Entropic particle transport: Higher-order corrections to the Fick-Jacobs diffusion equation

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Transport of point-size Brownian particles under the influence of a constant and uniform force field through a planar three-dimensional channel with smoothly varying, axis-symmetric periodic side walls is investigated. Here we employ an asymptotic analysis in the ratio between the difference of the widest and the most narrow constriction divided through the period length of the channel geometry. We demonstrate that the leading-order term is equivalent to the Fick-Jacobs approximation. By use of the higher-order corrections to the probability density we show that in the diffusion-dominated regime the average transport velocity is obtained as the product of the zeroth-order Fick-Jacobs result and the expectation value of the spatially dependent diffusion coefficient $D(x)$, which substitutes the constant diffusion coefficient in the common Fick-Jacobs equation. The analytic findings are corroborated with the precise numerical results of a finite element calculation of the Smoluchowski diffusive particle dynamics occurring in a reflection symmetric sinusoidal-shaped channel.

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I. INTRODUCTION

The transport of large molecules and small particles that are geometrically confined within pores, channels, or other quasi-one-dimensional systems has attracted attention in the last decade. This activity stems from the profitableness for shape and size selective catalysis, particle separation, and the dynamical characterization of polymers during their translocation [1–5]. In particular, the last theme, which aims at the experimental determination of the structural properties and the amino acid sequence in DNA or RNA when they pass through narrow openings or so-called bottlenecks, comprises challenges for technical developments of nanoscaled channel structures [5–8].

Along with the progress of experimental techniques the problem of particle transport through corrugated channel structures containing narrow openings and bottlenecks has given rise to recent theoretical activities to study diffusion dynamics occurring in such geometries [1]. Previous studies by Jacobs [9] and Zwanzig [10] ignited a revival of research on this topic. The so-called *Fick-Jacobs (FJ) approach* [9,10] accounts for the elimination of transverse stochastic degrees of freedom by assuming a fast equilibration in those transverse directions [9]. The theme found its application for particle transport through periodic channel structures [11] and designed single nanopores [12] exhibiting smoothly varying side walls. Several aspects of driven motion in the presence of applied external force fields and the quality of the FJ approach in the presence of an applied force field in corrugated structures has been the focus of recent studies [13–19].

Beyond the FJ approach, which is suitably applied to channel geometries with smoothly varying side walls, there exist yet other methods for describing the transport through varying channel structures such as cylindrical septate channels [20–22], tubes formed by spherical compartments [23,24], or channels containing abrupt changes of cross diameters [25].

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Our objective with this work is to provide a systematic treatment by using a series expansion in terms of a smallness parameter that specifies the channel corrugation for *biased* particle transport proceeding along a planar, three-dimensional periodic, reflection-symmetric channel for which the original, commonly employed (lowest-order) FJ approach fails because of extreme bending of the channel's side walls.

In Sec. II we introduce the model system: a Brownian particle in a confined channel geometry with reflection symmetric, irregular boundaries. The central findings, namely, the analytic expressions for the probability density and the average transport characteristics, are presented in Sec. III. In Sec. IV we employ our analytical results to a specific channel configuration consisting of sinusoidally varying side walls. Section V summarizes our findings.

II. TRANSPORT IN CONFINED STRUCTURES

Generic mass transport through confined structures such as irregular pores and channels occurs due to the combination of molecular diffusion, as quantified by the molecular diffusivity D and passive transport arising from either different particle concentrations maintained at the ends of the channel, an applied hydrodynamic velocity field, or an external, force-generating potential $U(x,y,z)$. Here we concentrate on constant force-driven transport where particles of dilute concentration (i.e., interaction effects can safely be neglected) are subjected to a fixed external force with magnitude F acting along the longitudinal direction of the channel $\mathbf{e}_x$, i.e., $U(x,y,z) = -F\,x$. The overdamped single Brownian particle then budges in a planar, three-dimensional periodic channel geometry of period L, constant height ΔH, and periodically varying transverse width. A sketch of a segment of the channel is depicted in Fig. 1. The shape of the side walls is described by the two boundary functions $\omega_\pm(x)$. As we restrict ourselves to reflection-symmetric confinements in the y direction, we set $\omega_\pm(x) \equiv \pm\omega(x)$.

The evolution of the probability density $P(\mathbf{q},t)$ of finding the particle at the local position $\mathbf{q} = (x,y,z)^T$ at time t is

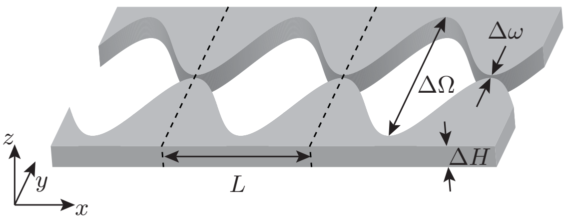

FIG. 1. Sketch of a segment of a reflection-symmetric sinusoidally varying channel that is confining the motion of the overdamped, pointlike Brownian particle. The periodicity of the channel structures is L, the height is ΔH, and the minimal and maximal channel widths are $\Delta\omega$ and $\Delta\Omega$, respectively. The size of a unit cell is indicated with the dashed lines.

governed by the three-dimensional Smoluchowski equation [26,27], i.e.,

$$\partial_t P(\mathbf{q},t) + \nabla_{\mathbf{q}} \cdot \mathbf{J}(\mathbf{q},t) = 0, \tag{1a}$$

where

$$\mathbf{J}(\mathbf{q},t) = \frac{F}{\eta} P(\mathbf{q},t)\, \mathbf{e}_x - \frac{k_B T}{\eta} \nabla_{\mathbf{q}} P(\mathbf{q},t) \tag{1b}$$

is the probability current of the probability density $P(\mathbf{q},t)$. The force strength acting on the Brownian particle is denoted by F, η is the friction coefficient, the Boltzmann constant is k_B, and T is the environmental temperature. Because of the impenetrability of the channel walls the probability current $\mathbf{J}(\mathbf{q},t) = (J^x, J^y, J^z)^T$ is subjected to the no-flux boundary condition, reading

$$\mathbf{J}(\mathbf{q},t) \cdot \mathbf{n} = 0, \quad \forall \mathbf{q} \in \text{channel wall}. \tag{2}$$

Here $\mathbf{n}$ denotes the out-pointing normal vector at the channel walls. The probability density satisfies the normalization condition $\int_{\text{unit-cell}} P(\mathbf{q},t)\, d^3\mathbf{q} = 1$ as well as the periodicity condition $P(x + m\,L, y, z, t) = P(x,y,z,t), \forall m \in \mathbb{Z}$. In the long-time limit the stationary probability density is defined as $P_{\text{st}}(\mathbf{q}) := \lim_{t\to\infty} P(\mathbf{q},t)$. Analogously, the stationary probability current reads $\mathbf{J}_{\text{st}}(\mathbf{q}) := \lim_{t\to\infty} \mathbf{J}(\mathbf{q},t)$.

