Diffusion in periodic two-dimensional channels formed by overlapping circles: Comparison of analytical and numerical results

Inti Pineda,¹ Marco-Vinicio Vazquez,¹ Alexander M. Berezhkovskii,²
and Leonardo Dagdug^{2,a)}

¹*Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa, Mexico, 09340 Distrito Federal, Mexico*

²*Mathematical and Statistical Computing Laboratory, Division of Computational Bioscience, Center for Information Technology, National Institutes of Health, Bethesda, Maryland 20892, USA*

(Received 8 September 2011; accepted 7 November 2011; published online 8 December 2011)

We study two-dimensional diffusion in a channel formed by periodic overlapping circles. Periodic variation of the channel width leads to the slowdown of diffusion along the channel axis. There are several approximate approaches, which allow one to analyze the slowdown. We use these approaches to derive five expressions for the effective diffusion coefficient of a point Brownian particle in the channel. To check the accuracy of the expressions we compare their predictions with the effective diffusion coefficient obtained from Brownian dynamics simulations. © 2011 American Institute of Physics. [doi:10.1063/1.3664179]

I. INTRODUCTION

In this paper we study diffusion in a periodic two-dimensional channel formed by overlapping circles of radius R , schematically shown in Fig. 1. The focus is on the effective diffusion coefficient, D_{eff} , that describes the motion of a point Brownian particle on times when the particle displacement significantly exceeds the channel period l , $l < 2R$. Due to varying channel geometry, D_{eff} is smaller than its counterpart in the straight channel, D_0 , which is identical to the particle diffusion coefficient in the absence of constraints. There are several approximate approaches, which allow one to analyze the effect of varying constrain geometry on diffusion. To evaluate the accuracy of different approaches, in the paper we find D_{eff} in Brownian dynamics simulations and compare our numerical results with the values of D_{eff} predicted theoretically using different approximations. One of our main results is Fig. 2 that illustrates the comparison. In this figure we show the ratio D_{eff}/D_0 as a function of the ratio a/R , where $a = \sqrt{R^2 - l^2/4}$ is the half-width of the openings connecting neighboring compartments of the channel.

Our interest in this problem was stimulated by growing interest in the scientific community to the study of transport in structures of periodically varying geometry (see review articles¹ and references therein). Usually, such problems are too complicated to be treated analytically and can be studied only numerically. The advantage of the system considered in the paper is that five analytical expressions for D_{eff} can be obtained using different approximations. We derive these expressions in Sec. II. Then, in Sec. III we discuss the expressions and compare them with the results of Brownian dynamics simulations.

II. ANALYTICAL RESULTS

Consider a point Brownian particle diffusing in a 2D-channel formed by overlapping circles schematically shown in Fig. 1. The pattern of the particle motion depends on the size of the openings or, equivalently, on the channel period, $l = 2\sqrt{R^2 - a^2}$. When the period is small compared to the circle radius R , and the opening width is close to $2R$ (Fig. 1(a)), the channel walls are only slightly corrugated, and the pattern of the particle motion is close to that in a straight channel. In this case one can describe the particle motion in terms of one-dimensional diffusion in periodic entropy potential, and find D_{eff} by means of the Lifson-Jackson formula.²

The pattern is qualitatively different when the openings are small, $a \ll R$, and the period is close to $2R$, $2R - l \ll R$ (Fig. 1(b)). In this case it takes a lot of time for the particle to find an opening through which it can escape to a neighboring compartment. When the search time is much larger than the characteristic relaxation time in an isolated compartment, R^2/D_0 , the particle equilibrates in the compartment much faster than it escapes. As a consequence, the particle motion can be described as a continuous-time random walk (RW) between centers of neighboring compartments,³ and D_{eff} can be found from the relation

$$D_{\text{eff}} \approx D_{\text{eff}}^{\text{RW}} = \frac{l^2}{2\tau}, \quad (2.1)$$

where τ is the mean particle lifetime in the compartment.

In this section we derive five expressions for D_{eff} using different approximations. These analytical results are discussed and compared with D_{eff} obtained from Brownian dynamics simulations in Sec. III.

