Trapping of diffusive particles by rough absorbing surfaces: Boundary smoothing approach

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We present analytical results for the first-passage statistics of Brownian particles near a comblike absorbing boundary. Our approach is based on the method of boundary homogenization (or boundary smoothing) when an equivalent flat boundary is introduced to maintain the same diffusion flux as the original rough boundary. By using the conformal invariance of the Laplace equation we derive an analytic expression for the position of an equivalent boundary in terms of its spatial period and amplitude. The main analytical results being initially obtained for the steady state system provide important insights into the statistical characteristics of diffusive transport near rough boundaries (high order moments of the trapping time statistics).

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I. INTRODUCTION

Diffusive transport in the presence of irregular interfaces is an essential ingredient of many natural phenomena and industrial processes. Illustrative examples include diffusion-controlled kinetics [1–10], transport properties of porous materials [11,12], and tracer dispersion in global geophysical systems (atmosphere, ocean, geological media [13,14]). Recently, these problems have drawn significant attention in relation to microfluidic devices [15,16,18]. In all these phenomena the interfacial complexity strongly influences the dynamics of the Brownian particles and often determines the overall properties of the diffusive transport in the system.

There is a vast amount of literature devoted to this subject (see Refs. [1–24], and references therein). The analytical approaches that are usually employed for these studies share an overarching mathematical goal, *viz.,* to find a solution of the underlying diffusion equation in domains with complex (and often irregular) boundaries. As a result, a number of advanced analytical methods have been developed to find such solutions. These methods vary significantly in complexity and fidelity ranging from simple engineering estimations to accurate predictions of the high order moments of the first-passage statistics of diffusive particles [1,2,7,14,15,17,19].

One of the simplest conceivable settings for studying the effect of surface complexity on diffusion transport is to analyze particle diffusion in a semi-infinite space lying on a complex boundary. In this case the boundary is kept at the constant concentration and the transport is driven by a concentration gradient imposed far from the boundary (or by the presence of another surface at which a constant concentration is held; see below). The aim of this analysis is to find the influence of surface irregularities on the transport properties of this system.

It is revealing initially to consider the diffusion transport in a 2D horizontal strip. In complex coordinates $z = x + iy$ this strip can be defined as $0 < \mathrm{Im}(z) < d$, where d is the thickness of strip. In the steady state, the particle concentration obeys the Laplace equation:

$$\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} = 0. \tag{1}$$

If the lower boundary is absorbing and concentration at the top boundary is kept constant, the boundary condition can be written in the form $C(x,0) = 0, C(x,d) = C_0$. In this case the solution of the solution of the Laplace equation is straightforward, $C = (J_0/D)y$, where D is diffusivity and $J_0 = DC_0/d$ is the concentration flux.

Consider gradual deformation of the flat boundary that transforms it to a rough surface with period W and amplitude H (Fig. 1). Our ultimate goal is to establish a relationship between the diffusion flux in this system J and the parameters H and W. Further simplification (used in the present study) can be achieved by imposing the limit $d \to \infty$ while keeping J_0 constant. This simplification translates the initial settings for the diffusion in the horizontal strip to the particle diffusion in the semi-infinite space where a boundary condition is formulated as a constant gradient of concentration far from the boundary.

A conventional way to characterize the effect of the surface irregularities on the diffusion transport is to introduce a so-called displacement length Δ [8,9,19,21]. This length is an offset of the flat absorbing boundary from the initial position at $y = 0$ that provides the same concentration flux as the absorbing boundary with irregularities. For any complex interface this length completely characterizes the change of diffusive flux in the system J, since for $d \gg \Delta$

$$J = \frac{J_0}{(1 - \Delta/d)}, \tag{2}$$

irrespective of the morphology of the interface and possible nontrivial distribution of concentration due to interface irregularities. Here J_0 is the diffusion flux in the system with plane boundaries, and the factor $1/(1 - \Delta/d)$ describes an increase or decrease of the diffusion flux in the system (depending on the sign of Δ). The displacement length Δ is determined by purely geometric parameters of the system, $\Delta \equiv \Delta(H,W)$ and obeys two apparent limiting conditions, $\Delta(0,W) = 0$ and $\Delta \to H$ as $H \to \infty$.

