

Interfacial territory covered by surface-mediated diffusion

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We consider a minimal model of heterogeneous catalysis in which a molecule performs surface-mediated diffusion inside a confining domain whose boundary contains catalytic sites. We explicitly take into account the combination of surface and bulk diffusion, and we obtain exact results for the mean and variance of the territory covered on the boundary by the particle before its exit in the case of a two-dimensional spherical domain. Depending on the relative positions of the entrance and exit points, very different behaviors with respect to the mean adsorption time of the molecule on the surface are found. We also determine both exact lower and upper bounds and an approximate expression of the probability of reacting with catalytic sites before exiting the domain. These results provide a quantitative measure of the efficiency of an idealized catalyst.

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I. INTRODUCTION

The territory covered by a diffusing particle is a key quantity of random walk theory, which has been the subject of a large number of works in various fields, ranging from physics and chemistry to ecology [1]. Interest in this observable comes mainly from its relation to the so-called Rosenstock trapping problem, where a random walk takes place in a medium containing a fraction q of immobile randomly distributed reactive sites, which trap the walker upon encounter [2]. Explicitly, the probability P_n that the walker has not been trapped along a given trajectory of n steps is written as $(1 - q)^{S_n}$, where S_n stands for the number of distinct sites visited after n steps and provides a direct measure of the territory covered by the walker. While the determination of the full distribution of S_n in dimension higher than 1 is a very difficult task, the mean and the leading behavior of the variance have been obtained [1,3]. Important extensions include the calculation of the mean number of distinct sites visited by p independent walkers [4] or the determination of the asymptotic behavior of the mean number of distinct sites visited on fractal structures [5,6]. Note that the difficulties of the statistical analysis of S_n are essentially the same as for its continuous counterpart, known as the Wiener Sausage and defined as the volume swept by a spherical Brownian particle of nonzero radius after a given time t [7].

Besides, interfacial reactions, for which molecules react on target sites located on the surface of a confining domain [8], play an important role in situations as various as heterogeneous catalysis [9], reactions in porous media, or biochemical reactions on DNA [10] and in vesicular systems [11–13]. The trajectories involved in such reactions, combining bulk and surface-mediated diffusion phases, can now be observed at the single molecule scale [14]. At the theoretical level, surface-mediated diffusion has generated a growing attention these last years [15–21]. Importantly, it has been recently shown to minimize reaction times by a proper tuning of the desorption rate from the surface and could thus constitute a general mechanism of enhancement and regulation of chemical and biological reactivity [17,18].

In this article, we raise the question of the interfacial territory covered by such a surface-mediated diffusion before

exiting a confining domain (see Fig. 1). More precisely, in the representative example of a two-dimensional (2D) spherical confining domain, (i) we calculate exactly the mean and the variance of the territory \mathcal{C} covered on the sphere by a Brownian molecule alternating phases of bulk and surface diffusion before exiting the domain by a point-like aperture; (ii) we show that, depending on the respective positions of the entrance and exit points, very different behaviors with respect to the affinity of the molecule for the surface emerge; surprisingly enough, the optimization of the mean territory $\langle \mathcal{C} \rangle$ as a function of the mean adsorption time turns out to be markedly different from the minimization of the mean reaction time derived in [17]; (iii) we apply these results to a trapping problem, by giving exact bounds as well as an approximate expression of the probability to react with traps covering the boundary of the domain, before exit. This quantity provides a measure of the efficiency of an idealized catalyst. Note that the 2D spherical geometry is chosen because it enables exact analytical derivations. The case of a three-dimensional (3D) spherical geometry requires the introduction of an aperture of finite extension and does not allow for an exact treatment. However, we believe that the conclusions obtained in the 2D geometry are qualitatively robust and would hold in other geometries relevant to heterogeneous catalysis.