A. Narrow openings

When the openings are narrow (Fig. 1(b)), one can map the particle motion onto the random walk and find the

^{a)} Author to whom correspondence should be addressed. Electronic mail: dagdug@mail.nih.gov.

FIG. 1. Schematic representation of periodic 2D-channels formed by overlapping circles with wide and narrow openings ($a = 0.8R$, $l = 1.2R$ and $a = 0.2R$, $l \approx 1.96R$ in panels (a) and (b), respectively) and corresponding entropy potentials, Eq. (2.7).

effective diffusion coefficient by means of Eq. (2.1). Thus, the problem of finding D_{eff} reduces to that of finding the mean particle lifetime in the compartment. We find this time using the result for the mean lifetime of a particle diffusing in a circle, perimeter of which contains n identical, non-overlapping, evenly spaced absorbing arcs.⁴ Denoting this mean lifetime by $\langle \tau(\sigma|n) \rangle$, where σ is the fraction of the perimeter occupied by the arcs, $0 < \sigma < 1$, we can write⁴

$$\langle \tau(\sigma|n) \rangle = \left[\frac{1}{8} + \frac{(1-\sigma)^2}{n} \ln \left(2.6 + \frac{0.7}{\sigma} \right) \right] \frac{R^2}{D_0}. \quad (2.2)$$

This is a generalization of the exact asymptotic ($\sigma \rightarrow 0$) result

$$\langle \tau(\sigma|n) \rangle = \frac{R^2}{nD_0} \ln \left(\frac{1}{\sigma} \right), \quad (2.3)$$

obtained by Ward and Keller⁵ and Holcman and Schuss.⁶

FIG. 2. Comparison of different expressions for D_{eff} , Eqs. (2.6), (2.18), (2.20), (2.22) and (2.24), with the effective diffusion coefficient obtained from Brownian dynamics simulations. Different panels show the comparison for different ranges of $\tilde{a} = a/R$.

When $n = 2$ and $\sigma = 2a/(\pi R)$, the mean lifetime, Eq. (2.2), is

$$\begin{aligned} & \left\langle \tau \left(\frac{2a}{\pi R} \middle| 2 \right) \right\rangle \\ &= \left[\frac{1}{4} + \left(1 - \frac{2a}{\pi R} \right)^2 \ln \left(2.6 + \frac{0.7\pi R}{2a} \right) \right] \frac{R^2}{2D_0}. \end{aligned} \quad (2.4)$$

Time τ is twice larger than time $\langle \tau(2a/(\pi R)|2) \rangle$ since the particle coming to a connecting opening escapes to the neighboring compartment and returns to the initial compartment with equal probability 1/2. Eventually, we have

$$\tau = \left[\frac{1}{4} + \left(1 - \frac{2a}{\pi R} \right)^2 \ln \left(2.6 + \frac{0.7\pi R}{2a} \right) \right] \frac{R^2}{D_0}. \quad (2.5)$$

Substituting this into Eq. (2.1) and using the relation $l = 2\sqrt{R^2 - a^2}$, we obtain

$$D_{eff}^{RW} = \frac{2(1 - \tilde{a}^2)D_0}{\left[\frac{1}{4} + \left(1 - \frac{2\tilde{a}}{\pi} \right)^2 \ln \left(2.6 + \frac{0.7\pi}{2\tilde{a}} \right) \right]}, \quad (2.6)$$

where $\tilde{a} = a/R$. The expression in Eq. (2.6) provides the exact asymptotic behavior of the effective diffusion coefficient as $\tilde{a} \rightarrow 0$. When deriving this result we have ignored the difference between the arc and its chord that is justified for narrow openings.

B. Wide openings

When the openings are wide (Fig. 1(a)), one can map the particle motion onto an effective one-dimensional description in terms of diffusion along the centerline of the channel in the presence of the entropy potential $U_{ent}(x)$ given by

$$\beta U_{ent}(x) = \ln \left(\frac{2R}{w(x)} \right), \quad (2.7)$$

where x is the particle coordinate measured along the centerline, $w(x)$ is the channel width as a function of x , $\beta = 1/(k_B T)$, k_B is the Boltzmann constant, and T is the absolute temperature. In Eq. (2.7) we count the entropy potential from its minima that correspond to the widest cross sections of the channel, $\max\{w(x)\} = 2R$. The entropy potentials for channels with wide and narrow openings are shown in Fig. 1.

