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 three-dimensional channel with smoothly varying periodic cross-section 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 derive an expression for the spatially dependent diffusion coefficient $D(x)$ which substitutes the constant diffusion coefficient present in the common Fick-Jacobs equation. In addition, 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 $\langle D(x) \rangle$. 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 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 [1,2]. In particular, the latter 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 the so-called bottlenecks, comprises challenges for technical developments of nanoscaled channel structures [3,4].

Along with the progress of the experimental techniques the problem of particle transport through corrugated channel structures containing narrow openings and bottlenecks has give rise to recent theoretical activities to study diffusion dynamics occurring in such geometries [1]. Previous studies by Jacobs [5] and Zwanzig [10] ignited a revival of doing research in this topic. The so-called Fick-Jacobs approach [5,10], 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 presence of applied external force fields and the quality of the Fick-Jacobs approach in presence of an applied force field in corrugated structures has been the focus of recent studies [13,14].

Beyond the Fick-Jacobs (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 like cylindrical septate channels [19,20], tubes formed by spherical compartments [22,23] or channels containing abrupt changes of cross diameters [24].

Our objective with this work is to provide a systematic treatment by using a series expansion in terms of a smallness parameter which specifies the channel corrugation for biased particle transport proceeding along an extended, three-dimensional periodic, reflection symmetric channel for which the original, commonly employed (lowest order) Fick-Jacobs 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 either from 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. in-
teraction effects can safely be neglected) are subjected to a fixed external force with magnitude \( F \) acting along the longitudinal direction of the channel \( e_x \), i.e., \( U(x, y, z) = -F x \). The overdamped single Brownian particle then budges in a three-dimensional periodic channel geometry of period \( L \), constant height \( \Delta H \), and periodically varying transverse width. A sketch of a segment of the channel is depicted in Fig. 1. The shape of the side walls are described by the two boundary functions \( \omega_\pm(x) \). As we restrict ourselves to reflection-symmetric confinements in \( y \)-direction, we set \( \omega_\pm(x) \equiv \pm \omega(x) \).

The evolution of the probability density \( P(q, t) \) of finding the particle at the local position \( q = (x, y, z)^T \) at time \( t \) is governed by the three-dimensional Smoluchowski equation \([25, 20]\), i.e.,

\[
\partial_t P(q, t) + \nabla_q \cdot J(q, t) = 0 , \tag{1a}
\]

where

\[
J(q, t) = \frac{F}{\eta} \frac{P(q, t)}{\eta} e_x - \frac{k_B T}{\eta} \nabla_q P(q, t) \tag{1b}
\]
is the probability current of the probability density \( P(q, t) \). The force strength acting on the Brownian particle is denoted by \( F \), \( \eta \) is the friction coefficient, while the Boltzmann constant is \( k_B \) and \( T \) refers to the environmental temperature. Because of the impenetrability of the channel walls the probability current \( J(q, t) = (J^x, J^y, J^z)^T \) is subjected to the no-flux boundary condition, reading

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

\( n \) denotes the out-pointing normal vector at the channel walls. The probability density satisfies the normalization condition \( \int_{\text{unit-cell}} P(q, t) \, d^3q = 1 \), 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 \( P_{\text{st}}(q) := \lim_{t \to \infty} P(q, t) \). Analogously, the stationary probability current reads \( J_{\text{st}}(q) := \lim_{t \to \infty} J(q, t) \).

