Trapping of diffusing particles by short absorbing spikes periodically protruding from reflecting base

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We study trapping of diffusing particles by a periodic non-uniform boundary formed by absorbing spikes protruding from a reflecting flat base. It is argued that such a boundary can be replaced by a flat uniform partially absorbing boundary with a properly chosen effective trapping rate. Assuming that the spikes are short compared to the inter-spike distance, we propose an approximate expression which gives the trapping rate in terms of geometric parameters of the boundary and the particle diffusivity. To validate this result, we compare some theoretical predictions based on the expression for the effective trapping rate with corresponding quantities obtained from Brownian dynamics simulations. <https://doi.org/10.1063/1.5040774>

I. INTRODUCTION

The conventional theory of diffusion-controlled reactions¹ deals with trapping of diffusing particles by smooth, uniform boundaries. For example, the Smoluchowski theory shows that the steady-state flux of particles diffusing to a perfectly absorbing sphere is the product of the particle concentration at infinity, C , and the Smoluchowski rate constant, k_{Sm} , $k_{Sm}C$, where $k_{Sm} = 4\pi DR$, with R and D denoting the sphere radius and the particle diffusivity. When the sphere is partially (not perfectly) absorbing, the steady-state flux is lower than its Smoluchowski counterpart since a particle coming to the sphere has a chance to escape to infinity. The maximum steady-state flux to a partially absorbing sphere (achieved when $D \rightarrow \infty$) is determined by the intrinsic rate constant, k , and given by the product kC . The Collins-Kimball formula for the rate constant, k_{CK} , provides a generalization of the Smoluchowski rate constant to the case of partially absorbing sphere,

$$k_{CK} = \frac{k_{Sm}k}{k_{Sm} + k} = k_{Sm}P_{tr}, \quad (1)$$

where P_{tr} is the trapping probability for a particle starting from the surface of the sphere,

$$P_{tr} = \frac{k}{k_{Sm} + k}. \quad (2)$$

The intrinsic rate constant is proportional to the surface area of the sphere, $4\pi R^2$. It can be written as the product of this area and the trapping rate, κ , that characterizes the trapping efficiency of the surface, $k = 4\pi R^2\kappa$. This allows one to write the trapping probability as

$$P_{tr} = \frac{\kappa R}{D + \kappa R}. \quad (3)$$

As κ increases from zero to infinity, the surface of the sphere changes from perfectly reflecting, $P_{tr} = 0$, to perfectly absorbing, $P_{tr} = 1$.

Berg and Purcell² generalized the Smoluchowski theory to the case of non-uniformly absorbing sphere. Specifically, they considered the steady-state flux of diffusing particles to N small non-overlapping absorbing discs of radius b randomly distributed over the surface of a large reflecting sphere of radius R , $b \ll R$, and derived an approximate expression for the rate constant, k_{BP} . Shoup and Szabo³ recognized that k_{BP} can be interpreted as the Collins-Kimball rate constant, $k_{BP} = k_{Sm}P_{tr}$, with the trapping probability given by

$$P_{tr} = \frac{bN}{\pi R + bN}, \quad (4)$$

and, hence, the intrinsic rate constant for the Berg-Purcell problem is $k = 4DbN$. Respectively, the trapping rate in this case is equal to $\kappa_{BP} = k/(4\pi R^2) = bDN/(\pi R^2)$. This may be considered as the first example of homogenization of non-uniform boundary conditions in diffusion-limited kinetics.

As can be seen from this example, boundary homogenization is the replacement of non-uniform boundary conditions by an effective uniform boundary condition with the trapping rate, κ , chosen so that to ensure that the homogenized boundary traps diffusing particles as the original non-uniform one. To discuss why such a replacement is possible, consider variation of the particle flux with the distance from the boundary. Although the flux is extremely complex near the boundary, it simplifies as the distance from the boundary increases. This happens because, due to diffusion, lateral components of the flux vanish with the distance and only its normal component survives. As a consequence, by analyzing the flux at sufficiently large distances from the boundary, one cannot discriminate whether this is the flux to a uniform or non-uniform boundary. This is the reason why one can homogenize the boundary. Up to now, we have discussed the steady-state flux and boundary homogenization in three dimensions, where

FIG. 1. Schematic representation of the original periodic boundary formed by absorbing spikes of height H protruding from a flat reflecting base and separated by the distance W [panel (a)] and the equivalent homogenized boundary [panel (b)], characterized by the effective trapping rate $\kappa(H, W)$ given in Eq. (5).

steady-state conditions arise naturally. Similar consideration can be repeated in two dimensions, where the steady-state may be achieved by fixing the particle concentration at some distance from the boundary. Of course, not any non-uniform boundary can be homogenized, but discussion of this issue is beyond the scope of this work.