We use the entropy potential to write the one-dimensional Smoluchowski equation for the particle propagator (the Green's function) in the channel, $G(x, t|x_0)$,

$$\frac{\partial G}{\partial t} = \frac{\partial}{\partial x} \left\{ D(x) e^{-\beta U_{ent}(x)} \frac{\partial}{\partial x} [e^{\beta U_{ent}(x)} G] \right\}, \quad (2.8)$$

where t is time, x_0 is the particle initial position at $t = 0$, and $D(x)$ is a position-dependent diffusion coefficient. The Smoluchowski equation in Eq. (2.8) is equivalent to the generalized Fick-Jacobs (FJ) equation:

$$\frac{\partial G}{\partial t} = \frac{\partial}{\partial x} \left\{ D(x) w(x) \frac{\partial}{\partial x} \left[\frac{G}{w(x)} \right] \right\}. \quad (2.9)$$

This equation with position-independent diffusion coefficient, $D(x) = D_0$, is known as ordinary FJ equation.⁷ Zwanzig (Zw) (Ref. 8) showed that a more accurate one-dimensional description of diffusion in systems of smoothly varying geometry is given by the generalized FJ equation that contains a position-dependent diffusion coefficient, Eq. (2.9). One can find a generalization of Zwanzig's analysis in Ref. 9.

For a 2D channel of varying cross section Zw derived⁸

$$D(x) \approx D_{Zw}(x) = \frac{D_0}{1 + \frac{1}{12} w'(x)^2}, \quad (2.10)$$

where $w'(x) = dw(x)/dx$. Based on heuristic arguments, Reguera and Rubi (RR) generalized the expression derived by Zwanzig and suggested¹⁰

$$D(x) \approx D_{RR}(x) = \frac{D_0}{\left(1 + \frac{1}{4} w'(x)^2 \right)^{1/3}}. \quad (2.11)$$

Kalinay and Percus (KP) obtained another expression for $D(x)$,¹¹

$$D(x) \approx D_{KP}(x) = 2 \frac{\arctan(w'(x)/2)}{w'(x)} D_0. \quad (2.12)$$

Recently, this expression was rederived by a different method by Martens *et al.*¹² Reduction of the two-dimensional diffusion in the channel to the effective one-dimensional description in terms of the generalized FJ equation is justified when $w'(x) \ll 1$.⁸ In such a case, the difference between the expressions for $D(x)$ given in Eqs. (2.10)–(2.12) can be neglected,

$$D_{Zw}(x) \approx D_{RR}(x) \approx D_{KP}(x) \approx \left(1 - \frac{1}{12} w'(x)^2 \right) D_0, \quad |w'(x)| \ll 1. \quad (2.13)$$

In what follows, we use the different expressions for $D(x)$ when deriving expressions for the effective diffusion coefficient of the particle in the channel.

Effective diffusion coefficient of a particle diffusing in a periodic potential $U(x)$, $U(x + l) = U(x)$, with periodic position-dependent diffusion coefficient $D(x)$, $D(x + l) = D(x)$, is given by the Lifson-Jackson formula,²

$$D_{eff} = \frac{1}{\langle e^{-\beta U(x)} \rangle \langle e^{\beta U(x)} / D(x) \rangle}, \quad (2.14)$$

where the angular brackets denote averaging over the period,

$$\langle f(x) \rangle = \frac{1}{l} \int_{x_0}^{x_0+l} f(x) dx. \quad (2.15)$$

In the case of the periodic entropy potential, Eq. (2.14) takes the form

$$D_{eff} = \frac{1}{\langle w(x) \rangle \langle 1/(D(x)w(x)) \rangle}. \quad (2.16)$$

We use this relation to find D_{eff} with different approximations for $D(x)$.

