Biased diffusion in tubes of alternating diameter: Analytical treatment in the case of strong bias

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This paper is devoted to the effective transport coefficients of a particle in a tube of alternating diameter. Analytical expressions are derived for the effective mobility and diffusivity under strong bias conditions, i.e., in the limiting case where the external biasing force tends to infinity. The expressions give the transport coefficients as functions of the geometric parameters of the tube and the external force. They show that the effective diffusivity is a linear function of the square of the external force, whereas the effective mobility is independent of the force. The problem of finding effective transport coefficients in a tube of alternating diameter is too complex to be analyzed by conventional methods. Therefore, the expressions are derived in the framework of an intuition-based approach and validated by Brownian dynamics simulations. The obtained results extend a short list of available analytical expressions for the effective transport coefficients. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4902552>]

I. INTRODUCTION

This paper is devoted to biased diffusion in three-dimensional tubes of alternating diameter, an example of which is shown in Fig. 1. During recent years, transport in quasi-one-dimensional structures of periodically varying geometry has attracted attention of many researchers because of its importance in various applications (see recent review articles¹ and references therein). Transport in such structures is characterized by the effective mobility, $\mu_{\text{eff}}(F)$, and diffusivity, $D_{\text{eff}}(F)$, where F is a constant uniform external biasing force. The goal of the theory is to establish the dependencies of the transport coefficients on the external force and geometric parameters of the system. This is a complicated problem that has mainly been studied numerically. In this paper we analytically determine the above mentioned dependencies for the tube shown in Fig. 1 in the limiting case of strong bias, $F \rightarrow \infty$. Our results extend a short list of available analytical expressions for the effective transport coefficients.

Even in the absence of an external bias, analytical expressions for $D_{\text{eff}}(0)$ are known only for a few geometries. If $D_{\text{eff}}(0)$ is known, the effective mobility, $\mu_{\text{eff}}(0)$, can be found using the Einstein relation, $\mu_{\text{eff}}(0) = \beta D_{\text{eff}}(0)$, where $\beta^{-1} = k_B T$ with the standard notations k_B and T for the Boltzmann constant and absolute temperature. The only known general result for $\mu_{\text{eff}}(0)$ and $D_{\text{eff}}(0)$ is that these transport coefficients are always smaller than their counterparts for a cylindrical tube μ_0 and D_0 . Kalinay² developed a perturbation theory to treat the effective transport coefficients at moderate bias. There is a unique system, tubes with periodic dead ends

schematically shown in Fig. 2, for which analytical expressions for $\mu_{\text{eff}}(F)$ and $D_{\text{eff}}(F)$ are known for arbitrary F .³

What is also known is asymptotic behavior of the transport coefficients in the limiting case of strong bias, $F \rightarrow \infty$. This asymptotic behavior is not universal and depends on the system geometry. When the tube radius is a smoothly varying function of a coordinate measured along the centerline of the tube, both transport coefficients approach their values in a cylindrical tube, μ_0 and D_0 .⁴ This happens because the particle is localized in the narrow cylinder passing through the tube bottlenecks. As a consequence, it is unaware of the varying tube geometry.

The situation is quite different when the tube radius changes abruptly. Here, the $F \rightarrow \infty$ asymptotic behaviors of $\mu_{\text{eff}}(F)$ and $D_{\text{eff}}(F)$ are known for the two tube geometries shown in Fig. 3. In a cylindrical tube separated into identical compartments by infinitely thin periodic partitions with circular apertures in their centers, shown in Fig. 3(a), the transport coefficients are functions of the ratio ν of the aperture radius a to the tube radius R , $\nu = a/R$. The effective mobility is independent of F and given by^{5,6}

$$\mu_{\text{eff}}(\infty) = \nu^2 \mu_0, \quad (1.1)$$

while the effective diffusivity is proportional to F^2 ,⁶

$$D_{\text{eff}}(F)|_{F \rightarrow \infty} = \frac{\nu^4}{4} (\nu^2 - 1 - 2 \ln \nu) (\beta F R)^2 D_0. \quad (1.2)$$

A distinctive feature of motion in the tube shown in Fig. 3(a) under strong bias conditions is that the particle “jumps”

FIG. 1. Schematic representation of a three-dimensional tube of alternating diameter formed by wide and narrow sections of radii R and a . The section lengths, respectively, are l_w and l_n .

between mobile and immobile states. In the former, the particle moves along the tube axis with velocity $\mu_0 F$ in the cylinder of radius a connecting the apertures. In the latter, the particle does not move along the tube because it is pressed against the partition by the external force.

In the tube shown in Fig. 3(b), the pattern of the particle motion under strong bias conditions depends on the external force direction.⁷ When $F \rightarrow +\infty$, the particle is localized in the cylinder connecting the apertures of the conical compartments, and therefore $\mu_{\text{eff}}(\infty) = \mu_0$ and $D_{\text{eff}}(\infty) = D_0$. When $F \rightarrow -\infty$, the particle jumps between the mobile and immobile state, and the transport coefficients are given by Eqs. (1.1) and (1.2).