The key quantities of particle transport through such periodic channels are the average particle velocity $\langle \dot{\mathbf{q}} \rangle$ and the effective diffusivity D_{eff}. The latter is given by

$$D_{\text{eff}} = \lim_{t\to\infty} \frac{\langle x^2(t)\rangle - \langle x(t)\rangle^2}{2t} \tag{3}$$

and can be calculated by means of the stationary probability density $P_{\text{st}}(\mathbf{q})$ using an established method taken from Ref. [28]. Once $P_{\text{st}}(\mathbf{q})$ is known, the mean particle velocity of Brownian particles can be computed by

$$\langle \dot{\mathbf{q}} \rangle \equiv \lim_{t\to\infty} \frac{\langle \mathbf{q}(t) \rangle}{t} = \int_{\text{unit-cell}} \mathbf{J}_{\text{st}}(\mathbf{q})\, d^3\mathbf{q}. \tag{4}$$

We next introduce dimensionless variables. In doing so, we measure longitudinal length and height as $\bar{x} = x/L$ and $\bar{z} = z/L$, respectively. For the rescaling of the y coordinate, we introduce the dimensionless aspect parameter ε: This is the difference of the widest cross section of the channel, i.e., $\Delta\Omega$, and the most narrow constriction at the bottleneck, i.e., $\Delta\omega$, in units of the period length, yielding

$$\varepsilon = \frac{(\Delta\Omega - \Delta\omega)}{L}. \tag{5}$$

In previous studies, the averaged half width [16,29,30] or the ratio of an imposed anisotropy of the diffusion constants $\varepsilon^2 = D_y/D_x$ [15,31] serves as expansion parameter. Contrarily in this work, the dimensionless value of ε characterizes the deviation of the boundary from the straight channel corresponding to $\varepsilon = 0$. The choice of ε is motivated by Ref. [13], where the authors have shown that the long-time dynamics of Brownian particles, when equilibration in the transverse direction is accomplished, is well described by the FJ equation as long as the extension of the bulges of the channel structures is small compared to the periodicity, i.e., $\varepsilon \ll 1$.

Following the reasoning in Ref. [29], we next measure, for the case of finite corrugation $\varepsilon \neq 0$, the transverse length y in units of εL, i.e., $y = \varepsilon L\, \bar{y}$, and, likewise, the boundary functions $\omega_\pm(x) = \varepsilon L\, h_\pm(x)$. Time is measured in units of $\tau = L^2\eta/(k_B T)$, which is twice the time the particle requires to overcome diffusively, at zero bias $F = 0$, the distance L, i.e., $\bar{t} = t/\tau$. The potential energy is rescaled by the thermal energy $k_{\text{B}}T$, i.e., for the considered situation with a constant force component in the longitudinal direction: $\overline{U} = -Fx/(k_{\text{B}}T) = -f\bar{x}$, with the dimensionless force magnitude [11,14]:

$$f = \frac{F\,L}{k_B\,T}. \tag{6}$$

The dimensionless forcing parameter f characterizes the ratio of the work $F\,L$ done on the particle when dragged by the constant force F along a distance of the period length L divided by the thermal energy $k_B T$. Note that for an adjustment of a certain value of f in an experimental setup one can modify either the force strength F or the temperature T. After scaling the probability distribution reads $\overline{P}(\bar{\mathbf{q}},\bar{t}) = \varepsilon\, L^3\, P(\mathbf{q},t)$; respectively, the probability current is given by $\overline{\mathbf{J}}(\bar{\mathbf{q}},\bar{t}) = \tau\, L^2\, (\varepsilon J^x, J^y, \varepsilon J^z)^T$. In the following we shall omit the overbar in our notation.

In dimensionless units, the Smoluchowski equation [see Eqs. (1)] reads

$$\partial_t P(\mathbf{q},t) + \nabla_{\mathbf{q}} \cdot \mathbf{J}(\mathbf{q},t) = 0, \tag{7a}$$

where $\nabla_{\mathbf{q}} = \left(\partial_x, \frac{1}{\varepsilon}\partial_y, \partial_z\right)^T$ and

$$\begin{aligned}\mathbf{J}(\mathbf{q},t) &= f\, P(\mathbf{q},t)\, \mathbf{e}_x - \nabla_{\mathbf{q}} P(\mathbf{q},t), \\ &= -e^{-U(\mathbf{q})} \nabla_{\mathbf{q}} [e^{U(\mathbf{q})} P(\mathbf{q},t)].\end{aligned} \tag{7b}$$

At steady state, Eq. (7a) becomes

$$\varepsilon^2 \partial_x J^x_{\text{st}} + \partial_y J^y_{\text{st}} + \varepsilon^2 \partial_z J^z_{\text{st}} = 0. \tag{8}$$

