) - \sin(zx) - \sin[z(1-x)]}{2z^2 \sin(z)}, \end{aligned} \quad (27)$$

we compute the mean FET as

$$\langle \mathcal{T} \rangle = \frac{r_0^2}{4D_1} \left[\frac{\cos(2\theta_0)}{\cos(2\Theta)} - 1 \right]. \quad (28)$$

Thanks to trigonometric relations, one finds

$$\cos(2\theta_0) = \frac{1 - \tan^2(\theta_0)}{1 + \tan^2(\theta_0)} = \frac{x_1^2 D_2 - x_2^2 D_1}{x_1^2 D_2 + x_2^2 D_1} \quad (29)$$

[and similar for $\cos(2\Theta)$]. After simplifications, we finally get a remarkably simple formula

$$\langle \mathcal{T} \rangle = \frac{x_1^2 - x_2^2}{2(D_2 - D_1)} = \frac{\delta(2x_1 - \delta)}{2(D_2 - D_1)}, \quad (30)$$

which is valid for $x_1 > x_2$ and $D_1 < D_2$ [note that this result could alternatively be derived by solving the Poisson Eq. (4) for the MFET]. This is precisely the MFPT for a single particle with the initial position x_2 and diffusivity $D_2 - D_1$ to a fixed absorbing endpoint x_1 of an interval $(0, x_1)$ with reflections at 0.² Thus, the mean FET for the problem with a slowly diffusing target (started at x_1) is the same as the mean FET for the problem with a fixed target at x_1 if the diffusivity D_2 of the rapidly diffusing particle is replaced with $D_2 - D_1$. However, this equivalence is only manifested at the level of

²Equation (30) can be easily found from the corresponding Green function on the interval $(0, x_1)$ with Dirichlet/Neumann boundary conditions at the endpoints, or by realizing that the problem is equivalent to that on an interval of doubled length $2x_1$ and two fully absorbing endpoints, whose solution is well-known from the literature, see, e.g., Ref. [4].

the mean FET, since already the variance is different for these two problems, as we show below.

The crucial difference between the two particles here is that the second particle [started from $x_2 \in (0, x_1)$] remains bound to a finite interval between 0 and the first particle (started from x_1), whereas the latter is bound to a half-line between the second particle and infinity. When $D_1 > D_2$, the first particle diffuses faster and can undertake very long excursions whose contributions make the mean FET infinite, as in the case of a single particle on the half-line with a fixed absorbing endpoint. In other words, as the slower second particle does not typically “catch” the first one until after a very long time, its diffusion is not relevant. In contrast, when the second particle diffuses faster ($D_2 > D_1$), the first particle cannot efficiently “run away” from it, and this setting is similar to diffusion on a finite interval, for which the mean FET is finite.

According to Eq. (3), the long-time decay Eq. (17) implies that the higher-order moment $\langle \mathcal{T}^k \rangle$ exists if $\Theta < \pi/(4k)$ and is given by

$$\begin{aligned} \langle \mathcal{T}^k \rangle &= 4k \sum_{n=1}^{\infty} \frac{1 - (-1)^n}{\pi n} \sin[v_n(\theta_0 + \Theta)] \\ &\quad \times \int_0^{\infty} dt t^{k-1} R_{v_n} \left(\frac{r_0}{\sqrt{D_1 t}} \right) \\ &= 2k \left(\frac{r_0^2}{D_1} \right)^k \sum_{n=1}^{\infty} \frac{1 - (-1)^n}{\pi n} \sin[v_n(\theta_0 + \Theta)] \varrho_k(v_n), \end{aligned} \quad (31)$$

where

$$\varrho_k(v) = \frac{\sqrt{2\pi}}{2^{3k+1}} \int_0^{\infty} \frac{dz}{z^{k+1/2}} e^{-z} [I_{\frac{v+1}{2}}(z) + I_{\frac{v-1}{2}}(z)]. \quad (32)$$

For integer-order moment k , one can use the following Laplace transform [93]

$$\begin{aligned} &\int_0^{\infty} dt e^{-pt} t^{\mu} I_{\nu}(at) \\ &= \frac{a^{\nu} \Gamma(\mu + \nu + 1)}{2^{\nu} p^{\mu+\nu+1} \Gamma(\nu + 1)} \\ &\quad \times {}_2F_1 \left(\frac{\mu + \nu + 1}{2}, \frac{\mu + \nu + 2}{2}; \nu + 1; \frac{a^2}{p^2} \right) \end{aligned} \quad (33)$$

(where ${}_2F_1(a, b; c; z)$ is the Gauss hypergeometric function) to obtain

$$\varrho_k(v) = (k-1)! \prod_{j=1}^k \frac{1}{v^2 - (2j)^2}, \quad (34)$$

which completes the computation of the k th order moment:

$$\begin{aligned} \langle \mathcal{T}^k \rangle &= 2(k!) (r_0^2/D_1)^k \sum_{n=1}^{\infty} \frac{1 - (-1)^n}{\pi n} \sin[v_n(\theta_0 + \Theta)] \\ &\quad \times \prod_{j=1}^k \frac{1}{v_n^2 - (2j)^2}. \end{aligned} \quad (35)$$

Using again the summation identity in Eq. (27), we get

$$\langle \mathcal{T}^2 \rangle = -\frac{r_0^2}{6D_1} \langle \mathcal{T} \rangle + \frac{(r_0^2/D_1)^2}{96} \left[\frac{\cos(4\theta_0)}{\cos(4\Theta)} - 1 \right],$$

whence

$$\langle \mathcal{T}^2 \rangle = \frac{(x_1^2 - x_2^2)(5x_1^2 D_2 + 5x_2^2 D_1 - x_1^2 D_1 - x_2^2 D_2)}{12(D_2 - D_1)(D_1^2 + D_2^2 - 6D_1 D_2)}. \quad (36)$$

The variance then is

$$\begin{aligned} \sigma_{\mathcal{T}}^2 &= \frac{x_1^4 - x_2^4}{6(D_2 - D_1)^2} \\ &\quad \times \frac{6(x_1^2 - x_2^2)D_1 D_2 + (x_1^2 + x_2^2)(D_2^2 - D_1^2)}{(x_1^2 + x_2^2)(D_1^2 + D_2^2 - 6D_1 D_2)}. \end{aligned} \quad (37)$$

Note that the condition $\Theta < \pi/8$ (with $k = 2$) is equivalent to $D_1/D_2 < 3 - 2\sqrt{2} \approx 0.1716$, which is precisely one of the roots of the quadratic polynomial in the denominator. When D_1/D_2 approaches this value, the variance diverges, whereas the mean remains finite.