This work focuses on the effective transport coefficients in tubes of alternating diameter (Fig. 1) under strong bias conditions. Our goal is to find analytical expressions for $\mu_{\text{eff}}(\infty)$ and $D_{\text{eff}}(F)|_{F \rightarrow \infty}$ as functions of the geometric parameters, a , R , l_n , and l_w (see Fig. 1), as well as the F -dependence of the effective diffusivity. As $l_n \rightarrow 0$, narrow sections of the tube become infinitely thin partitions and the transport coefficients are given by Eqs. (1.1) and (1.2). In the opposite limit, when $l_n \rightarrow \infty$, the particle essentially moves in a cylindrical tube of radius a and the transport coefficients are μ_0 and D_0 . Thus, our goal is to describe the transition between the two limits.

In a tube of alternating diameter, under strong bias conditions the particle also jumps between mobile and immobile states, where it moves along the tube axis with velocity $\mu_0 F$ or is pressed against the wall by the external force, respectively. As a consequence, the effective mobility can be written as

$$\mu_{\text{eff}}(\infty) = P_m(z, \nu) \mu_0, \quad (1.3)$$

where $P_m(z, \nu)$ is the steady-state probability of finding the particle in the mobile state when it is in the cylinder of radius a around the tube axis, and $z = l_n/l_w$. We show that the probability $P_m(z, \nu)$ monotonically increases from ν^2 to unity as z increases from zero to infinity (Fig. 5).

FIG. 2. Schematic representation of a tube with periodic dead ends.

FIG. 3. Schematic representation of a cylindrical tube separated into identical compartments by infinitely thin periodic partitions (a) and a periodically tapering tube (b).

We will see that the effective diffusivity is given by

$$D_{\text{eff}}(F)|_{F \rightarrow \infty} = [B(z, \nu)(\beta F R)^2 + P_m(z, \nu)] D_0, \quad (1.4)$$

where function $B(z, \nu)$ varies from $\nu^4(\nu^2 - 1 - 2 \ln \nu)/4$ at $z = 0$ to zero as $z \rightarrow \infty$. The transition between the two limiting values is either monotonic or non-monotonic, depending on the value of the radii ratio ν (Fig. 6). The transition is non-monotonic for small ν and monotonic when ν approaches unity. A critical value of ν , where the z -dependence of function $B(z, \nu)$ changes its behavior is $\nu^* \approx 0.68$.

Finally, we mention that the effective transport coefficients describe the particle motion at sufficiently long times. In view of this circumstance, the question of how to describe the motion at intermediate times naturally arises. This is a very complicated question even in the absence of bias ($F = 0$). In this case D_0 is larger than D_{eff} that characterizes the mean square displacement of the particle at sufficiently long times, $\langle \Delta x^2(t) \rangle = 2D_{\text{eff}}t$. As a consequence, at intermediate times $\langle \Delta x^2(t) \rangle$ grows with time slower than a linear function. This transient behavior of $\langle \Delta x^2(t) \rangle$ can be mistakenly interpreted as anomalous diffusion. A discussion of how to discriminate between the transient behavior and anomalous diffusion at $F = 0$ is given in Ref. 8. In the presence of bias ($F \neq 0$), the question of how to describe the particle motion at intermediate times is even more complicated. The reason is that not only the second moment, but the first two moments of the particle displacement are involved: the first moment determines $\mu_{\text{eff}}(F)$ and both moments determine $D_{\text{eff}}(F)$. Concluding this brief discussion, we point out that the focus of this study is on the effective transport coefficients. Therefore, the much more complicated problem of description of the particle motion at intermediate times is beyond the scope of our analysis.

Our consideration contains some heuristic arguments. Therefore the obtained analytical results have been validated by Brownian dynamics simulations. The outline of the paper is as follows. We consider the effective mobility and diffusivity in Secs. II and III, respectively. Section IV contains a summary of the obtained results and some concluding remarks.

II. EFFECTIVE MOBILITY

To find the effective mobility, Eq. (1.4), we need to know the steady-state probability $P_m(z, \nu)$ of finding the particle

moving along the tube in the cylinder of radius a around the tube axis. This probability is a sum of the steady-state probabilities of finding the particle, moving along the tube, in the wide and narrow tube sections, $P_m^{(w)}(z, \nu)$ and $P_m^{(n)}(z, \nu)$, respectively,

$$P_m(z, \nu) = P_m^{(w)}(z, \nu) + P_m^{(n)}(z, \nu). \quad (2.1)$$

We assume that the ratio of these probabilities is equal to the ratio of the lengths of the wide and narrow sections. Then $P_m^{(n)}(z, \nu)$ can be written as

$$P_m^{(n)}(z, \nu) = \frac{l_n}{l_w} P_m^{(w)}(z, \nu) = z P_m^{(w)}(z, \nu). \quad (2.2)$$

Let $P_{im}(z, \nu)$ be the steady-state probability of finding the particle in the immobile state. The three probabilities satisfy the normalization condition,

$$P_m^{(w)}(z, \nu) + P_m^{(n)}(z, \nu) + P_{im}(z, \nu) = 1, \quad (2.3)$$

which is used in calculating the probability $P_m(z, \nu)$.

