Effective diffusivity of a Brownian particle in a two-dimensional periodic channel of abruptly alternating width

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We study diffusion of a Brownian particle in a two-dimensional periodic channel of abruptly alternating width. Our main result is a simple approximate analytical expression for the particle effective diffusivity, which shows how the diffusivity depends on the geometric parameters of the channel: lengths and widths of its wide and narrow segments. The result is obtained in two steps: first, we introduce an approximate one-dimensional description of particle diffusion in the channel, and second, we use this description to derive the expression for the effective diffusivity. While the reduction to the effective one-dimensional description is standard for systems of smoothly varying geometry, such a reduction in the case of abruptly changing geometry requires a new methodology used here, which is based on the boundary homogenization approach to the trapping problem. To test the accuracy of our analytical expression and thus establish the range of its applicability, we compare analytical predictions with the results obtained from Brownian dynamics simulations. The comparison shows excellent agreement between the two, on condition that the length of the wide segment of the channel is equal to or larger than its width.

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I. INTRODUCTION

Diffusion in complex media plays a key role in a huge variety of natural (including biological) and technological processes ranging, for example, from transport in nanoporous silicon [1] and crowded biological extracellular and intracellular environments [2–4] to transport in carbon nanotubes [5,6] and micro- and nanofluidic devices used for a wide range of separation technologies [7–17]. Transport in two-dimensional systems possesses specific properties that attract attention of researchers [10–15]. For example, Karzbrun *et al.* used a series of linked two-dimensional compartments for modelling artificial cells [15]. Since such systems are very complicated, a main tool for studying transport in them is stochastic simulations. However, the situation simplifies when the system has spatial periodicity. The reason is that at sufficiently long times, when the mean particle displacement is much greater than the system period, one can coarse-grain the particle motion and describe it as free diffusion characterized by an effective diffusivity D_{eff}. As an example of transport in such systems, we mention diffusion in periodic porous media and nanostructures [18–20]. The goal of the theory is to find D_{eff} as a function of the geometric parameters of the system.

Although the problem of finding D_{eff} for an arbitrary periodic three-dimensional tube or two-dimensional channel has no solution, it can be obtained for systems of smoothly varying geometry (see below). In this paper we consider the opposite limiting case, where the system geometry changes abruptly. Specifically, we study diffusion in a two-dimensional periodic channel formed by alternating wide and narrow segments of lengths L and l and widths W and w, respectively, schematically shown in Fig. 1. To find D_{eff} as a function of these geometric parameters we adopt the method proposed earlier [21] to find D_{eff} in a three-dimensional cylindrical tube of abruptly changing radius. Our main result for D_{eff} is given in Eqs. (13) and (14). The former is the standard expression for the effective diffusivity in term of the tortuosity, and the latter is a simple analytical expression for the tortuosity as a function of the abovementioned geometric parameters. The predictions of this expression perfectly agree with the tortuosity values obtained from Brownian dynamics simulations over the entire range of the geometric parameters, on condition that the width of the wide channel segment does not exceed its length, $W \leqslant L$. It is worth mentioning that while in tubes and channels of smoothly varying geometry D_{eff} is controlled by the entropy potential, this potential does not appear in our analysis. The reason is that the approach we use here to find D_{eff} differs from the conventional one applicable for smooth periodic geometries.

A frequently used approach to finding D_{eff} in periodic three-dimensional tubes and two-dimensional channels of smoothly varying geometry involves two steps: (1) introduction of an approximate one-dimensional description of particle diffusion along the system axis and (2) derivation of an expression for D_{eff} in the framework of this description. When the geometry is a smooth function of the x

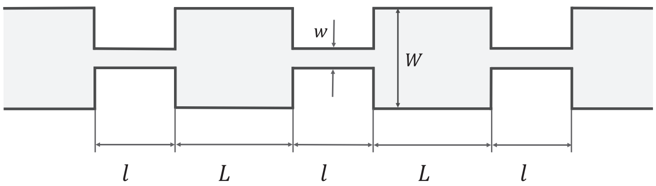

FIG. 1. Two-dimensional periodic channel formed by alternating wide and narrow segments of lengths L and l and widths W and w, respectively.

coordinate measured along the tube/channel axis, the simplest one-dimensional description is given by the Fick-Jacobs equation [22]

$$\frac{\partial G(x,t|x_0)}{\partial t} = D_0 \frac{\partial}{\partial x}\left[A(x)\frac{\partial}{\partial x}\frac{G(x,t|x_0)}{A(x)}\right], \tag{1}$$

where $G(x,t|x_0)$ is the particle propagator (Green's function), which is the distribution function of the particle position x at time t, conditional on that the particle started from x_0 at $t=0$, D_0 is the intrinsic particle diffusivity, and $A(x)$ is the cross-section area $\pi R^2(x)$ of the tube of radius $R(x)$ or the channel width $h(x)$ in the three-dimensional and two-dimensional cases, respectively. It has been shown [23–33] that a more accurate reduction to the one-dimensional description results in a position-dependent diffusivity $D(x)$. Then the propagator satisfies a modified Fick-Jacobs equation,

$$\frac{\partial G(x,t|x_0)}{\partial t} = \frac{\partial}{\partial x}\left[D(x)A(x)\frac{\partial}{\partial x}\frac{G(x,t|x_0)}{A(x)}\right]. \tag{2}$$