In recent years, boundary homogenization has been used to treat various problems with smooth non-uniform boundaries.^{4–25} Here, for the first time, we extend the theory to the case of rough, non-uniform boundaries. Our interest in trapping of diffusing particles by such boundaries is motivated by the fact that problems of this type are ubiquitous in physics, chemistry, biology, and technological applications. Examples include^{26–34} transport through porous membranes, electric current through microelectrodes, heterogeneous catalysis, ligand binding to cell surface receptors, sensing systems, and smart antibacterial coatings, to mention just a few.

Boundary roughness and non-uniformity make treatment of such problems highly non-trivial. Here we discuss homogenization of a rough non-uniform boundary shown in Fig. 1(a). More specifically, we study trapping of particles diffusing on a flat surface by absorbing spikes periodically protruding from a smooth reflecting base. The boundary structure (the spike height, H , and the inter-spike distance, W) determines the steady-state flux and, hence, the trapping rate, κ . Our goal is to find this rate as a function of the geometric parameters of the boundary, $\kappa(H, W)$, as illustrated in Fig. 1.

The main result of this work is an approximate expression for the trapping rate in terms of H and W as well as the particle diffusivity, which is applicable when the inter-spike distance significantly exceeds the spike height,

$$\kappa(H, W) = \frac{\pi D}{W \ln[1/\sin(\pi H/W)]}, \quad H \ll W. \quad (5)$$

This expression is obtained in Sec. II and tested numerically using Brownian dynamics (BD) simulations in Sec. III. Some concluding remarks are made in Sec. IV.

II. DERIVATION

We obtain the expression for $\kappa(H, W)$ in Eq. (5) using some heuristic arguments and then validate the result by Brownian dynamics simulations. Our derivation exploits the known exact result for the effective trapping rate of a flat boundary

FIG. 2. Schematic representation of the original periodic boundary formed by absorbing intervals of length l separated by reflecting intervals of length $L - l$, where L is the period of the boundary [panel (a)], and the equivalent homogenized boundary [panel (b)], characterized by the effective trapping rate $\kappa_{MMS}(l, L)$ given in Eq. (6).

consisting of alternating absorbing and reflecting intervals of lengths l and $L - l$, respectively, where L is the period of the boundary (see Fig. 2). This trapping rate is given by the Moizhes-Muratov-Shvartsman formula,¹¹

$$\kappa_{MMS}(l, L) = \frac{\pi D}{L \ln[1/\sin(\pi l/(2L))]} \quad (6)$$

More than six decades ago, Moizhes,³⁵ who studied electrostatic problems of electric field near complex electrodes, derived a formula for an effective uniform boundary condition for the electric field on the surface of a flat electrode made of alternating metallic and dielectric strips. Muratov and Shvartsman¹¹ applied this formula to find the effective surface trapping rate, Eq. (6).

Consider trapping of point particles freely diffusing in a strip shown in Fig. 3(a), assuming that their starting points are uniformly distributed over the strip area. The strip boundaries are formed by absorbing spikes of height H periodically protruding from reflecting bases as in the boundary shown in Fig. 1. The strip width W is equal to the distance between neighboring spikes, whose height is assumed to be significantly smaller than W . The strip width and the inter-spike distance are chosen to be equal intentionally because this will allow us to convert the trapping problem with rough, periodic, non-uniform boundaries into one with smooth, periodic, non-uniform boundaries. The latter boundaries can be “homogenized” by means of the formula in Eq. (6), and this will allow us to use κ_{MMS} to find $\kappa(H, W)$.

Due to the system periodicity, it is sufficient to consider trapping of the particles in the elementary cell shown in Fig. 3(b) assuming that the absorbing spikes protruding from the opposite bases are connected by reflecting partitions. This elementary cell is also the elementary cell of the strip shown in Fig. 3(c). Although the new strip has the same width and periodicity, W , as the original strip, there is an important difference between the two. The flat boundaries of the new strip contain absorbing intervals of length $2H$, separated by reflecting intervals, of length $W - 2H$, while the rough boundaries of the initial strip are formed by absorbing spikes of height H , separated by longer reflecting intervals of length W .

