Biased diffusion in tubes of alternating diameter: Numerical study over a wide range of biasing force

Yurii A. Makhnovskii,¹ Alexander M. Berezhkovskii,² Anatoly E. Antipov,³
and Vladimir Yu. Zitserman⁴

¹*Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninsky Prospekt 29, Moscow 119991, Russia*

²*Mathematical and Statistical Computing Laboratory, Division of Computational Bioscience, Center for Information Technology, National Institutes of Health, Bethesda, Maryland 20819, USA*

³*Faculty of Fundamental Physics and Chemical Engineering, Moscow State University, GSP-1, 1-51 Leninskie Gory, Moscow 119991, Russia*

⁴*Joint Institute for High Temperatures, Russian Academy of Sciences, Izhorskaya 13, Bldg. 2, Moscow 125412, Russia*

(Received 26 July 2015; accepted 16 October 2015; published online 2 November 2015)

This paper is devoted to particle transport in a tube formed by alternating wide and narrow sections, in the presence of an external biasing force. The focus is on the effective transport coefficients—mobility and diffusivity, as functions of the biasing force and the geometric parameters of the tube. Dependences of the effective mobility and diffusivity on the tube geometric parameters are known in the limiting cases of no bias and strong bias. The approximations used to obtain these results are inapplicable at intermediate values of the biasing force. To bridge the two limits Brownian dynamics simulations were run to determine the transport coefficients at intermediate values of the force. The simulations were performed for a representative set of tube geometries over a wide range of the biasing force. They revealed that there is a range of the narrow section length, where the force dependence of the mobility has a maximum. In contrast, the diffusivity is a monotonically increasing function of the force. A simple formula is proposed, which reduces to the known dependences of the diffusivity on the tube geometric parameters in both limits of zero and strong bias. At intermediate values of the biasing force, the formula catches the diffusivity dependence on the narrow section length, if the radius of these sections is not too small. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4934728>]

I. INTRODUCTION

Particle transport in three-dimensional tubes and two-dimensional channels of periodically varying geometry is described by effective transport coefficients—mobility μ_{eff} and diffusivity D_{eff} , which allow one to find the first two moments of the particle displacement along the tube/channel axis at sufficiently long times, when a typical particle displacement exceeds the period of the system. The problem of transport in such quasi-one-dimensional periodic systems is a special case of a more general class of problems of transport in the presence of varying geometrical constraints, the so-called entropic transport. These problems attract attention of many researchers because they arise in modeling various physical, geological, biological, and technological processes. Recent review articles^{1–6} and references therein provide an overview of the current state-of-the-art in the field.

In the present paper, we study the effective transport coefficients in a tube of alternating diameter schematically shown in Fig. 1. The tube is formed by wide (w) and narrow (n) sections of radii R and a , $R \geq a$, and lengths l_w and l_n , respectively, so that the system period is $l_w + l_n$. The focus is on the dependences of the transport coefficients on the external biasing force F directed along the tube axis. The force dependences of the effective mobility and diffusivity

in such tubes were studied earlier in the limiting case of infinitely thin narrow sections ($l_n = 0$).^{7–9} Here, we extend that study and consider narrow sections of arbitrary thickness, which we will call partitions. Analytical expressions giving the effective transport coefficients as functions of the tube geometric parameters are available only in the limiting cases of $F = 0$ ^{10,11} and $F \rightarrow \infty$.¹²

The aim of the present work is to study the transition between the asymptotic results mentioned above. Unfortunately, there is no simple coarse-grained picture of the particle dynamics in the tube shown in Fig. 1 at intermediate values of F , which would allow us to develop an approximate transport theory. Therefore, the transition between the limiting behaviors of μ_{eff} and D_{eff} as F increases from zero to infinity is studied numerically using Brownian dynamics simulations. This is done for a representative set of values of the geometric parameters, the partition thickness, and the radii ratio a/R . The simulation results reveal a non-trivial F -dependence of the effective mobility. It turns out that in a certain range of the geometric parameters, this force dependence is non-monotonic. The mobility first increases, reaches a maximum, and then decreases, approaching its large F asymptotic value from above. We suggest a qualitative explanation of this behavior. In addition, based on the simulation results, we propose a simple interpolation formula that connects the

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 .

known asymptotic expressions for D_{eff} at $F = 0$ and $F \rightarrow \infty$ and works reasonably well at intermediate values of F for the entire range of the geometric parameters unless the radii ratio, a/R , is not too small.