Planar three-dimensional channel structures composed of two parallel horizontal layers in the z direction and two perpendicular side walls are often found in experimental setups for microfluidic devices [32–34]. We postulate that (1) the dynamics in the z direction is decoupled from the dynamics in the x and y directions and (2) the shape of the lower and upper boundary depends neither on x nor on y. Consequently, the separation ansatz $P_{st}(x,y,z) = p_{\rm st}(x,y)\,\zeta(z)$ under consideration of the boundary condition

$$J^z_{\rm st} = 0, \quad \text{at } z = 0 \quad \text{and} \quad z = \Delta H/L, \tag{9}$$

results in a nontrivial solution for $\zeta(z)$ for $J^z_{\rm st}(\mathbf{q}) = 0$ everywhere within the channel. For the considered situation, i.e., there is only a constant force acting in the x direction, the form function $\zeta(z)$ equals the inverse of the dimensionless channel height, i.e., $\zeta = L/\Delta H$. Note that the presented separation technique can also be applied for more complex forcing scenarios with an additional force component in the z direction such as a gravitational or a buoyant force. Assuming a general potential landscape $U(x,y,z) = V(x,y) + W(z)$ defined within the channel, the used separation ansatz for the stationary solution results in

$$P_{\rm st}(x,y,z) = p_{\rm st}(x,y)\frac{e^{-W(z)}}{\int_0^{\Delta H/L} dz\, e^{-W(z)}}. \tag{10}$$

Consequently, this allows a reduction of the problem's dimensionality from three dimensions to two dimensions:

$$\varepsilon^2 \partial_x J^x_{\rm st} + \partial_y J^y_{\rm st} = 0, \tag{11}$$

where the transport of Brownian particles is delimited by entropic barriers caused by geometrical confinements like the bottlenecks of the channel structure. The two-dimensional transport problem was investigated in symmetric [11,13,14,29,35,36] as well as in asymmetric [15–17,25] channels. Note that even in the case of a more general substrate potential given by $U(\mathbf{q}) = V(x,y) + W(z)$, the two-dimensional problem [Eq. (11)] does not depend on the potential $W(z)$.

For the considered dimensionless channel geometry $\pm h(x)$ the outward-pointing normal vector at the perpendicular side walls is given by $\mathbf{n} = \left(-h'(x), \pm 1{,}0\right)^T / \sqrt{1 + h'(x)^2}$ with the prime denoting the differentiation with respect to x. Therefore, the no-flux boundary condition Eq. (2) can be written as

$$\pm \varepsilon^2 h'(x)\, J^x_{\rm st} = J^y_{\rm st}, \quad \forall y \in \pm h(x). \tag{12}$$

Finally, we define the marginal one-dimensional probability density in the force direction $p_{\rm st}(x)$ as follows:

$$p_{\rm st}(x) = \int_{-h(x)}^{h(x)} dy \int_0^{\Delta H/L} dz\, P_{\rm st}(x,y,z). \tag{13}$$

III. ASYMPTOTIC ANALYSIS

We apply the asymptotic analysis [29–31] to the problem stated by Eq. (11) and Eq. (12). In doing so, we use for the stationary probability density $p_{st}(x,y)$ (the index st will be omitted in the following) the ansatz

$$p(x,y) = \sum_{n=0}^{\infty} \varepsilon^{2n} p_n(x,y) \tag{14}$$

and for the probability flux

$$\mathbf{J}(x,y) = \sum_{n=0}^{\infty} \varepsilon^{2n} \mathbf{J}_n(x,y) \tag{15}$$

in the form of a formal perturbation series in even orders of the parameter ε. Substituting these expressions into Eq. (11), we find

$$0 = \partial_y J^y_0(x,y) + \sum_{n=1}^{\infty} \varepsilon^{2n}\left[\partial_x J^x_{n-1}(x,y) + \partial_y J^y_n(x,y)\right], \tag{16a}$$

and the no-flux boundary condition at the channel walls $y = \pm h(x)$ [Eq. (12)] turns into

$$0 = -J^y_0(x,y) + \sum_{n=1}^{\infty} \varepsilon^{2n}[\pm h'(x) J^x_{n-1}(x,y) - J^y_n(x,y)]. \tag{16b}$$

Each order p_n has to obey the periodic boundary condition $p_n(x+m,y) = p_n(x,y), \forall m \in \mathbb{Z}$, and $p(x,y)$ has to be normalized for every value of ε.

Consequently, the average particle velocity is given by

$$\langle \dot{x} \rangle = \langle \dot{x} \rangle_0 + \sum_{n=1}^{\infty} \varepsilon^{2n}\left[f\,\langle p_n(x,y)\rangle_{x,y} - \langle \partial_x p_n(x,y)\rangle_{x,y}\right]. \tag{17}$$

In Eq. (17) the average of an arbitrary function $k(x,y)$ is defined as the integral over the cross section in y and over one period divided by the period length, which is one in the considered scaling, i.e., $\langle k(x,y)\rangle_{x,y} = \int_0^1 dx \int_{-h(x)}^{h(x)} dy\, k(x,y)$. In Sec. III A we demonstrate that the zeroth order of the perturbation series expansion coincides with the FJ equation [9,10]. Referring to Refs. [11,37] an expression for the average velocity $\langle \dot{x} \rangle_0$ is known. Moreover, in Sec. III B the higher-order corrections to the probability density are derived. Using those results we are able to obtain corrections (see Sec. III C) to the average velocity beyond the zeroth-order FJ approximation presented in the next section.

A. Zeroth order: The Fick-Jacobs equation

For the zeroth order, Eqs. (16) read

$$\partial_y J^y_0(x,y) = -\partial_y\left(e^{-V}\partial_y\left(e^{V} p_0(x,y)\right)\right) = 0, \tag{18a}$$

supplemented with the corresponding no-flux boundary condition

$$J^y_0(x,y) = 0, \forall y \in \text{wall}. \tag{18b}$$

Consequently,

$$p_0(x,y) = g(x)\, e^{-V(x,y)}, \tag{19}$$

where $g(x)$ is an unknown function which has to be determined from the second-order $O\left(\varepsilon^2\right)$ balance given by Eq. (16a):

$$0 = \partial_x(e^{-V} g'(x)) + \partial_y(e^{-V}\partial_y(e^{V} p_1(x,y))). \tag{20}$$