Since the probabilities $P_{im}(z, \nu)$ and $P_m^{(w)}(z, \nu)$ are proportional to the areas $\pi(R^2 - a^2)$ and πa^2 , respectively, their ratio is proportional to the ratio of these areas,

$$\frac{P_{im}(0, \nu)}{P_m^{(w)}(0, \nu)} \propto \frac{R^2 - a^2}{a^2} = \nu^{-2} - 1. \quad (2.4)$$

Exact solutions for the probability ratio can be found only in two limiting cases of $z = 0$ and ∞ . As shown in the Appendix, when $z = \infty$ the ratio is

$$\left. \frac{P_{im}(z, \nu)}{P_m^{(w)}(z, \nu)} \right|_{z \rightarrow \infty} = \frac{1}{2}(\nu^{-2} - 1). \quad (2.5)$$

It is impossible to generalize the derivation given in the Appendix to the case of finite z . The reason is that we cannot find the steady-state radial distribution at the entrance to the wide section of the tube from the narrow one. Nevertheless, the ratio can be found in the opposite limiting case of infinitely thin partitions ($z = 0$). Using some general arguments it has been shown that in this case the ratio is⁶

$$\frac{P_{im}(0, \nu)}{P_m^{(w)}(0, \nu)} = \frac{R^2 - a^2}{a^2} = \nu^{-2} - 1. \quad (2.6)$$

Consider the probability ratio $P_{im}(z, \nu)/P_m^{(w)}(z, \nu)$, normalized to its value at $z = 0$, $\nu^{-2} - 1$. According to Eqs. (2.5) and (2.6), this normalized probability ratio decreases from unity at $z = 0$ to one half at $z = \infty$, independent of ν . Since we cannot find an analytical solution for the normalized probability ratio at arbitrary z , we obtained this ratio numerically from Brownian dynamics simulations and found that the ratio is independent of ν not only at $z = \infty$, but over the entire range of z , i.e., over the entire range of the partition thickness (see Table I). (Hereafter we interchangeably use the terms partition and narrow section of the tube.) Denote the normalized probability ratio by $\varphi(z)$,

$$\varphi(z) = \frac{P_{im}(z, \nu)}{(\nu^{-2} - 1)P_m^{(w)}(z, \nu)}. \quad (2.7)$$

As z increases from zero to infinity, function $\varphi(z)$ monotonically decreases from unity to one half.

TABLE I. Values of function $\varphi(z)$ obtained from Brownian dynamics simulations at $\nu = 0.1, 0.3$, and 0.7 , with $\beta FR = 10^5$, and predicted by Eq. (2.9).

$z = l_n/l_w$	$\nu = a/R$			Eq. (2.9)
	0.1	0.3	0.7	
0	0.99	0.99	0.99	1
0.1	0.74	0.76	0.77	0.77
0.3	0.67	0.67	0.67	0.70
0.5	0.62	0.63	0.63	0.62
0.7	0.59	0.60	0.59	0.59
0.9	0.58	0.59	0.57	0.57
1	0.56	0.56	0.55	0.57
2	0.53	0.53	0.52	0.53
5	0.52	0.51	0.52	0.51
10	0.51	0.51	0.51	0.50
20	0.51	0.51	0.51	0.50
50	0.51	0.50	0.50	0.50
100	0.50	0.51	0.49	0.50

To provide a rationale for the ν -independence of the normalized probability ratio, consider radial displacement of the particle moving along the tube axis in a wide section of the tube. The mean time spent by such a particle in the wide section, τ_w , is given by

$$\tau_w = \frac{l_w}{\mu_0 F}. \quad (2.8)$$

As $F \rightarrow \infty$, time τ_w approaches zero. As a consequence, the radial displacement during this time, which is proportional to $\sqrt{D_0 \tau_w}$, is much smaller than $R - a$. This implies that the particle escaping from the mobile state, when traversing the wide section, is unaware of the existence of the reflecting boundary at $r = R$. We believe that this is ultimately the reason why the normalized probability ratio $\varphi(z)$, Eq. (2.7), is independent of ν .

Figure 4 shows function $\varphi(z)$ obtained from Brownian dynamics simulations at $\nu = 0.3$ (symbols). We found that $\varphi(z)$ can be reasonably well approximated by a simple formula,

$$\varphi(z) = \frac{1}{2}(e^{-2\sqrt{z}} + 1), \quad (2.9)$$

shown in Fig. 4 by solid curves, which varies from unity at $z = 0$ to its large- z limiting asymptotic value $\varphi(\infty) = 0.5$. One can see that $\varphi(z)$ falls from $\varphi(0) = 1$ to approximately 0.56 at $z = 1$ and then slowly goes to 0.5 as $z \rightarrow \infty$. The maximum relative error of the approximation formula does not exceed 5%.

According to Eq. (2.7), the steady-state probability of finding the particle in the immobile state is

$$P_{im}(z, \nu) = (\nu^{-2} - 1)\varphi(z)P_m^{(w)}(z, \nu). \quad (2.10)$$

Substituting this and $P_m^{(n)}(z, \nu)$ in Eq. (2.2) into Eq. (2.3), we arrive at a linear equation for the probability $P_m^{(w)}(z, \nu)$. Solving this equation we obtain

$$P_m^{(w)}(z, \nu) = \frac{1}{1 + z + (\nu^{-2} - 1)\varphi(z)}. \quad (2.11)$$

FIG. 4. Function $\varphi(z)$. Symbols are the values of $\varphi(z)$ obtained from Brownian dynamics simulations at $\nu = 0.3$ and $\beta FR = 10^5$. Solid curves are drawn using the approximation formula in Eq. (2.9).