The outline of the paper is as follows: Known dependences of the transport coefficients on the tube geometric parameters at $F = 0$ and $F \rightarrow \infty$ are discussed in Section II. Our simulation results are presented in Section III, and some concluding remarks are made in Section IV.

II. PRELIMINARIES

The goal of the theory of entropic transport in periodic systems is to find μ_{eff} and D_{eff} as functions of the parameters determining the system geometry as well as the external biasing force. The effective transport coefficients are formally defined as $\mu_{\text{eff}} = (1/F) \langle \Delta x(t|F) \rangle / t|_{t \rightarrow \infty}$, $D_{\text{eff}} = \langle (\Delta x(t|F) - \langle \Delta x(t|F) \rangle)^2 \rangle / (2t)|_{t \rightarrow \infty}$, where $\Delta x(t|F)$ is the particle displacement in time t in the presence of the external biasing force F , and the angular brackets, $\langle \dots \rangle$, denote the averaging over realizations of the particle stochastic trajectory. Varying system's geometry makes it impossible to obtain exact analytical results for μ_{eff} and D_{eff} . Even approximate analytical expressions for these functions are known only for a few systems and mainly in the absence of bias, $F = 0$. One can find a brief discussion of known analytical results for μ_{eff} and D_{eff} in Ref. 12.

For the tube shown in Fig. 1, asymptotic expressions for the effective transport coefficients at $F = 0$ and $F \rightarrow \infty$ are derived in Refs. 10–12, where their accuracy is validated by Brownian dynamics simulations. A key step in the derivations is the approximate reduction of the initial three-dimensional particle dynamics to the effective one-dimensional one. Unfortunately, this strategy does not work at intermediate values of the biasing force. As a consequence, as mentioned earlier, it is impossible to develop an approximate transport theory for this range of F . This is why we study the transition between the asymptotic analytical results for μ_{eff} and D_{eff} by means of Brownian dynamics simulations.

A tube of alternating diameter is characterized by the four parameters, l_w , l_n , R , and a (see Fig. 1). For further discussion, it is convenient to introduce three dimensionless geometric parameters of the tube, $z = l_n/l_w$, $\nu = a/R$, and l_w/R . In addition, we introduce a dimensionless biasing force f , defined as $f = FR/(k_B T)$, where k_B and T are the Boltzmann constant and the absolute temperature. Finally, we use the particle mobility and diffusivity in space with no constraints, μ_0 and D_0 , as scaling factors for the effective mobility and diffusivity, to introduce dimensionless transport coefficients denoted by μ

and D ,

$$\mu = \frac{\mu_{\text{eff}}}{\mu_0}, \quad D = \frac{D_{\text{eff}}}{D_0}. \quad (2.1)$$

The dimensionless transport coefficients are functions of the dimensionless biasing force f and the three dimensionless geometric parameters z , ν , and l_w/R . For purely cylindrical tubes, these functions are equal to unity for all values of f .

In the absence of bias, the transport coefficients are related by the Einstein relation, $D_{\text{eff}}/\mu_{\text{eff}}|_{f=0} = D_0/\mu_0 = k_B T$. Therefore, the dimensionless transport coefficients are identical in this limiting case. They are given by^{10,11}

$$\mu|_{f=0} = D|_{f=0} = \frac{\nu^2(1+z)^2}{(\nu^2 + M(\nu) + z)(1 + z\nu^2)}, \quad l_w/R \geq 1, \quad (2.2)$$

where

$$M(\nu) = \frac{\pi\nu(1-\nu^2)^2}{2(l_w/R)(1 + 1.37\nu - 0.37\nu^4)}. \quad (2.3)$$