It can be seen that in such an approach the problem of calculation of the modified diffusion flux is translated to a calculation of the displacement length Δ. In spite of its clear definition and a variety of methods for the analytical treatment of confined diffusion, the problem of calculation of the displacement length for a given interface is still a challenging task even for simple geometries (for numerical calculations

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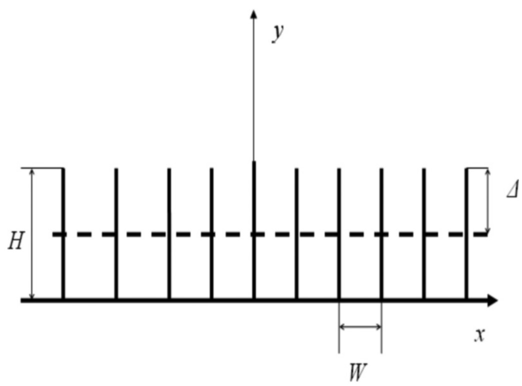

FIG. 1. Comblike model of a rough absorbing boundary.

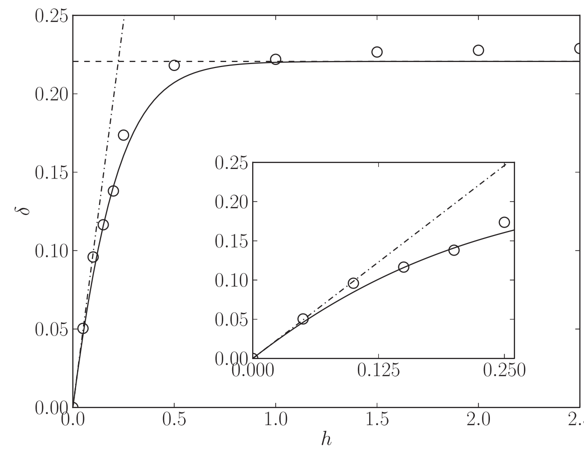

FIG. 2. Position of the effective boundary: $\delta = \Delta/H$, as function of the ratio $h = H/W$. The solid line is the theoretical prediction, Eq. (3). Symbols (○) are the results of the Brownian dynamics simulations. Dashed lines are asymptotic behavior $\delta = h$ for $h \ll 1$ and $\delta = (\ln 2)/\pi$ and for $h \gg 1$.

see Refs. [8,9,19,21], and references therein). For smooth and small-amplitude boundary irregularities perturbation methods usually provide consistent estimations (as a small correction to the zero-order solution corresponding to the position of the unperturbed interface) [15,21]. The task of finding the displacement length becomes more challenging for nonsmooth boundaries and smooth boundaries with nontrivial morphology (e.g, trapping zones, profound dead ends, small openings, etc.).

One of the common features of these boundaries is that they have complex (and even intermittent) distribution of diffusion fluxes and strongly nonuniform accessibility of the boundary to the diffusive particles. A transport process near such boundaries can exhibit a variety of new phenomena such as distinctive active zones, surface screening, trapping entrances, etc. [6,8,9,14,19,21]. Consequently, a conventional perturbation analysis is not applicable to these cases, and any zero-order approximation for the position of an equivalent boundary may be completely misleading. This necessitates a development of some alternative analytical methods for finding the position of the equivalent smooth boundary (e.g., conformal mapping, mixed boundary conditions) [2,9,14,18,19,22]. A wealth of computational techniques have also been proposed for numerical simulation of these phenomena [6,8,9].