As said earlier, this expression differs from the variance for an effective problem of a particle diffusing with diffusion coefficient $D_2 - D_1$ to a fixed target at x_1 :

$$\sigma_{\mathcal{T}, \text{eff}}^2 = \frac{x_1^4 - x_2^4}{6(D_2 - D_1)^2}. \quad (38)$$

Indeed, Eq. (37) can be written as

$$\sigma_{\mathcal{T}}^2 = \sigma_{\mathcal{T}, \text{eff}}^2 W(x_2/x_1, D_2/D_1), \quad (39)$$

where

$$W(x, \eta) = 1 - 2 \frac{1 - 6\eta + x^2}{(1 + x^2)(1 - 6\eta + \eta^2)}, \quad (40)$$

for $0 \leq x \leq 1$ and $\eta > \eta_0 = 1/(3 - 2\sqrt{2}) \approx 5.8284$. One can easily check that for any $0 \leq x \leq 1$, $W(x, \eta)$ is a monotonously decreasing function of η , which varies from $+\infty$ at $\eta = \eta_0$ to 1 as $\eta \rightarrow \infty$. In other words, the variance $\sigma_{\mathcal{T}}^2$ is always greater than $\sigma_{\mathcal{T}, \text{eff}}^2$ but approaches the latter as $\eta = D_2/D_1$ goes to infinity. In turn, the dependence of $W(x, \eta)$ on $x = x_2/x_1$ is rather weak.

IV. INTERVAL

In this section, we consider the FET problem for two particles diffusing on an interval $\Omega = (0, L)$, which is equivalent to anisotropic diffusion on the square $(0, L) \times (0, L)$. As this domain is bounded, the governing diffusion operator, $D_1 \partial^2/\partial x_1^2 + D_2 \partial^2/\partial x_2^2$, has a discrete spectrum, its eigenfunctions form a complete basis in the space of square-integrable functions on $\Omega \times \Omega$, and the survival probability admits a spectral expansion [94]. In particular, the survival probability decays exponentially

$$S(t|x_1, x_2) \propto \exp(-t/T) \quad (t \rightarrow \infty), \quad (41)$$

with the decay time $T(D_1, D_2)$, determined by the smallest eigenvalue of the diffusion operator. This behavior is in sharp contrast with the power-law decay Eq. (17) for diffusion on a half-line.

We treat separately two cases: $D_1 = D_2$, for which an exact solution and much more advanced analysis are possible (Sec. IV A), and $D_1 \neq D_2$, for which we focus on the long-time limit (Sec. IV B).

A. Equal diffusivities

We search for the distribution of the first-encounter time for two particles diffusing with equal diffusivities, $D_1 = D_2$, on an interval $(0, L)$ with reflecting endpoints. As discussed in Sec. II, the $N = 2$ problem is equivalent to two-dimensional diffusion on the square $(0, L) \times (0, L)$ with reflecting edges and absorbing diagonal. Our previous assumption $x_1 > x_2$ implies that the particle is actually restricted to the isosceles right triangle $\Omega = \{0 < x_1 < L, 0 < x_2 < x_1\}$ with reflecting edges and absorbing hypotenuse. For this domain, one can construct the eigenfunctions of the Laplace operator by antisymmetrizing the known eigenfunctions on the square:

$$u_{n_1, n_2}(x_1, x_2) = c_{n_1, n_2} [\cos(\pi n_1 x_1 / L) \cos(\pi n_2 x_2 / L) - \cos(\pi n_2 x_1 / L) \cos(\pi n_1 x_2 / L)], \quad (42)$$

with the indices $0 \leq n_1 < n_2$, and the normalization coefficients are

$$c_{n_1, n_2} = \frac{2}{L} \frac{1}{\sqrt{(1 + \delta_{n_1, 0})(1 + \delta_{n_2, 0})}}. \quad (43)$$

As this set of eigenfunctions is complete (see Appendix A and [95–98]), the survival probability can be written as a spectral decomposition:

$$S(t|x_1, x_2) = \sum_{n_1=0}^{\infty} \sum_{n_2 > n_1}^{\infty} b_{n_1, n_2} u_{n_1, n_2}(x_1, x_2) e^{-D_1 t \lambda_{n_1, n_2}}, \quad (44)$$

where $\lambda_{n_1, n_2} = \pi^2(n_1^2 + n_2^2)/L^2$ and

$$b_{n_1, n_2} = \int_{\Omega} dx_1 dx_2 u_{n_1, n_2}(x_1, x_2) = \frac{2L^2 c_{n_1, n_2} (1 - (-1)^{n_1 + n_2})}{\pi^2(n_2^2 - n_1^2)}. \quad (45)$$

This expression is a particular form of the general antisymmetrized expression for N vicious walkers provided in Ref. [71]. An alternative spectral representation of the survival probability was derived in Ref. [76]:

$$S(t|x_1, x_2) = \frac{4}{\pi^2} \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} e^{-D_1 t \lambda'_{n_1, n_2}} \times \frac{\sin\left[\frac{\pi(n_1+1/2)(x_1-x_2)}{L}\right] \sin\left[\frac{\pi(n_2+1/2)(x_1+x_2)}{L}\right]}{(n_1+1/2)(n_2+1/2)}, \quad (46)$$

where $\lambda'_{n_1, n_2} = 2\pi^2[(n_1+1/2)^2 + (n_2+1/2)^2]/L^2$. The decay time in the long-time limit is simply

$$T(D_1, D_1) = \frac{1}{D_1 \lambda_{0,1}} = \frac{L^2}{\pi^2 D_1}. \quad (47)$$

In the long-time limit, the double sum in Eq. (44) is essentially determined by a single decay mode associated with

$T(D_1, D_1)$, and one obtains

$$S(t|x_1, x_2) \approx \frac{8}{\pi^2} \{\cos(\pi x_2/L) - \cos(\pi x_1/L)\} e^{-D_1 \pi^2 t/L}. \quad (48)$$

In the particular case $x_1 = L$, the average of Eq. (48) over a uniform distribution of x_2 on the interval $[0, L]$ yields

$$S_{\text{uniform}}(t) \simeq \frac{8}{\pi^2} e^{-D_1 \pi^2 t/L} \quad (t \rightarrow \infty). \quad (49)$$

This expression will be compared to the target problem discussed below (see Sec. IV A 1).