The expression in Eq. (2.2) is applicable for all z and ν on condition that $l_w/R \geq 1$. This constraint arises because Eq. (2.2) was derived using the method of boundary homogenization,¹³ which in this particular case is applicable only when the length of the wide sections is equal to or larger than its radius.¹⁴ As follows from Eq. (2.2), in the absence of bias, the transport coefficients are smaller than unity (their counterparts for a purely cylindrical tube) when $\nu < 1$ and the partitions are of finite thickness, $z < \infty$. Comparison with the results obtained from Brownian dynamics simulations shows that Eq. (2.2) predicts the transport coefficients with relative error within 3%.¹⁰

Analytical expressions for the dimensionless transport coefficients are also available in the opposite limiting case of strong bias, $f \rightarrow \infty$, where they are given by¹²

$$\mu|_{f \rightarrow \infty} = \frac{\nu^2 K(z)}{1 - \nu^2 + \nu^2 K(z)}, \quad (2.4)$$

$$D|_{f \rightarrow \infty} = \mu|_{f \rightarrow \infty} + f^2 B(z, \nu). \quad (2.5)$$

Functions $K(z)$ and $B(z, \nu)$ in the above expressions are

$$K(z) = \frac{2(1+z)}{1 + \exp(-2\sqrt{z})}, \quad (2.6)$$

$$B(z, \nu) = \frac{\nu^4 K(z)}{8[1 + \nu^2(K(z) - 1)]^3} \times \left\{ (1 - \nu^2)^2 - [4 \ln \nu + (1 - \nu^2)(3 - \nu^2)] K(z) \right\}. \quad (2.7)$$

One can see that the transport coefficients in Eqs. (2.4) and (2.5) are independent of the dimensionless length of the wide sections, l_w/R . This parameter determines the force range where the expressions in Eqs. (2.4) and (2.5) are applicable,

$$f \gg \frac{(l_w/R)}{(1 - \nu)^2}. \quad (2.8)$$

Note that this constraint on f is independent of the partition thickness. One can find a detailed discussion of transport in the case of strong bias in Ref. 12.

Expressions in Eqs. (2.2), (2.4), and (2.5) describe variations of the transport coefficients as the dimensionless partition thickness z changes from zero to infinity. These expressions show that both dimensionless transport coefficients approach unity as z tends to infinity. This might be expected based on common sense arguments, since the particle spends practically all time in the narrow sections, i.e., in a cylindrical tube of radius a . The z -dependences of μ and D in the limiting cases of zero and strong bias are illustrated in Fig. 2. One can see that the smaller the ν , the slower the dimensionless mobility and diffusivity approach unity. The figure also shows that the mobility approaches its limiting value from below both at $f = 0$ and $f = \infty$. In contrast, the way how the diffusivity approaches its limiting value depends on f : at $f = 0$, where $D = \mu$, the diffusivity approaches its limiting value from below, while in the strong bias limit, it approaches from above. In addition, D approaches unity at large f much slower than at $f = 0$, whereas the rate with which μ approaches unity at small and large f is almost the same.

The fact that μ and D differ from unity as $f \rightarrow \infty$ at finite values of z , including $z = 0$ (see Fig. 2), is quite in contrast with

the behavior of both transport coefficients in tubes of smoothly varying geometry. The latter always approach unity in the strong bias limit, $f \rightarrow \infty$, while the former approach unity only as $z \rightarrow \infty$ (see Fig. 2). This difference in the behavior of μ and D is a consequence of the abrupt changes of the tube radius.¹² One can find a comparative study of biased diffusion in tubes of smoothly and abruptly varying geometry in Ref. 8 and a detailed discussion of biased diffusion in tubes formed by spherical compartments in Ref. 15.