II. MAIN RESULTS

In this paper we present analytical results for diffusion transport towards a 2D comblike absorbing boundary (see Fig. 1), which can be considered as quite a general model of an extremely rough interface (i.e., when rough interface can be characterized by two parameters, *viz.,* by its period W and the amplitude of inhomogeneities H). As the main result of our study we deduce that for particles that are released sufficiently far from this comblike boundary it is equivalent to a flat absorbing boundary positioned at $y = l$, where $l = H - \Delta$, $\Delta = \delta W$ and the nondimensional parameter δ is given by the simple expression

$$\delta = \frac{1}{\pi} \ln\left[\frac{2}{1+\exp(-2\pi h)}\right], \quad h = H/W. \tag{3}$$

For $h \ll 1$, $\delta \simeq h$, and for $h \gg 1$, δ exponentially approaches to its saturation value $\delta \simeq (\ln 2)/\pi$ (see Fig. 2). The first limit is intuitively clear: in the limit of small irregularities the absorbing boundary simply works as an unperturbed flat boundary, which coincides with the bottom of the comb structure. In the opposite limit, $h \gg 1$ (i.e., sharp irregularities of large amplitude), the comblike boundary also behaves like a flat interface, but now with some offset from its top. This offset is independent of the amplitude of the boundary spikes (since particles never reach the bottom of the structure) and is proportional to the boundary period with a universal prefactor [which is according to Eq. (3) given by a surprisingly simple formula $\delta = (\ln 2)/\pi$]. It is noteworthy that the value of this prefactor happens to be rather small ($\approx$0.22), and this implies that in the limit of spiky and dense irregularities most particles will be trapped near the very top of the comblike structure. In other words, the expression $[(\ln 2)/\pi]W$ gives an estimation for the length-scale of the so-called "active zones" of particle trapping [24], which can be difficult (or even impossible) to deduce by other means. Equation (3) provides an insightful description of the transition from a sparse to dense profile of the comblike boundary and predicts an associated position of an equivalent smooth boundary. We argue that this simple model reveals some universal properties of particle diffusion and trapping near rough surfaces (see discussion at the end of the paper). The theoretical conjecture (3) is supported by Brownian particle simulations.

III. THEORETICAL FRAMEWORK

In order to make analytical progress on the problem of diffusion transport near a comblike absorbing boundary we employ the well-known property of conformal invariance of the underlying Laplace equation and the associated boundary conditions [2,15,17,25].

In the context of the present study it means that since $C = J_0 \mathrm{Im}(z)$ is a solution for the half-space, then $C = J_0 \mathrm{Im}[\omega(z)]$ is a solution for the comblike boundary, where $\mathrm{Im}(\cdot)$ denotes the imaginary part of its argument and $\omega(z)$ is a conformal map between the two domains.

Far from the boundary $[z \gg \max(H,W)]$ the effect of boundary irregularities diminishes, so here we have $\omega(z) \approx z$.

The next term in the far field expansion for $\omega(z)$ is a constant, so it can be written in the form $\omega(z) \approx (z - z_0)$. This constant determines the offset l of the "effective" boundary from the original flat boundary [$l = \mathrm{Im}(z_0)$] [9,19]. Indeed, the value of l is boundary specific since it is determined by the conformal map $\omega(z)$.

Now we derive the specific expression for z_0 and Δ for a comblike boundary as depicted in Fig. 1. The conformal map of the half space with the flat boundary in coordinates $z = x + iy$ to the half space with the comblike boundary in coordinates $\omega = u(x,y) + iv(x,y)$ can be implemented in three consecutive steps [25]. We exploit the periodicity of the comblike structure and consider its single period (i.e., a semi-infinite strip $-W \leqslant x \leqslant 0$ and $y > 0$; see Fig. 1). This periodicity implies that if we find a conformal transformation for a single period, then under the same transformation all other sections will be transformed to their corresponding images (the symmetry principle [25]). For a single period of the comb we can introduce reflective boundaries, so that it will have absorbing boundaries between $0 < y < H$ and reflective boundaries $H < y < \infty$. The reflective boundaries have no effect on the vertical transport of particles.

