Effective diffusion coefficient of a Brownian particle in a periodically expanded conical tube

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Diffusion in a tube of periodically varying diameter occurs slower than that in a cylindrical tube because diffusing particles get trapped in wells of the periodic entropy potential which is due to variation of the tube cross-section area. To quantify the slowdown one has to establish a relation between the effective diffusion coefficient of the particle and the tube geometry, which is a very complicated problem. Here we show how to overcome the difficulties in the case of a periodically expanded conical tube, where we find an approximate solution for the effective diffusion coefficient as a function of the parameters determining the tube geometry.

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Diffusion in systems of varying geometry is a hot topic actively studied during the past decade. The reason is that problems involving diffusion in such systems are ubiquitous in nature and technology. Examples include transport in porous media and materials [1], controlled drug delivery [2], transport in spiny dendrites [3], and channel-facilitated membrane transport [4], to mention just a few. This Brief Report considers unbiased diffusion in a periodically expanded conical tube whose radius linearly increases from its minimum value a to its maximum value R over the tube period L, as shown in Fig. 1(a). Variation of the tube radius leads to the slowdown of the particle diffusion along the tube axis, since the particle gets trapped in the wells of the entropy potential [see Fig. 1(b)]. The goal of this study is to quantify the slowdown and to establish its relation to the tube geometry. The focus is on the coarse-grained description of motion at sufficiently long times when the particle displacement significantly exceeds the tube period, and the motion can be treated as effective free diffusion along the tube axis, characterized by the diffusion coefficient D_{eff}. Our main result is the formula in Eq. (16), which gives D_{eff} as a function of the geometric parameters of the tube. It is worth mentioning that tubes of this type have been made [5], and their application as a controlled drug release device has been discussed in the literature [6]. Although biased diffusive transport in such systems has been studied in recent papers [7] devoted to the force-dependent mobility, entropic rectification, and separation of particles of different sizes, the case of unbiased diffusion has not been considered in the literature yet. The present work fills this gap.

The problem of constructing a coarse-grained description and finding D_{eff} in a tube of periodically varying diameter has a straightforward solution when the tube diameter is a slowly varying function of the coordinate x measured along the tube axis. The solution involves two steps: (1) Reduction to the modified Fick-Jacobs equation [8–10], which describes the particle motion as one-dimensional diffusion along the tube axis in the presence of a periodic entropy potential with periodic position-dependent diffusion coefficient. (2) Finding D_{eff} using the Lifson-Jackson formula [11], which gives the effective diffusion coefficient for such a motion.

This strategy does not work for the tube shown in Fig. 1(a) since the tube diameter changes abruptly. To obtain D_{eff} in this case, we adapt the strategy used in Ref. [12] to find the effective diffusion coefficient of a particle in a tube of alternating diameter. Specifically, we map the particle motion onto a continuous time random walk among neighboring sites separated by the tube period L. For such random walks D_{eff} is given by

$$D_{\text{eff}} = L^2/(2\tau), \tag{1}$$

where τ is the mean particle lifetime on a site, which is the mean first-passage time of the particle from a starting point $x = x_0$ to one of the points located at $x = x_0 \pm L$. In this way the problem of finding D_{eff} reduces to that of finding the mean first-passage time τ.

To solve the latter problem, we first reformulate the initial three-dimensional description of the particle motion in the tube in terms of an approximate one-dimensional description which contains two elements: (1) diffusion in the entropy potential on intervals where the tube radius is a smooth function of x, and (2) matching the solutions at points where the tube radius abruptly changes from R to a. The former is described by the modified Fick-Jacobs equation [8] with a renormalized diffusion coefficient [8–10]. The matching conditions are obtained as follows: (i) To describe the entrance of the particle into the narrow part of a cone from the wide part of the neighboring cone, we treat the cone base containing