Using this together with Eqs. (2.1) and (2.2), we get the following expression for the steady-state probability of finding the particle in the mobile state:

$$P_m(z, \nu) = \frac{1 + z}{1 + z + (\nu^{-2} - 1)\varphi(z)}. \quad (2.12)$$

This allows us to find the effective mobility, Eq. (1.3), as a function of the tube geometric parameters,

$$\mu_{\text{eff}}(\infty) = \frac{1 + z}{1 + z + (\nu^{-2} - 1)\varphi(z)} \mu_0, \quad (2.13)$$

which is one of the main results of this section. One can see that the effective mobility in Eq. (2.13) reduces to that in Eq. (1.1) at $z = 0$ and to μ_0 as $z \rightarrow \infty$. The difference between $\mu_{\text{eff}}(\infty) = \nu^2 \mu_0$ at $z = 0$ and μ_0 is most pronounced for small ν , $\nu \ll 1$. Here $\mu_{\text{eff}}(\infty)$ can be reliably approximated by μ_0 only when $z \gg 1$ and hence the partition thickness, l_n , significantly exceeds l_w . The corresponding inequality that follows from Eq. (2.13) is given by

$$z \gg \nu^{-2}, \quad \nu \ll 1. \quad (2.14)$$

In Fig. 5 we compare the z -dependencies of $P_m(z, \nu)$ predicted by Eq. (2.12), with function $\varphi(z)$ given by Eq. (2.9), (solid curves) and the mobility ratios $\mu_{\text{eff}}(\infty)/\mu_0$ obtained from Brownian dynamics simulations (symbols). The comparison is made for $\nu = 0.1, 0.3$, and 0.7 . One can see excellent agreement between the theoretical predictions and simulation results. As mentioned above, the smaller ν , the slower the probability $P_m(z, \nu)$ approaches unity as $z \rightarrow \infty$. Finally, we point out that deviation of function $\varphi(z)$ from unity is especially important when ν is small, and hence $\nu^2 \ll 1$. In such a case, $P_m(z, \nu)$ in Eq. (2.12) is inversely proportional to $\varphi(z)$ at not too large z ,

$$P_m(z, \nu) \approx (1 + z) \frac{\nu^2}{\varphi(z)}, \quad (2.15)$$

FIG. 5. The mobility ratio $\mu_{\text{eff}}(\infty)/\mu_0 = P_m(z, \nu)$ as a function of z for $\nu = 0.1, 0.3$, and 0.7 . Symbols are the values of the ratio obtained from Brownian dynamics simulations with $\beta FR = 10^5$. Solid curves are drawn using Eq. (2.12) with function $\varphi(z)$ given by Eq. (2.9).

and, therefore, variation of the function $\varphi(z)$ cannot be neglected.

III. EFFECTIVE DIFFUSIVITY

To find the effective diffusivity, consider the particle motion in the tube shown in Fig. 1 under strong bias conditions, assuming that the cumulative times spent by the particle in the mobile and immobile states, respectively, are t_m and $t - t_m$, where t is the total observation time. Since the particle moves along the tube only in the mobile state, the first two moments of the particle displacement, Δx , along the tube axis are

$$\langle \Delta x(t_m) \rangle = \mu_0 F t_m \quad (3.1)$$

and

$$\langle \Delta x^2(t_m) \rangle = (\mu_0 F t_m)^2 + 2D_0 t_m. \quad (3.2)$$

Time t_m is a random variable. Denoting the averaging over t_m at a fixed value of the total observation time by $\langle \cdots \rangle_t$, we can write the first two moments above averaged over t_m as

$$\langle \langle \Delta x(t_m) \rangle \rangle_t = \mu_0 F \langle t_m \rangle_t \quad (3.3)$$

and

$$\langle \langle \Delta x^2(t_m) \rangle \rangle_t = (\mu_0 F)^2 \langle t_m^2 \rangle_t + 2D_0 \langle t_m \rangle_t, \quad (3.4)$$

where $\langle t_m \rangle_t$ and $\langle t_m^2 \rangle_t$ are the first two moments of the cumulative residence time spent by the particle in the mobile state. Using Eqs. (3.3) and (3.4), the variance of the particle displacement along the tube axis during time t , $\sigma_{\Delta x}^2(t)$, can be written as

$$\begin{aligned} \sigma_{\Delta x}^2(t) &= \langle \langle \Delta x^2(t_m) \rangle \rangle_t - \langle \langle \Delta x(t_m) \rangle \rangle_t^2 \\ &= (\mu_0 F)^2 \sigma_{t_m}^2(t) + 2D_0 \langle t_m \rangle_t, \end{aligned} \quad (3.5)$$

where $\sigma_{t_m}^2(t)$ is the variance of the cumulative time t_m , conditional on that the total observation time is equal to t ,

$$\sigma_{t_m}^2(t) = \langle t_m^2 \rangle_t - \langle t_m \rangle_t^2. \quad (3.6)$$

By definition, the effective diffusivity is

$$D_{\text{eff}}(F) = \lim_{t \rightarrow \infty} \frac{\sigma_{\Delta x}^2(t)}{2t}. \quad (3.7)$$