Introducing the entropy potential $U_{\mathrm{entr}}(x)$,

$$\beta U_{\mathrm{entr}}(x) = -\ln\left(A(x)/A_{\max}\right), \tag{3}$$

where β is the inverse absolute temperature measured in the energy units, and $A_{\max}$ is the maximum value of $A(x)$ (the minimum value of $U_{\mathrm{entr}}(x)$ is zero, and $U_{\mathrm{entr}}(x) \geqslant 0$), one can write Eq. (2) as the Smoluchowski equation,

$$\frac{\partial G(x,t|x_0)}{\partial t} = \frac{\partial}{\partial x}\left[D(x)e^{-\beta U_{\mathrm{entr}}(x)}\frac{\partial}{\partial x}\left(e^{\beta U_{\mathrm{entr}}(x)}G(x,t|x_0)\right)\right]. \tag{4}$$

Several approximate expressions for $D(x)$ have been proposed in the literature. Since $D(x)$ is always smaller than D_0, it is convenient to write $D(x)$ as

$$D(x) = D_0/K(x). \tag{5}$$

Here are expressions for function $K(x)$ proposed by Zwanzig [23] (Zw), Reguera and Ruby [24] (RR), and Kalinay and Percus [25–29] (KP):

$$K_{\mathrm{Zw}}(x) = \begin{cases} 1+R'(x)^2/2, & \text{for a 2D tube} \\ 1+h'(x)^2/12, & \text{for a 3D channel} \end{cases}, \tag{6}$$

$$K_{\mathrm{RR}}(x) = \begin{cases} \sqrt{1+R'(x)^2}, & \text{for a 3D tube} \\ \sqrt[3]{1+h'(x)^2/4}, & \text{for a 2D channel} \end{cases}, \tag{7}$$

$$K_{\mathrm{KP}}(x) = \begin{cases} \sqrt{1+R'(x)^2}, & \text{for a 3D tube} \\ \frac{h'(x)/2}{\arctan(h'(x)/2)}, & \text{for a 2D channel} \end{cases}, \tag{8}$$

where $R'(x) = dR(x)/dx$ and $h'(x) = dh(x)/dx$. More complex expressions for $K(x)$ has been proposed in the literature [32,33].

Having in hand the Smoluchowski equation, Eq. (4), with a periodic entropy potential, Eq. (3), one cand find the effective diffusivity by the Lifson-Jackson formula, [34] which is an exact result,

$$D_{\mathrm{eff}} = \frac{1}{\langle e^{-\beta U_{\mathrm{entr}}(x)}\rangle\langle e^{\beta U_{\mathrm{entr}}(x)}/D(x)\rangle}, \tag{9}$$

where the angular brackets denote averaging over the period L of the system,

$$\langle f(x)\rangle = \frac{1}{L}\int_0^L f(x)dx. \tag{10}$$

Coming back to the geometric notations, we can write

$$D_{\mathrm{eff}} = \frac{1}{\langle A(x)\rangle\langle 1/(D(x)A(x))\rangle} = \frac{D_0}{\langle A(x)\rangle\langle K(x)/A(x)\rangle}. \tag{11}$$

In the Fick-Jacobs approximation $K(x)=1$, and Eq. (11) reduces to

$$D_{\mathrm{eff}} = \frac{D_0}{\langle A(x)\rangle\langle 1/A(x)\rangle}. \tag{12}$$

The reduction to the one-dimensional description and finding the effective diffusivity discussed above are applicable in the case of a smoothly varying geometry of the system. In the present paper the focus is on diffusive transport in the opposite limiting case, where the system geometry changes abruptly. Specifically, we study diffusion in a two-dimensional periodic channel formed by alternating wide and narrow segments schematically shown in Fig. 1. Although the reduction to the one-dimensional description discussed above is inapplicable here, nevertheless, such a reduction is possible by a different method based on the "boundary homogenization" (see below). In this method, particle motion in the intervals corresponding to the wide and narrow segments is described as free one-dimensional diffusion along the channel axis with the intrinsic diffusivity D_0. The transition between neighboring intervals is described as trapping by an infinitely thin boundary separating the intervals, whose trapping rate is a function of the side from which the particle comes to the boundary. We discuss this reduction in detail in Sec IV, where the expression for D_{eff} is derived. Note that similar approach to the reduction to the one-dimensional description has been applied to diffusion in a three-dimensional tube of abruptly changing radius in Refs. [21,35]. Kalinay and Percus [36] provided an analytical verification of this approach for both two-dimensional channels and three-dimensional tubes.

While our approach is based on the reduction to an effective one-dimensional description, an alternative approach to finding D_{eff} in a periodic two-dimensional channel was recently proposed by Mangeat, Guerin, and Dean [37]. These authors did not rely on the reduction to a one-dimensional description and considered a general case of a 2D periodic channel of smoothly varying width in the presence of infinitely thin partitions and the width discontinuities at certain points. They developed a first order perturbation theory considering the ratio $\varepsilon = a/\mathcal{L}$, where a is the minimum channel width, as a small parameter, and assuming that the leading term in the expansion in ε is given by the expression in Eq. (12) with $A(x) = h(x)$.