Using boundary homogenization, we can replace the non-uniform boundary conditions on the boundaries of the strip shown in Fig. 3(c) by effective uniform boundary conditions characterized by the trapping rate $\kappa_{MMS}(2H, W)$ [see Fig. 3(d)]. Then the trapping by rough non-uniform boundaries shown in

FIG. 3. Schematic representation of the strip restricted by two periodic boundaries shown in Fig. 1(a) [panel (a)]. The strip width is equal to the inter-spike distance W . Dashed lines show boundaries of elementary cells of the system. A single elementary cell shown in panel (b) is simultaneously an elementary cell of the strip shown in panel (c), which has the same width and periodicity, W , as the initial strip. In contrast to the strip shown in panel (a), the boundaries of this strip do not have absorbing spikes separated by the distance W . Instead, its flat boundaries contain absorbing intervals of length $2H$, separated by reflecting intervals of length $W - 2H$. This strip with homogenized boundaries is shown in panel (d).

Fig. 3(a) becomes equivalent to that by the flat uniform boundaries shown in Fig. 3(d), and hence $\kappa(H, W) = \kappa_{MMS}(2H, W)$. Substituting here the explicit expression for $\kappa_{MMS}(2H, W)$, we arrive at the expression for the effective trapping rate in Eq. (1),

$$\kappa(H, W) = \kappa_{MMS}(2H, W) = \frac{\pi D}{W \ln[1/\sin(\pi H/W)]}. \quad (7)$$

As follows from the above equation, each absorbing spike of height H “acts” as an absorbing interval of length $2H$. However, this is only true when the inequality $H \ll W$ is fulfilled. This inequality constrains the range of applicability of the expression for the effective trapping rate in Eq. (7), whereas Eq. (6) for $\kappa_{MMS}(l, L)$ is valid for an arbitrary length l of the absorbing interval, $0 \leq l \leq L$.

III. COMPARISON WITH BROWNIAN DYNAMICS SIMULATIONS

To validate the above expression for the effective trapping rate, we compare the mean particle lifetime in the asymmetric elementary cell shown in Fig. 4(a) obtained from Brownian dynamics simulations with its counterpart predicted by the

FIG. 4. Schematic representation of the asymmetric elementary cell of width a used in our Brownian dynamics simulations [panel (a)] and its homogenized version [panel (b)].

theory, which assumes the effective uniform boundary condition [see Fig. 4(b)]. In deriving Eq. (7), we use the strip of width $a = W$. Now we consider the strip width a as a free parameter. It is intuitively clear that boundary homogenization is applicable for sufficiently large values of a , where the effective trapping rate is independent of the strip width. When this happens, the mean particle lifetimes in the strips shown in Figs. 4(a) and 4(b) are equal. The goal of our simulations is to check this fact and to establish the range of applicability of the obtained expression for $\kappa(H, W)$.

One can easily find the mean particle lifetime in the strip with a uniform boundary shown in Fig. 4(b) since its derivation reduces to the solution of a simple one-dimensional problem. Consider a particle diffusing in the interval of length a terminated by partially absorbing end-points [see Fig. 4(b)]. The mean particle lifetime, considered as a function of its starting point x and denoted by $\tau(x)$, satisfies³⁶

$$D \frac{d^2 \tau(x)}{dx^2} = -1, \quad 0 < x < a, \quad (8)$$

subject to radiation boundary conditions at the end points,

$$D \frac{d\tau(x)}{dx} \Big|_{x=0} = \kappa \tau(0), \quad -D \frac{d\tau(x)}{dx} \Big|_{x=a} = \kappa \tau(a), \quad (9)$$

where $\kappa = \kappa(H, W)$ is the boundary trapping rate. Solving Eq. (8), we find

$$\tau(x) = \frac{1}{2} \left(\frac{a}{\kappa} + \frac{ax}{D} - \frac{x^2}{D} \right). \quad (10)$$

Averaging this mean lifetime over the particle starting point, we arrive at the expression for the mean lifetime of interest, denoted by $\langle \tau \rangle_a$,

$$\langle \tau \rangle_a = \frac{1}{a} \int_0^a \tau(x) dx = \frac{a}{2\kappa} + \frac{a^2}{12D}. \quad (11)$$

Substituting here the expression for $\kappa(H, W)$ in Eq. (2), we obtain

$$\langle \tau \rangle_a = \frac{aW}{2\pi D} \ln \left[\frac{1}{\sin(\pi H/W)} \right] + \frac{a^2}{12D}. \quad (12)$$

This is a theoretically predicted dependence of the mean lifetime on the spike height and the inert-spike distance. One can readily see that Eq. (12) has a limited range of applicability: it

fails when the spike height exceeds the half of the inter-spike distance, as $\sin(\pi H/W)$ becomes negative at $H > W$. The same is true for the expression for $\kappa(H, W)$ in Eq. (5), which is valid only when $H \ll W$.