Substituting here $\sigma_{\Delta x}^2(t)$ in Eq. (3.5) we obtain

$$D_{\text{eff}}(F)|_{F \rightarrow \infty} = (\mu_0 F)^2 \lim_{t \rightarrow \infty} \frac{\sigma_{t_m}^2(t)}{2t} + D_0 \lim_{t \rightarrow \infty} \frac{\langle t_m \rangle_t}{t}. \quad (3.8)$$

As $t \rightarrow \infty$, the ratio $\langle t_m \rangle_t/t$ approaches $P_m(z, \nu)$,

$$\lim_{t \rightarrow \infty} \frac{\langle t_m \rangle_t}{t} = P_m(z, \nu). \quad (3.9)$$

As shown below, under certain conditions, the long-time asymptotic behavior of the variance $\sigma_{t_m}^2(t)$ is given by

$$\begin{aligned} \sigma_{t_m}^2(t) = & \frac{R^2 t}{2D_0} \frac{\nu^4 K(z)^2}{[1 + (K(z) - 1)\nu^2]^3} \\ & \times \left[\nu^2 - 1 - 2 \ln \nu - \frac{1}{2K(z)}(1 - \nu^2)^2(K(z) - 1) \right], \end{aligned} \quad (3.10)$$

where function $K(z)$ is defined as

$$K(z) = \frac{1 + z}{\varphi(z)}. \quad (3.11)$$

This function is responsible for the variance dependence on the partition thickness.

Substituting the relations in Eqs. (3.9) and (3.10) into Eq. (3.8) and using the Einstein relation, $\mu_0 = \beta D_0$, we arrive at the expression for the effective diffusivity in Eq. (1.4) with function $B(z, \nu)$ given by

$$\begin{aligned} B(z, \nu) = & \frac{\nu^4 K(z)^2}{4[1 + (K(z) - 1)\nu^2]^3} \\ & \times \left[\nu^2 - 1 - 2 \ln \nu - \frac{1}{2K(z)}(1 - \nu^2)^2(K(z) - 1) \right]. \end{aligned} \quad (3.12)$$

This is one of the main results of this section. Thus, one can find the effective diffusivity, $D_{\text{eff}}(F)|_{F \rightarrow \infty}$, as a function of the geometric parameters of the tube and the external force using Eq. (1.4) with functions $P_m(z, \nu)$ and $B(z, \nu)$ given by Eqs. (2.12) and (3.12), respectively.

Function $B(z, \nu)$ is a three-dimensional surface over the strip $0 \leq z < \infty$, $0 < \nu \leq 1$, which has a bell-shaped form as a function of ν in every $z = \text{const}$ cross section [$B(z, \nu)$ vanishes at $\nu = 0$ and 1, having a maximum in between]. Panel (a) of Fig. 6 shows the ν -dependence of this function for $z = 0$ (infinitely thin partitions),

$$B(0, \nu) = \frac{\nu^4}{4}(\nu^2 - 1 - 2 \ln \nu). \quad (3.13)$$

As z (and hence the partition thickness) tends to infinity, function $B(z, \nu)$ approaches zero. Panel (b) of Fig. 6 shows the z -dependencies of $B(z, \nu)$ at $\nu = 0.1, 0.3$, and 0.7 .

FIG. 6. Function $B(z, \nu)$. The ν -dependence of this function at $z = 0$ is shown in panel (a), and its z -dependencies at $\nu = 0.1, 0.3$, and 0.7 are shown in panel (b). Symbols are the values of $B(z, \nu)$ obtained from Brownian dynamics simulations with $\beta FR = 10^5$. Solid curves are drawn using Eqs. (3.12) and (3.13).

The z -dependence of $B(z, \nu)$ is non-monotonic when ν is small. It changes the behavior and becomes monotonic as ν approaches unity. A critical value $\nu = \nu^*$, at which the z -dependence changes its character can be determined from the requirement $dB(z, \nu)/dz|_{z=0} = 0$. We use this to find that ν^* is a root of the equation,

$$7\nu^4 - 12\nu^2 + 4(2 - 3\nu^2)\ln \nu + 5 = 0. \quad (3.14)$$

Solving this equation we obtained $\nu^* \approx 0.68$. In Fig. 6 the symbols show the values of function $B(z, \nu)$ obtained from Brownian dynamics simulations, while the solid curves represent the dependencies predicted by Eq. (3.10) with function $K(z)$ defined in Eq. (3.11), in which function $\varphi(z)$ is given by

FIG. 7. Two-dimensional square-well potential $U(r)$, Eq. (3.15).

Eq. (2.9). One can see that the theoretically predicted function $B(z, \nu)$ perfectly agrees with the simulation results.

Concluding this section, we outline the derivation of the expression for $\sigma_m^2(t)$ in Eq. (3.10). When the partitions are infinitely thin ($z = 0$), $\sigma_m^2(t)$ is the variance of the cumulative time spent by a particle, freely diffusing in a circle of radius R , inside a concentric smaller circle of radius a . In this case $K(0) = 1$, and Eq. (3.10) reduces to the result published in Ref. 9. A general formalism developed in Ref. 9 is applicable not only for free diffusion, but also for diffusion in an arbitrary multidimensional potential. To derive the expression in Eq. (3.10), we considered diffusion in the circle of radius R in the presence of a radially symmetric square-well potential $U(r)$ of the form

$$U(r) = \begin{cases} 0, & a < r < R \\ -\Delta U, & 0 < r < a \end{cases}, \quad (3.15)$$

shown in Fig. 7.