The conformal mapping is implemented in three steps. First, we use a constant scaling $\omega_1(z) = \pi(z/W)$ to ensure that the boundary has period π. Second, we apply the transformation $\omega_2(z) = (\cos z)/\cosh(\pi h)$ that maps the strip into the upper half-space. The numerical prefactor $1/\cosh(\pi h)$ ensures that the tips of the absorbing boundary maps to the correct locations at the boundary of the half-space. Finally, we use map $\omega_3 = \arccos[\omega_2(z)]$ to transfer the upper half-space back to a semi-infinite strip $-\pi \leqslant x \leqslant 0, y > 0$ with the vertical reflective boundaries and absorbing bottom. Combining three subsequent steps we arrive at solution of the Laplace equation in the new domain:

$$C(z) = J_0 \mathrm{Im}[\omega(z)], \tag{4}$$

where $\omega(z) = \arccos[(\cos z)/\cosh(\pi h)]$.

In line with the above comments the offset from the original flat boundary $l = \mathrm{Im}(z_0)$ can easily be derived from the expansion of $C(z)$ for $z \to \infty$ by applying the identity $\arccos z = -i \ln(z + i\sqrt{1 - z^2})$ in Eq. (4) and comparing the limiting behavior of Eq. (4) with the asymptotic expression $C(z) = J_0 \mathrm{Im}(z - z_0)$. Then the relation $\Delta = H - l$ eventually leads to Eq. (3).

IV. NUMERICAL SIMULATIONS

In order to validate the analytical conjecture (3) we ran a Monte Carlo particle simulation, based on the numerical algorithms described in Refs. [6,26] to model the temporal characteristics of the diffusion process, observing the time taken for system of Brownian particles to reach the absorbing boundary. To ensure that the simulation converges, a flat reflective boundary, parallel to the x axis at $y = L \gg \max(W,H)$, was introduced to have convergence of the mean first passage time of the diffusive particles (since the mean passage time in the half space is infinite [17]). The periodicity of boundary on the x axis allows us to introduce additional reflective boundaries at $x = \pm W$, and we ran simulation for only one period of the comb structure.

Particles are released from below the upper reflective boundary, uniformly distributed in the range $-\pi < x < 0$. Results from simulation included the mean first passage time to the boundary $\langle T \rangle$, its higher statistical moments $\langle T^n \rangle$, and the probability distribution function (PDF) of the first passage time, $P(T)$. The number of particles in the simulations were gradually increased until an acceptable bound on the errors of $\langle T \rangle$ was reached. For 10^6 particles a relative error of estimation was less than 0.2% at the 95% confidence limit.

To estimate the position of the flat boundary that is equivalent to the comblike structure we calculate the offset of the equivalent boundary from the top of the calculation domain: $L_{\mathrm{eff}} = \sqrt{2D\langle T \rangle}$. Then the offset δ entering in Eq. (3) is related to L_{eff} by the apparent formula $\delta = L_{\mathrm{eff}} - L$.

We performed numerical simulations for the different values of L, and for each L we estimated the equivalent boundary offset δ. For each realization of the comblike structure (uniquely defined by parameter $h = H/W$) we calculated the saturation limit $\delta = (L_{\mathrm{eff}} - L)/W$ as $L \to \infty$ and compared this limit with Eq. (3). We remark that the very existence of this limit is an indication of the effect of boundary smoothing. That is, an equivalence exists for the comblike absorbing interface and the flat boundary. These results are presented in Fig. 3. We found a consistently accurate match between the results obtained from Brownian dynamics simulations and the analytical prediction given by Eq. (3).

The estimation of the effective boundary offset l presented above involves only the first statistical moment of the particle trapping time T and does not elaborate on the effect of fluctuations of T on estimation of the position of the effective boundary. Evidently, in the case of large fluctuations this position may not be statistically viable revealing a failure of the boundary smoothing approach for a given rough interface. The effect of T fluctuations can be estimated from more accurate analysis of the trapping time statistics that would involve the higher order statistical moments. It is also reasonable to expect that if under some conditions the comblike structure behaves like a flat absorbing boundary, then the PDF