The key quantities of particle transport through such periodic channels are the average particle velocity \( \langle \dot{q} \rangle \) and the effective diffusivity \( D_{\text{eff}} \). 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 \( P_{\text{st}}(q) \) using an established method taken from Ref. [27]. Once \( P_{\text{st}}(q) \) is known, the mean particle velocity of Brownian particles can be computed by

\[
\langle \dot{q} \rangle = \lim_{t \to \infty} \frac{\langle q(t) \rangle}{t} = \int_{\text{unit-cell}} J_{\text{st}}(q) \, d^3q . \tag{4}
\]

We next introduce dimensionless variables. In doing so, we measure longitudinal length and height as \( x = x/L \) and \( z = z/L \), respectively. For the rescaling of the \( y \)-coordinate, we introduce the dimensionless aspect parameter \( \varepsilon \): This is the difference of the widest crosssection 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

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

The dimensionless value of \( \varepsilon \) characterizes the deviation of the boundary from the straight channel which amounts to \( \varepsilon = 0 \). Following the reasoning in Ref. [28], we next measure, for the case of finite corrugation \( \varepsilon \neq 0 \), the transverse length \( y \) in units of \( \varepsilon L \), i.e. \( y = \varepsilon L \tilde{y} \) and, likewise, the boundary functions \( h_\pm(x) = \omega_\pm(x)/\varepsilon L \). Time is measured in units of \( \tau = \varepsilon L^2 \eta/(k_B T) \) which is twice the time the particle assumes to overcome diffusively, at zero bias \( F = 0 \), the distance \( L \), i.e., \( \tilde{t} = t/\tau \). The potential energy is rescaled by the thermal energy \( k_B T \), i.e., for the considered situation with a constant force component in channel direction: \( \tilde{U} = -F x/(k_B T) = -f \tilde{\tau} \), with the dimensionless force magnitude \([11, 14]\):

\[
f = \frac{F L}{k_B T} . \tag{6}
\]

The dimensionless forcing parameter \( f \) is given as 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 \( \underline{P}(\underline{q}, \tilde{\tau}) = \varepsilon L^3 \tilde{P}(\tilde{q}, \tilde{t}) \), respectively, the probability current is given by \( \underline{J}(\underline{q}, \tilde{\tau}) = \tau L^2 (\varepsilon \tilde{J}^x, \varepsilon \tilde{J}^y, \varepsilon \tilde{J}^z)^T \). In the following, we shall omit the overbar in our notation.

In dimensionless units, the Smoluchowski equation, cf. Eqs. (1), reads:

\[
\partial_t P(q, t) + \nabla_q \cdot J(q, t) = 0 , \tag{7a}
\]

where

\[
\nabla_q = (\partial_x, \frac{1}{\varepsilon} \partial_y, \partial_z)^T \quad \text{and} \quad J(q, t) = f \tilde{P}(\tilde{q}, \tilde{t}) e_x - \nabla_{\tilde{q}} \tilde{P}(\tilde{q}, \tilde{t}) . \tag{7b}
\]
At steady state, Eq. (7a) becomes:

$$\varepsilon^2 \partial_x J_{st}^x + \partial_y J_{st}^y + \varepsilon^2 \partial_z J_{st}^z = 0 .$$  \hspace{1cm} (8)

Because (i) the dynamics in z-direction is decoupled from the dynamics in x and y-direction and (ii) the shape of the lower and upper boundary depends neither on x nor on y, the separation ansatz $P_{st}(x,y,z) = p_{st}(x,y)\zeta(z)$ and the boundary condition

$$J_{st}^z = 0 , \text{ at } z = 0 \text{ and } z = \Delta H/L ,$$  \hspace{1cm} (9)

results in a non-trivial solution for $\zeta(z)$ for $J_{st}^z(q) = 0$ everywhere within the channel. For the considered situation, i.e. there is only a constant force acting in 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. 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

$$p_{st}(x,y,z) = p_{st}(x,y) \frac{e^{-W(z)}}{\Delta H/L} \int_0^{\Delta H/L} dz e^{-W(z)} .$$  \hspace{1cm} (10)

Consequently, this allows a reduction of the problem’s dimensionality from 3D to 2D:

$$\varepsilon^2 \partial_x J_{st}^x + \partial_y J_{st}^y = 0 .$$  \hspace{1cm} (11)