From Eq. (2), the probability density of the FET is given as

$$H(t|x_1, x_2) = D_1 \sum_{n_1=0}^{\infty} \sum_{n_2=n_1+1}^{\infty} b_{n_1, n_2} u_{n_1, n_2}(x_1, x_2) \lambda_{n_1, n_2} \times e^{-D_1 t \lambda_{n_1, n_2}}. \quad (50)$$

The mean and higher-order moments of the FET can be obtained from Eq. (3):

$$\langle \mathcal{T}^k \rangle = k! \sum_{n_1=0}^{\infty} \sum_{n_2 > n_1}^{\infty} \frac{b_{n_1, n_2}}{(D_1 \lambda_{n_1, n_2})^k} u_{n_1, n_2}(x_1, x_2). \quad (51)$$

In Appendix B, we employ the summation technique to partly evaluate this double sum. In particular, we derive the following expression for the mean FET (for $x_1 \geq x_2$):

$$\langle \mathcal{T} \rangle = \frac{(x_1 - x_2)[2L^2 + 6x_2(L - x_1) - (x_1 - x_2)^2]}{12D_1 L} + \frac{L^2}{D_1} \sum_{n=1}^{\infty} \frac{\cos(\pi n \frac{x_2}{L}) v_n(\frac{x_1}{L}) - \cos(\pi n \frac{x_1}{L}) v_n(\frac{x_2}{L})}{(\pi n)^3}, \quad (52)$$

where $v_n(x) = \frac{\cosh[\pi n(1-x)] - (-1)^n \cosh(\pi n x)}{\sinh(\pi n)}$ (for $x_1 < x_2$, one needs just to exchange x_1 and x_2). An alternative spectral representation of the mean FET, based on Eq. (46), was derived in Ref. [76]:

$$\langle \mathcal{T} \rangle = \frac{(x_1 - x_2)[L - (x_1 - x_2)/2]}{2D_1} - \frac{L^2}{D_1} \sum_{k=0}^{\infty} \frac{\sin\left[\frac{\pi(k+1/2)(x_1-x_2)}{L}\right]}{\pi^3(k+1/2)^3} \times \frac{\sinh\left[\frac{\pi(k+1/2)(x_1+x_2)}{L}\right] + \sinh\left[\frac{\pi(k+1/2)(2L-x_1-x_2)}{L}\right]}{\sinh[\pi(2k+1)]}. \quad (53)$$

Tejedor *et al.* discussed approximations for this exact relation, in particular, when both particles are initially close to an endpoint of the interval [76].

It is well known that the fluctuations in the values of \mathcal{T} in many first-passage time problems can be enormous [4, 10, 99, 100]. Equation (51) allows us to compare $\langle \mathcal{T} \rangle$ and the standard deviation $\sigma_{\mathcal{T}} = \sqrt{\langle \mathcal{T}^2 \rangle - \langle \mathcal{T} \rangle^2}$ in the present case of two particles in an interval (Fig. 3). We see that the standard deviation is larger, and even much larger in some cases, than the mean FET when the initial positions of the particles are close. For example, we see that the standard deviation is always larger than the mean FET when both particles start

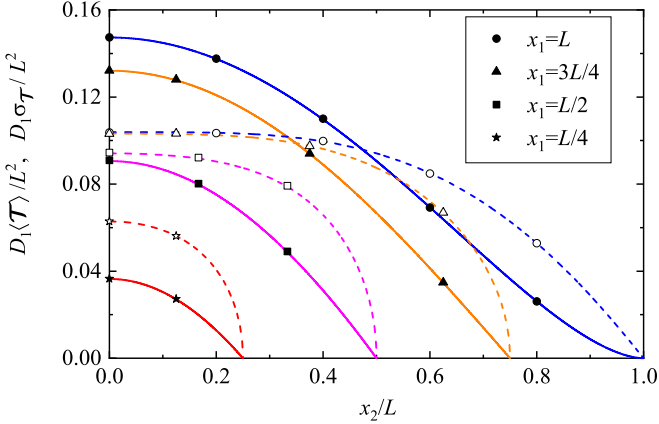


FIG. 3. Normalized mean FET (solid lines) and standard deviation (dashed lines) versus the initial position of the left particle for several initial positions of the right particle. The symbols show simulation results with 10^6 runs, obtained for $L = 1000$ and particles with diffusion coefficient $D_1 = D_2 = 1/2$.

in the same half of the interval. This is illustrated with more detail in Fig. 4 where a contour plot of the ratio $\sigma_T/\langle T \rangle$ on the x_1 - x_2 plane is shown.

1. Comparison with the problem of a diffusing particle in a sea of diffusing traps

By symmetry, the above problem with $x_1 = L$ can be mapped to an equivalent problem where particle 1 starts at the middle of an interval $(0, 2L)$, and is surrounded by particle 2 (which starts at x_2 and has diffusivity $D_2 = D_1$), and a fictitious mirror particle 2' (which is originally located at $2L - x_2$ and follows symmetrically the trajectory of the particle 2). One could thus wonder to what extent this problem is similar to other problems in which the distance to the nearest neighbors on a one-dimensional setting determines the survival probability of the particle.

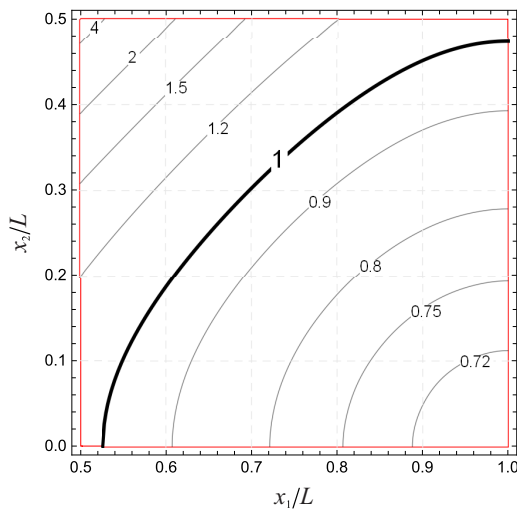


FIG. 4. Contour plot of $\sigma_T/\langle T \rangle$ on the plane of initial positions x_1 - x_2 . Contour lines corresponding to several values of this ratio (which is shown as a label) are provided.

One such problem is the computation of the survival probability of a diffusing pointlike target with diffusivity D_1 in a sea of identical noninteracting point traps, each of them diffusing with diffusivity $D_2 = D_1$. The traps are initially scattered at random with a global density ρ on the infinite real line. In the limit $t \rightarrow \infty$, it can be shown that the survival probability of the target averaged over an ensemble of initial conditions is $S_{\text{target}}(t) \simeq e^{-4\rho(D_2 t/\pi)^{1/2}}$ [38–40]. Taking the density value $\rho = 1/L$ and $D_2 = D_1$ yields

$$S_{\text{target}}(t) \simeq e^{-4(D_1 t/\pi)^{1/2}/L} \quad (t \rightarrow \infty), \quad (54)$$

i.e., an asymptotic decay that is slower than the one prescribed by Eq. (49).

In the target problem, there are large trap density fluctuations which entail the formation of large gaps between the target and the closest traps in certain statistical realizations. In contrast, the maximum distance from particle 2 (and its mirror particle 2') to the target at any time can never exceed the value L in our expanded system. This accelerates the decay of the survival probability with respect to that observed in the target problem, despite the fact that in the latter more than just two particles (actually, an infinite number of them) are available to kill the target, since the traps can overpass each other.