The well depth ΔU was chosen so that the ratio of the equilibrium probabilities of finding the particle inside and outside the circle of radius a was equal to the ratio of the probabilities $P_m(z, \nu)$ and $P_{im}(z, \nu)$. This requirement leads to

$$\beta \Delta U = \ln \left[(v^{-2} - 1) \frac{P_m(z, \nu)}{P_{im}(z, \nu)} \right]. \quad (3.16)$$

Using $P_m(z, \nu)$ in Eq. (2.12) one can check that the probability ratio in the above equation is

$$\frac{P_m(z, \nu)}{P_{im}(z, \nu)} = \frac{1 + z}{(v^{-2} - 1)\varphi(z)}. \quad (3.17)$$

Substituting this into Eq. (3.16), we arrive at the expression

$$\beta \Delta U = \ln \left[\frac{1 + z}{\varphi(z)} \right], \quad (3.18)$$

which determines the depth of the potential well as a function of z . Thus it turns out that the well depth is independent of the radii ratio ν and depends only on the section lengths ratio z . The radii ratio determines the size of the square well measured in units of the wide section radius. Comparing Eqs. (3.11) and (3.18), one can see the relation between the well depth and function $K(z)$,

$$K(z) = e^{\beta \Delta U}. \quad (3.19)$$

To derive the expression for $\sigma_m^2(t)$ in Eq. (3.10) we applied the formalism developed in Ref. 9 to diffusion in the two-dimensional square-well potential $U(r)$, Eq. (3.15), with the z -dependent well depth given by Eq. (3.18). The key step of our approach is the replacement of the initial three-dimensional problem by an effective two-dimensional one.

Excellent agreement between the theoretically predicted function $B(z, \nu)$ and the simulation results validates our intuition-based approach.

The formalism developed in Ref. 9 also helps to understand why the z -dependence of function $B(z, \nu)$ is non-monotonic at small ν and monotonic as ν approaches unity. Using the results of Ref. 9, it can be shown that the long-time asymptotic behavior of $\sigma_m^2(t)$, Eq. (3.10), can be written as

$$\sigma_m^2(t) = 2P_m(z, \nu)P_{im}(z, \nu)\tau_{\text{rel}}(z, \nu)t, \quad t \rightarrow \infty, \quad (3.20)$$

where $\tau_{\text{rel}}(z, \nu)$ is a relaxation time, which is a smooth function of its arguments z and ν . Substituting $\sigma_m^2(t)$ in Eq. (3.20) into Eq. (3.8) and using the Einstein relation, $\mu_0 = \beta D_0$, we obtain

$$B(z, \nu) = \frac{D_0 \tau_{\text{rel}}(z, \nu)}{R^2} P_m(z, \nu) P_{im}(z, \nu). \quad (3.21)$$

Both the non-monotonic z -dependence of function $B(z, \nu)$ at small ν and the change in the character of this dependence at ν larger than ν^* are due to the z -dependence of the product of the probabilities, $P_m(z, \nu)P_{im}(z, \nu) = P_m(z, \nu)(1 - P_m(z, \nu))$. Therefore, let us consider the z -dependencies of this product at different values of the radii ratio ν .

The product reaches its maximum value of 1/4 when $P_m(z, \nu) = 1/2$. If $P_m(0, \nu) = \nu^2$ is smaller than 1/2, i.e., $\nu < 1/\sqrt{2} \approx 0.71$, the product first increases with z , until $P_m(z, \nu)$ reaches the value of 1/2, and then decreases. If $P_m(0, \nu)$ is larger than 1/2, i.e., $\nu > 1/\sqrt{2} \approx 0.71$, the product monotonically decreases with z . The z -dependence of the product changes its behavior from non-monotonic to monotonic at $\nu_1^* = 1/\sqrt{2} \approx 0.71$. The two critical values of the radii ratio ν , $\nu^* \approx 0.68$, and $\nu_1^* \approx 0.71$, differ because the picture of the z -dependence of the product of the probabilities is modified by the presence of the relaxation time, $\tau_{\text{rel}}(z, \nu)$, which enters into the expression for the function $B(z, \nu)$ in Eq. (3.21).

IV. CONCLUDING REMARKS

In this paper we study the effective transport coefficients in tubes of alternating diameter (Fig. 1) under strong bias conditions. Our main results are the expression for the effective mobility in Eq. (2.13) and the expression for the effective diffusivity in Eq. (1.4), with functions $P_m(z, \nu)$ and $B(z, \nu)$ given in Eqs. (2.12) and (3.12), respectively. The expressions give the effective transport coefficients as functions of the geometric parameters of the tube. As the length of the narrow sections vanishes, the expressions reduce to the known results for the transport coefficients for a cylindrical tube separated into identical compartments by infinitely thin periodic partitions with circular apertures in their centers, Eqs. (1.1) and (1.2).