The outline of the present paper is as follows. In the next Sec II we give and discuss the obtained expression for D_{eff}, which is the main result of our work. Since the effective diffusivity is always smaller than the intrinsic one, it is convenient to write the former as

$$D_{\text{eff}} = D_0/T, \tag{13}$$

where T is the tortuosity, defined as the ratio D_0/D_{eff}, and formulate our main result in terms of the tortuosity. The derived expression for the tortuosity shows how T depends on the lengths L and l and widths W and w of the wide and narrow sections of the channel. These dependences are compared with the results obtained from Brownian dynamics simulations, as described in Sec III. A derivation of our expression for the tortuosity is given in Sec IV. Some concluding remarks are made in the final Sec V.

II. MAIN RESULT

Our main result is an expression for the tortuosity T, which, by means of Eq. (13), shows how the effective diffusivity D_{eff} of the channel illustrated in Fig. 1 depends on its geometric parameters:

$$T = \frac{D_0}{D_{\text{eff}}} = 1 + \frac{1}{\mathcal{L}^2}\left[Ll\frac{(1-\nu)^2}{\nu} + (LW + lw)\varphi(\nu)\right], \tag{14}$$

where $\mathcal{L} = L + l$ is the channel period, $\nu = w/W$ is the ratio of the widths of the narrow and wide segments, and function $\varphi(\nu)$ is given by

$$\varphi(\nu) = (2/\pi)\ln(1/\sin(\pi\nu/2)). \tag{15}$$

The expression in Eq. (14) is derived in Sec IV, assuming that the width of the wide section does not exceed its length $W \leqslant L$. As explained below, this condition guarantees good agreement between D_{eff} predicted by the theory and obtained from Brownian dynamics simulations.

One can see that the tortuosity is equal to 1 for a straight channel of constant width ($\nu = 1$) and greater than 1 when $\nu < 1$. The tortuosity monotonically increases as ν decreases at fixed values of the segment lengths. As ν and hence the width of the narrow segment approaches zero, the tortuosity diverges, and D_{eff} vanishes, as it must be. In general, the value of T depends on the interplay between ν and the lengths L and l of the two segments. The expression in Eq. (14) shows that the tortuosity approaches 1 as the length of one of the two segments tends to infinity at fixed values of other parameters.

The situation is different when the lengths of both segments tend to infinity at fixed l/L ratio. Here the sum in the square brackets in Eq. (14) is determined by the first term. As a result, this equation reduces to

$$T = 1 + \xi(1-\xi)(1-\nu)^2/\nu, \tag{16}$$

where $\xi = l/(L + l)$ is the fraction of the period occupied by the narrow segment. Note that one can derive this expression for the tortuosity formally using Eq. (12) for D_{eff} obtained for a channel of smoothly varying geometry. Indeed, according to this equation,

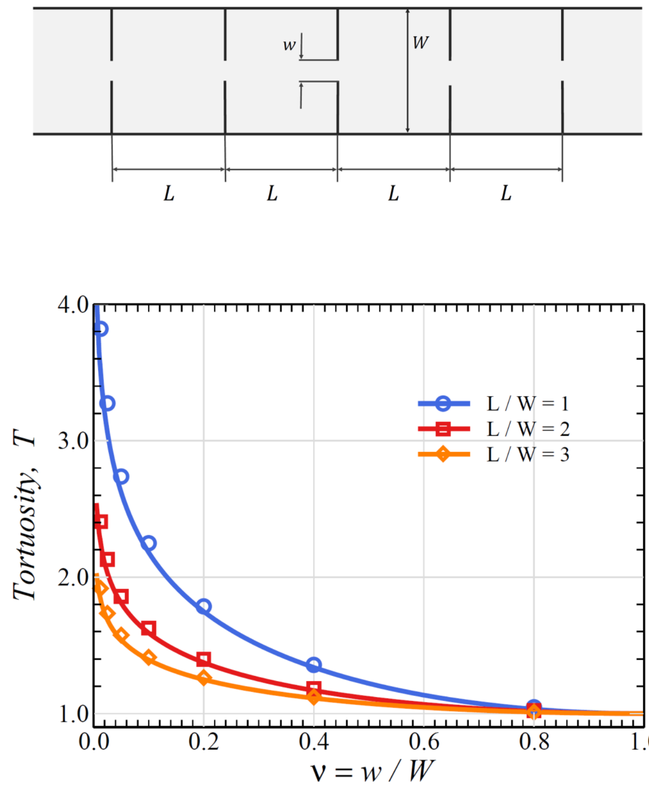

FIG. 2. Compartmentalized channel (upper panel) and the tortuosity in such a channel as a function of $\nu = w/W$ for $L/W = 1$, 2, and 3 from top to bottom (lower panel). Solid curves are the dependences given by Eq. (21), and symbols are the tortuosity values obtained from our simulations.

$$T = \frac{D_0}{D_{\text{eff}}} = \langle h(x)\rangle\langle 1/h(x)\rangle. \tag{17}$$

In our case of the channel of alternating width we have

$$\langle h(x)\rangle = \frac{1}{L+l}(LW + lw) \tag{18}$$

and

$$\langle 1/h(x)\rangle = \frac{1}{L+l}\left(\frac{L}{W} + \frac{l}{w}\right). \tag{19}$$

Substituting these expressions into Eq. (17), we arrive at

$$T = \frac{1}{\mathcal{L}^2}\left[\mathcal{L}^2 + l^2 + lL\left(\nu + \frac{1}{\nu}\right)\right] = 1 + \frac{lL}{\mathcal{L}^2}\,\frac{(1-\nu)^2}{\nu}, \tag{20}$$

which is the expression for the tortuosity in Eq. (16).