Besides this practical relevance in the context of heterogeneous catalysis, the theoretical analysis of this problem raises two important new issues: (i) contrarily to standard approaches that consider the covered territory S_n in an unbounded space at a deterministic observation time n , we consider the covered territory in a *confined* domain and at a *random* time N , which is the first exit time of the particle from the domain; (ii) we go beyond the standard Brownian motion and consider surface-mediated diffusion, whose theoretical description has been established only recently. The problem is therefore challenging since even the statistics of the stopping time N for surface-mediated diffusion is nontrivial, as shown in [17,18].

II. THE MODEL

As an archetype of confined interfacial systems, we consider a molecule inside a disk H of radius R (Fig. 1), alternating phases of surface diffusion on ∂H with diffusion coefficient

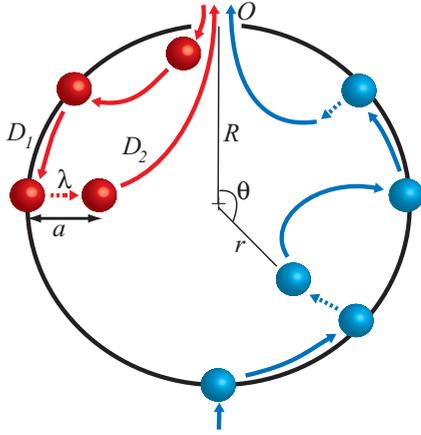


FIG. 1. (Color online) Model of surface-mediated diffusion in a confining domain, showing an example of a return trajectory (in red, left), for which the particle enters and exits the domain by the same point O . In the case of a crossing trajectory (in blue, right) the entrance point is opposite to the exit.

D_1 and phases of bulk diffusion inside H with diffusion coefficient D_2 . The time spent during each surface phase is assumed to follow an exponential law with the desorption rate λ , which is reminiscent of first-order kinetics. At each desorption event, the molecule is assumed to be radially ejected at a distance a from the surface (as otherwise it would be instantaneously readsorbed). Although formulated for any value of this parameter a smaller than R , in most situations of physical interest $a \ll R$. We assume that the molecule is instantaneously adsorbed on the surface upon encounter; the case of a radiative boundary condition used for instance in [21] can be easily incorporated but is not presented here for the sake of simplicity. The random variable we are interested in is the territory $\mathcal{C}(\mathbf{r}_S)$ covered on the boundary of the disk, ∂H , by a molecule started from the source point S , before exiting the domain through the pointlike aperture O . Note that the molecule can then exit the domain only during phases of surface diffusion. The territory $\mathcal{C}(\mathbf{r}_S)$ can be written as

$$\mathcal{C}(\mathbf{r}_S) = \int_{\partial H} I_O(\mathbf{r}_T | \mathbf{r}_S) d\mathbf{r}_T, \quad (1)$$

where $I_O(\mathbf{r}_T | \mathbf{r}_S)$ is the indicator function equal to 1 if the point T is reached by the molecule before exit and 0 otherwise. Since it does not depend on the time spent in bulk excursions, \mathcal{C} is clearly independent of the diffusion coefficient D_2 .

We will consider below two typical configurations that are relevant to heterogeneous catalysis: the case of crossing, in which particles enter the domain from the point opposite to the exit ($\theta = \pi$), and the case of return, where particles enter and exit the domain by the same zone ($\theta = 0$) (see Fig. 1). First, we show that simple conclusions can be obtained in the case of a uniform distribution of the entrance point.

III. MEAN TERRITORY COVERED BEFORE EXIT

By using the definition (1), the mean territory $\langle \mathcal{C}(\mathbf{r}_S) \rangle$ can be written as

$$\langle \mathcal{C}(\mathbf{r}_S) \rangle = \int_{\partial H} \Pi_O(\mathbf{r}_T | \mathbf{r}_S) d\mathbf{r}_T, \quad (2)$$

where the splitting probability $\Pi_O(\mathbf{r}_T | \mathbf{r}_S)$ is defined as the probability that the particle reaches a target point T on the surface ∂H of H before exiting the domain at O , starting from S . In the case of a uniform distribution of \mathbf{r}_S , or more generally any spherically symmetric distribution, this expression can be drastically simplified since the splitting probability averaged over the initial distribution reads, for symmetry reasons, as $\overline{\Pi_O(\mathbf{r}_T | \mathbf{r}_S)} = 1/2$. Finally, we obtain the very simple result