Under the strong bias conditions, the effective mobility is independent of the external biasing force, F . It approaches its value μ_0 in a purely cylindrical tube as the partition thickness tends to infinity. In contrast, the effective diffusivity is a linear function of F^2 . The derivative $dD_{\text{eff}}(F)/dF^2|_{F \rightarrow \infty}$ depends on the partitions thickness and vanishes as the thickness tends to infinity. As a consequence, the effective diffusivity reduces to its value D_0 in a purely cylindrical tube in this

limiting case. This reduction to D_0 should not be confused with the reduction of the effective diffusivity to D_0 in a tube of smoothly varying periodic geometry. The latter occurs at a fixed tube geometry when the external force becomes large enough,⁴ while the former is controlled by the tube geometry rather than the force strength. The increase of the force at fixed geometry does not lead to the reduction to D_0 .

The obtained analytical results for the effective transport coefficients for tubes of alternating diameter under strong bias conditions complement known analytical results for these quantities in such systems in the opposite limit of weak bias.¹⁰ It would be interesting to see the behavior of the effective transport coefficients over the entire range of the biasing force. This would bridge the results in the two limiting cases mentioned above.

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APPENDIX: DERIVATION OF EQ. (2.5)

Here we derive an expression for the probability ratio, $P_{im}(z, \nu)/P_m^{(w)}(z, \nu)$, in the limiting case of very long partitions (narrow sections of the tube). We assume that the partitions are so long that the mean time required for the particle to traverse the partition, $l_n/(\mu_0 F)$, significantly exceeds the intra-partition relaxation time which is proportional to a^2/D_0 . Therefore, a particle entering a wide tube section from the narrow one is uniformly distributed over the entrance area, πa^2 . In this limiting case, the probability $P_m^{(n)}(z, \nu)$ is close to unity, whereas the probabilities $P_m^{(w)}(z, \nu)$ and $P_{im}(z, \nu)$ are negligibly small. However, their ratio remains finite and, as we will see, is given by Eq. (2.5).

In deriving this result, we take advantage of the fact that, by the definition of strong bias, time τ_w , Eq. (2.8), satisfies the inequality

$$\sqrt{D_0 \tau_w} \ll a, \quad R - a. \quad (\text{A1})$$

As a consequence, the probability that a particle, entering a wide section from the narrow one, escapes from the cylinder of radius a around the tube axis during its passage through the wide section is very low. Therefore, the probability $P_m^{(w)}$ (hereafter we omit the arguments of the probabilities $P_m^{(w)}$ and P_{im}) can be written as the product of the two-dimensional (2d) reduced probability density¹¹ of the particle distribution over the cylinder cross-section, denoted by p_{2d} , and the cylinder

cross-section area, πa^2 ,

$$P_m^{(w)} = \pi a^2 p_{2d}. \quad (\text{A2})$$

To find the probability P_{im} , consider the two-dimensional probability density of the particle on the partition wall. Denoting this probability density by $w(r)$, $a < r < R$, we can write the probability P_{im} as

$$P_{im} = 2\pi \int_a^R w(r) r dr. \quad (\text{A3})$$

The steady-state probability density $w(r)$ is maintained by the steady-state probability flux coming to the wall from the bulk of the wide section. This flux is formed by those realizations of the particle trajectory that escape from the cylinder of radius a during the wide section passage time τ_w .

We denote the total steady-state flux to the wall by J and its radial distribution by $j(r)$, $a < r < R$,

$$J = \int_a^R j(r) dr. \quad (\text{A4})$$

The probability density $w(r)$ satisfies

$$\frac{D_0}{r} \frac{d}{dr} \left(r \frac{dw(r)}{dr} \right) + \frac{j(r)}{2\pi r} = 0, \quad a < r < R, \quad (\text{A5})$$

subject to reflecting and absorbing boundary conditions at $r = R$ and $r = a$, respectively,

$$\left. \frac{dw(r)}{dr} \right|_{r=R} = w(a) = 0. \quad (\text{A6})$$

The probability density $w(r)$ is a sum of the contributions maintained by the steady-state fluxes coming to the wall at different distances from the entrance to the narrow section. Therefore,

$$w(r) = \int_a^R w(r|r') dr', \quad (\text{A7})$$

where $w(r|r')$ satisfies

$$\frac{D_0}{r} \frac{d}{dr} \left(r \frac{dw(r|r')}{dr} \right) + \frac{j(r')}{2\pi r'} \delta(r - r') = 0, \quad a < r < R, \quad (\text{A8})$$

subject to the same boundary conditions at $r = a$ and R as $w(r)$ (see Eq. (A6)).