Integrating the latter over the cross section in y:

$$0 = \partial_x\left(\int_{-h(x)}^{h(x)} dy\, e^{-V(x,y)} g'(x)\right) + h'(x) J^x_0[x,-h(x)] + h'(x) J^x_0[x,h(x)] - J^y_1[x,h(x)] + J^y_1[x,-h(x)], \tag{21}$$

and taking the no-flux boundary conditions Eq. (16b) into account, one obtains

$$0 = \partial_x \left(e^{-A(x)} g'(x)\right), \tag{22}$$

where the effective potential $A(x)$ is explicitly given by

$$e^{-A(x)} = \int_{-h(x)}^{h(x)} dy\, e^{-V(x,y)}. \tag{23}$$

For the problem at hand, i.e., for $V(x,y) = -f\,x$, as well for potentials where x enters only linearly and where x is not multiplicative coupled to the other spatial coordinates [36,38,39], the stationary probability density within the zeroth order reads

$$p_0(x,y) = e^{-V(x,y)} g(x) = \frac{e^{-V(x,y)} \int_x^{x+1} e^{A(x')} dx'}{\int_0^1 dx e^{-A(x)} \int_x^{x+1} e^{A(x')} dx'}. \tag{24}$$

Moreover, the marginal probability density Eq. (13) becomes

$$p_0(x) = e^{-A(x)}\, g(x). \tag{25}$$

Expressing next $g(x)$ by $p_0(x)$ [see Eq. (22)] then yields the celebrated stationary FJ equation

$$0 = \partial_x \left(e^{-A(x)} \partial_x \left[e^{A(x)}\, p_0(x)\right]\right) \tag{26}$$

derived previously in Refs. [9,10,40]. Thus, we find the result that the leading-order term of the asymptotic analysis is equivalent to the FJ equation.

Note that the above presented derivation of the FJ equation is limited neither to reflection symmetric channel geometries [15–17] nor to the particularly chosen external potential: $V(x,y) = -f\,x$ [36,38,39,41]. Further, the differential equation determining the unknown function $g(x)$ [see Eq. (22)] is the same for the dynamics of a Brownian particle evolving in an energetic potential $V_{\mathrm{en}}(x,y)$ leading to a confinement in the y direction, with the natural boundary conditions $J_n^y(x, y = \pm\infty) = 0$ [10,42]. Therefore, in zeroth order and for the given scaling, an appropriately chosen confining energetic potential $V_{\mathrm{en}}(x,y)$ obeying $\int_{-\infty}^{\infty} dy \exp[-V_{\mathrm{en}}(x,y)] = \int_{-h(x)}^{h(x)} dy \exp[-V(x,y)]$ results in the same transport characteristics as those induced by the confining channel with the boundary functions $h_\pm(x)$ [43,44].

The average particle current is calculated by integrating the probability flux J_0^x over the unit cell [37,45]

$$\langle \dot{x}(f)\rangle_0 = \int_0^1 dx \int_{-h(x)}^{h(x)} dy\, J_0^x(x,y)$$
$$= \frac{1 - e^{-f}}{\int_0^1 dx\, e^{-A(x)} \int_x^{x+1} e^{A(x')}\, dx'}. \tag{27}$$

In the spirit of linear response theory, the mobility in units of the free mobility $1/\eta$ is defined by the ratio of the mean particle current Eq. (27) and the applied force f, yielding

$$\eta\, \mu_0(f) = \frac{\langle \dot{x}(f)\rangle_0}{f}. \tag{28}$$

In general, the stationary probability density of finding an overdamped Brownian particle budging in a two-dimensional periodic geometry is sufficiently described by Eq. (26) as long as the extension of the bulges of the channel structures is small compared to the periodicity, i.e., $\varepsilon \ll 1$. We next address the higher-order corrections $p_n(x,y)$ of the probability density, which become necessary for more winding structures.

B. Higher-order contributions to the Fick-Jacob equation

According to Eq. (16a), one needs to iteratively solve

$$\partial_y^2 p_n(x,y) = \mathfrak{L}\, p_{n-1}(x,y), \quad n \geqslant 1, \tag{29}$$

in consideration of the boundary condition [Eq. (16b)]. In Eq. (29) we make use of the operator $\mathfrak{L}$, reading $\mathfrak{L} = \left(f\,\partial_x - \partial_x^2\right)$. Applied n times this yields the expression

$$\mathfrak{L}^n = \sum_{k=0}^{n} \binom{n}{k} (-1)^k f^{n-k} \frac{\partial^{\,n+k}}{\partial\, x^{n+k}}. \tag{30}$$

Each solution of the second-order partial differential equation [Eq. (29)] possesses two integration constants $d_{n,1}$ and $d_{n,2}$. The first, $d_{n,1}$, is determined by the no-flux boundary condition Eq. (16b), while the second provides the normalization condition $\langle p(x,y)\rangle_{x,y} = 1$. In what follows we use the normalization constant of the probability density $p(x,y)$ via the zeroth order $\langle p_0(x,y)\rangle$. As a consequence, we have

$$\langle p_0(x,y)\rangle_{x,y} = \int_0^1 dx \int_{-h(x)}^{h(x)} dy\, p_0(x,y) = 1, \tag{31a}$$

$$\langle p_n(x,y)\rangle_{x,y} = 0, \quad \forall n \geqslant 1, \tag{31b}$$

with the constraint that

$$\int_{-h(x)}^{h(x)} dy\, p_n(x,y) \neq 0, \quad \forall n \geqslant 1, \tag{31c}$$

in order to prevent that the marginal probability density [Eq. (13)] equals the FJ results [see Eq. (25)] for an arbitrary value of ε, i.e., $p(x) = p_0(x)$. Further, we have to emphasize that the centered functions

$$p_n(x,y) \longmapsto \frac{p_n(x,y) - \langle p_n(x,y)\rangle}{\langle p(x,y)\rangle}, \quad \text{for } n \geqslant 1, \tag{32}$$

are not probability densities anymore because they can assume negative values for a given x and y. The calculation of the average particle velocity [Eq. (17)] simplifies to

$$\langle \dot{x}\rangle = \langle \dot{x}\rangle_0 - \sum_{n=1}^{\infty} \varepsilon^{2n} \langle \partial_x p_n(x,y)\rangle_{x,y}. \tag{33}$$

We find that the average particle current (1) is composed of the FJ result $\langle \dot{x}\rangle_0$ [see Eq. (27)] and (2) becomes corrected by the sum of the averaged derivatives of the higher orders $p_n(x,y)$. One immediately notices that the second integration constant $d_{n,2}$ does not influence the result for the average particle velocity [Eq. (33)].