$$\langle \mathcal{C}(\mathbf{r}_S) \rangle = \pi R. \quad (3)$$

Quite unexpectedly, $\langle \mathcal{C}(\mathbf{r}_S) \rangle$ is therefore *independent* of λ . This is in strong contrast with the behavior of the mean first-passage time to the exit zone averaged over the initial distribution (sometimes referred to in the literature as the narrow escape time problem [13,16,22,23]), which can display a nonmonotonic behavior with the desorption rate λ [17,18].

We now turn to the case of a fixed entrance point, which leads to strikingly different behaviors. As shown in Eq. (2), the calculation of the mean territory requires the determination of the splitting probabilities. These splitting probabilities satisfy the following backward equations [24]:

$$\frac{D_1}{R^2} \frac{\partial^2}{\partial \theta^2} \Pi_1(\theta) + \lambda [\Pi_2(R - a, \theta) - \Pi_1(\theta)] = 0, \quad (4)$$

$$\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} \right) \Pi_2(r, \theta) = 0, \quad (5)$$

where $\Pi_1(\theta) \equiv \Pi_O(\mathbf{r}_T | \mathbf{r}_S \equiv (R, \theta))$ stands for the splitting probability for a particle started from the adsorbed state at a position defined on the surface by the polar angle θ , and $\Pi_2(r, \theta) \equiv \Pi_O(\mathbf{r}_T | \mathbf{r}_S \equiv (r, \theta))$ is the splitting probability for a particle started from the point (r, θ) in the bulk. In Eqs. (4) and (5), the first term stands for the diffusion, respectively, on the surface and in the bulk, while the second term in Eq. (4) describes desorption events. These equations have to be completed by the boundary conditions:

$$\Pi_2(R, \theta) = \Pi_1(\theta), \quad (6)$$

which describes the adsorption events, and

$$\Pi_1(0) = \Pi_1(2\pi) = 0, \quad \Pi_1(\theta_T) = 1, \quad (7)$$

which come from the very definition of the splitting probabilities, where $\theta_O \equiv 0$ and θ_T are the polar angles of O and T . Note that these boundary conditions involve two targets O and T , requiring us to deal separately with two intervals $[0, \theta_T]$ and $[\theta_T, 2\pi]$. Explicitly, by considering Π_2 as a source term in the Poisson-type Eq. (4), the solution for $\theta \in [0, \theta_T]$ can be written as

$$\begin{aligned} \Pi_1(\theta) = & \frac{\sinh \omega \theta}{\sinh \omega \theta_T} + \frac{\omega}{\sinh \omega \theta_T} \int_0^{\theta_T} \Pi_2(R - a, \theta') \\ & \times \sinh(\omega \min[\theta, \theta']) \sinh(\omega(\theta_T - \max[\theta, \theta'])) d\theta', \end{aligned} \quad (8)$$

where we have used the dimensionless variable $\omega \equiv R\sqrt{\lambda/D_1}$. Similarly, the solution for $\theta \in [\theta_T, 2\pi]$ is

$$\begin{aligned} \Pi_1(\theta) &= \frac{\sinh \omega(2\pi - \theta)}{\sinh \omega(2\pi - \theta_T)} + \frac{\omega}{\sinh \omega(2\pi - \theta_T)} \\ &\times \int_{\theta_T}^{2\pi} \Pi_2(R - a, \theta') \sinh(\omega(\min[\theta, \theta'] - \theta_T)) \\ &\times \sinh(\omega(2\pi - \max[\theta, \theta'])) d\theta'. \end{aligned} \quad (9)$$