Another type of the tortuosity dependence on the channel parameters arises when the length of the narrow segment vanishes, $l = 0$. Here, the channel is a set of compartments of length L and width W ($L \geqslant W$) separated by infinitely thin partitions containing connecting windows of width w in their centers, as shown in Fig. 2, upper panel. In this case $\mathcal{L} = L$,

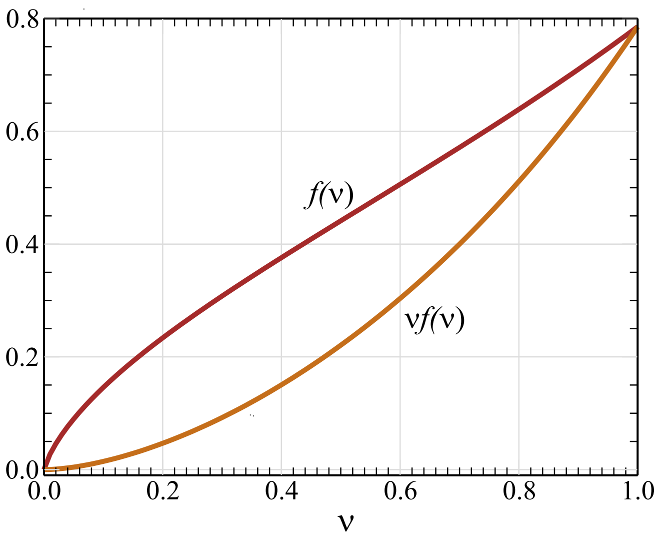

FIG. 3. Functions $f(\nu)$, Eq. (23), and $\nu f(\nu)$.

and the expression in Eq. (14) simplifies and reduces to

$$T = 1 + \frac{W}{L}\varphi(\nu). \tag{21}$$

This expression gives the tortuosity of a compartmentalized channel as a function of two dimensionless parameters: the width ratio $\nu = w/W$ and the dimensionless compartment length L/W. The tortuosity dependence on ν is illustrated in Fig. 2, lower panel by solid curves drawn at three values of L/W: $L/W = 1$, 2, and 3. Symbols in this figure show the values of the tortuosity obtained from Brownian dynamics simulations discussed in the following Sec III. One can see excellent agreement between our theoretical predictions and the simulation results.

To study the l-dependence of the tortuosity at fixed values of L, W, and ν, it is convenient to write Eq. (14) as

$$T = 1 + \frac{L(1-\nu)^2}{\mathcal{L}^2\nu}(Wf(\nu) + \alpha l), \tag{22}$$

where function $f(\nu)$ and factor α are

$$f(\nu) = \frac{\nu}{(1-\nu)^2}\varphi(\nu) \tag{23}$$

and

$$\alpha = 1 + \frac{W}{L}\nu f(\nu). \tag{24}$$

Plots presented in Fig. 3 show that functions $f(\nu)$ and $\nu f(\nu)$ monotonically increase from zero to $\pi/4$ as ν goes from zero to 1. As a consequence, factor α is constrained by the inequality $1 < \alpha < 2$, and the first term in the parenthesis in Eq. (22) can be neglected when the length of the narrow part of the channel significantly exceeds the width of its wide part, $l \gg W$. In this case the tortuosity, Eq. (22), takes the form

$$T = 1 + \alpha\frac{lL(1-\nu)^2}{\mathcal{L}^2\nu}. \tag{25}$$

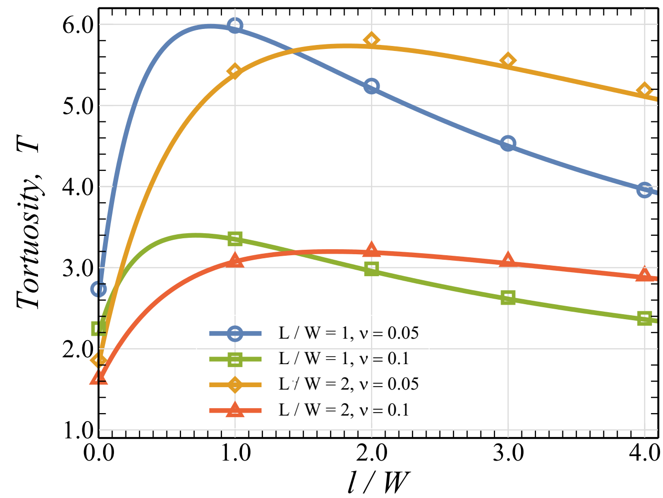

FIG. 4. Tortuosity dependence on the length l of the narrow segment at fixed values of the length of the wide segment L and the segment width ratio $\nu = w/W$. Solid curves are theoretical dependences predicted by Eq. (14), symbols are simulation results. Two upper curves correspond to $\nu = 0.05$. Two lower curves correspond to $\nu = 0.1$.