III. RESULTS AND DISCUSSION

As discussed in Section II, the transport coefficients are known in the limiting cases of zero and strong bias. To bridge the gap between the two limits, we obtained μ and D at intermediate values of f from Brownian dynamics simulations. The simulation details are discussed in the Appendix. This was done for $f = 10^{-2}, 10^{-1}, 1, 10, 10^2, 10^3, 10^4$, and 10^5 at different values of the geometric parameters. Specifically, the partition thickness was $z = 0, 0.1, 1, 10$, and 100 , the radii ratio was $\nu = 0.1, 0.3$, and 0.7 , and the dimensionless wide section length was $l_w/R = 1$. In this section, we present and discuss our simulation results in order, first the mobility and then the diffusivity.

A. Effective mobility

The force dependences of the mobility at different values of z and ν are shown in Fig. 3. At $z = 0$ (infinitely thin partitions), the mobility monotonically decreases as the biasing force increases, as illustrated in Fig. 3(a). The question arises what happens to this dependence as the partition thickness increases. As follows from Eqs. (2.2) and (2.4), both $\mu|_{f=0}$ and $\mu|_{f \rightarrow \infty}$ approach unity, as $z \rightarrow \infty$. In addition, $\mu|_{f=0}$ is greater than $\mu|_{f \rightarrow \infty}$ at small z . However, $\mu|_{f \rightarrow \infty}$ grows with z faster than $\mu|_{f=0}$ and becomes greater than $\mu|_{f=0}$ at sufficiently large z . This is illustrated in Fig. 2(a).

One might expect that the mobility at a fixed value of z (constant partition thickness) and ν is a monotonic function of f , which varies smoothly from $\mu|_{f=0}$ to $\mu|_{f \rightarrow \infty}$ as f increases from zero to infinity. In reality, this is not necessarily the case. The simulation results show that there is a range of the partition thickness where the f -dependence of the mobility has a maximum. This is illustrated in panels (b)–(d) of Fig. 3. It is interesting that, independent of the partition thickness and the radii ratio, the mobility has a maximum at the same value of the biasing force, $f = 10$. The results presented in panels (b)–(d) of Fig. 3 show that the smaller the radii ratio, ν , the stronger is the effect.

Using Eq. (2.4), one can check that $\mu|_{f \rightarrow \infty}$ monotonically increases with the partition thickness for all ν (see Fig. 2(a)). The z -dependence of $\mu|_{f=0}$ is a function of ν , which changes its behavior from non-monotonic (at small ν) to monotonic, as ν increases and approaches unity. The smaller the ν , the stronger the non-monotonicity is pronounced (see Fig. 2(a)). This non-monotonicity disappears with the increase of the biasing force as illustrated in Fig. 4.

To rationalize the nontrivial behavior of the mobility discussed above, we indicate that this behavior results from

FIG. 2. Dimensionless mobility μ (panel (a)) and diffusivity D (panel (b)) as functions of the dimensionless partition thickness z in the limiting cases of no bias (solid curves) and strong bias (dashed curves) given by Eqs. (2.2), (2.4), and (2.5), respectively. The dependences are shown for three values of the radii ratio $\nu = 0.1, 0.3$, and 0.7 , which are indicated near the curves. In panel (b), the z -dependences of the diffusivity in the strong bias limit are given for $f = 1000$.

FIG. 3. Dimensionless mobility μ as a function of the biasing force f at different values of the dimensionless partition thickness z , for three values of the radii ratio, $\nu = 0.1$ (red circles), 0.3 (blue squares), and 0.7 (green stars). Panels (a)–(d) show the dependences at $z = 0, 1, 10$, and 100 , respectively. The dashed and dotted lines show the asymptotic values of the mobility at $f = 0$ and $f \rightarrow \infty$.

the interplay of opposite tendencies. The monotonic decrease of the mobility with the increase of the biasing force at $z = 0$, shown in Fig. 3(a), is due to the fact that the force pushing the particles to the infinitely thin partitions makes them unable to participate in the conduction process. As the force tends