At the same time, Eq. (5) is easily shown to be satisfied by the following Fourier series:

$$\Pi_2(r, \theta) = \alpha_0 + \sum_{n=1}^{\infty} \left(\frac{r}{R}\right)^n [\alpha_n \cos(n\theta) + \beta_n \sin(n\theta)], \quad (10)$$

with unknown coefficients α_n and β_n . Substituting Eq. (10) into Eqs. (8) and (9), using the boundary condition (6), and projecting onto the functions $\cos(n\theta)$ and $\sin(n\theta)$ lead to an infinite hierarchy of equations for α_n and β_n , $n \in \mathbb{N}$, which can be decoupled. Lengthy but standard calculations lead finally to

$$\begin{aligned} \Pi_2(r, \theta) &= \frac{1}{2} + T(\theta_T) \sum_{n=1}^{\infty} \frac{(r/R)^n}{(1 - k_n)(\omega^2 + n^2)} \\ &\times \sin\left(n \frac{\theta_T}{2}\right) \sin\left[n \left(\theta - \frac{\theta_T}{2}\right)\right], \end{aligned} \quad (11)$$

where

$$\begin{aligned} T(\theta_T) &\equiv \frac{g(\theta_T)}{1 - g(\theta_T) \sum_{n \geq 1} \frac{k_n \cos n\theta_T - 1}{1 - k_n} \frac{1}{\omega^2 + n^2}}, \\ g(\theta_T) &\equiv \omega \frac{\sinh \omega\theta_T + \sinh \omega(2\pi - \theta_T) + \sinh 2\pi\omega}{\pi \sinh \omega\theta_T \sinh \omega(2\pi - \theta_T)}, \\ k_n &\equiv x^n \frac{\omega^2}{\omega^2 + n^2}, \quad \text{and } x \equiv 1 - \frac{a}{R}. \end{aligned} \quad (12)$$

Several comments are in order. (i) As expected, both limits $\lambda \rightarrow 0$ (i.e., $\omega \rightarrow 0$) and $a \rightarrow 0$ of the splitting probability when starting from the absorbed state are given by a piecewise linear function, which corresponds to pure one-dimensional (1D) diffusion, without unbinding [24]. (ii) The limit $\lambda \rightarrow \infty$ leads to the uniform probability $1/2$: indeed the molecule stays an infinitely short time bound to the surface and is unable to reach any target by 1D diffusion. (iii) In the specific case of a uniform distribution of the entrance point, it can be checked from Eq. (11) that the splitting probability is equal to $1/2$, in agreement with the general result (3). (iv) The limit $a \rightarrow R$ corresponds actually to rebinding positions uniformly distributed on the surface and leads to the simple expression

$$\Pi_2(r, \theta) = \frac{1}{2} + g(\theta_T) \sum_{n=1}^{\infty} \frac{(r/R)^n}{\omega^2 + n^2} \sin n \frac{\theta_T}{2} \sin n \left(\theta - \frac{\theta_T}{2}\right), \quad (13)$$

where the second term stands for the splitting probability before the first desorption, whereas the first term stands for a perfect redistribution after the first desorption event. This regime can be seen as a mean-field approximation of the problem, which could be related to the approach developed

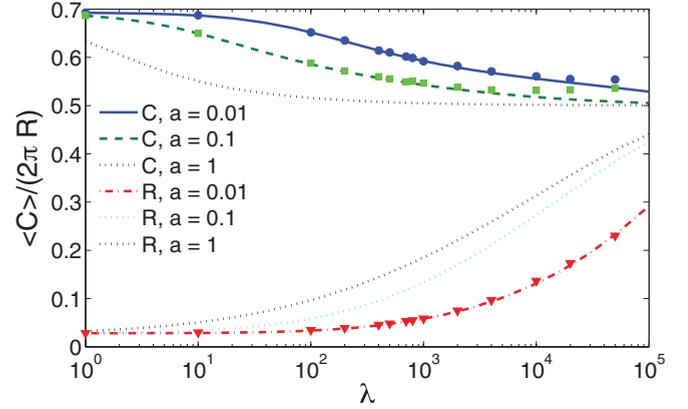


FIG. 2. (Color online) The normalized mean covered territory as a function of the desorption rate λ , with $D_1 = 1$ (arb. units), $R = 1$ (arb. units) for both crossing [C, starting point = $(r = R, \theta = \pi)$] and return [R, starting point = $(r = 0.99, \theta = 0)$] cases. Exact results (lines) are compared to Monte Carlo numerical simulations (symbols). The case $a = 1$ corresponds to the mean-field approximation obtained from (13).

in [16,25–27]; we stress that it is found here to substantially deviate from the exact result, which shows that the correlations induced by bulk excursions cannot be neglected (see Fig. 2).