For the first-order correction, the determining equation is

$$\partial_y^2 p_1(x,y) = \mathfrak{L}\, p_0(x,y) = \frac{\langle \dot{x}\rangle_0}{2}\, \partial_x \left(\frac{1}{h(x)}\right), \tag{34}$$

and after integrating twice over y, we obtain

$$p_1(x,y) = -\frac{\langle \dot{x} \rangle_0}{2} \left(\frac{h'(x)}{h^2(x)} \right) \frac{y^2}{2!}. \tag{35}$$

Hereby, as previously required above, the first integration constant $d_{1,1}(x)$ is set to 0 in order to fulfill the no-flux boundary condition, and the second must provide the normalization condition [Eq. (31b)], i.e., $d_{1,2} = 0$. Consequently, the first correction to the probability density becomes positive if the confinement is constricting, i.e., for $h'(x) < 0$ and $\langle \dot{x} \rangle_0 \neq 0$. In contrast, the probability density becomes less in unbolting regions of the confinement, i.e., for $h'(x) > 0$. Note that the first-order correction scales linearly with the average particle current $\langle \dot{x} \rangle_0$. Overall the break of spatial symmetry observed within numerical simulations in previous works [13,41] is reproduced by this very first-order correction. Particularly, with increasing forcing, the probability for finding a particle close to the constricting part of the confinement increases; see Refs. [13,41].

Upon recursively solving, we obtain for the higher-order corrections $n \geqslant 1$ as

$$p_n(x,y) = \mathfrak{L}^n p_0(x,y) \frac{y^{2n}}{2n!} + d_{n,2} + \sum_{k=1}^{n} \mathfrak{L}^{n-k} d_{k,1}(x) \frac{|y|^{2(n-k)+1}}{(2(n-k)+1)!}, \tag{36}$$

with the integration constants for the nth order reading

$$d_{n,1}(x) = -\frac{1}{2} \partial_x \left(\int_{-h(x)}^{h(x)} dy \, J^x_{n-1}(x,y) \right), \tag{37a}$$

$$d_{n,2} = -\left(\int_0^1 dx \sum_{k=1}^{n} \frac{h^{2(n-k)+2}}{(2(n-k)+2)!} \mathfrak{L}^{n-k} d_{k,1}(x) + \int_0^1 dx \, \mathfrak{L}^n p_0(x,y) \frac{h^{2n+1}}{(2n+1)!} \right) \Big/ \int_0^1 dx \, h(x). \tag{37b}$$

Note that for the considered case of an *axis-symmetric channel*, with respect to the y axis, each correction term $p_n(x,y)$ results in a first contribution involving even powers in y only and, in addition, of a sum over odd powers of $|y|$.

The stationary probability density $p(x,y)$ is obtained by summing all correction terms $p_n(x,y)$ [see Eq. (14)]. Accordingly, all terms with odd powers $|y|^{2k+1}, k \in \mathbb{N}$, vanish identically because these are proportional to $\sum_{n=1}^{\infty} \varepsilon^{2n} d_{n,1} = -\varepsilon^2 \partial_x \left(\int_{-h(x)}^{h(x)} dy \, J^x(x,y) \right)/2$. The latter expression equals zero in the stationary case [see Eq. (11)]. Consequently, the stationary probability density simplifies to read

$$p(x,y) = p_0(x,y) + \sum_{n=1}^{\infty} \varepsilon^{2n} \left(\mathfrak{L}^n p_0(x,y) \frac{y^{2n}}{(2n)!} + d_{n,2} \right). \tag{38}$$

Because $\mathfrak{L}\, p_0(x,y) \propto \langle \dot{x}(f) \rangle_0$, the two-dimensional probability density equals the zeroth-order contribution $p(x,y) = p_0(x,y) =$ const. for all values of ε for the case that the external force $f = 0$.

The presented derivation of $p(x,y)$ is valid here only for an axis-symmetric channel where no transverse potential force is acting on the particles, i.e., $\partial_y V(x,y) = 0$.

Further, according to Eq. (33), it follows that the average particle current scales with the average particle current obtained from the FJ formalism $\langle \dot{x} \rangle_0$ for all values of ε. In the following, we derive an expression for the mean particle current based on the above presented perturbation series expansion for the stationary probability density $p(x,y)$.

C. Corrections to the mean particle velocity

In Sec. III A, we could show that the dynamics of Brownian particles in confined structures can be described approximatively by the FJ equation [see Eq. (26)]. Zwanzig [10] obtained this one-dimensional equation from the full two-dimensional Smoluchowski equation upon eliminating the transverse degree of freedom. This approximation neglects the influence of relaxation dynamics in the transverse direction, supposing that it is infinitely fast. In a more detailed view, we must notice that diffusing particles pile up, or miss, at the curved wall if the channel is getting narrower or wider as they can flow out from or toward the wall in the y direction only at finite time. These effects are described by the higher expansion orders $p_n(x,y)$ presented in Eq. (36).

Next we derive an estimate for the mean particle current $\langle \dot{x}(f) \rangle$ based on the higher expansion orders $p_n(x,y)$. Referring to Eq. (33), the average particle current (1) is composed of the FJ result $\langle \dot{x} \rangle_0$ [see Eq. (27)] and (2) becomes corrected by the sum of the averaged derivatives of the higher orders $p_n(x,y)$. Consequently, it plays no role whether one uses the original expansion terms defined by Eq. (16a) or the centered ones, given by Eq. (32).