Note, that the 2D transport problem was investigated in symmetric \cite{11, 13, 15, 28, 30} and asymmetric \cite{16, 24} channels. For an arbitrary dimensionless channel geometry $h_{\pm}(x)$ the outwards pointing normal vector at the perpendicular side walls is given by $n = (\mp h_{\pm}(x), \pm 1, 0) / \sqrt{1 + h_{\pm}(x)^2}$ with the prime denoting the differentiation with respect to $x$. Therefore, the no-flux boundary condition Eq. (2) can be written as

$$\varepsilon^2 h_{\pm}'(x) J_{st}^x = J_{st}^x , \forall y \in h_{\pm}(x) .$$  \hspace{1cm} (12)

Note that even in the case of a more general substrate potential given by $U(q) = V(x,y) + W(z)$ the 2D problem Eq. (11) does not dependent on the potential $W(z)$.

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

$$p_{st}(x) = \int_{h_{-}(x)}^{h_{+}(x)} dy \int_0^{\Delta H/L} dz \ p_{st}(x,y,z) .$$  \hspace{1cm} (13)

### III. ASYMPTOTIC ANALYSIS

We apply the asymptotic analysis \cite{28, 31, 32} 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

$$p(x,y) = \sum_{n=0}^{\infty} \varepsilon^{2n} p_n(x,y) ,$$  \hspace{1cm} (14)

and for the probability flux

$$J(x,y) = \sum_{n=0}^{\infty} \varepsilon^{2n} J_n(x,y)$$  \hspace{1cm} (15)

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

$$0 = \partial_y J_0^y(x,y) + \sum_{n=1}^{\infty} \varepsilon^{2n} \left\{ \partial_x J_n^x(x,y) + \partial_y J_n^y(x,y) \right\} ,$$  \hspace{1cm} (16a)

and the no-flux boundary condition at the channel walls Eq. (12) turns into

$$0 = - J_0^y(x,y) + \sum_{n=1}^{\infty} \varepsilon^{2n} \left\{ h_{\pm}'(x) J_{n-1}^x(x,y) - J_n^y(x,y) \right\} .$$  \hspace{1cm} (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 $\varepsilon$.

Consequently, the average particle velocity is given by

$$\langle \dot{x} \rangle = \langle \dot{x} \rangle_0 + \sum_{n=1}^{\infty} \varepsilon^{2n} \{ f(p_n(x,y))_{x,y} - \langle \partial_x p_n(x,y) \rangle_{x,y} \} .$$  \hspace{1cm} (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. $\langle k(x,y) \rangle_{x,y} = \int_0^1 dx \int_{-\Delta(x)}^{\Delta(x)} dy \ k(x,y)$. In Sec. III A we demonstrate that the zeroth order of the perturbation series expansion coincides with the Fick-Jacobs equation \cite{11, 11}. Referring to \cite{11, 33} an expression for the average velocity $\langle \dot{x} \rangle_0$ is known. Moreover, in Sec. III B the higher orders of the probability density are derived. Using those results we are able to obtain corrections, see in Sec. III C to the average velocity beyond the zeroth order Fick-Jacobs approximation presented in the next section.

#### A. Zeroth Order: the Fick-Jacobs equation

For the zeroth order, Eqs. (16) read

$$\partial_y J_0^y(x,y) = - \partial_y e^{-V(x,y)} \partial_y \left( e^{V(x,y)} p_0(x,y) \right) = 0 ,$$  \hspace{1cm} (18a)
supplemented with the corresponding no-flux boundary condition

\[ J_0^y(x, y) = 0, \forall y \in \text{wall}. \quad (18b) \]

Consequently,

\[ p_0(x, y) = g(x) e^{-V(x,y)}, \quad (19) \]

where \( g(x) \) is an unknown function which has to be determined from the second order \( O(\varepsilon^2) \) balance given by Eq. (16a). Integrating the latter over the cross-section in \( y \) and taking the no-flux boundary conditions Eq. (16b) into account, one obtains

\[ 0 = \partial_x \left( e^{-A(x)} g'(x) \right), \quad (20) \]