Finally, the exact result (11) together with Eq. (2) provides an explicit expression of the mean territory $\langle \mathcal{C}(\mathbf{r}_S) \rangle$. Importantly, this result shows that the mean territory displays very different dependencies on λ controlled by the position of the starting point \mathbf{r}_S [see Figs. 2 and 3(a)]. In the case of crossing when the particle starts from a point $(r, \theta) = (R, \pi)$ opposite to the exit, the mean territory $\langle \mathcal{C}(\mathbf{r}_S) \rangle$ is a monotonically decreasing function of the desorption rate λ . In the opposite case of return when the particle enters and exits the domain by the same zone [the starting point being $(r, \theta) = (R - a, 0)$, with $a \ll R$], $\langle \mathcal{C}(\mathbf{r}_S) \rangle$ is, in contrast, a monotonically increasing function of λ . Last, quite remarkably, one can show that $\langle \mathcal{C}(\mathbf{r}_S) \rangle$ can also be nonmonotonic and present a maximum as a function of λ , for a specific region of starting points roughly located around $\theta = \pi/2$. The corresponding starting zone is shown in Fig. 3(b). These various behaviors can be intuitively understood as follows. In the case of return, at low desorption rate λ , trajectories are likely to be very short and localized in the neighborhood of the entrance and exit zone O . Increasing λ then favors longer trajectories away from O and therefore increases $\langle \mathcal{C}(\mathbf{r}_S) \rangle$. On the other hand, in the case of crossing, a low desorption rate implies long trajectories along the boundary to reach the exit, and increasing λ reduces $\langle \mathcal{C}(\mathbf{r}_S) \rangle$ by favoring bulk excursions. The combination of both effects for intermediate points yields the nonmonotonic variation. Such behaviors will have important consequences in the context of heterogeneous catalysis, as discussed below.

IV. FLUCTUATIONS OF THE TERRITORY COVERED BEFORE EXIT

The previous analysis can be extended to study the fluctuations of \mathcal{C} . In fact, it is easily seen from (1) that the second moment $\langle \mathcal{C}^2 \rangle$ can also be written in terms of splitting

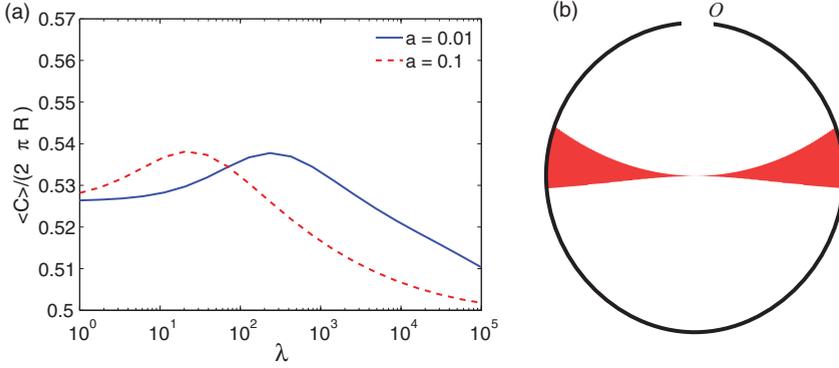


FIG. 3. (Color online) (a) The normalized mean covered territory (exact result) as a function of the desorption rate λ , with $D_1 = 1$ (arb. units), $R = 1$ (arb. units) for the starting point $(r = R, \theta = 1.38)$. (b) Map of the starting positions (in red) leading to optimization of the mean covered territory as a function of the desorption rate λ .