For our further analysis, it is convenient to nondimensionalize Eq. (12) by dividing its both sides by the factor $aW/(2\pi D)$ and to write the nondimensionalized equation as

$$\frac{2\pi D \langle \tau \rangle_a}{aW} - \frac{\pi a}{6W} = \ln \left[\frac{1}{\sin(\pi H/W)} \right] = \frac{\pi D}{W \kappa(H, W)}. \quad (13)$$

At sufficiently large a , where the replacement of the original rough, non-uniform boundary by the effective flat, partially absorbing one is justified, the left-hand side of Eq. (13) is independent of a and given by the expression on the right-hand side of this equation.

To check this fact, we use Brownian dynamics (BD) simulations, where we determine the mean lifetime for uniform distribution of the particle starting point over the area of the elementary cell shown in Fig. 4(a). This mean lifetime, denoted by $\langle \tau \rangle_a^{BD}$, is used to find function $f(a|H, W)$ defined by [cf. the left-hand side of Eq. (13)]

$$f(a|H, W) = \frac{2\pi D \langle \tau \rangle_a^{BD}}{aW} - \frac{\pi a}{6W}. \quad (14)$$

We study the a -dependence of this function for several values of the ratio H/W that characterizes the roughness of the original boundary, $H/W = 0.05, 0.1, 0.2$, and 0.3 . For each value of H/W , we find $f(a|H, W)$ for $a/W = 0.5, 1, 2, 3, 4, 5, 6$. Our simulations show that as a increases, function $f(a|H, W)$ decreases and approaches its plateau value. The value of a , at which the plateau value is achieved, denoted by a^* , depends on the spike height, H ; the higher the spikes are, the wider strips are required to make function $f(a|H, W)$ independent of a . We find that $a^*/W = 1$ for $H/W = 0.05$ and 0.1 , $a^*/W = 3$ for $H/W = 0.2$, and $a^*/W = 4$ for $H/W = 0.3$.

In Fig. 5, we compare the plateau value of function $f(a|H, W)$ with the ratio predicted by the theory, Eq. (13),

FIG. 5. Comparison of the theoretically predicted dependence of the plateau value of the function $f(a|H, W)$ [defined in Eq. (14)] on the ratio H/W with the simulation results. The solid curve represents the theoretical dependence given in Eq. (13). Symbols are the plateau values of $f(a|H, W)$ obtained from Brownian dynamics simulations.

$\pi D / (W \kappa(H, W)) = \ln[1/\sin(\pi H/W)]$. One can see a good agreement between the theoretical predictions (solid curve) and numerical results (symbols) at $H/W \leq 0.1$. Here the relative error of the theoretical estimate of the plateau value of the function $f(a|H, W)$ is less than 3%. Thus, the proposed approximate replacement of the original boundary by the effective one is justified when the inequality $H/W \leq 0.1$ is fulfilled. At $H/W = 0.2$, the relative error of the theoretically predicted plateau value of the function $f(a|H, W)$ is about 15%. The fact that the proposed expression for $\kappa(H, W)$, Eq. (5), fails at $H/W = 0.2$ is not surprising since here the plateau value is reached at $a^*/W = 3$, whereas the derivation of this expression assumes that $a^*/W \leq 1$.

IV. CONCLUDING REMARKS

To summarize, this paper analyzes trapping of diffusing particles by a rough, non-uniform boundary, as shown in Fig. 1. An approximate expression for the effective boundary trapping rate is proposed assuming that the spike height is small compared to the inter-spike distance. This expression, Eq. (5), represents the trapping rate as a function of the geometric parameters of the boundary and the particle diffusivity. The range of applicability of Eq. (5) has been established by comparing theoretical predictions based on this equation with the results obtained from Brownian dynamics simulations. The comparison shows that Eq. (5) “works” reasonably well when the spike height does not exceed one-tenth of the inter-spike distance. It would be interesting to learn what happens at larger values of the spike height when this height becomes comparable or larger than the distance between neighboring spikes.

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