Finally, it is also worth noting that the decay observed in our one-dimensional problem is similar to that observed in the three-dimensional target problem with diffusing target of finite extent [101]; in both cases, the decay is exponential, since the reflecting boundaries and the increased dimensionality, respectively, facilitate the mixing of the reactants and accelerate the decay of the survival probability.

B. Unequal diffusivities

Here we investigate the mean FET $\langle T \rangle$ and the decay time $T(D_1, D_2)$ for the case $D_1 \neq D_2$. In particular, we will consider the cases in which one of the diffusivities is much smaller than the other, say $\epsilon^2 = D_2/D_1 \ll 1$.

1. Mean FET

In Ref. [78], Tzou *et al.* studied Eq. (4) and found the following asymptotic expression for the mean FET for $\epsilon \ll 1$:

$$\frac{D_1 \langle T \rangle}{L^2} = u^0(\bar{x}_1, \bar{x}_2, \epsilon) + \epsilon V_1(\bar{x}_1, \bar{x}_2/\epsilon) + \epsilon^2 V_2(\bar{x}_1, \bar{x}_2/\epsilon), \quad (55)$$

where

$$u^0(\bar{x}_1, \bar{x}_2, \epsilon) = (1 + \epsilon^2) \left(\bar{x}_1 - \bar{x}_2 - \frac{\bar{x}_1^2}{2} + \frac{\bar{x}_2^2}{2} \right) \quad (56)$$

is the outer solution, and

$$V_1(x, \eta) = - \sum_{n=0}^{\infty} \frac{2}{\alpha_n^2} e^{-\alpha_n \eta} \sin(\alpha_n x), \quad (57)$$

$$V_2(x, \eta) = \int_0^{\infty} \frac{d\omega \hat{F}(\omega)}{\cosh(2\pi\omega)} \cosh[2\pi\omega(x-1)] \cos(2\pi\omega\eta), \quad (58)$$

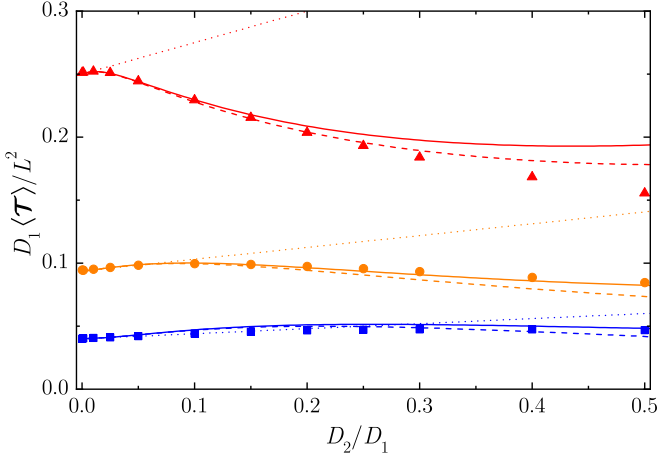


FIG. 5. Scaled mean FET $\langle T \rangle$ vs. the ratio D_2/D_1 (with $D_1 = 0.5$) for $\{x_1/L = 0.75, x_2/L = 0.25\}$ (triangles, $L = 500$), $\{x_1/L = 0.75, x_2/L = 0.5\}$ (circles, $L = 500$), and $\{x_1/L = 0.9, x_2/L = 0.7\}$ (squares, $L = 1000$). The symbols show simulation results with 10^6 runs. The dotted line is the outer solution Eq. (56), the dashed line is the uniform solution Eq. (55) when one term is retained in the infinite series, whereas the solid line is the same solution with ten terms retained.

$\hat{F}(\omega)$ being the Fourier cosine transform of

$$f(\eta) = \eta \sum_{n=0}^{\infty} \frac{2}{\alpha_n^2} e^{-\alpha_n \eta}, \quad (59)$$

$\alpha_n = (n + 1/2)\pi$, and $\bar{x} = x/L$. In Fig. 5 we compare these expressions with simulation results. We see that when the diffusivity of one of the particles is much smaller than the diffusivity of the other, i.e., for $D_2 \ll D_1$, Eq. (56) is a simple and accurate expression for estimating the mean FET, $\langle T \rangle$, especially when the two particles start close to each other.

In the limiting case of $D_2 \rightarrow 0$, i.e., for $\epsilon \rightarrow 0$, one gets

$$\langle T \rangle = \frac{2L(x_1 - x_2) - x_1^2 + x_2^2}{2D_1}, \quad (60)$$

which is just the mean FPT of a diffusive particle with diffusion coefficient D_1 that starts at x_1 and is surrounded by an absorbing frontier at x_2 and a reflecting barrier at L [see Eq. (30) and the discussion below this equation].

Note that Tzou *et al.* in Ref. [78] did not assess the accuracy of their asymptotic formulas. They were mainly interested by the question whether, to survive, it is better for one of the particles to move randomly or remain immobile.

2. Decay time

In the case $D_1 \neq D_2$, one can still stretch the original square along one coordinate into a rectangle to get isotropic diffusion (Fig. 6). In particular, the smallest eigenvalue λ_{\min} of the Laplace operator in the right triangle with (reflecting) Neumann boundary conditions on legs $(0, L_1)$ and $(0, L_2)$ (with $L_1 = L$ and $L_2 = L\sqrt{D_1/D_2}$ resulting from stretching) and (absorbing) Dirichlet boundary condition on the hypotenuse

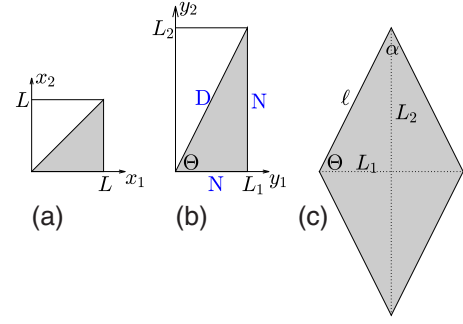


FIG. 6. Schematic illustration of the first-encounter problem for two particles with unequal diffusivities $D_2 < D_1$ on the interval $(0, L)$. (a) The original first-encounter problem is mapped onto anisotropic diffusion in a square $(0, L) \times (0, L)$ with diffusivities D_1 and D_2 along coordinates x_1 and x_2 . The condition $x_1 > x_2$ restricts the starting point to the isosceles right triangle (gray region). (b) In new variables $y_1 = x_1$ and $y_2 = x_2\sqrt{D_1/D_2}$, this problem is equivalent to isotropic diffusion in the right triangle with legs $(0, L_1)$ and $(0, L_2)$, where $L_1 = L$ and $L_2 = L\sqrt{D_1/D_2}$. The larger angle of the triangle is $\Theta = \text{atan}(L_2/L_1) = \text{atan}(\sqrt{D_1/D_2})$. Neumann (N) boundary condition is imposed on both legs, whereas Dirichlet (D) boundary condition is imposed on the hypotenuse. (c) Due to the reflection symmetry of the ground eigenfunction of the Laplace operator, the smallest Laplacian eigenvalue λ_{\min} in the above triangle can be determined from that in the rhombus with the size $\ell = \sqrt{L_1^2 + L_2^2}$ and the acute angle $\alpha = \pi - 2\Theta$, where a Dirichlet boundary condition is imposed on all edges.

determines the decay time T ,

$$T(D_1, D_2) = \frac{1}{D_1 \lambda_{\min}(D_1, D_2)}. \quad (61)$$

Unfortunately, the eigenvalues and eigenfunctions of the Laplace operator are not known for arbitrary right triangles.