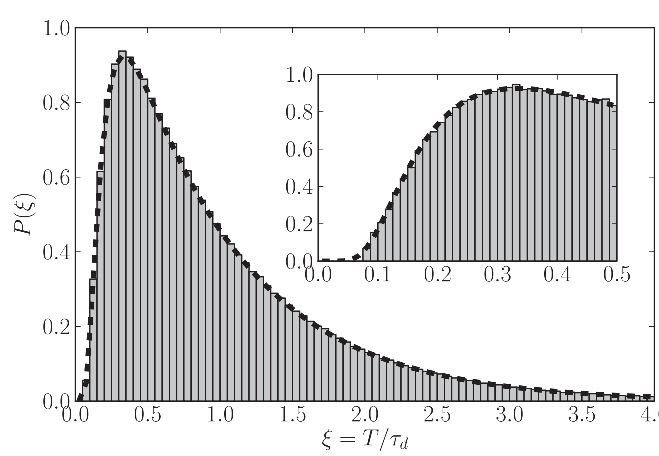

FIG. 3. Universal PDF of the normalized trapping time of the Brownian particles in the vicinity of the comblike boundary, $P(\xi)$, $\xi = T/\tau_d$: particle simulations (histogram) and theoretical predictions given by Eq. (5) for the equivalent flat boundary (dashed line): $h = 0.5$.

of the first passage time of particles in the vicinity of this structure, $P(T)$, should resemble that of the particles in the one-dimensional interval with the absorbing and reflecting boundaries separated by the distance L_{eff} (provided boundary smoothing does occur). The similarity between these PDFs would immediately imply that *all* statistical moments of the particle trapping time converge to those for the particles near the flat boundary and the preceding estimation of Δ based on the mean value of T is statistically viable.

An implicit formula for $P(T)$ for an one-dimensional interval with absorbing and reflecting boundaries can be easily written in terms of the inverse Laplace transform of the well-known expression [17]

$$\hat{P}(s) = 1/[\cosh(\sqrt{s\tau_d})], \quad \tau_d = L_{\mathrm{eff}}^2/D, \quad L_{\mathrm{eff}} = L + \delta. \tag{5}$$

Since τ_d is the only parameter of this function it leads to the following conclusions. First, the PDFs derived for all possible comblike boundaries (with any value of $h = H/W$) can be presented in a self-similar form, i.e., in terms of one nondimensional variable $\xi = T/\tau_d$ and should collapse to a single universal curve. Second, the the shape of this curve should be in agreement with the theoretical prediction given by Eq. (5) irrespective of the value of H/W.

To validate these conjectures we calculated the inverse Laplace transform of Eq. (5) numerically and then compared it with the PDFs of the trapping times calculated from our particle simulations. The results are depicted in Fig. 3. We observe that the results of particle simulations are in a reasonable agreement with the analytical predictions given by Eqs. (3) and (5). This agreement is a convincing argument for the particle statistics equivalence between the comblike structure and the flat absorbing boundary positioned at $y = \Delta$, although "geometrically" these interfaces look strikingly different.

V. CONCLUDING REMARKS

To summarize, we have presented an analytical framework for the first-passage statistics of Brownian particles near a rough absorbing interface (comblike structure). Our approach is based on the method of boundary homogenization (or boundary smoothing) when an equivalent flat boundary is introduced to maintain the same diffusion flux as to the original rough boundary. We present an analytical expression for the position of the equivalent boundary in terms of its period and amplitude of roughness. Our main result being initially obtained for the steady state system provides important insights into the statistical characteristics of diffusion transport in this case (high order moments of the trapping time statistics).

Although the theoretical results presented above have been derived for a simplified morphology of a rough boundary we may expect that some properties of diffusion transport reported above may be quite generic. We argue that the statistics of particles trapped by rough absorbing boundaries with more complex geometric irregularities should resemble some similarities with the theoretical conjectures deduced for the comblike boundaries. For instance, similar results should be valid the for a comb boundary with spikes of nonzero (but still relatively small) thickness. Moreover, according to Eq. (3) at the large spikes limit, when $h = H/W \gg 1$) particles never reach the bottom of the structure [since the scale of penetration length is given by $Y \simeq (\log 2)W/\pi \ll H$], so the specifics of the boundary profile at a distance greater than Δ from its top become irrelevant, and one should recover similar trapping statistics for all spiky surfaces characterized by similar values of parameter h. To support this conjecture and provide specific numerical examples we compare our analytical result $(\ln 2)/\pi \approx 0.22$ and numerical values obtained in Ref. [9] for the periodic fractal-like interfaces at the limit $h \gg 1$: $\delta = 0.27$ (von Koch fractal) and $\delta = 0.26$ (Minkowski fractal). The analytical result for the absorbing interface composed from the equilateral triangles $\delta = 1 - \sqrt{3}/4 + 3\log(3)/(4\pi) \approx 0.30$ [9] is also in reasonable agreement.