FIG. 4. Dimensionless mobility μ as a function of the dimensionless partition thickness z at different values of the biasing force f , for three values of the radii ratio, $\nu = 0.1$ (red circles), 0.3 (blue squares), and 0.7 (green stars). Panels (a)–(c) show the dependences at $f = 1, 10$, and 100 , respectively. The mobility values at $z = 0.01$ given in the panels are those at $z = 0$, assuming that the two are equal.

to infinity, the probability for the particle to participate in the conduction reaches a minimum value equal to ν^2 . This is why the mobility in Eq. (2.4) reduces to ν^2 at $z = 0$ (as follows from Eq. (2.6), $K(0) = 1$). However, when the partitions are of finite thickness, $z > 0$, a moderate biasing force leads to the increase of the mobility (see panels (b)–(d) in Fig. 3). The reason is that a particle entering a narrow cylinder from a wide section has a probability to pass through the narrow section, which is a function of the biasing force.¹⁶ As the force increases from zero to infinity, this probability increases from $1/[2(1 + 2z/(\pi\nu))]$ at $f = 0$ to unity in the limiting case of strong bias. Thus, the biasing force facilitates the particle passage through the partitions that leads to the increase of the mobility.

FIG. 5. Dimensionless diffusivity D as a function of the biasing force f at different values of the dimensionless partition thickness z , for three values of the radii ratio, $\nu = 0.1$ (red circles), 0.3 (blue squares), and 0.7 (green stars). Panels (a)–(d) show the dependences at $z = 0, 1, 10$, and 100 , respectively. The dashed and dotted lines show the asymptotic values of the diffusivity at $f = 0$ and its asymptotic behaviors at $f \rightarrow \infty$.

The fact that the mobility first increases with the biasing force (see Fig. 3, panels (b)–(d)) shows that for the parameter sets studied in our simulations, the force dependence of the mobility at $f \leq 10$ is determined by the increasing passage

probability. The decrease of the mobility at larger values of f is presumably a consequence of the decreasing ability of the particle to participate in the conduction process induced by the biasing force.

B. Effective diffusivity

In contrast to the non-monotonic f -dependence of the mobility, the diffusivity is a monotonic function of the biasing force. As f increases, the diffusivity grows from its value at $f = 0$, given by Eq. (2.2), approaching its asymptotic form in Eq. (2.5), as $f \rightarrow \infty$. The f -dependence of the diffusivity is illustrated in Fig. 5.

The asymptotic expression in Eq. (2.5) gives the diffusivity as the sum of two terms. Replacing the first term, $\mu|_{f \rightarrow \infty}$, in this expression by μ , we arrive at the following formula:

$$D = \mu + f^2 B(z, \nu), \quad (3.1)$$

which reduces to $D|_{f=0}$, Eq. (2.2), and $D|_{f \rightarrow \infty}$, Eq. (2.5), in the limiting cases of zero and strong bias. In view of the fact that Eq. (3.1) has correct asymptotic behavior in both limiting cases, the question arises how well this simple expression describes the diffusivity over the entire range of f .

To answer this question, we use our simulation results to calculate the ratios of the diffusivities predicted by Eq. (3.1) to their counterparts obtained from the simulations. These ratios are close to unity for all z and ν at zero and strong bias and deviate from unity at intermediate values of the biasing force. Table I gives the diffusivity ratio as a function of f , z , and ν . This table shows that the expression in Eq. (3.1) works reasonably well at $\nu = 0.7$: It predicts the diffusivity with relative error less than 10% for all values of f and z except three points ($f = 10$, $z = 0$), ($f = 10^2$, $z = 0$), and ($f = 10^2$, $z = 1$), where the relative errors, respectively, are 33%, 20%, and 19%. The situation is getting worse as ν decreases. At $\nu = 0.3$, the largest deviations of the ratio from unity are 0.43 at $f = 10$, $z = 0$, 0.54 at $f = 1$, $z = 10$, and 0.57 at $f = 100$, $z = 0$, i.e., Eq. (3.1) predicts about twice smaller values of the diffusivity than the simulations for these (f, z) points. The situation becomes even worse at $\nu = 0.1$, where the ratio has

TABLE I. The ratio of the diffusivity predicted by Eq. (3.1) to its counterpart obtained from Brownian dynamics simulations as a function of f , z , and ν .