However, the limiting case of one slowly diffusing particle, $D_2 \ll D_1$, can be worked out. Note that, in this case, one deals with strongly elongated triangles. Due to Neumann boundary conditions on the two legs, the original right triangle can be quadrupled by double reflection along each leg, yielding a rhombus with absorbing boundary condition on all four sides. This operation does not change the smallest eigenvalue. As $D_2 \ll D_1$, the obtuse angle 2Θ of the rhombus is close to π , whereas the acute angle $\alpha = 2\Theta_0 = \pi - 2\Theta = 2 \text{atan}(\sqrt{D_2/D_1})$ is small. In Ref. [102], the following asymptotic behavior for the smallest eigenvalue was derived:

$$\lambda_{\min} \simeq \frac{\pi^2}{\ell^2 \alpha^2} \left[1 - \frac{2^{2/3} a'_1}{\pi^{2/3}} \alpha^{2/3} + O(\alpha^{4/3}) \right], \quad (62)$$

where ℓ is the side length, $\alpha \ll 1$ is the angle, and $a'_1 \approx -1.0188$ is the first zero of the derivative of the Airy function. In our setting, $\ell^2 = L_1^2 + L_2^2 = L^2(1 + D_1/D_2)$ and $\alpha = 2\Theta_0$ so that

$$\lambda_{\min} \simeq \frac{\pi^2}{4L^2(1 + D_2/D_1)} \frac{D_2/D_1}{\text{atan}^2(\sqrt{D_2/D_1})} \times \left(1 - \frac{2^{4/3} a'_1}{\pi^{2/3}} \text{atan}^{2/3}(\sqrt{D_2/D_1}) + \dots \right). \quad (63)$$

Expectedly, the smallest eigenvalue multiplied by L^2 is just a function of D_2/D_1 . As a consequence, the decay time reads

$$T(D_1, D_2) \simeq \frac{4L^2}{\pi^2 D_1} \frac{(D_1 + D_2) \operatorname{atan}^2(\sqrt{D_2/D_1})}{D_2} \times \left(1 + \frac{2^{4/3} a'_1}{\pi^{2/3}} \operatorname{atan}^{2/3}(\sqrt{D_2/D_1}) + \dots \right). \quad (64)$$

In the limit $D_2 \rightarrow 0$, the decay time approaches a constant, $T(D_1, 0^+) = 4L^2/(\pi^2 D_1)$. We emphasize that this limit is different from the one obtained in the case of a static target fixed at x_2 and a particle diffusing on the interval (x_2, L) , for which the decay time is $T(D_1, 0) = 4(L - x_2)^2/(\pi^2 D_1)$. In other words, the limit $D_2 \rightarrow 0$ is singular, i.e.,

$$\lim_{D_2 \rightarrow 0} T(D_1, D_2) = T(D_1, 0^+) \neq T(D_1, 0). \quad (65)$$

In fact, even when D_2 is very small but strictly positive, the memory of the starting position x_2 of the slow particle is lost in the long-time limit, implying that x_2 does not influence the timescale of the slowest decaying mode. In this respect, the decay time $T(D_1, D_2)$ is considerably different from the mean FET, which depends on both starting point x_1 and x_2 , see Fig. 5.

Figure 7(a) shows the behavior of the smallest eigenvalue λ_{\min} as a function of D_2/D_1 . At $D_2 = D_1$, we recover the square case considered in Sec. IV A, with $L^2 \lambda_{\min} = \pi^2$. In turn, as D_2 decreases, $L^2 \lambda_{\min}$ also decreases and reaches the value $\pi^2/4$. One can see that the asymptotic Eq. (63) accurately captures the behavior of λ_{\min} for $D_2/D_1 \lesssim 0.01$. It is worth noting that the next-order correction term appearing in the second line of Eq. (63) is necessary because the leading term alone (dashed line) fails to reproduce well the behavior. Figure 7(b) further illustrates that $T(D_1, D_2)$ is not a function of $D_1 + D_2$ alone (as in the free case) but depends on both D_1 and D_2 in a more intricate fashion.

V. CONCLUSIONS

In this paper, we investigated the impact of confinement on the FET distribution for two diffusing particles. In spite of the practical importance of this problem in chemical physics and related disciplines, it has received little attention in comparison with other first-passage problems, even for one-dimensional systems. We focused on two settings: a half-line and an interval. In the half-line case, the survival probability $S(t|x_1, x_2)$ and the related probability density $H(t|x_1, x_2)$ of the FET were already formally known, but had not been studied in detail, in particular in the short-time limit. We thus carried out a thorough analysis of both short- and long-time asymptotic behaviors, as well as a comparison with the free case (without reflecting endpoint at the origin). In addition, we derived and discussed the behavior of the mean FET and its variance.

The case of an interval was even less studied. Both $S(t|x_1, x_2)$ and $H(t|x_1, x_2)$, as well as the moments of the FET, can be written in terms of explicit spectral expansions in the case of equal diffusivities. We compared the mean FET and its standard deviation to quantify the role of fluctuations of the FET. We also compared the behavior for two particles with the