When $\nu W/L \to 0$, factor α approaches unity, and Eq. (25) reduces to the expression for the tortuosity in Eq. (16).

The l-dependence of the tortuosity is illustrated in Fig. 4 (solid curves) at two values of the dimensional length of the wide section of the channel, $L/W = 1$ and 2, and two values of the segment width ratio, $\nu = 0.05$ and 0.1. One can see that the tortuosity first increases with l, reaches a maximum, and then decrease approaching 1, as $l \to \infty$. Symbols shown in Fig. 4 are the values of the tortuosity obtained from Brownian dynamics simulation, as explained in the following Sec III. One can see excellent agreement between our theoretical and simulation results.

III. BROWNIAN DYNAMICS SIMULATIONS

In this section we discuss Brownian dynamics simulations that we run to validate our analytical result for the tortuosity, Eq. (14). To find the tortuosity in Brownian dynamics simulations we take advantage of the relation between this quantity and the mean first-passage time of a diffusing particle from its starting position (averaged over the channel cross-section) to one of the two absorbing boundaries separated from the starting position by the channel period. Denoting this mean first-passage time by τ we can write the relation as

$$T = \frac{2D_0\tau}{\mathcal{L}^2}. \tag{26}$$

This relation follows from the definition of the effective diffusivity in term of the mean first-passage time,

$$D_{\mathrm{eff}} = \frac{\mathcal{L}^2}{2\tau}. \tag{27}$$

Substituting this into the definition of the tortuosity, $T = D_0/D_{\mathrm{eff}}$, we arrive at the relation in Eq. (26).

Thus, to find the tortuosity we need to know the mean first-passage time obtained from Brownian dynamics simulations.

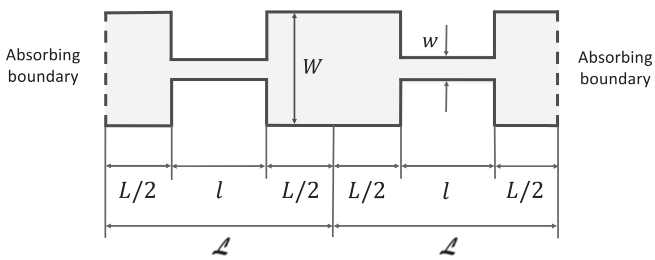

FIG. 5. Channel geometry used in our simulations. Particles start in the middle of the wide segment of the channel and are trapped by absorbing boundaries separated from the starting cross section by the period $\mathcal{L} = L + l$.

To this end, we run the simulations in the two-dimensional channel in the geometry shown in Fig. 5. In our simulations we run $N = 25\,000$ trajectories of Brownian particles whose starting points were uniformly distributed over the channel cross section located in the middle of its wide segment. The trajectories were terminated as soon as they cross one of the two absorbing boundaries, located at distance $\mathcal{L}$ from the starting cross section, for the first time (see Fig. 5). The lifetimes of individual trajectories t_i, $i = 1, 2, ..., N$, were used to find the mean first-passage time, denoted by $\tau_{\rm sim}$,

$$\tau_{\rm sim} = \frac{1}{N}\sum_{i=1}^{N} t_i, \tag{28}$$

which was substituted into Eq. (26) to find the tortuosity. In our simulations we set $W = D_0 = 1$ and took the dimensionless time step Δt measured in units of $W^2/(2D_0)$ to be $\Delta t = 10^{-7}$.

The value of the tortuosity obtained from Brownian dynamics simulations are compared with their theoretically predicted counterparts in Figs. 2, lower panel, and 4. The former illustrate the tortuosity dependence on the segment width ratio $\nu = w/W$ in compartmentalized channels ($l = 0$) of different periods $\mathcal{L} = L$. The latter shows the tortuosity dependence on the length l of the narrow segment at several values of L and ν. As mentioned earlier, the theoretical predictions are in perfect agreement with the tortuosity values obtained from the simulations that were run for channels with sufficiently long wide segments, whose lengths satisfied $L \geqslant W$. This guarantees the applicability of boundary homogenization, an approximation that is central for our approach to the problem (see Ref. [38] and the following Sec IV for more details).

IV. DERIVATION

A key step in our approach to finding the effective diffusivity and tortuosity is the introduction of an approximate one-dimensional description of the particle diffusion in the channel. This can be done using the result obtained for the problem of trapping of particles diffusing in three dimensions by a flat surface which is periodically, with period W, covered by parallel absorbing strips of width w, $w \leqslant W$. It turns out that this striped surface, in what concerns trapping, is equivalent to a uniformly absorbing surface characterized by a properly chosen trapping rate κ. This can be understood if one takes into account the fact that the lateral component of the diffusion flux to the surface vanishes as the distance from the surface increases. As a consequence, significantly far away from the surface the flux becomes indistinguishable from the flux to a uniformly absorbing surface, and the trapping problem becomes essentially one-dimensional.