Burada *et al.* [13] have presented a validity criteria for the FJ approach. They have shown that the critical value of the force magnitude up to which the FJ equation holds depends on $1/\varepsilon^2$. Here we are mainly interested in the effect of winding structures on the average velocity, and thus we concentrate on the limit $|f| \ll 1$. Then the n-times-applied operator $\mathfrak{L}$ [see Eq. (30)] simplifies to $\mathfrak{L}^n = (-1)^n \frac{\partial^{2n}}{\partial x^{2n}}$. Similar to the authors of Ref. [15], we make the ansatz that all but the first derivative of the boundary function $h(x)$ are negligible. Then the partial derivative of $p_n(x,y)$ simplifies to

$$\partial_x p_n(x,y) = \langle \dot{x} \rangle_0 (-1)^{n+1} \frac{(h')^{2n}}{2\, h^{2n+1}} y^{2n} + O(h''(x)). \tag{39}$$

Integrating the latter over the channel's width, inserting the result into Eq. (33), and calculating the sum over ε^2 yields our main finding:

$$\lim_{f \to 0} \langle \dot{x}(f) \rangle \simeq \lim_{f \to 0} \langle \dot{x}(f) \rangle_0 \left\langle \frac{\arctan\left(\varepsilon h'(x)\right)}{\varepsilon h'(x)} \right\rangle_x. \tag{40}$$

There the average is taken over one period, which is one in the considered scaling, i.e., $\langle \cdot \rangle_x = \int_0^1 \cdot \, dx$. In Eq. (40), we identify $\arctan\left(\varepsilon h'(x)\right)/\varepsilon h'(x)$ with the spatially dependent diffusion coefficient $D(x)$ derived by Kalinay and Percus [15] for two-dimensional channel geometries:

$$\lim_{f\to 0}\langle\dot{x}(f)\rangle = \lim_{f\to 0}\langle\dot{x}(f)\rangle_0 \langle D(x)\rangle_x + O\left(h''(x)\right). \quad (41)$$

In the diffusion-dominated regime, the average transport velocity is therefore obtained as the product of the zeroth-order FJ result and the expectation value of the spatially dependent diffusion coefficient $\langle D(x)\rangle$. In the Appendix, we derive the expression for the spatially dependent diffusion constant based on the above presented perturbation series expansion in the average slope parameter ε.

In the linear response limit, i.e., for $|f| \ll 1$, the Sutherland-Einstein relation emerges [46,47] and reads in dimensionless units

$$\lim_{f\to 0}\mu(f) = \lim_{f\to 0} D_{\text{eff}}(f). \quad (42)$$

Thus, the effective diffusion coefficient D_{eff} is determined by the mobility $\mu = \lim_{f\to 0}\langle\dot{x}(f)\rangle/f$. Consequently, if the average current $\langle\dot{x}(f)\rangle_0$ [or the effective diffusion coefficient $D^0_{\text{eff}}(f)$] are known in the zeroth order, the higher-order corrections to both quantities can be obtained according to Eq. (41).

IV. APPLICATION OF THE THEORY TO A SINUSOIDALLY SHAPED CHANNEL

In this section we validate the obtained analytic predictions [Eq. (41)] with precise numerical simulations concerning one single pointlike Brownian particle moving with a corrugated sinusoidally shaped geometry [13,14]. The dimensionless boundary function $h(x)$ reads

$$h_\pm(x) = \pm h(x) = \pm\frac{1}{4}\left(\frac{1+\delta}{1-\delta} + \sin(2\pi\, x)\right) \quad (43)$$

and is illustrated in Fig. 1. Note that in absence of the scaling each channel geometry is determined by the period L, the maximum width $\Delta\Omega$, and the width at the bottleneck $\Delta\omega$. Upon scaling all lengths are measured in units of the period L. Consequently the parameter $\delta\Omega$ denotes the ratio of the maximum width $\Delta\Omega$ and the period L, namely, $\delta\Omega = \Delta\Omega/L$. Equivalently, it holds that $\delta\omega = \Delta\omega/L$. Within this scaling the period of the channel equals one.

In addition, one notices that the dimensionless boundary function $h(x)$ is solely governed by the aspect ratio of the minimal and maximal channel width $\delta = \delta\omega/\delta\Omega$. Obviously different realizations of channel geometries can possess the same value of δ. The number of orders have to taken into account in the perturbation series [Eq. (14)]; respectively, the applicability of the *Fick-Jacob approach* to the problem depends only on the value of the slope parameter $\varepsilon = \delta\Omega\,(1-\delta)$ for a given aspect ratio δ. For clarity, the impact of the maximum $\delta\Omega$ and minimum width $\delta\omega$ on the expansion parameter ε and on the aspect ratio δ, respectively, is illustrated in Fig. 2.

According to the Sutherland-Einstein relation [Eq. (42)] the mobility equals the effective diffusion coefficient (in the dimensionless units) for $f \ll 1$ [46]. Consequently, it is sufficient to discuss the behavior of the mobility $\mu(f)$. Referring to Sec. III C, the higher-order corrections to the mobility are given by the product of the FJ result and the expectation value of the spatially dependent diffusion coefficient $D(x)$ [see Eq. (41)].

First, we obtain the mobility μ_0 within the zeroth-order (FJ approximation). In the diffusion-dominated regime, the analytic expression for the mobility within the FJ approach [see Eqs. (27) and (28)] simplifies to the Lifson-Jackson formula [13,48]:

$$\mu_0 := \lim_{f\to 0}\mu_0(f) = \frac{1}{\langle h(x)\rangle\left\langle\frac{1}{h(x)}\right\rangle} = \lim_{f\to 0} D_{\text{eff}}(f). \quad (44)$$

For the exemplarily considered channel geometry [Eq. (43)] the mobility attains the asymptotic value

$$\lim_{f\to 0}\mu_0(f) = \frac{2\sqrt{\delta}}{1+\delta} = \frac{2\sqrt{1-\varepsilon/\delta\Omega}}{2-\varepsilon/\delta\Omega}. \quad (45)$$

One notices that in the diffusion-dominated regime, $|f| \ll 1$, the mobility of one single particle is determined only by the geometry, more precisely by the aspect ratio δ. In the limit of vanishing bottleneck width, i.e., $\delta \to 0$, the mobility tends to 0. In contrast, for straight channels corresponding to $\delta = 1$, i.e., $\varepsilon = 0$, the mobility equals its free value, which is one in the considered scaling.