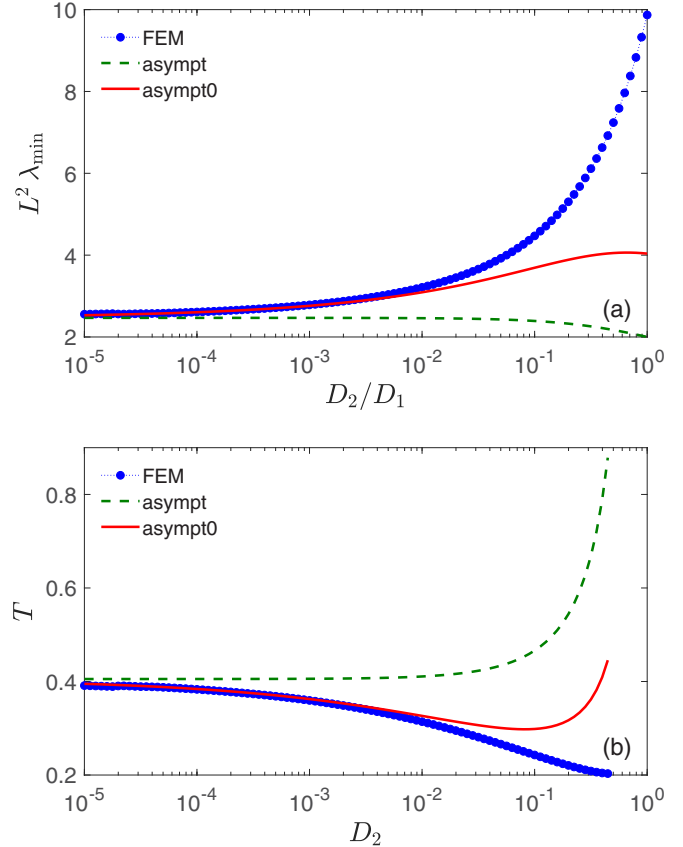


FIG. 7. (a) Smallest eigenvalue of the diffusion operator as a function of D_2/D_1 for two particles diffusing on an interval $(0, L)$ with diffusivities D_1 and D_2 . Filled circles show the eigenvalue obtained numerically by a finite element method in Matlab PDEtool, whereas solid and dashed lines represent the asymptotic Eq. (63), with and without the subdominant term, respectively. (b) Associated decay time T vs. D_2 as obtained from Eq. (61) for $D_1 + D_2 = 1$ and $L = 1$.

problem of a diffusing particle in a sea of diffusing traps, and found a faster decay of the survival probability in the former case. Finally, we investigated the case of unequal diffusivities in the limit $D_2 \ll D_1$. First, we checked the quality of the asymptotic approximation for the mean FET reported in Ref. [78]. Second, we obtained another asymptotic relation for the decay time characterizing the survival probability and the probability density in the long-time limit.

As shown by our results, geometric confinement implies the onset of additional time scales associated with the diffusion times of the particles to the reflecting boundaries. Even in the case of a single boundary, subtle effects emerge, e.g., the FET probability density may be peaked at times earlier or later than in the free case depending on the parameter choice. In the case when particle 1 diffuses slowly, the mean FET is equal to the mean FPT for a single particle with diffusivity $D_2 - D_1$ moving between the origin and an absorbing point at x_1 , but the variances are different. In the presence of two boundaries (an interval), fluctuations of the FET can also be important. Moreover, we showed that the mean FET and the decay time are different and exhibit sophisticated dependences on both diffusivities D_1 and D_2 . This observation breaks a common

intuitive thought, inspired by the free case, that only $D_1 + D_2$ matters. Finally, we illustrated that the limit $D_2 \rightarrow 0$ is singular by deriving the asymptotic behavior of the decay time. In other words, the long-time behavior of the survival probability is different for an immobile target ($D_2 = 0$) and for a very slowly diffusing target ($D_2 \approx 0$). This observation may question common assumptions of static targets in biological systems, in which everything is moving.

As we have seen, the additional scales introduced by boundaries result in the onset of very rich behavior and drastic modifications with respect to the free case. Even in simple settings, it is often not possible to obtain exact analytic results, as exemplified by the computation of the dominant decay mode in the interval problem. From a broader perspective, a variety of processes (fluorescence, phosphorescence, and luminescence quenching, reactions of solvated electrons, proton transfer, radical recombination reactions, enzyme-ligand interactions, etc.) have been shown to display reaction rates that are often of the same order of magnitude as the predictions of Smoluchowski's theory [1,2], but still display important deviations. Assessing the role of boundary effects in some of these systems may help to better quantify these discrepancies.

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APPENDIX A: COMPLETENESS OF THE EIGENBASIS FOR THE ISOSCELES RIGHT TRIANGLE

In this Appendix, we prove that the Laplacian eigenbasis used in Sec. IV A is complete. Even though this result should be known, we could not find its proof in the literature.

The starting point of the proof is the fact that the functions

$$\phi_{n_1 n_2}(x_1, x_2) = c_{n_1 n_2} \cos(\pi n_1 x_1 / L) \cos(\pi n_2 x_2 / L), \quad (A1)$$

$$(n_1, n_2 = 0, 1, 2, \dots),$$

with Eq. (43), form a complete set of (orthonormal) eigenfunctions of the Laplace operator on a square of side L with reflecting boundaries. In other words, any square-integrable function f on the square can be decomposed in this basis:

$$f(x_1, x_2) = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} b_{n_1 n_2} \phi_{n_1 n_2}(x_1, x_2), \quad (A2)$$

where

$$b_{n_1 n_2} = \langle \phi_{n_1 n_2} | f \rangle = \int_0^L \int_0^L \phi_{n_1 n_2}(x_1, x_2) f(x_1, x_2) dx_1 dx_2. \quad (A3)$$

Let us now assume that f has the symmetry $f(x_1, x_2) = -f(x_2, x_1)$. This symmetry has the following implications for the values of the Fourier coefficients $b_{n_1 n_2}$:

(i) $b_{nn} = 0$. In fact, by definition

$$b_{nn} = \langle \phi_{nn} | f \rangle = \frac{2}{L} \int_0^L \int_0^L F(x_1, x_2) dx_1 dx_2, \quad (A4)$$

where, for $n \neq 0$,

$$F(x_1, x_2) = \cos(\pi n x_1 / L) \cos(\pi n x_2 / L) f(x_1, x_2). \quad (A5)$$

But note that, due to the symmetry of f , $F(x_1, x_2) = -F(x_2, x_1)$. This implies that the integral $\int_0^L \int_0^L F(x_1, x_2) dx_1 dx_2$ over the lower triangle $\Omega = \{0 \leq x_1 \leq L, 0 \leq x_2 \leq x_1\}$ is equal (but with opposite sign) to the integral over the upper triangle $\bar{\Omega} = \{0 \leq x_1 \leq L, 0 \leq x_1 \leq x_2\}$. Therefore, $b_{nn} = 0$. The proof for $n = 0$ is straightforward.

(ii) $b_{n_1 n_2} = -b_{n_2 n_1}$. In fact, by definition

$$b_{n_2 n_1} = \frac{2}{L} \int_0^L \int_0^L \cos(\pi n_2 x_1 / L) \cos(\pi n_1 x_2 / L) f(x_1, x_2) dx_1 dx_2 \quad (A6)$$

or, using the property $f(x_1, x_2) = -f(x_2, x_1)$,

$$b_{n_2 n_1} - \frac{2}{L} \int_0^L \int_0^L \cos(\pi n_1 x_2 / L) \times \cos(\pi n_2 x_1 / L) f(x_2, x_1) dx_2 dx_1 = -b_{n_1 n_2}. \quad (A7)$$

This is also true if $n_1 = 0$ or $n_2 = 0$.