An exact solution for κ is given by the Moizhes-Muratov-Shvartsman formula,

$$\kappa = \frac{\pi D_0}{W \ln\{1/\sin[\pi w/(2W)]\}}, \tag{29}$$

where D_0, as before, is the particle intrinsic diffusivity. This expression for κ was obtained by Muratov and Shvartsman, [39] who carried over to diffusion-limited kinetics the exact result obtained for the corresponding electrostatic problem by Moizhes [40]. The same trapping rate characterizes absorption of particles diffusing in a semi-infinite plane restricted by a linear boundary containing alternating absorbing and reflecting intervals of length w and $W-w$, respectively. Because of the symmetry, κ in Eq. (29) is also the exact effective trapping rate for particles diffusing in a semi-infinite strip of width W with reflecting side boundaries terminated by a reflecting interval containing an absorbing window of width w in its center. As shown in Ref. [38], Eq. (29) provides a good approximation for the trapping rate in the case of a strip of finite length L, on condition that this length satisfies $L \geqslant W/2$. The replacement of nonuniform boundary conditions by an effective uniform one, called boundary homogenization, allows one to introduce a one-dimensional description of trapping of a particle diffusing in the two-dimensional chamber of size $L \times W$ by the absorbing window of length w, located in the center of the chamber wall of length W. Here we require that the length of the wide segment satisfies $L \geqslant W$ as, according to our results, this guarantees good agreement between our theoretical predictions and simulations.

In our one-dimensional description of diffusion, we use boundary homogenization to describe the entrance of the particle into the narrow segment of the channel from the wide one. The exit of the particle from the narrow segment, i.e., its transition to one of the two neighboring wide segments, is also described as trapping by uniform partially absorbing boundaries at the segment ends. These boundaries are characterized by the trapping rate κ'. The two trapping rates, κ and κ', are not independent. They must satisfy the relation $\kappa W = \kappa' w$, which follows from the condition of detailed balance [41,42]. As a consequence, we have

$$\kappa' = \kappa\frac{W}{w} = \frac{\pi D_0}{w \ln\{1/\sin[\pi w/(2W)]\}}. \tag{30}$$

Thus, our one-dimensional description replaces diffusion in the two-dimensional periodic channel shown in Fig. 1 by free one-dimensional diffusion within each repeating interval of length L and l with interval boundaries characterized by two trapping rates κ and κ', as shown in Fig. 6. The former characterizes trapping of particles diffusing in an interval of length L (corresponding to a wide segment of the channel) upon approaching its boundary. The latter does the same for particles diffusing in an interval of length l, which corresponds to a narrow segment.

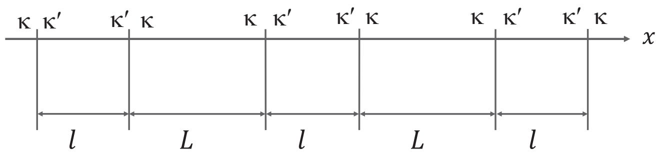

FIG. 6. Effective one-dimensional description of particle diffusion in a two-dimensional channel shown in Fig. 1.

In the rest of this section, we find the tortuosity in the framework of the one-dimensional description illustrated by Fig. 6. The effective diffusivity here is given by Eq. (27). Correspondingly, the tortuosity is given by Eq. (26). So, to find the tortuosity, we derive an expression for τ, substitute this expression in Eq. (26), and, after some manipulations, we recover our result for the tortuosity in Eq. (14).

It is convenient to choose the center of an interval of length L corresponding to a wide section of the channel as the origin and as the particle starting point. To find τ, consider a steady state where a constant flux j is injected at the origin and injected particles are trapped by two absorbing boundaries located at points $\pm\mathcal{L}$, where $\mathcal{L} = L + l$ is the system period as shown in Fig. 7. There is a simple exact relation between τ, j, and the steady state number of particles in the system, denoted by N,

$$\tau = N/j, \quad N = \int_{-\mathcal{L}}^{\mathcal{L}} c(x)dx = 2\int_0^{\mathcal{L}} c(x)dx, \tag{31}$$

where $c(x)$ is the steady-state concentration of the particles, and factor 2 in front of the second integral accounts for the symmetry of function $c(x)$, $c(-x) = c(x)$. Thus, to find τ we need to know the steady-state concentration in the interval $0 < x < \mathcal{L}$.

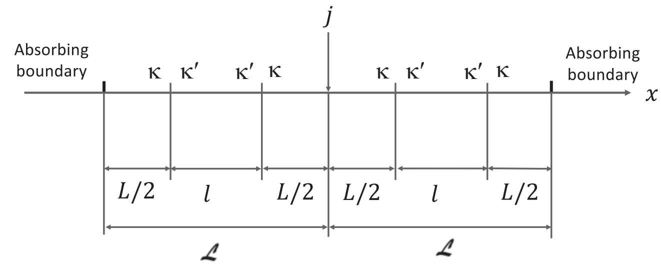

FIG. 7. Illustration of the one-dimensional model used to find the mean first-passage time τ.