Taking $D(x) = D_0$, we find that the effective diffusion coefficient, D_{eff}^{FJ} , predicted by the ordinary FJ equation is given by

$$D_{eff}^{FJ} = \frac{D_0}{\langle w(x) \rangle \langle 1/w(x) \rangle}. \quad (2.17)$$

After performing the integrations, we obtain

$$D_{eff}^{FJ} = \frac{2(1 - \tilde{a}^2)D_0}{[\arcsin(\sqrt{1 - \tilde{a}^2}) + \tilde{a}\sqrt{1 - \tilde{a}^2}] \arcsin(\sqrt{1 - \tilde{a}^2})}. \quad (2.18)$$

Substituting into Eq. (2.16) $D(x) = D_{Zw}(x)$, Eq. (2.10), we obtain D_{eff}^{Zw} , which is given by

$$D_{eff}^{Zw} = \frac{D_0}{\langle w(x) \rangle \langle (1 + w'(x)^2/12)/w(x) \rangle} = \frac{\langle 1/w(x) \rangle D_{FJ}}{\langle (1 + w'(x)^2/12)/w(x) \rangle}. \quad (2.19)$$

Carrying out the integrations, we find

$$D_{eff}^{Zw} = \frac{3\tilde{a} \arcsin(\sqrt{1 - \tilde{a}^2}) D_{eff}^{FJ}}{2\tilde{a} \arcsin(\sqrt{1 - \tilde{a}^2}) + \sqrt{1 - \tilde{a}^2}}. \quad (2.20)$$

Choosing $D(x) = D_{RR}(x)$, Eq. (2.11), we obtain D_{eff}^{RR} , which is given by

$$D_{eff}^{RR} = \frac{D_0}{\langle w(x) \rangle \langle (1 + w'(x)^2/4)^{1/3}/w(x) \rangle} = \frac{\langle 1/w(x) \rangle D_{FJ}}{\langle (1 + w'(x)^2/4)^{1/3}/w(x) \rangle}. \quad (2.21)$$

After some manipulations, this reduces to

$$D_{eff}^{RR} = \frac{\arcsin(\sqrt{1 - \tilde{a}^2}) D_{eff}^{FJ}}{\int_0^{\arcsin(\sqrt{1 - \tilde{a}^2})} \frac{d\varphi}{(\cos \varphi)^{2/3}}}. \quad (2.22)$$

Finally, substituting into Eq. (2.16) $D(x) = D_{KP}(x)$, Eq. (2.12), we obtain D_{eff}^{KP} , which is given by

$$D_{eff}^{KP} = \frac{D_0}{\langle w(x) \rangle \langle w'(x)/[2w(x) \arctan(w'(x)/2)] \rangle} = \frac{\langle 1/w(x) \rangle D_{FJ}}{\langle w'(x)/[2w(x) \arctan(w'(x)/2)] \rangle}. \quad (2.23)$$

It can be shown that this reduces to

$$D_{eff}^{KP} = \frac{\arcsin(\sqrt{1 - \tilde{a}^2}) D_{eff}^{FJ}}{\int_0^{\arcsin(\sqrt{1 - \tilde{a}^2})} \frac{\tan \varphi}{\varphi} d\varphi}. \quad (2.24)$$

Expressions for the effective diffusion coefficient given in Eqs. (2.6), (2.18), (2.20), (2.22) and (2.24) are main results of this section.

III. DISCUSSION

As the tube period l increases from zero to $2R$, the width of the connecting openings, $2a = \sqrt{4R^2 - l^2}$, decreases from $2R$ to zero. As a result, the effective diffusion coefficient decreases from D_0 to zero. The exact asymptotic behavior of D_{eff} , as $a \rightarrow 0$, is given by the expression in Eq. (2.6), which in this limiting case takes the form

$$D_{eff}^{RW} \approx \frac{2D_0}{\ln(1/\tilde{a})}, \quad \tilde{a} \rightarrow 0. \quad (3.1)$$

Other formulas for D_{eff} , given in Eqs. (2.18), (2.20), (2.22) and (2.24), work when a is close to R and D_{eff} is close to D_0 . From these formulas one can see that D_{eff}^{FJ} , D_{eff}^{Zw} , D_{eff}^{RR} , and D_{eff}^{KP} tend to D_0 as $\tilde{a} \rightarrow 1$.