Using the results $b_{n_1 n_2} = -b_{n_2 n_1}$ and $b_{nn} = 0$, one finds that any function $f(x_1, x_2)$ with the property $f(x_1, x_2) = -f(x_2, x_1)$ can be uniquely represented in terms of the eigenfunctions $u_{n_1, n_2}(x_1, x_2) = \phi_{n_1 n_2}(x_1, x_2) - \phi_{n_2 n_1}(x_1, x_2)$ with $0 \leq n_1 < n_2$. Note, however, that the property $f(x_1, x_2) = -f(x_2, x_1)$ does not imply any restriction on the value of f on the lower triangle Ω . Thus, any square-integrable function $f(x_1, x_2)$ defined on Ω can be uniquely represented in terms of the eigenfunctions $u_{n_1, n_2}(x_1, x_2) = \phi_{n_1 n_2}(x_1, x_2) - \phi_{n_2 n_1}(x_1, x_2)$ with $0 \leq n_1 < n_2$. In other words, $u_{n_1, n_2}(x_1, x_2)$ with $0 \leq n_1 < n_2$ form a complete set of Laplacian eigenfunctions on Ω .

APPENDIX B: MFET FOR THE INTERVAL

In this Appendix, we present a lengthy and technical derivation of the mean FET of two particles diffusing with equal diffusivities on the interval $(0, L)$ with reflecting endpoints. We start by rewriting Eq. (51) explicitly as

$$\langle \mathcal{T}^k \rangle = C_k \sum_{n_1=0}^{\infty} \sum_{n_2 > n_1}^{\infty} \frac{1 - (-1)^{n_1 + n_2}}{(1 + \delta_{n_1, 0})(\alpha_{n_2}^2 - \alpha_{n_1}^2)(\alpha_{n_1}^2 + \alpha_{n_2}^2)^k} \times [\cos(\alpha_{n_1} x_1) \cos(\alpha_{n_2} x_2) - \cos(\alpha_{n_1} x_2) \cos(\alpha_{n_2} x_1)],$$

where $\alpha_n = \pi n$, $C_k = 8(k!)(L^2/D_1)^k$, and we rescaled x_1 and x_2 by L for shorter notations. Note that here we have assumed that $x_1 \geq x_2$. As this expression is antisymmetric with respect to the exchange $x_1 \leftrightarrow x_2$, one would need to change the sign for $x_1 < x_2$.

We first separate the term with $n_1 = 0$, for which we get

$$S_k^{(0)} = \frac{C_k}{2} \sum_{n_2=1}^{\infty} \frac{1 - (-1)^{n_2}}{\alpha_{n_2}^{2(k+1)}} [\cos(\alpha_{n_2} x_2) - \cos(\alpha_{n_2} x_1)]. \tag{B1}$$

We use the summation identities [92]

$$\sum_{n=1}^{\infty} \frac{\cos(\alpha_n x)}{s + \alpha_n^2} = \frac{\cosh(\sqrt{s}(1-x))}{2\sqrt{s} \sinh(\sqrt{s})} - \frac{1}{2s}, \tag{B2a}$$

$$\sum_{n=1}^{\infty} \frac{\cos(\alpha_n x)(-1)^n}{s + \alpha_n^2} = \frac{\cosh(\sqrt{s}x)}{2\sqrt{s} \sinh(\sqrt{s})} - \frac{1}{2s}, \tag{B2b}$$

to compute

$$F(s, x) = \sum_{n=1}^{\infty} \frac{(1 - (-1)^n) \cos(\alpha_n x)}{s + \alpha_n^2} = \frac{\cosh(\sqrt{s}(1-x)) - \cosh(\sqrt{s}x)}{2\sqrt{s} \sinh(\sqrt{s})}. \tag{B3}$$

Evaluating the k th derivative of this identity at $s = 0$, one gets

$$S_k^{(0)} = \frac{C_k (-1)^k}{2(k!)} \lim_{s \rightarrow 0} \frac{\partial^k [F(s, x_2) - F(s, x_1)]}{\partial s^k}. \tag{B4}$$

Now we switch to the evaluation of the double sum with $n_1 > 0$ and $n_2 > n_1$:

$$S_k^{(1)} = \frac{C_k}{2} \sum_{n_1=1}^{\infty} \sum_{n_2 \neq n_1} \frac{1 - (-1)^{n_1+n_2}}{\alpha_{n_2}^2 - \alpha_{n_1}^2} \frac{1}{(\alpha_{n_1}^2 + \alpha_{n_2}^2)^k} \times [\cos(\alpha_{n_1} x_1) \cos(\alpha_{n_2} x_2) - \cos(\alpha_{n_1} x_2) \cos(\alpha_{n_2} x_1)],$$

where we have employed the symmetry of the summand expression with respect to the exchange $n_1 \leftrightarrow n_2$ to symmetrize the second sum. Our goal is to evaluate exactly the second sum over n_2 :

$$W_{k, n_1} = \sum_{n_2 \neq n_1} \frac{1 - (-1)^{n_1+n_2}}{\alpha_{n_2}^2 - \alpha_{n_1}^2} \frac{1}{(\alpha_{n_1}^2 + \alpha_{n_2}^2)^k} \times [\cos(\alpha_{n_1} x_1) \cos(\alpha_{n_2} x_2) - \cos(\alpha_{n_1} x_2) \cos(\alpha_{n_2} x_1)],$$

so that

$$S_k^{(1)} = \frac{C_k}{2} \sum_{n_1=1}^{\infty} W_{k, n_1}. \tag{B5}$$

For this purpose, we evaluate the following sum:

$$U_k(s, x) = \sum_{n=1}^{\infty} \frac{\cos(\alpha_n x)(-1)^n}{(\alpha_n^2 - s)(\alpha_n^2 + s)^k}.$$

Using the identity

$$\frac{1}{(\alpha_n^2 - s)(\alpha_n^2 + s)^k} = \frac{(2s)^{-k}}{(\alpha_n^2 - s)} - \sum_{j=1}^k \frac{(2s)^{j-k-1}}{(\alpha_n^2 + s)^j}, \tag{B6}$$

we can evaluate this sum with the help of Eq. (B2b):

$$U_k(s, x) = \frac{1}{(2s)^k} \left[-\frac{\cos(\sqrt{s}x)}{2\sqrt{s} \sinh(\sqrt{s})} + \frac{1}{2s} \right]$$

$$- \sum_{j=0}^{k-1} (2s)^{j-k} \frac{(-1)^j}{j!} \frac{\partial^j}{\partial s^j} \left[\frac{\cosh(\sqrt{s}x)}{2\sqrt{s} \sinh(\sqrt{s})} - \frac{1}{2s} \right] = \frac{1}{2s^{k+1}} - \frac{1}{(2s)^k} \frac{\cos(\sqrt{s}x)}{2\sqrt{s} \sinh(\sqrt{s})} - \sum_{j=0}^{k-1} (2s)^{j-k} \frac{(-1)^j}{j!} \frac{\partial^j}{\partial s^j} \frac{\cosh(\sqrt{s}x)}{2\sqrt{s} \sinh(\sqrt{s})}.$$