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

\[ e^{-A(x)} = \int_{-h(x)}^{+h(x)} dy e^{-V(x,y)}. \quad (21) \]

For the problem at hand, i.e. for \( V(x, y) = -fx \), as well for potentials where \( x \) enters only linearly and where \( x \) is not multiplicatively coupled to the other spatial coordinates \( \mathbf{30, 31, 32} \), the stationary probability density within the zeroth order reads

\[ p_0(x, y) = e^{-V(x,y)} g(x) = e^{-V(x,y)} \int_0^{x+1} dx' \int_{-h(x)}^{+h(x)} dy e^{-A(x')} dx', \quad (22) \]

In addition, the marginal probability density Eq. (13) becomes

\[ p_0(x) = e^{-A(x)} g(x). \quad (23) \]

Expressing next \( g(x) \) by \( p_0(x) \), see Eq. (20), then yields the celebrated stationary Fick-Jacobs equation

\[ 0 = \partial_x \left( e^{-A(x)} \partial_x e^{A(x)} p_0(x) \right) \quad (24) \]

derived previously in Ref. \[ 9, 11, 36 \]. Thus, we find the result that the leading order term of the asymptotic analysis is equivalent to the FJ-equation. Please note that the differential equation determining the unknown function \( g(x) \), cf. Eq. (20), is the same for the dynamics of a Brownian particle evolving in an energetic potential \( V_{en}(x, y) \) leading to a confinement in \( y \)-direction, with the natural boundary conditions \( J_0^y(x, y = \pm \infty) = 0 \). \[ 10, 32 \]. Therefore, in zeroth order and for the given scaling, an appropriately chosen confining energetic potential \( V_{en}(x, y) \) obeying \( \int_{-\infty}^{\infty} dy \exp(-V_{en}(x, y)) = \int_{-h(x)}^{h(x)} dy \exp(-V(x, y)) \) results in the same transport characteristics as those induced by the confining channel with the boundary functions \( h_{\pm}(x) \). \[ 37 \].

The average particle current is calculated by integrating the probability flux \( J_0^x \) over the unit-cell \[ 33, 35 \]

\[ \langle \dot{x}(f) \rangle_0 = \int_0^1 dx \int_{h_-(x)}^{h_+(x)} dy J_0^x(x, y) = \frac{1 - e^{-f}}{\int_0^1 dx e^{-A(x)} \int_x^{x+1} e^{A(x')} dx'}. \quad (25) \]

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. (25) and the applied force \( f \) yielding

\[ \eta \mu_0 (f) = \frac{\langle \dot{x}(f) \rangle_0}{f}. \quad (26) \]

B. Higher order contributions to the Fick-Jacobs equation

We next address the higher order corrections \( p_n(x, y) \) of the probability density. According to Eq. (16a), one needs to iteratively solve

\[ \partial_x^2 p_n(x, y) = \Sigma p_{n-1}(x, y), \quad n \geq 1, \quad (27) \]

under consideration of the boundary condition Eq. (16b). In Eq. (27), we make use of the operator \( \Sigma \), reading \( \Sigma = (f \partial_x - \partial_x f) \). Applied \( n \)-times yields the expression

\[ \Sigma^n = \sum_{k=0}^{n} \binom{n}{k} (-1)^k f^{n-k} \frac{\partial^{n+k}}{\partial x^{n+k}}. \quad (28) \]