ν	z	f						
		0	1	10	10^2	10^3	10^4	10^5
0.1	0	1.00	0.93	0.23	0.17	0.47	0.76	0.95
	1	1.00	0.73	0.15	0.58	0.76	0.90	0.99
	10	0.99	0.21	0.23	0.64	0.90	0.97	1.02
	100	0.99	0.25	0.78	1.20	1.01	1.00	1.00
0.3	0	0.95	0.97	0.43	0.57	0.81	0.93	0.98
	1	0.97	0.84	0.69	0.89	1.00	1.01	1.01
	10	0.99	0.54	0.88	1.01	1.00	0.99	1.00
	100	1.00	0.80	1.02	1.03	1.00	0.99	0.97
0.7	0	1.00	1.01	1.33	1.20	1.07	1.03	1.01
	1	1.01	0.95	0.99	1.19	1.06	1.01	1.01
	10	1.00	0.97	0.93	1.07	1.00	0.99	1.00
	100	1.00	1.00	0.97	1.03	1.01	0.99	1.01

the minimum value of 0.15 at $f = 10$ and $z = 1$. The ratio has close values 0.17 and 0.21 at $f = 1$, $z = 10$ and $f = 10^2$, $z = 10$, respectively.

To summarize, the simple formula in Eq. (3.1) not only correctly describes the dependence of the diffusivity on the tube geometric parameters in the asymptotic zero- and strong-bias regimes but also catches the behavior of the diffusivity at intermediate values of the biasing force unless the radius ratio, ν , is not too small.

As shown in Fig. 2(b), the diffusivity dependence on the partition thickness may be both monotonic and non-monotonic. At $f = 0$, the dependence is non-monotonic at small ν . As ν increases and approaches unity, the dependence changes its character and becomes monotonic. In the strong

bias regime, the dependence is non-monotonic at $\nu = 0.1$ and $\nu = 0.3$, but monotonic at $\nu = 0.7$. In the first case, the diffusivity first increases with z , reaches a maximum and then decreases, approaching unity from above. In the second case, the diffusivity monotonically decreases, as z increases from zero to infinity, from its maximum value at $z = 0$ to unity as $z \rightarrow \infty$.

The transition of the diffusivity from its zero-bias pattern to its strong-bias pattern is illustrated in Fig. 6. At $f = 100$, all three z -dependences of the diffusivity shown in panel (c) follow their strong-bias patterns: monotonically decreasing z -dependence at $\nu = 0.7$, and non-monotonic z -dependences with maxima at $\nu = 0.1$ and $\nu = 0.3$. (For $\nu = 0.1$, we have only the increasing part of the dependence since the maximum is located at $z > 100$.)

The situation becomes more complex at $f = 1$ and 10 (see panels (a) and (b)). It looks like that the z -dependence of the diffusivity at $f = 1$ and $\nu = 0.7$ follows the zero-bias pattern: the diffusivity monotonically increases with z , approaching unity from below. At this value of the biasing force, $f = 1$, the z -dependences of the diffusivity at $\nu = 0.1$ and $\nu = 0.3$ are similar. They have two extrema: the diffusivities first decrease, reach their minima, than increase, reach their maxima, and then decrease again, approaching unity from above. (In Fig. 6(a), we have only the increasing parts of these dependences since their maxima are located at $z > 100$.)

As the biasing force increases from $f = 1$ to $f = 10$, the pattern of the z -dependence of the diffusivity at $\nu = 0.7$ changes from its zero-bias monotonic increase to its strong-bias monotonic decrease. The z -dependence of the diffusivity at $f = 10$ and $\nu = 0.3$ also follows its strong-bias pattern with one extremum, maximum at $z = 10$. At the same time, the z -dependence of the diffusivity at $\nu = 0.1$ and $f = 10$ is similar to that at $f = 1$: it has two extrema, a minimum and a maximum, which is located at $z > 100$.