Evaluating the period-averaged value of $D(x)$, i.e., considering all higher-order corrections apart from than scaling with higher derivatives of the boundary function $h(x)$, we obtain from Eq. (41)

$$\begin{aligned}\mu :&= \lim_{f\to 0}\mu(f) = \mu_0\,\langle D(x)\rangle \\ &= \frac{4\sqrt{1-\varepsilon/\delta\Omega}}{2-\varepsilon/\delta\Omega}\,\frac{\operatorname{asinh}(\pi\varepsilon/2)}{\pi\,\varepsilon}\end{aligned} \quad (46)$$

for the mobility μ and the effective diffusion coefficient D_{eff} in units of its free values, respectively.

In Fig. 3 we depict the dependence of the $\mu(f)$ (triangles) and $D_{\text{eff}}(f)$ (circles) on the slope parameter ε for $f = 10^{-3}$. The numerical results are obtained by solving the stationary

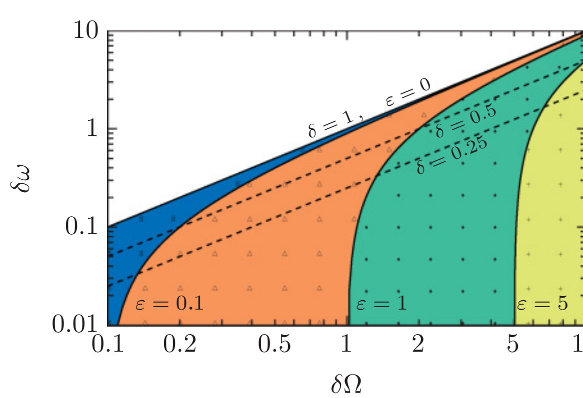

FIG. 2. (Color online) Schematic sketch of the dependence of the expansion parameter $\varepsilon = \delta\Omega - \delta\omega$ and the aspect ratio $\delta = \delta\omega/\delta\Omega$ on the maximum width $\delta\Omega$; respectively, the width at the bottleneck $\delta\omega$ in units of the period L. The dashed lines correspond to $\delta = 1$,0.5,0.25 (from above), and the colored areas illustrate pairs of $(\delta\Omega,\delta\omega)$, where $\varepsilon \leqslant 0.1$ (blue, circles), $\varepsilon \leqslant 1$ (red, triangles), $\varepsilon \leqslant 5$ (green, dots), and $\varepsilon > 5$ (yellow, plus signs).

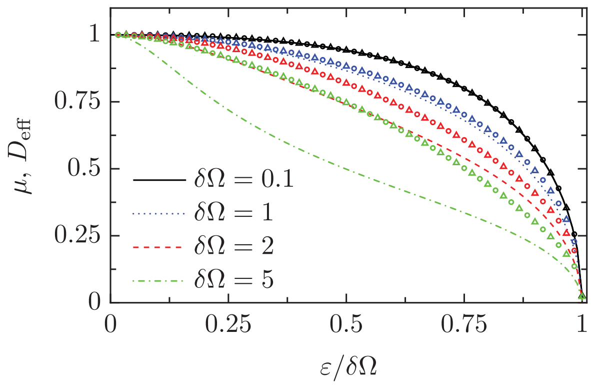

FIG. 3. (Color online) Comparison of the analytic theory versus precise numerics (in dimensionless units): The mobility and the effective diffusion constant for a Brownian particle moving inside a channel confinement are depicted as function of the ratio of slope parameter ε and maximal channel width $\delta\Omega$ for different values $\delta\Omega = 0.1,1,2,5$ and bias $f = 10^{-3}$ (corresponding to the diffusion-dominated regime). The symbols correspond to the numerical obtained mobility (triangles) and the effective diffusion coefficient (circles). The lines correspond to analytic higher-order results; see Eq. (46). The zeroth-order FJ results given by Eq. (45) collapse to a single curve hidden by the solid line.

Smoluchowski equation [Eq. (1a)] using the finite-element method [49] and subsequently calculating the average particle current [Eq. (4)]. In order to determine the effective diffusion coefficient $D_{\rm eff}(f)$, one has to solve numerically the reaction-diffusion equation for the *B-field* [28,29]. Note that the numerical results for the effective diffusion coefficient $D_{\rm eff}(f)$ and the mobility $\mu(f)$ coincide for all values of ε, thus corroborating the Sutherland-Einstein relation. In addition, the FJ result, given by Eq. (45), and the higher-order result [see Eq. (46)] are depicted in Fig. 3.

For the case of smoothly varying channel geometry, i.e., $\delta\Omega \ll 1$, the analytic expressions are in excellent agreement with the numerics, indicating the applicability of the FJ approach. As long as the extension of the bulges of the channel structures is small compared to the periodicity, sufficiently fast transversal equilibration, which serves as a fundamental ingredient for the validity of the FJ approximation, is taking place. In virtue of Eq. (5), the slope parameter is defined by $\varepsilon = \delta\Omega - \delta\omega$, and hence the maximal value of ε equals $\delta\Omega$; see Fig. 2. Consequently the influence of the higher expansion orders $\varepsilon^{2n}\,\langle\partial_x p_n(x,y)\rangle$ on the average velocity [Eq. (33)] and mobility, respectively, becomes negligible if the maximum channel's width $\delta\Omega$ is small.

With increasing maximum width the difference between the FJ result and the numerics is growing. Specifically, the FJ approximation resulting in Eq. (45) overestimates the mobility μ and the effective diffusion coefficient $D_{\rm eff}$. The higher-order corrections need to be included and consequently provide a good agreement for a wide range of ε values for maximum widths $\delta\Omega$ on the scale to the length of the channel, i.e., $\delta\Omega \sim 1$; see the dotted line in Fig. 3. Further increasing the maximum width $\delta\Omega$ diminishes the range of applicability of the derived higher-order corrections. This is due to the neglect of the higher derivatives of the boundary function $h(x)$. Put differently, the higher derivatives of $h(x)$ become significant for $\delta\Omega \gg 1$.