Now we can come back to the sum W_{n_1} , which can be split into four terms:

$$W_{k, n_1} = \cos(\alpha_{n_1} x_1) [V_{k, n_1}^{(1)}(x_2) - (-1)^{n_1} V_{k, n_1}^{(2)}(x_2)] - \cos(\alpha_{n_1} x_2) [V_{k, n_1}^{(1)}(x_1) - (-1)^{n_1} V_{k, n_1}^{(2)}(x_1)],$$

where

$$V_{k, n_1}^{(1)}(x) = \sum_{n_2 \neq n_1} \frac{\cos(\alpha_{n_2} x)}{(\alpha_{n_2}^2 - \alpha_{n_1}^2)(\alpha_{n_1}^2 + \alpha_{n_2}^2)^k}, \tag{B7}$$

$$V_{k, n_1}^{(2)}(x) = \sum_{n_2 \neq n_1} \frac{\cos(\alpha_{n_2} x)(-1)^{n_2}}{(\alpha_{n_2}^2 - \alpha_{n_1}^2)(\alpha_{n_1}^2 + \alpha_{n_2}^2)^k}. \tag{B8}$$

These sums can be evaluated by using $U_k(s)$. In fact, replacing $\alpha_{n_1}^2$ with s in the above expressions, one can first evaluate these sums for $s \neq \alpha_{n_1}^2$ by adding and subtracting the term $n_2 = n_1$, and then take the limit $s \rightarrow \alpha_{n_1}^2$:

$$V_{k, n_1}^{(1)}(x) = \lim_{s \rightarrow \alpha_{n_1}^2} \left[U_k(s, 1-x) - \frac{\cos(\alpha_{n_1} x)}{(\alpha_{n_1}^2 - s)(s + \alpha_{n_1}^2)^k} \right],$$

$$V_{k, n_1}^{(2)}(x) = \lim_{s \rightarrow \alpha_{n_1}^2} \left[U_k(s, x) - \frac{\cos(\alpha_{n_1} x)(-1)^{n_1}}{(\alpha_{n_1}^2 - s)(s + \alpha_{n_1}^2)^k} \right].$$

The subtracted term removes the singularity in $U_k(s, 1-x)$ and $U_k(s, x)$ as $s \rightarrow \alpha_{n_1}^2$. This completes our formal evaluation of the moment $\langle \mathcal{T}^k \rangle$, which is just the sum of $S_k^{(0)}$ and $S_k^{(1)}$ given above.

Let us apply this general evaluation to get the mean FET $\langle \mathcal{T} \rangle$. For $k = 1$, we have $C_1 = 8L^2/D_1$ and

$$S_1^{(0)} = \frac{4}{D_1} \left(\frac{x_2^3 - x_1^3}{12L} - \frac{x_2^2 - x_1^2}{8} \right). \tag{B9}$$

To evaluate the contribution $S_1^{(1)}$, we first find

$$U_1(s, x) = \frac{1}{4s} \left[\frac{2}{s} - \frac{\cos(\sqrt{s}x)}{\sqrt{s} \sinh(\sqrt{s})} - \frac{\cosh(\sqrt{s}x)}{\sqrt{s} \sinh(\sqrt{s})} \right]. \tag{B10}$$

Then we compute the limit

$$V_{1, n_1}^{(2)}(x) = \frac{1}{4\alpha_{n_1}^4} \left\{ 2 - \frac{\alpha_{n_1} \cosh(\alpha_{n_1} x)}{\sinh \alpha_{n_1}} + (-1)^{n_1} \left[\frac{3}{2} \cos(\alpha_{n_1} x) + x \alpha_{n_1} \sin(\alpha_{n_1} x) \right] \right\},$$

and $V_{1, n_1}^{(1)}(x) = V_{1, n_1}^{(2)}(1-x)$. Combining these results, we get

$$W_{1, n} = \frac{\cos(\alpha_n x_1) w_n(x_2) - \cos(\alpha_n x_2) w_n(x_1)}{4\alpha_n^4}, \tag{B11}$$

where

$$w_n(x) = 2[1 - (-1)^n] - \alpha_n \sin(\alpha_n x) - \frac{\alpha_n}{\sinh \alpha_n} \{ \cosh[\alpha_n(1-x)] - (-1)^n \cosh(\alpha_n x) \}.$$

As a consequence, the above expression allows one to split $S_1^{(1)}$ into three contributions:

$$S_1^{(1)} = S_1^{(1,1)} + S_1^{(1,2)} + S_1^{(1,3)},$$

where

$$S_1^{(1,1)} = \frac{C_1}{2} \sum_{n=1}^{\infty} \frac{(1 - (-1)^n)[\cos(\alpha_n x_1) - \cos(\alpha_n x_2)]}{2\alpha_n^4},$$

$$S_1^{(1,2)} = \frac{C_1}{2} \sum_{n=1}^{\infty} \frac{\sin[\alpha_n(x_1 - x_2)]}{4\alpha_n^3},$$

$$S_1^{(1,3)} = \frac{C_1}{2} \sum_{n=1}^{\infty} \frac{\cos(\alpha_n x_2)v_n(x_1) - \cos(\alpha_n x_1)v_n(x_2)}{4\alpha_n^3},$$

with

$$v_n(x) = \frac{\cosh[\alpha_n(1-x)] - (-1)^n \cosh(\alpha_n x)}{\sinh \alpha_n}. \quad (\text{B12})$$

Note that $S_1^{(1,1)} = -S_1^{(0)}/2$. The second sum can be easily computed by taking the derivative of Eq. (B2a) with respect to x and s and evaluating the limit $s \rightarrow 0$:

$$\sum_{n=1}^{\infty} \frac{\sin(\alpha_n x)}{\alpha_n^3} = \frac{x(1-x)(2-x)}{12}, \quad (\text{B13})$$

from which

$$S_1^{(1,2)} = \frac{(x_1 - x_2)(L - x_1 + x_2)(2L - x_1 + x_2)}{12D_1L}. \quad (\text{B14})$$

In summary, we conclude for $x_1 \geq x_2$ that

$$\langle \mathcal{T} \rangle = \frac{(x_1 - x_2)[2L^2 + 6x_2(L - x_1) - (x_1 - x_2)^2]}{12D_1L} + \frac{L^2}{D_1} \times \sum_{n=1}^{\infty} \frac{\cos(\alpha_n x_2/L)v_n(x_1/L) - \cos(\alpha_n x_1/L)v_n(x_2/L)}{\alpha_n^3},$$

with $v_n(x)$ given by Eq. (B12), and $\alpha_n = \pi n$. For $x_1 < x_2$, one just needs to exchange x_1 and x_2 .

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