It is interesting that the formula for D_{eff}^{KP} , Eq. (2.24), obtained using the KP approximation for $D(x)$, Eq. (2.12),

correctly predicts the asymptotic behavior of D_{eff} in both limiting cases,

$$D_{eff}^{KP} \approx D_0 \times \begin{cases} \frac{2}{\ln(1/\tilde{a})}, & \tilde{a} \rightarrow 0 \\ 1, & \tilde{a} \rightarrow 1. \end{cases} \quad (3.2)$$

The formula for D_{eff}^{Zw} , Eq. (2.20), obtained using Zwanzig's approximation for $D(x)$, Eq. (2.10), predicts linear dependence on $\tilde{a}$ in the limit of narrow openings,

$$D_{eff}^{Zw} \approx \frac{12}{\pi} \tilde{a} D_0, \quad \tilde{a} \rightarrow 0. \quad (3.3)$$

Two other formulas for D_{eff} , D_{eff}^{FJ} and D_{eff}^{RR} , given in Eqs. (2.18) and (2.22), respectively, predict finite values of D_{eff} , as $a \rightarrow 0$,

$$D_{eff}^{FJ} \rightarrow \frac{8}{\pi^2} D_0 \approx 0.81 D_0, \quad \tilde{a} \rightarrow 0, \quad (3.4)$$

$$D_{eff}^{RR} \rightarrow \frac{4D_0}{\pi \int_0^{\pi/2} \frac{d\varphi}{(\sin \varphi)^{2/3}}} \approx 0.35 D_0, \quad \tilde{a} \rightarrow 0. \quad (3.5)$$

To check the accuracy of different expressions for the effective diffusion coefficient, Eqs. (2.6), (2.18), (2.20) and (2.22), we found D_{eff} in Brownian dynamics simulations and compared the theoretical predictions with the numerical results. Two different methods of determining the effective diffusion coefficient were used in the simulations. (1) We found the mean squared displacement along the channel axis of the particle, which was initially uniformly distributed over the compartment, as a function of time, $\langle \Delta x^2(t) \rangle$. Then D_{eff} was obtained as one half of the plateau value of the slope of this function,

$$D_{eff} = \frac{1}{2} \lim_{t \rightarrow \infty} \frac{d\langle \Delta x^2(t) \rangle}{dt}. \quad (3.6)$$

(2) We found the mean transit time, $\langle t \rangle$, of the particle between neighboring openings for uniform distribution of the starting point over the opening, and obtained D_{eff} by means of the relation

$$D_{eff} = \frac{l^2}{2\langle t \rangle}. \quad (3.7)$$

In addition, we checked that $\langle t \rangle$ was one quarter of the similar mean time for transitions between second neighboring openings. One can learn more about this method of determining D_{eff} in Ref. 13. In both cases the numerical results were obtained by averaging over 5×10^4 trajectories. The time step in the simulations was $10^{-6} R^2/D_0$. Collisions of the trajectory with the channel walls were treated as elastic. We found that the relative difference in D_{eff} obtained by the two methods is smaller than 3%, which is the accuracy of our numerical results.

We compare different expressions for the effective diffusion coefficient with D_{eff} found from Brownian dynamics simulations in Fig. 2. One can see that the formula for the effective diffusion coefficient obtained using the ordinary FJ equation, D_{eff}^{FJ} , Eq. (2.18), is applicable only when $\tilde{a} \geq 0.8$ (Fig. 2(a)). The expression in Eq. (2.20) giving D_{eff}^{Zw} , which

FIG. 3. Schematic representation of a square lattice of circular obstacles (panel (a)) and equivalent channels (panels (b) and (c)).

was obtained using the Zwanzig formula for $D(x)$, Eq. (2.10), has a wider range of applicability, $\tilde{a} \geq 0.6$ (Fig. 2(a)). Although D_{eff}^{RW} , Eq. (2.22) fails at very small openings $\tilde{a} < 0.01$ (Fig. 2(c)), it is close to the numerical results for $\tilde{a} \geq 0.01$ (Figs. 2(a) and 2(b)). One can see excellent agreement between D_{eff}^{RW} , Eq. (2.6), and numerical results at very small openings, $\tilde{a} \leq 0.01$ (Fig. 2(c)). The best approximation for the effective diffusion coefficient over the entire range of the opening size is provided by D_{eff}^{KP} given in Eq. (2.24) (Figs. 2(a)–2(c)).