IV. CONCLUDING REMARKS

This paper is devoted to the effective mobility and diffusivity of particles moving in tubes of alternating diameter, an example of which is schematically shown in Fig. 1. These transport coefficients are functions of both the biasing force and the tube geometric parameters. At fixed values of the dimensionless wide section length, l_w/R , and the radii ratio, ν , the dimensionless transport coefficients, defined in Eq. (2.1), are two-dimensional surfaces over the plane of the force f and narrow section length z , both are measured in dimensionless units.

The simulation results presented in Figs. 3 and 5 illustrate the f -dependences of the transport coefficients in the constant z cross sections, $z = 0, 1, 10$, and 100 , of the surfaces $\mu_\nu(f, z)$ and $D_\nu(f, z)$, with three values of the radii ratio, $\nu = 0.1, 0.3$, and 0.7 , for a wide range of f , $f = 10^{-2}, 10^{-1}, 1, 10, 10^2, 10^3, 10^4$, and 10^5 . The results presented in Figs. 4 and 6 illustrate the z -dependences of the transport coefficients in the constant f cross sections of these surfaces, at $f = 1, 10$, and 100 . At $f = 0$, these dependences are illustrated in Fig. 2.

The simulations show that the diffusivity, considered as a function of f , smoothly increases from its zero-bias limiting

FIG. 6. Dimensionless diffusivity D as a function of the dimensionless partition thickness z at different values of the biasing force f , for three values of the radii ratio, $\nu = 0.1$ (red circles), 0.3 (blue squares), and 0.7 (green stars). Panels (a)–(c) show the dependences at $f = 1, 10$, and 100 , respectively. The diffusivity values at $z = 0.01$ given in the panels are those at $z = 0$, assuming that the two are equal.

value, Eq. (2.2), to the strong-bias asymptotic behavior given by Eq. (2.5). As mentioned earlier, there is no simple approximate picture of the particle dynamics in the tube shown in Fig. 1 at intermediate values of f , and, as a consequence, there is no theory leading to analytical expressions for the transport coefficients in this range of the biasing force. In view of this circumstance, to connect the two limits, we proposed a simple interpolation formula for the diffusivity, Eq. (3.1), and used the simulation results to test its accuracy. This formula reduces to the known asymptotic expressions in Eqs. (2.2) and (2.5) in the zero- and strong-bias limits, and provides a reasonably accurate description of the diffusivity as a function of z at intermediate values of the biasing force, unless the radii ratio, ν , is not too small.

The force dependence of the mobility is more complex than that of the diffusivity. While the latter is monotonic (Fig. 5), the simulations showed that the former may have a maximum (Fig. 3). We suggested a qualitative explanation of such non-monotonic behavior in Section III A. The explanation is based on the idea that the force dependence of the mobility is determined by the competition of two opposite tendencies. This non-monotonic behavior makes it difficult to propose a simple empirical formula which would cover the entire range of the force, as we managed to do in the case of the diffusivity.

ACKNOWLEDGMENTS

A.E.A. and V.Yu.Z. thank the Russian Foundation for Basic Research for partial support (Grant No. 14-03-00343). A.E.A. gratefully acknowledges the support of the Ministry of Education and Science of Russia (Grant No. 14.607.21.0002). V.Yu.Z. is grateful for partial support to the Program of Basic Research no.1 of Presidium of Russian Academy of Sciences “Fundamental Problems of Mathematical Modeling” (supervisor academician V. B. Betelin). A.M.B. was supported by the Intramural Research Program of the NIH, Center for Information Technology.