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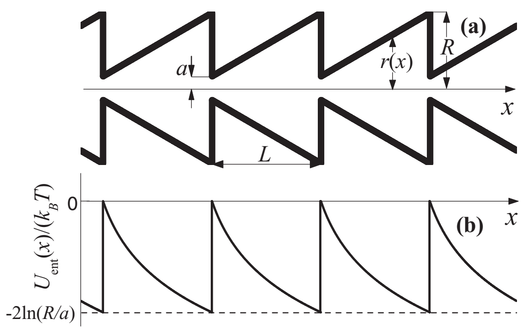

FIG. 1. Schematic representation of a periodically expanded conical tube [panel (a)] and corresponding entropy potential $U_{ent}(x)$ defined as $U_{ent}(x)/k_BT = -\ln\{A[r(x)]/A(a)\} = -2\ln[r(x)/a]$, where k_B is the Boltzmann constant and T is the absolute temperature [panel (b)].

the entrance as a uniform partially absorbing boundary. The trapping efficiency of such a boundary is characterized by the trapping rate κ_{wn}, where the subscript "wn" indicates that this rate is related to the wide-to-narrow transitions of the particle. (ii) When describing transitions of the particle in the opposite, narrow-to-wide (nw) direction, we also treat the boundary separating the two cones as partially absorbing characterized by the rate κ_{nw}. To find this rate we use the detailed balance condition (the requirement of no net flux across the boundary at equilibrium), which leads to the following relation between the two trapping rates:

$$\kappa_{wn}A(R) = \kappa_{nw}A(a), \tag{2}$$

where $A(r) = \pi r^2$ is the area of the cone cross section of radius r, perpendicular to the tube axis.

The replacement of the cone base containing the entrance into the neighboring cone by a uniform partially absorbing cone base is an example of the so-called boundary homogenization (BH) (see Refs. [13,14], and references therein). The reason why such a replacement is possible can be understood if one considers a steady-state flux of diffusing particles to the cone base containing an absorbing spot in its center. The point is that this flux becomes indistinguishable from the steady-state flux to the partially absorbing cone base with correctly chosen trapping rate at distances larger than the base radius. Recently we have used BH to study diffusion in cylindrical tubes of abruptly changing diameter [12,15,16].

Here, for the first time, we apply BH in the presence of the entropy potential which is due to varying diameter of the conical tube. This potential "pushes" diffusing particles towards the cone base [see Fig. 1(b)]. We found κ_{wn} in the presence of the entropy potential by means of Brownian dynamics simulations, following the same computer-assisted BH strategy as that used in Ref. [14] to determine the effective trapping rate for particles diffusing in a cylindrical tube containing an absorbing disk in the center of its end wall. In view of the fact that the reduction to the modified Fick-Jacobs equation is applicable only when the radius variation rate λ, $\lambda = (R-a)/L$, does not exceed unity [17], we numerically studied BH in the same range of λ, $\lambda \leqslant 1$. To our surprise, we found that κ_{wn} is practically independent of λ and well described by the formula proposed in Ref. [14] by fitting numerical results obtained for a cylindrical tube ($\lambda = 0$). This formula gives the trapping rate as a function of the ratio ν of the tube radius R to the radius a of the absorbing spot, $\nu = a/R$,

$$\kappa_{wn} = \frac{4D_0}{\pi R}\nu f(\nu) = \frac{4D_0}{\pi a}\nu^2 f(\nu), \tag{3}$$

where D_0 is the particle diffusion coefficient in a cylindrical tube and function $f(\nu)$ is given by $f(\nu) = (1 + 1.37\nu - 0.37\nu^4)/(1-\nu^2)^2$. As ν increases from zero to 1, $f(\nu)$ monotonically increases from unity to infinity.

Although we have no arguments explaining why κ_{wn} is practically independent of λ for the entire range of ν, $0 < \nu \leqslant 1$, we point out that this independence can be rationalized in the limiting cases of ν close to zero and $\nu = 1$. Indeed, it is obvious that κ_{wn} tends to infinity as $\nu \to 1$ for all λ because the entire cone base is perfectly absorbing in this limiting case. In the opposite limiting case of small ν, using the Hill-Berg-Purcell (HBP) formula [18] for the rate constant of a perfectly absorbing disk of radius a on a flat reflecting wall, $k_{HBP} = 4D_0 a$, it can be shown that $\kappa_{wn} = 4D_0 a/(\pi R^2)$ independent of λ.