Slowdown of diffusion in the channel formed by overlapping circles (Fig. 1) analyzed above should not be confused with slowdown of diffusion on a planar surface containing circular obstacles arranged in a square lattice (Fig. 3(a)) discussed in Ref. 14. The problem of finding the effective dif-

fusion coefficient in the second case can be reduced to that of finding D_{eff} in an equivalent channel. Two examples of such a channel are shown in Figs. 3(b) and 3(c). One can see that shapes of these channels are quite different from the shape of the channel shown in Fig. 1. This is why the slowdown of diffusion due to the presence of obstacles considered in Ref. 14 differs from the slowdown discussed above.

In summary, we have studied effective diffusion coefficient of a point Brownian particle in a periodic two-dimensional channel formed by overlapping circles (Fig. 1) with the goal to compare different approximations. Our main results are the approximate expressions for the effective diffusion coefficient given in Eqs. (2.6), (2.18), (2.20), (2.22) and (2.24), as well as the comparison of their predictions with D_{eff} obtained from Brownian dynamics simulations in Fig. 2. Finally, we note that the present study complements our similar study in three dimensions¹⁵ devoted to diffusion in a cylindrically symmetric tube of periodically varying diameter formed by overlapping spheres, in which we also compared different approximations for the effective diffusion coefficient found analytically with D_{eff} obtained from Brownian dynamics simulations.

ACKNOWLEDGMENTS

I.P. thanks CONACyT for partial support. We are grateful to Super Computer Division of Universidad Autonoma Metropolitana-Iztapalapa for the use of their computational facilities. This study was supported by the Intramural Research Program of the National Institutes of Health (NIH), Center for Information Technology.

- ¹P. S. Burada, P. Hanggi, F. Marchesoni, G. Schmid, and P. Talkner, *ChemPhysChem* **10**, 45 (2009); P. Hanggi and F. Marchesoni, *Rev. Mod. Phys.* **81**, 387 (2009).
- ²S. Lifson and J. L. Jackson, *J. Chem. Phys.* **36**, 2410 (1962).
- ³A. M. Berezhkovskii, V. Yu. Zitserman, and S. Y. Shvartsman, *J. Chem. Phys.* **118**, 7146 (2003); A. M. Berezhkovskii, V. Yu. Zitserman, and S. Y. Shvartsman, *J. Chem. Phys.* **119**, 6991 (2003).
- ⁴A. M. Berezhkovskii and A. V. Barzykin, *Phys. Rev. E* **82**, 011114 (2010).
- ⁵M. J. Ward and J. B. Keller, *SIAM J. Appl. Math.* **74**, 770 (1993).
- ⁶D. Holcman and Z. Schuss, *J. Stat. Phys.* **117**, 975 (2004).
- ⁷M. N. Jacobs, *Diffusion Processes* (Springer, New York, 1967).
- ⁸R. Zwanzig, *J. Phys. Chem.* **96**, 3926 (1992).
- ⁹A. M. Berezhkovskii and A. Szabo, *J. Chem. Phys.* **135**, 074108 (2011).
- ¹⁰D. Reguera and J. M. Rubi, *Phys. Rev. E* **64**, 061106 (2001).
- ¹¹P. Kalinay and J. K. Percus, *Phys. Rev. E* **74**, 041203 (2006).
- ¹²S. Martens, G. Schmid, L. Schimansky-Geier, and P. Hanggi, *Phys. Rev. E* **83**, 051135 (2011).
- ¹³L. Dagdug and A. M. Berezhkovskii, *J. Chem. Phys.* **131**, 056101 (2009).
- ¹⁴D. Holcman, N. Hoze, and Z. Schuss, *Phys. Rev. E* **84**, 021906 (2011).
- ¹⁵M.-V. Vazquez, A. M. Berezhkovskii, and L. Dagdug, *J. Chem. Phys.* **129**, 046101 (2008).