APPENDIX: BROWNIAN DYNAMICS SIMULATIONS

To find the mobility μ and diffusivity D , defined in Eq. (2.1), one needs to know the long-time behavior of the mean and variance of the particle displacement $\Delta x(t|F)$ along the tube axis, which are determined by the first two moments of the displacement. These moments were obtained

by averaging over $3 \times 10^4 - 10^5$ trajectories generated by numerical integration of the overdamped Langevin equation. The integration was performed using the Euler algorithm. In simulations, we used dimensionless time defined as physical time measured in units of R^2/D_0 . The dimensionless time step of the integration was different at different values of f , varying from 10^{-7} at large f to 10^{-5} at $f = 0$. The number of time steps was large enough to avoid transient effects and guarantee the independence of the obtained values of μ and D of the simulation time. Depending on the values of f , z , and ν , this number varied from 2×10^7 to 2×10^{10} . Because of the system periodicity, the particle motion was considered only on one period of the tube. When the particle escaped from one side of the period, it was instantly injected from the opposite side. The way we used to handle particle collisions with the reflecting tube walls is described in detail in Ref. 9. Estimates showed that the relative error of μ and D obtained from the simulations does not exceed 5%.

¹P. Hanggi and F. Marchesoni, *Rev. Mod. Phys.* **81**, 387 (2009).

²P. S. Burada, P. Hänggi, F. Marchesoni, G. Schmid, and P. Talkner, *ChemPhysChem* **10**, 45 (2009).

³P. Malgaretti, I. Pagonabarraga, and J. M. Rubi, *Front. Phys.* **1**, 21 (2013).

⁴P. C. Bressloff and J. M. Newby, *Rev. Mod. Phys.* **85**, 135 (2013).

⁵M. Borromeo, *Acta Phys. Pol., B* **44**, 1037 (2013).

⁶S. Bezrukov, L. Schimansky-Geier, and G. Schmid, eds., *Eur. Phys. J.: Spec. Top.* **233**(14) (2014), topical issue on Brownian Motion in Confined Geometries, http://link.springer.com/journal/11734/topicalCollection/AC_e5ea2f7e0945d2d4024a32affe52af8b/page/1.

⁷F. Marchesoni, *J. Chem. Phys.* **132**, 166101 (2010).

⁸A. M. Berezhkovskii, L. Dagdug, Yu. A. Makhnovskii, and V. Yu. Zitserman, *J. Chem. Phys.* **132**, 221104 (2010).

⁹Yu. A. Makhnovskii, A. M. Berezhkovskii, L. V. Bogachev, and V. Yu. Zitserman, *J. Phys. Chem. B* **115**, 3992 (2011).

¹⁰Yu. A. Makhnovskii, A. M. Berezhkovskii, and V. Yu. Zitserman, *Chem. Phys.* **367**, 110 (2010).

¹¹A. E. Antipov, Yu. A. Makhnovskii, V. Yu. Zitserman, and S. M. Aldoshin, *Khim. Fiz.* **33**, 78 (2014) [*Russ. J. Phys. Chem. B* **8**, 752 (2014)].

¹²V. Yu. Zitserman, A. M. Berezhkovskii, A. E. Antipov, and Yu. A. Makhnovskii, *J. Chem. Phys.* **141**, 214103 (2014).

¹³A. M. Berezhkovskii, Yu. A. Makhnovskii, M. I. Monine, V. Yu. Zitserman, and S. Y. Shvartsman, *J. Chem. Phys.* **121**, 11390 (2004); Yu. A. Makhnovskii, A. M. Berezhkovskii, and V. Yu. Zitserman, *ibid.* **122**, 236102 (2005); A. M. Berezhkovskii, M. I. Monine, C. B. Muratov, and S. Y. Shvartsman, *ibid.* **124**, 036103 (2006); C. B. Muratov and S. Y. Shvartsman, *Multiscale Model. Simul.* **7**, 44 (2008).

¹⁴A. M. Berezhkovskii, A. V. Barzykin, and V. Yu. Zitserman, *J. Chem. Phys.* **131**, 224110 (2009).

¹⁵A. M. Berezhkovskii and L. Dagdug, *J. Chem. Phys.* **133**, 134102 (2010).

¹⁶A. M. Berezhkovskii, M. A. Pustovoi, and S. M. Bezrukov, *J. Chem. Phys.* **116**, 9952 (2002).