V. SUMMARY AND CONCLUSION

In summary, we have considered the transport of point-sized Brownian particles under the influence of a constant and uniform force field through a planar three-dimensional, axis-symmetric channel. The latter exhibits a constant height and periodically varying side walls.

We have presented a systematic treatment of particle transport by using a series expansion of the stationary probability density in terms of a smallness parameter that specifies the corrugation of the channel walls. In particular, it turns out that the leading-order term of the series expansion is equivalent to the well-established *Fick-Jacobs approach* [9,10]. The higher-order corrections to the probability density become significant for extreme bending of the channel's side walls. Analytic results for each order of the perturbation series have been derived. Interestingly, within the presented perturbation theory, all higher-order corrections to the stationary probability distribution and the average particle current scale with the average particle current obtained from the FJ formalism. Accordingly, in the linear response regime, i.e., for small forcing $|f| \ll 1$, the mean particle velocity is then given by the product of the average particle current obtained from the FJ formalism and the expectation value of the spatially dependent diffusion coefficient $D(x)$. Moreover, due to the Sutherland-Einstein relation, the above statement also holds good for the effective diffusion coefficient.

Finally, we have applied our analytic results to a specific example, namely, the particle transport through a channel with sinusoidally varying side walls. We corroborate our theoretical predictions for the mobility and the effective diffusion coefficient with precise numerical results of a finite-element calculation of the stationary Smoluchowski equation. Moreover, by using the higher-order corrections we present an alternative derivation for the spatially dependent diffusion coefficient $D(x)$, which substitutes the constant diffusion coefficient present in the common FJ equation based on assumptions similar to those suggested by Kalinay and Percus.

In conclusion, the consideration of the higher-order corrections leads to a substantial improvement of the FJ approach, which corresponds to the zeroth order in our perturbation analysis, toward more winding side walls of the channel.

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APPENDIX: SPATIALLY DEPENDENT DIFFUSION COEFFICIENT $D(x)$

Below we present an alternatively derivation for the spatially dependent diffusion coefficient $D(x)$, which was previously derived by Kalinay and Percus (KP) [15,17]. The concept of $D(x)$ was introduced by Zwanzig [10] and subsequently supported by the study of Reguera and Rubi [40]. Zwanzig obtained the FJ equation [see Eq. (26)] from the full two-dimensional Smoluchowski equation upon eliminating the transverse degree of freedom supposing infinitely fast relaxation.

The first systematically treatment taking the finite diffusion time into account was presented by Kalinay and Percus [15,17]. Their suggested mapping procedure enables the derivation of higher-order corrections in terms of an expansion parameter $\varepsilon_{\rm KP}^2$, which is the ratio of the diffusion constants in the longitudinal and transverse directions. The projection technique based on an imposed anisotropy in the diffusion equation which is equivalent to scaling the transverse lengths by $\varepsilon_{\rm KP}$ [31]. Within this scaling, the fast transverse modes (transients) separate from the slow longitudinal ones and can be projected out by integration over the transverse directions. KP suggested an operator procedure mapping the solutions of the corrected FJ equation back onto the space of solutions of the original two-dimensional problem. The resulting recurrence scheme provides systematical corrections to the FJ equation [17].

In the spirit of KP, we determine the spatially dependent diffusion coefficient $D(x)$ based on the presented results for the perturbation series expansion [see Eq. (38)]. Reguera and Rubi [40] derived the corrected stationary FJ equation within the framework of mesoscopic nonequilibrium thermodynamics:

$$0 = -\partial_x J^x(x) = \frac{\partial}{\partial x}\left[D(x)\, e^{-A(x)}\frac{\partial}{\partial x}\left(e^{A(x)}p(x)\right)\right]. \quad \text{(A1)}$$

In the limit of small force strengths, i.e., for $|f| \ll 1$, diffusion is the dominating process. Integrating the two-dimensional stationary Smoluchowski equation [Eq. (11)] over the cross section in y, and taking the no-flux boundary condition [Eq. (12)] into account, one derives an alternative definition of the marginal probability current $J^x(x)$, equivalent to Eq. (A1):

$$\begin{aligned} -J^x(x) &= D(x)\,h(x)\partial_x\left(\frac{p(x)}{h(x)}\right) \\ &= \int_{-h(x)}^{h(x)} \partial_x p(x,y)\,dy. \end{aligned} \quad \text{(A2)}$$

The second equality determines the sought-after spatially dependent diffusion coefficient $D(x)$. Note that $D(x)$ is solely determined by derivatives of $p(x,y)$ and $p(x)$. Hence, it plays no role whether one uses the original expansion terms defined by Eq. (16a) or the centered ones, given by Eq. (32). In compliance with Ref. [15], we make the ansatz that all but the first derivative of the boundary function $h(x)$ are negligible. Moreover, in the limit $|f| \ll 1$, the n-times-applied operator $\mathfrak{L}$ [see Eq. (30)] simplifies to $\mathfrak{L}^n = (-1)^n \frac{\partial^{2n}}{\partial x^{2n}}$, yielding

$$\partial_x \mathfrak{L}^n p_0(x,y) = \langle \dot{x}\rangle_0 (-1)^{n+1}(2n)!\frac{(h')^{2n}}{2\,h^{2n+1}} + O[h''(x)]. \quad \text{(A3)}$$

Inserting the probability densities into Eq. (A2), one finds that

$$\begin{aligned} D(x) &= \sum_{n=0}^{\infty} \varepsilon^{2n}(-1)^n \frac{(h')^{2n}}{2n+1} + O[h''(x)] \\ &\simeq \frac{\arctan\left(\varepsilon h'(x)\right)}{\varepsilon h'(x)} \end{aligned} \quad \text{(A4)}$$

for the spatially dependent diffusion coefficient $D(x)$ in the diffusion-dominated regime, i.e., for $|f| \ll 1$. Note that in contrast to KP we concentrate on the stationary process, which is, in fact, the only state necessary for deriving $D(x)$. Following KP's argumentation, we derive the identical result for $D(x)$ avoiding their presented operator algebra.

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