Each solution of the second order partial differential equation Eq. (27) possesses two integration constants \( d_{n,1} \) and \( d_{n,2} \). The first one, \( d_{n,1} \), 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

\[ \langle p_0(x, y) \rangle_{x,y} = \int_0^1 dx \int_{h_-(x)}^{h_+(x)} dy p_0(x, y) = 1, \quad (29a) \]

\[ \langle p_n(x, y) \rangle_{x,y} = 0, \quad \forall n \geq 1, \quad (29b) \]

with the constraint that

\[ \int_{h_-(x)}^{h_+(x)} dy p_n(x, y) \neq 0, \quad \forall n \geq 1, \quad (29c) \]
in order to prevent that the marginal probability density Eq. (13) equals the FJ results, cf. Eq. (25), for an arbitrary value of $\varepsilon$, i.e. $p(x) = p_0(x)$. Further, we have to emphasize that the centered functions

$$p_n(x, y) \mapsto \frac{p_n(x, y) - \langle p_n(x, y) \rangle}{\langle p(x, y) \rangle}, \quad \text{for } n \geq 1,$$

(30)

are no 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

$$\langle \dot{x} \rangle = \langle \dot{x}_0 \rangle - \sum_{n=0}^{\infty} \varepsilon^{2n} \langle \partial_x p_n(x, y) \rangle_{x,y}.$$

(31)

We find that the average particle current is composed of (i) the Fick-Jacob result $\langle \dot{x}_0 \rangle$, cf. Eq. (25), and (ii) 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. (31).

For the first order correction, the determining equation is

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

(32)

and after integrating twice over $y$, we obtain

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

(33)

Hereby, as previously requested 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. (29b), i.e. $d_{1,2} = 0$. Consequently, the first correction to the probability density becomes positive if the confinement is constraining, 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 $h'(x) > 0$. Please note, that the first order correction scales linearly with the average particle current $\langle \dot{x}_0 \rangle$. Overall, the break of spatial symmetry observed within numerical simulations in previous works [13, 39] is reproduced by this very first order correction. Particularly, with increasing forcing, the probability for finding a particle close to the constraining part of the confinement increases, cf. Ref. [13, 39].

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

$$p_n(x, y) = \sum_{n}^{} p_n(x, y) \frac{y^{2n}}{2n!} + d_{n,2} +$$

$$+ \sum_{k=1}^{n} \varepsilon^{n-k} d_{k,1}(x) \frac{|y|^{2(n-k)+1}}{(2(n-k)+1)!},$$

(34)

with the integration constants for the $n$-th order

$$d_{n,1}(x) = -\partial_x \left( \int_0^x dy J_{n-1}^x (x, y) \right),$$

(35a)

$$d_{n,2} = \left( \int_0^1 dx \sum_{k=1}^{n} \varepsilon^{n-k} d_{k,1}(x) \right) \frac{h^{2(n-k)+2}}{(2(n-k)+2)!}$$

$$+ \int_0^1 dx \sum_{k=1}^{n} \varepsilon^{n-k} d_{k,1}(x) \frac{h^{2n+1}}{(2n+1)!} \frac{1}{\int_0^1 dx h(x)}.$$  

(35b)

As expected, for a reflection symmetric channel in $y$-direction each order $p_n(x, y)$ results as well in a reflection symmetric function. The latter consists of a term proportional to even powers in $y$ and in addition of a sum of odd powers of $|y|$, caused by the no-flux boundary conditions. Since each integration constant $d_{n,1}(x)$ with $n > 1$ is determined by the probability current of the previous order, every order $p_n(x, y)$ is proportional to the average current of the zeroth order $\langle \dot{x}_0 \rangle$. Consequently, the 2D probability density equals the zeroth order $p(x, y) = p_0(x, y) = const$ for all values of $\varepsilon$ in absence of an external force $f = 0$. Further, it follows that the average particle current Eq. (31) scales with the average particle current obtained from the Fick-Jacob formalism $\langle \dot{x}_0 \rangle$ for all values of $\varepsilon$.

C. Spatially diffusion coefficient $D(x)$

With Sec. IIIA we could show that the dynamics of Brownian particles in confined structures can be described approximatively by the FJ-equation, cf. Eq. (24). Zwanzig [10] obtained this 1D equation from the full 2D Smoluchowski equation upon eliminating the transverse degree of freedom. This approximation neglects the influence of relaxation dynamics in transverse direction, supposing that it is infinitely fast. In a more detailed view, we have to 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 towards the wall in $y$ direction only at finite time. These effects are described by the higher expansion orders $p_n(x, y)$ presented in Eq. (34). In the following, we aim at deriving a dynamical equation of Smoluchowski-type, but with a diffusion coefficient that depends on the longitudinal channel coordinate $x$.