To find τ, consider a particle initially located at point x_0 which is between points $x = 0$ and $x = L$, $0 < x_0 < L$, assuming that the tube radius changes its value from R to a at points $x = nL$, $n = 0, \pm1, \pm2, \ldots$. Let $G(x,t|x_0)$ be the particle propagator (Green's function), which is the probability density of finding the particle at point x, $x_0 - L < x < x_0 + L$, at time t, conditional on that the particle starts from $x = x_0$ at $t = 0$. The propagator satisfies the modified Fick-Jacobs equation on the intervals $x_0 - L < x < 0$, $0 < x < L$, and $L < x < x_0 + L$, absorbing boundary conditions at points $x = x_0 \pm L$, and matching conditions at points $x = 0$ and $x = L$. The particle survival probability for time t, $S(t)$, is related to the propagator by

$$S(t) = \int_{x_0-L}^{x_0+L} G(x,t|x_0)dx. \tag{4}$$

Using $S(t)$, we can find the probability density of the particle lifetime, $\varphi(t) = -dS(t)/dt$, and the mean lifetime,

$$\tau = \int_0^\infty t\varphi(t)dt = \int_0^\infty S(t)dt. \tag{5}$$

Substituting here the expression for $S(t)$ in Eq. (4), we can write τ as

$$\tau = \int_{x_0-L}^{x_0+L} F(x|x_0)dx, \tag{6}$$

where

$$F(x|x_0) = \int_0^\infty G(x,t|x_0)dt. \tag{7}$$

The expression in Eq. (6) has a transparent physical interpretation. The product $F(x|x_0)dx$ is the mean cumulative time spent by the particle in the interval of length dx around point x. Thus, Eq. (6) gives τ as a sum of the mean cumulative times spent by the particle at all points of the entire interval $(x_0 - L\,,\; x_0 + L)$.

In the tube under study, the tube radius $r(x)$ is a periodic function of x, $r(x+nL) = r(x)$, $n = 0, \pm 1, \pm 2, \ldots,$ with $r(x)$ given by

$$r(x) = a + \lambda x, \qquad 0 < x < L. \tag{8}$$

As x increases from zero to L, the tube radius grows from a to its maximum value $R = a + \lambda L$. Since $dr(x)/dx = \lambda =$ const, the diffusion coefficient entering into the modified Fick-Jacobs equation is a position-independent function of λ, which we denote by D_λ. Thus the propagator $G(x,t|x_0)$ is a solution to

$$\frac{\partial G}{\partial t} = D_\lambda \frac{\partial}{\partial x}\left\{A[r(x)]\frac{\partial}{\partial x}\frac{G}{A[r(x)]}\right\} \tag{9}$$

on the intervals $x_0 - L < x < 0$, $0 < x < L$, and $L < x < x_0 + L$, subject to the initial condition $G(x,0|x_0) = \delta(x - x_0)$ and absorbing boundary conditions at the end points, $G|_{x_0 \pm L} = 0$. At the matching (m) points, $x_m = 0$ and L, the propagator satisfies the matching conditions,

$$\begin{aligned} D_\lambda A(R)\,\frac{\partial}{\partial x}\frac{G}{A\,[r(x)]}\bigg|_{x=x_m-0} &= D_\lambda A(a)\,\frac{\partial}{\partial x}\frac{G}{A\,[r(x)]}\bigg|_{x=x_m+0} \\ &= \kappa_{nw} G|_{x=x_m+0} - \kappa_{wn}\, G|_{x=x_m-0}\,. \end{aligned} \tag{10}$$

The first equality in Eq. (10) guarantees conservation of the total flux across the boundary, while the second one provides the relation between the flux and the propagators on the two sides of the boundary, which follows from BH.