probabilities:

$$\langle C^2(\mathbf{r}_S) \rangle = 2 \int_{\partial H^2} \Pi_{O, T_1}(\mathbf{r}_{T_2} | \mathbf{r}_{T_2}) \Pi_{O, T_1}(\mathbf{r}_{T_2} | \mathbf{r}_S) d\mathbf{r}_{T_1} d\mathbf{r}_{T_2}, \quad (14)$$

where $\Pi_{O, T_1}(\mathbf{r}_{T_2} | \mathbf{r}_S)$ stands for the probability of reaching the target T_2 before O and T_1 , starting from S . Actually, these three-target splitting probabilities can be calculated and shown to be expressed conveniently in terms of the mean first-passage times t_{ji} from i to j , whose expression is given in [18] [see Eqs. (5), (10), and (11) with $\epsilon = 0$]:

$$\begin{aligned} \Pi_{T_2, T_3}(T_1 | S) &= [(t_{2S} - t_{3S})(t_{12} - t_{13}) \\ &\quad + t_{23}(t_{23} + 2t_{1S} - t_{13} - t_{12} - t_{2S} - t_{3S})] \\ &\quad \times \frac{1}{t_{23}^2 + t_{12}^2 + t_{13}^2 - 2(t_{13}t_{12} + t_{23}t_{12} + t_{23}t_{13})}. \end{aligned} \quad (15)$$

The final analytical expression for $\langle C^2(\mathbf{r}_S) \rangle$, not shown for the sake of simplicity, yields the reduced variance of the territory \mathcal{C} , which is plotted in Fig. 4 in both cases of crossing and return. Importantly, this shows that the fluctuations are much larger in the case of return than in the case of crossing; moreover, in this latter case, the fluctuations are found to only weakly depend

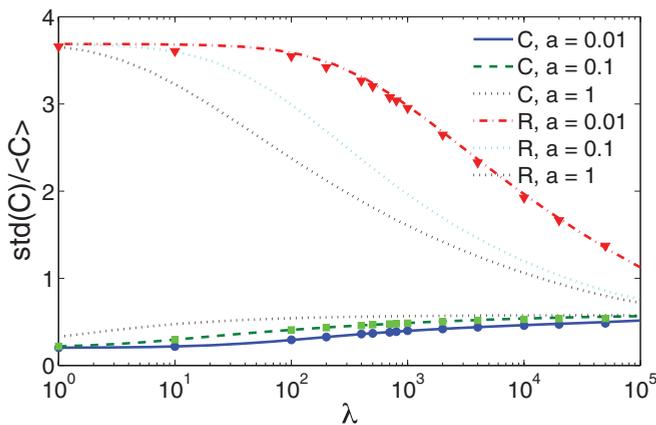


FIG. 4. (Color online) The normalized standard deviation of \mathcal{C} as a function of the desorption rate λ , with $D_1 = 1$ (arb. units), $R = 1$ (arb. units) for both crossing [C, starting point = $(r = R, \theta = \pi)$] and return [R, starting point = $(r = 0.99, \theta = 0)$] cases. Exact results (lines) are compared to Monte Carlo numerical simulations (symbols).

on λ . The large fluctuations in the case of return originate from the significant probability of extremely short trajectories that exit the domain within their first interfacial excursion.