The concept of a spatially dependent diffusion coefficient $D(x)$ was introduced by Zwanzig [10] and subsequently supported by the study of Reguera and Rubi [38]. The main idea is to combine all marginal higher orders corrections $p_n(x)$ into a one-dimensional function $D(x)$, effectively acting on the marginal probability density $p(x)$. In Ref. [38] the corrected stationary
FJ-equation has the form

$$0 = -\partial_x J^x(x) = \frac{\partial}{\partial x} D(x) e^{-A(x)} \frac{\partial}{\partial x} e^{A(x)} p(x) ,$$  \hspace{1cm} (36)

and was derived therein within the framework of mesoscopic non-equilibrium thermodynamics. Kalinay and Percus [15] used a rigorous mapping of the 2D diffusion equation onto the reduced dimension and derived an expansion of the diffusion coefficient $D(x)$, which represents corrections to the FJ-equation.

In this spirit we now determine the spatial dependent diffusion coefficient $D(x)$ based on the presented results for the perturbation series expansion Eq. (34). We concentrate on the limit of small force strengths $|f| \ll 1$, so that diffusion is the dominating process. Integrating the 2D stationary Smoluchowski equation Eq. (11) over the cross-section in $y$, and respecting the no-flux boundary condition Eq. (12), one derives an alternative definition of the marginal probability current $J^x(x)$, equivalent to Eq. (36):

$$-J^x(x) = D(x) h(x) \partial_x \left( \frac{p(x)}{h(x)} \right) = \int_{-h(x)}^{h(x)} \partial_x p(x, y) dy .$$  \hspace{1cm} (37)

The second equality determines the sought-after spatial 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. (10) or the centered ones, given by Eq. (36). In compliance with Ref. [13], we make the ansatz that all but the first derivative of the boundary function $h(x)$ are negligible. Then, the integration constants $a_{n,1}(x)$ equal 0 as they can been shown to be proportional to higher derivatives of $h(x)$. Moreover, in the limit $|f| \ll 1$, the $n$-times applied operator $\mathcal{L}$, cf. Eq. (28), simplifies to $\mathcal{L}^n = (-1)^n \frac{\partial^{2n}}{\partial x^{2n}}$. Moreover

$$\mathcal{L}^n p_0 = \langle \dot{x} \rangle_0 (-1)^n (2n - 1)! \frac{(h')^{2n-1}}{2^n h^{2n}} + O(h''(x)) .$$  \hspace{1cm} (38)

Inserting the probability densities into Eq. (37), one finds that

$$D(x) = \sum_{n=0}^{\infty} \varepsilon^{2n} (-1)^n \frac{(h')^{2n}}{2^n h^{2n+1}} + O(h''(x))$$

$$\simeq \frac{\arctan (\varepsilon h'(x))}{\varepsilon h'(x)}$$  \hspace{1cm} (39)

for the spatially dependent diffusion coefficient $D(x)$ in the diffusion dominated regime, i.e. when $|f| \ll 1$. Note, that this expression for $D(x)$ was obtained previously by Kalinay and Percus [15] within a quite different expansion approach.