Correspondingly, the function $F(x|x_0)$, defined in Eq. (7), satisfies the equation which is obtained by integrating Eq. (9) with respect to time from zero to infinity. Using the initial conditions for the propagator, we find that on the intervals $x_0 - L < x < 0$, $0 < x < L$, and $L < x < x_0 + L$, $F(x|x_0)$ is a solution to

$$D_\lambda \frac{\partial}{\partial x}\left\{A\,[r(x)]\,\frac{\partial}{\partial x}\frac{F}{A\,[r(x)]}\right\} = -\delta(x - x_0). \tag{11}$$

At the matching points it satisfies the matching conditions that follow from Eq. (10),

$$\begin{aligned} D_\lambda A(R)\,\frac{\partial}{\partial x}\frac{F}{A\,[r(x)]}\bigg|_{x=x_m-0} &= D_\lambda A(a)\,\frac{\partial}{\partial x}\frac{F}{A\,[r(x)]}\bigg|_{x=x_m+0} \\ &= \kappa_{nw} F|_{x=x_m+0} - \kappa_{wn}\, F|_{x=x_m-0}\,. \end{aligned} \tag{12}$$

Finally, at the end points $x = x_0 \pm L$ this function satisfies absorbing boundary conditions, $F|_{x_0\pm L} = 0$, as the propagator does.

We find $F(x|x_0)$ by integrating Eq. (11). Substituting the result into Eq. (6) and performing the integration, we obtain

$$\tau = \left(\int_0^L A\,[r(x)]\,dx\right)\left(\int_0^L A\,[r(x)]^{-1}\,dx + D_\lambda/\sqrt{A(R)A(a)\kappa_{wn}\kappa_{nw}}\right)\bigg/(2D_\lambda)\,. \tag{13}$$

Using this we can write $D_{\rm eff}$ defined in Eq. (1) as

$$D_{\rm eff} = \frac{D_\lambda}{\langle A[r(x)]\rangle[\langle 1/A[r(x)]\rangle + D_\lambda/(L\sqrt{A(R)A(a)\kappa_{wn}\kappa_{nw}})]}, \tag{14}$$

where $\langle f(x)\rangle$ denotes averaging of a function $f(x)$ over the tube period, $\langle f(x)\rangle = \int_0^L f(x)dx/L$. One can check that for $r(x)$ given in Eq. (8) we have $\langle 1/A[r(x)]\rangle = 1/\sqrt{A(R)A(a)}$. This allows us to write Eq. (14) in the following form:

$$D_{\rm eff} = \frac{D_\lambda}{\langle A[r(x)]\rangle\langle 1/A[r(x)]\rangle[1 + D_\lambda/(L\sqrt{\kappa_{wn}\kappa_{nw}})]}. \tag{15}$$

The explicit dependence of $D_{\rm eff}$ on the geometric parameters of the tube, which is the main result of this Brief Report, is given by

$$D_{\rm eff} = \frac{D_0}{[1 + \lambda^2 l^2/[3(1+\lambda l)]][\sqrt{1+\lambda^2} + \pi(1+\lambda l)/(4 l f(\nu)|_{\nu=1/(1+\lambda l)})]}, \tag{16}$$

where $l = L/a$ and we have used the Reguera-Rubi formula [9] for D_λ, $D_\lambda = D_0/\sqrt{1+\lambda^2}$. To illustrate the slowdown of diffusion, in Fig. 2 we show the ratio $D_0/D_{\rm eff}$, predicted by Eq. (16), as a function of λ for $l = 5,\ 10,\ 25,\ 50$, and 100. In this figure we also give the values of the ratio obtained from three-dimensional Brownian dynamics simulations, which are shown by symbols. One can see that the theoretically predicted behavior is in good agreement with the simulation results.