This concentration satisfies

$$\frac{j}{2} = -D_0\frac{dc(x)}{dx}, \quad 0 < x < \frac{L}{2}, \quad \frac{L}{2} < x < l + \frac{L}{2}, \quad l + \frac{L}{2} < x < \mathcal{L}. \tag{32}$$

At points of contacts, $x = L/2$ and $x = l + L/2$ the concentration makes jumps, which are controlled by the trapping rates κ and κ'. The concentrations on the two sides of the contact points satisfy

$$\frac{j}{2} = \begin{cases} \kappa c\left(\frac{L}{2} - \varepsilon\right) - \kappa' c\left(\frac{L}{2} + \varepsilon\right) \\ \kappa' c\left(l + \frac{L}{2} - \varepsilon\right) - \kappa c\left(l + \frac{L}{2} + \varepsilon\right) \end{cases}, \quad \varepsilon \to 0. \tag{33}$$

Finally, the concentration vanishes at $x = \mathcal{L}$, where the absorbing boundary is located,

$$c(L + l) = 0. \tag{34}$$

Integrating Eq. (32) subject to the boundary conditions in Eqs. (33) and (34), we arrive at

$$c(x) = \frac{j}{2D_0} \times \begin{cases} L + l\kappa'/\kappa - x + 2D_0/\kappa, & 0 \leqslant x < L/2 \\ (1 + \kappa/\kappa')L/2 + l - x + D_0/\kappa', & L/2 < x < l + L/2. \\ \mathcal{L} - x, & l + L/2 < x \leqslant \mathcal{L} \end{cases} \tag{35}$$

We use this to find τ by Eq. (31). The result is

$$\tau = \frac{2}{j}\int_0^{\mathcal{L}} c(x)dx = \frac{1}{2D_0}\left[L^2 + l^2 + Ll\left(\frac{\kappa}{\kappa'} + \frac{\kappa'}{\kappa}\right)\right] + \frac{l}{\kappa'} + \frac{L}{\kappa}. \tag{36}$$

Substituting here the expressions for κ and κ', Eqs. (29) and (30), we can write the above result for time τ as

$$\tau = \frac{1}{2D_0}\left[L^2 + l^2 + Ll\left(\nu + \frac{1}{\nu}\right)\right] + (LW + lw)\varphi(\nu). \tag{37}$$

This leads to the following expression for the tortuosity, Eq. (26),

$$T = \frac{1}{\mathcal{L}^2}\left[L^2 + l^2 + Ll\left(\nu + \frac{1}{\nu}\right) + (LW + lw)\varphi(\nu)\right]. \tag{38}$$

One can check that this is identical to the expression for the tortuosity in Eq. (14) using the relation

$$L^2 + l^2 + Ll\left(\nu + \frac{1}{\nu}\right) = \mathcal{L}^2 + Ll\frac{(1-\nu)^2}{\nu}. \tag{39}$$

V. CONCLUDING REMARKS

The present paper is devoted to diffusion of Brownian particles in two-dimensional periodic channels of abruptly changing geometry. More specifically, the focus is on the particle effective diffusivity D_{eff} in a channel of alternating width schematically shown in Fig. 1. We write D_{eff} as the ratio of the particle intrinsic diffusivity D_0 to the tortuosity T which describes the lowering of D_{eff} compared to D_0, Eq. (13). The main result of our study is the expression for the tortuosity in Eq. (14), which gives the tortuosity as a function of the geometric parameters: lengths L and l and widths W and w of the wide and narrow segments of the channel. Our analysis has demonstrated a nontrivial dependence of the effective diffusivity on these parameters. For example, the nonmonotonicity in the tortuosity (and hence effective diffusivity) dependence on the length l of the narrow segment shown in Fig. 4.

To find the tortuosity, and hence effective diffusivity, we introduce an approximate one-dimensional description of two-dimensional diffusion in the channel. Since the channel width changes abruptly, the conventional reduction to the one-dimensional description (which assumes that the channel width is a slowly varying function) is inapplicable in our case. Therefore, to introduce such a description we take advantage of an exact result for the trapping problem in diffusion-limited kinetics obtained using the boundary homogenization approach. This is discussed in detail in Sec IV, where the expression for the tortuosity, Eq. (14), is derived.

As discussed in Sec III, this expression is applicable for the entire range of the geometric parameters L, l, W, and w of the channel on condition that the length of the wide segment exceeds or is equal to its width, $L \geqslant W$. Since our result for the tortuosity, Eq. (14), is obtained in the framework of an approximate one-dimensional description of the particle diffusion in the channel, we tested its predictions against the values of the tortuosity obtained from Brownian dynamics simulations. Comparison showed excellent agreement between our theoretical and simulation results when the condition $L \geqslant W$ is fulfilled.

It is worth mentioning that although we consider point Brownian particles, this is not a severe restriction, since a finite size of the particle can be easily taken into account by renormalizing the widths w and W of the channel segments. In this work we study periodic channels of alternating width, which have a very simple shape of their elementary cells. It would be interesting to generalize the above analysis to the case of channels in which the elementary cells have more complex shape. Another interesting direction for future work is to develop a theory of biased transport in channels of abruptly changing geometry.

Data availability statement. The data that support the findings of this study are available from the corresponding author upon reasonable request.