V. PROBABILITY OF REACTION

We now turn to applications to heterogeneous catalysis and assume that the surface of the domain S is covered by pointlike catalytic sites, distributed according to a Poisson law of density μ . We then consider as above a reactive particle which enters the domain at a specific point, performs surface-mediated diffusion, and can irreversibly react with the catalytic sites. The above analysis enables the determination of both rigorous lower and upper bounds and an accurate approximation of the probability \mathcal{P} that reaction occurs before the reactive particle exits the domain. We start from the well-known expression $\mathcal{P}(\mathbf{r}_S) = \langle 1 - e^{-\mu \mathcal{C}(\mathbf{r}_S)} \rangle$ [1]. First, by using convexity inequalities, this yields the exact bounds

$$\mu \langle \mathcal{C}(\mathbf{r}_S) \rangle - \frac{1}{2} \mu^2 \langle \mathcal{C}^2(\mathbf{r}_S) \rangle \leq \mathcal{P}(\mathbf{r}_S) \leq 1 - e^{-\mu \langle \mathcal{C}(\mathbf{r}_S) \rangle}, \quad (16)$$

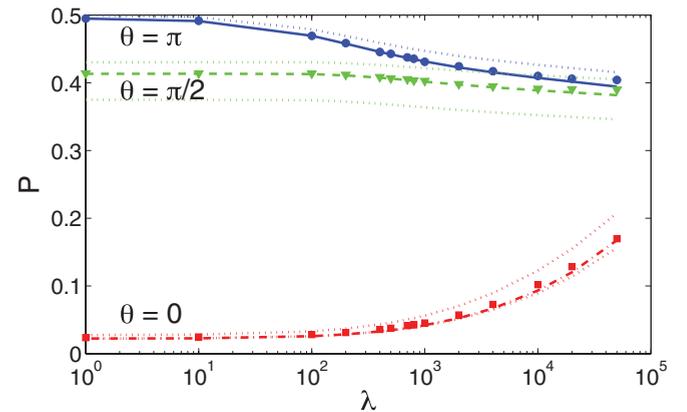


FIG. 5. (Color online) The reaction probability \mathcal{P} as a function of the desorption rate λ , with $D_1 = 1$ (arb. units), $R = 1$ (arb. units), $a/R = 0.1$, and $\mu = 1$ (arb. units). The three sets of curves correspond, respectively, to three starting points: $(r, \theta) = (R, \pi)$ (upper set, blue), $(r, \theta) = (R, \pi/2)$ (middle set, green), and $(r, \theta) = (R - a, 0)$ (lower set, red). Numerical simulations (symbols) are compared to the cumulant approximation (17) (thick lines), while dotted lines represent the exact upper and lower bounds (16).

where $\langle \mathcal{C}(\mathbf{r}_S) \rangle$ and $\langle \mathcal{C}^2(\mathbf{r}_S) \rangle$ are determined explicitly above. Second, the standard cumulant approximation [1,28] yields

$$\mathcal{P}(\mathbf{r}_S) \simeq 1 - \exp\left(-\mu \langle \mathcal{C}(\mathbf{r}_S) \rangle + \frac{\mu^2}{2} (\langle \mathcal{C}^2(\mathbf{r}_S) \rangle - \langle \mathcal{C}(\mathbf{r}_S) \rangle^2)\right), \quad (17)$$

which can be written explicitly using the results above. This last expression provides a quantitative measure of the efficiency of an idealized catalyst. In turn, it yields the minimal catalyst density μ required to ensure a given reaction probability \mathcal{P} . In both cases of crossing and return, the cumulant approximation yields a very good estimate for the reaction probability, at least for low catalytic sites density (see Fig. 5). In the case of crossing, the highest catalytic efficiency is obtained for small desorption rate λ , in strong contrast with the case of return, for which the highest catalytic efficiency is obtained for high λ . This shows that the geometry of a catalytic domain can deeply impact its efficiency, as quantified by our approach.

VI. CONCLUSION

In conclusion, we have considered a minimal model of heterogeneous catalysis in which a molecule performs surface-mediated diffusion inside a confining domain whose boundary contains catalytic sites. Exact results for the mean and variance of the covered territory on the boundary by the particle before its exit have been obtained in the case of a 2D spherical domain. We have shown that, depending on the relative positions of the entrance and exit points, very different behaviors with respect to the mean adsorption time of the molecule on the surface emerge. We also determined both exact bounds and an approximate expression of the probability of reacting with catalytic sites before exiting the domain. This quantity provides a measure of the efficiency of an idealized catalyst.

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