In summary, the analytical framework presented in this study provides a simple, but consistent and rigorous, approach for the analytical treatment of complex phenomenology of particle diffusion and absorbtion near complex boundaries.

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[1] D. ben-Avraham and S. Havlin, *Diffusion and Reaction in Fractals and Disordered Systems* (Cambridge University Press, Cambridge, 2000).
[2] M. Z. Bazant, Proc. R. Soc. A **460**, 1433 (2004).
[3] M. Z. Bazant, Phys. Rev. E **73**, 060601 (2006).
[4] O. Bénichou and R. Voituriez, Phys. Rep. **539**, 225 (2014).
[5] D. S. Grebenkov, Phys. Rev. Lett. **95**, 200602 (2005).
[6] P. Levitz, D. S. Grebenkov, M. Zinsmeister, K. M. Kolwankar, and B. Sapoval, Phys. Rev. Lett. **96**, 180601 (2006).
[7] D. S. Grebenkov, M. Filoche, and B. Sapoval, Phys. Rev. E **73**, 021103 (2006).
[8] M. Brady and C. Pozrikidis, Proc. R. Soc. Lond. A **442**, 571 (1993).
[9] M. G. Blyth and C. Pozrikidis, Int. J. Heat Mass Transfer **46**, 1329 (2003).
[10] P. R. Nair and M. A. Alam, Phys. Rev. Lett. **99**, 256101 (2007).
[11] S. Torquato, *Heterogeneous Materials* (Springer, New York, 2002).
[12] G. Drazer and J. Koplik, Phys. Rev. E **62**, 8076 (2000).
[13] J. R. Ledwell, E. T. Montgomery, K. L. Polzin, L. C. St. Laurent, R. W. Schmitt, and J. M. Toole, Nature (London) **403**, 179 (2000).
[14] G. Boffetta, A. Celani, D. Dezzani, and A. Seminara, Geoph. Res. Lett. **35**, L03615 (2008).
[15] H. Bruus, *Theoretical Microfluidics* (Oxford University Press, Oxford, 2008).

[16] K. D. Dorfman and H. Brenner, Phys. Rev. E **65**, 021103 (2002).
[17] S. Redner, *A Guide to First Passage Processes* (Cambridge University Press, Cambridge, 2001).
[18] P. R. Nair and M. A. Alam, Fractals **18**, 461 (2010).
[19] D. Vandembroucq and S. Roux, Phys. Rev. E **55**, 6171 (1997).
[20] A. Singer, Z. Schuss, and D. Holcman, J. Stat. Phys. **122**, 491 (2006).
[21] K. Sarkar and A. Prosperetti, Proc. R. Soc. Lond. A **451**, 425 (1995).
[22] A. M. Berezhkovskii, M. I. Monine, C. B. Muratov, and S. Y. Shvartsman, J. Chem. Phys. **124**, 036103 (2006).
[23] C. B. Muratov and S. Y. Shvartsman, Multiscale Model. Simul. **7**, 44 (2008).
[24] A. Rozanova-Pierrat, D. S. Grebenkov, and B. Sapoval, Phys. Rev. Lett. **108**, 240602 (2012).
[25] R. Schinzinger and A. A. Laura, *Conformal Mapping: Methods and Applications* (Dover Publications, New York, 2003).
[26] A. M. Berezhkovskii, V. Zaloj, and N. Agmon, Phys. Rev. E **57**, 3937 (1998).