Finally, we discuss the asymptotic behavior of the effective diffusion coefficient given in Eq. (16) in the limiting cases of $\lambda = 0$ and $\lambda l \gg 1$. As follows from Eq. (16), when the tube is cylindrical ($\lambda = 0$) $D_{\rm eff}$ reduces to D_0, as it must be. In the limiting case of large λl, $D_{\rm eff}$ takes the form

$$D_{\rm eff} = \frac{3D_0}{\lambda l(\sqrt{1+\lambda^2} + \pi\lambda/4)}, \quad \lambda l \gg 1, \tag{17}$$

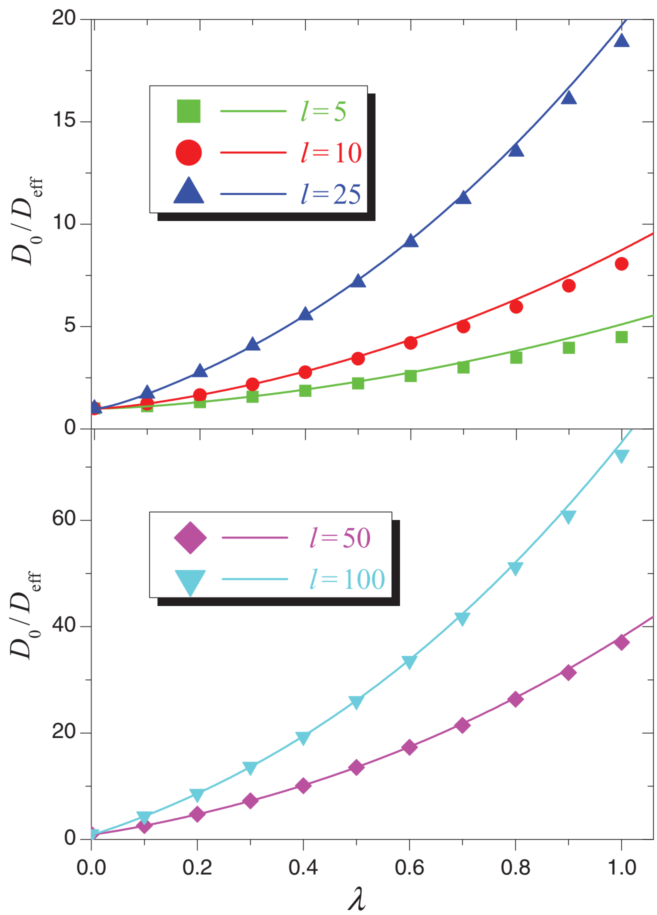

FIG. 2. (Color online) The ratio $D_0/D_{\rm eff}$ as a function of the radius variation rate λ at fixed values of the dimensionless tube period $l = L/a$. Solid curves are the theoretically predicted dependencies drawn using Eq. (16). Symbols are the values of the ratio obtained from three-dimensional Brownian dynamics simulations.

which shows that at a fixed value of λ, $\lambda \neq 0$, $D_{\rm eff}$ approaches zero with increasing tube period as $1/l = a/L$. This is a consequence of the fact that as λl increases, the barrier in the entropy potential [Fig. 1(b)] becomes higher and higher, since the ratio $a/R = 1/(1+\lambda l)$ becomes smaller and smaller.

In summary, although at first sight the problem of finding the effective diffusion coefficient for the periodically expanded conical tube shown in Fig. 1(a) looks hopeless because of the complex tube geometry, we managed to find an approximate solution for $D_{\rm eff}$, Eq. (16), which is the main result of this Brief Report. In deriving Eq. (16) we used the modified Fick-Jacobs equation and treated the cone base containing the entrance into the neighboring cone as a uniform partially absorbing cone base. Its trapping rate was determined in computer-assisted boundary homogenization. We found that the rate is insensitive to the presence of the entropy potential and well described by the formula obtained for a cylindrical tube in Ref. [14]. It is worth mentioning that both boundary homogenization [16] and the reduction to the Fick-Jacobs equation [19] are applicable only when the tube period is larger than the diameter of the openings connecting neighboring cones. This condition supplements the above-mentioned requirement that the radius variation rate should not exceed unity [17]. If this condition is not met, Eq. (16) fails. However, the slowdown of diffusion due to the varying tube diameter in this case is small and can be neglected. Comparison shows that predictions of the formula in Eq. (16) agree well with the values of $D_{\rm eff}$ obtained from three-dimensional Brownian dynamics simulations over a wide range of the parameters determining the tube geometry.

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