The solution to Eq. (A8) is

$$w(r|r') = \frac{j(r')}{2\pi D_0} \times \begin{cases} \ln(r/a), & a < r < r' \\ \ln(r'/a), & r' < r < R \end{cases}. \quad (\text{A9})$$

Since τ_w is very short and satisfies the inequality in Eq. (A1), the flux J is localized in a thin ring near the entrance to the narrow section, whose width is proportional to $\sqrt{D_0 \tau_w}$. As a consequence, on the most part of the partition wall outside the ring $w(r|r')$ is independent of r and given by

$$w(r|r') = \frac{j(r')}{2\pi D_0} \ln(r'/a) \simeq \frac{j(r')}{2\pi D_0 a} (r' - a). \quad (\text{A10})$$

Substituting this into Eq. (A7), we obtain

$$w(r) = \frac{1}{2\pi D_0 a} \int_a^R (r' - a) j(r') dr'. \quad (\text{A11})$$

Introducing the radial distribution function of the flux defined as the ratio $j(r)/J$, we can write Eq. (A11) as

$$w(r) = \frac{J}{2\pi D_0 a} \langle r - a \rangle, \quad (\text{A12})$$

where $\langle r - a \rangle$ is the mean distance of the flux landing point from the entrance to the narrow section located at $r = a$,

$$\langle r - a \rangle = \frac{1}{J} \int_a^R (r - a) j(r) dr. \quad (\text{A13})$$

We find the probability P_{im} by substituting $w(r)$ in Eq. (A12) into Eq. (A3) and performing the integration. The result is

$$P_{im} = \frac{J \langle r - a \rangle}{2D_0 a} (R^2 - a^2). \quad (\text{A14})$$

Then for the probability ratio of interest we obtain

$$\frac{P_{im}}{P_m^{(w)}} = \frac{J \langle r - a \rangle}{\pi a D_0 p_{2d}} \frac{R^2 - a^2}{2a^2}. \quad (\text{A15})$$

In what follows we find the total flux J landing on the partition wall and the mean distance $\langle r - a \rangle$ and demonstrate that their product is equal to $\pi a D_0 p_{2d}$. This means that Eq. (A15) is identical to Eq. (2.5).

The total steady-state flux through the system, denoted by I , is given by

$$I = \frac{P_m^{(w)}}{\tau_w} = \frac{\pi a^2 p_{2d}}{\tau_w}, \quad (\text{A16})$$

where we have used the expression for $P_m^{(w)}$ in Eq. (A2). The flux J can be written as the product of the flux I and the particle escape probability from the cylinder of radius a during the wide section passage time τ_w , denoted by P_{esc} ,

$$J = P_{esc} I. \quad (\text{A17})$$

To find the escape probability we again take advantage of the fact that time τ_w is very short and satisfies the inequality in Eq. (A1). This allows us to replace the round boundary of the cylinder by a flat one.

Let ξ be a coordinate normal to this flat boundary, chosen so that $\xi > 0$ and $\xi < 0$ correspond to the particle position outside and inside the cylinder, respectively. Consider a particle entering a wide section from the narrow one at distance $|\xi_0|$ from the boundary, $\xi_0 < 0$, at time $t = 0$. During the time τ_w , the particle freely diffuses along ξ . Therefore, when the particle approaches the partition wall, its propagator along ξ is

$$G(\xi, \tau_w | \xi_0) = \frac{1}{\sqrt{4\pi D_0 \tau_w}} e^{-(\xi - \xi_0)^2 / (4D_0 \tau_w)}. \quad (\text{A18})$$

The probability of finding this particle outside the cylinder, $P_{esc}(\xi_0)$, is given by

$$P_{esc}(\xi_0) = \int_0^\infty G(\xi, \tau_w | \xi_0) d\xi = \frac{1}{2} \operatorname{erfc} \left(\frac{|\xi_0|}{\sqrt{4D_0 \tau_w}} \right), \quad (\text{A19})$$

where $\operatorname{erfc}(z)$ is the complimentary error function. This shows that the probability $P_{esc}(\xi_0)$ quickly decreases from its maximum value of 0.5 at $\xi_0 = 0$ to zero as the initial position ξ_0 deepens into the cylinder. The probability P_{esc} is obtained by averaging $P_{esc}(\xi_0)$ over ξ_0 , using $2\pi a / (\pi a^2) = 2/a$ as the probability density of the particle initial position. The result is

$$P_{esc} = \frac{2}{a} \int_{-\infty}^0 P_{esc}(\xi_0) d\xi_0 = \frac{2}{a} \sqrt{\frac{D_0 \tau_w}{\pi}}. \quad (\text{A20})$$

Using this together with Eqs. (A16) and (A17), we find that the total flux J landing on the partition wall from the bulk of the wide section is given by

$$J = 2a p_{2d} \sqrt{\frac{\pi D_0}{\tau_w}}. \quad (\text{A21})$$

We use the propagator in Eq. (A18) to define the probability density $\rho(\xi)$ of the landing point,

$$\begin{aligned} \rho(\xi) &= \frac{2}{a P_{esc}} \int_{-\infty}^0 G(\xi, \tau_w | \xi_0) d\xi_0 \\ &= \sqrt{\frac{\pi}{4D_0 \tau_w}} \operatorname{erfc} \left(\frac{\xi}{\sqrt{4D_0 \tau_w}} \right). \end{aligned} \quad (\text{A22})$$

Identifying $\langle r - a \rangle$ with the mean value of the landing point, we obtain

$$\langle r - a \rangle = \int_0^\infty \xi \rho(\xi) d\xi = \frac{1}{2} \sqrt{\pi D_0 \tau_w}. \quad (\text{A23})$$

This and Eq. (A21) for the flux J allows one to check that

$$\frac{J \langle r - a \rangle}{\pi a D_0 p_{2d}} = 1, \quad (\text{A24})$$

and hence Eq. (A15) is identical to Eq. (2.5).

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