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[1] D. Kondrashova *et al.*, Sci. Rep. **7**, 40207 (2017).
[2] C. Nicholson and J. M. Phillips, J. Physiol. **321**, 225 (1981); C. Nicholson, P. Kamali-Zare, and L. Tao, Compute. Vis. Sci. **14**, 309 (2011).
[3] S. K. Ghosh, A. G. Cherstvy, and R. Metzler, Phys. Chem. Chem. Phys. **17**, 1847 (2015).
[4] S. K. Ghosh, A. G. Cherstvy, D. S. Grebenkov, and R. Metzler, New J. Phys. **18**, 013027 (2016).
[5] M. S. Dresselhaus, G. Dresselhaus, and P. Avouris, *Carbon Nanotubes: Synthesis, Structure, Properties, and Applications* (Springer, Berlin, 2001).
[6] L. Bowman, *Carbon Nanotubes Handbook* (NY Research Press, New York, NY 2015).
[7] T. M. Squires and S. R. Quake, Rev. Mod. Phys. **77**, 977 (2005).
[8] G. Hu and D. Li, Chem. Eng. Sci. **62**, 3443 (2007).
[9] B. J. Kirby, *Micro- and Nanoscale FluidMechanics: Transport in Microfluidic Devices* (Cambridge University Press, Cambridge, UK 2010).
[10] A. Shamloo and A. Mashhandian, Phys. Fluids **30**, 012002 (2018).
[11] Y. Xu, Adv. Mater. **30**, 1702419 (2018).
[12] L. Zhang and M. Jaronies, Chem. Soc. Rev. **49**, 6039 (2020).
[13] J. Han and H. G. Craighead, Science **288**, 1026 (2000).
[14] M. Zhang, P. Zhao, P. Li, Y. Ji, G. Liu, and W. Jin, ACS Nano **15**, 5209 (2021).
[15] E. Karzbrun, A. M. Tayar, V. Noireaux, and R. H. Bar-Ziv, Science **345**, 829 (2014).
[16] F. Moghadam and H. B. Park, 2D Mater. **6**, 042002 (2019).
[17] H. Zhan, Z. Xiong, C. Cheng, Q. Liang, J. Z. Liu, and D. Li, Adv. Mater. **32**, 1904562 (2019).
[18] A. E. Saetz, J. C. Perfetti, and I. Rusinek, Transp. Porous Media **6**, 143 (1991).
[19] D. J. Bergman, K. J. Dunn, L. M. Schwartz, and P. P. Mitra, Phys. Rev. E. **51**, 3393 (1995).
[20] R. Raccis, A. Nikoubashman, M. Retsch *et al.*, ACS Nano **5**, 4607 (2011).
[21] Yu. A. Makhnovskii, A. M. Berezhkovskii, and V. Yu. Zitserman, Chem. Phys. **367**, 110 (2010).
[22] M. H. Jacobs, *Diffusion Processes* (Springer, New York, 1967).
[23] R. Zwanzig, J. Phys. Chem. **96**, 3926 (1992).
[24] D. Reguera and J. M. Rubí, Phys. Rev. E **64**, 061106 (2001).
[25] P. Kalinay and J. K. Percus, J. Chem. Phys. **122**, 204701 (2005).
[26] P. Kalinay and J. K. Percus, Phys. Rev. E **72**, 061203 (2005).
[27] P. Kalinay and J. K. Percus, Phys. Rev. E **74**, 041203 (2006).
[28] P. Kalinay and J. K. Percus, J. Stat. Phys. **123**, 1059 (2006).
[29] P. Kalinay and J. K. Percus, Phys. Rev. E **78**, 021103 (2008).
[30] R. M. Bradley, Phys. Rev. E **80**, 061142 (2009).
[31] A. Berezhkovskii1 and A. Szabo, J. Chem. Phys. **135**, 074108 (2011).
[32] M. Sivan and O. Farago, Phys. Rev. E **98**, 052117 (2018).
[33] M. Sivan and O. Farago, Phys. Rev. E **99**, 022141 (2019).
[34] S. Lifson and J. L. Jackson, J. Chem. Phys. **36**, 2410 (1962).
[35] A. M. Berezhkovskii, A. V. Barzykin, and V. Yu. Zitserman, J. Chem. Phys. **131**, 224110 (2009).
[36] P. Kalinay and J. K. Percus, Phys. Rev. E **82**, 031143 (2010).
[37] M. Mangeat, T. Guerin, and D. S. Dean, J. Chem. Phys. **149**, 124105 (2018).
[38] L. Dagdug, A. M. Berezhkovskii, V. Yu. Zitserman, and S. M. Bezrukov, Phys. Rev. E **103**, 012135 (2021).
[39] C. B. Muratov and S. Y. Shvartsman, Multiscale Model. Simul. **7**, 44 (2008).
[40] B. Ya. Moizhes, Zh. Tech. Fiz. **25**, 167 (1955) (in Russian).
[41] S. M. Bezrukov, A. M. Berezhkovskii, M. A. Pustovoit, and A. Szabo, J. Chem. Phys. **113**, 8206 (2000).
[42] A. M. Berezhkovskii, A. Szabo, and H.-X. Zhou, J. Chem. Phys. **135**, 075103 (2011).