In what follows, we evaluate the average particle current Eq. (31) by means of the spatially dependent diffusion coefficient $D(x)$. According to $\lim_{f \to 0} \langle \dot{x} \rangle = \int_0^1 dx J^x(x)$, it follows that in the small force limit the mean particle velocity is proportional to the expectation value of the spatially dependent diffusion coefficient, yielding the main finding

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

$$\simeq \lim_{f \to 0} \langle \dot{x}(f) \rangle_0 \left\langle \frac{\arctan (\varepsilon h'(x))}{\varepsilon h'(x)} \right\rangle_x .$$  \hspace{1cm} (40)

In Eq. (40), the average of an arbitrary function $k(x)$ is defined as the integral over one period divided by the period length which is one in the considered scaling, i.e., $\langle k(x) \rangle_x = \int_0^1 k(x) dx$. In the linear response limit, i.e. for $|f| \ll 1$, the Sutherland-Einstein relation emerges Ref. [40,11], reading in dimensionless units:

$$\lim_{f \to 0} \mu(f) = \lim_{f \to 0} D_{\text{eff}}(f),$$  \hspace{1cm} (41)

the effective diffusion coefficient $D_{\text{eff}}$ 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 $D_{\text{eff}}(f)$) are known in the zeroth order, the higher order corrections to both quantities can be obtained according to Eq. (40).

IV. APPLICATION OF THE THEORY TO A SINUSOIDALLY SHAPED CHANNEL

In the following we validate the obtained analytic predictions Eq. (40) with precise numerical simulations concerning one single point-like Brownian particle moving with a corrugated sinusoidally-shaped geometry Ref. [12,14]. The dimensionless boundary function $h(x)$ reads

$$h_{\pm}(x) = \pm h(x) = \pm \frac{1}{4} \left( 1 + \frac{\delta}{1 - \delta} + \sin(2\pi x) \right) ,$$  \hspace{1cm} (42)

and is illustrated in Fig. 1. Please 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 $L$, viz., $\delta \Omega = \Delta \Omega / L$. 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 $\delta$. 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 $\delta$. For clarity, the impact of the maximum of $\delta \Omega$ and minimum
width $\delta \omega$ on the expansion parameter $\varepsilon = \delta \Omega - \delta \omega$, respectively, the aspect ratio $\delta$ is illustrated in Fig. 2.

According to the Sutherland-Einstein relation Eq. (41) the mobility equals the effective diffusion coefficient (in the dimensionless units) for $f \ll 1$ [40]. 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. (40).

First, we obtain the mobility $\mu_0$ within the zeroth-order (Fick-Jacobs approximation). In the diffusion dominated regime, the analytic expression for the mobility within the FJ-approach, cf. Eqs. (25) and (26), simplifies to the Lifson-Jackson formula [13, 12].

\[
\mu_0 := \lim_{f \to 0} \mu_0(f) = \frac{1}{\langle h(x) \rangle} = \lim_{f \to 0} D_{\text{eff}}(f). \quad (43)
\]

For the exemplarily considered channel geometry Eq. (42) the mobility attains the asymptotic value

\[
\lim_{f \to 0} \mu_0(f) = \frac{2 \sqrt{\delta}}{1 + \delta} = \frac{2 \sqrt{1 - \varepsilon/\delta \Omega}}{2 - \varepsilon/\delta \Omega}. \quad (44)
\]

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 $\delta$. 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 scaling with higher derivatives of the boundary function $h(x)$, we obtain from Eq. (40):

\[
\mu := \lim_{f \to 0} \mu(f) = \mu_0 \langle D(x) \rangle = \frac{4 \sqrt{1 - \varepsilon/\delta \Omega}}{2 - \varepsilon/\delta \Omega} \frac{\sinh (\pi \varepsilon/2)}{\pi \varepsilon}. \quad (45)
\]

for the mobility $\mu$ and the effective diffusion coefficient $D_{\text{eff}}$ 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 $\varepsilon$ for $f = 10^{-3}$. The numerical results are obtained by solving the stationary Smoluchowski equation Eq. (13) using finite element method [43] and subsequently calculating the average particle current Eq. (4). In order to determine the effective diffusion coefficient $D_{\text{eff}}(f)$, one has to solve numerically the reaction-diffusion equation for the $B$-field [27, 28]. Note, that the numerical results for the effective diffusion coefficient $D_{\text{eff}}(f)$ and the mobility $\mu(f)$ coincide for all values of $\varepsilon$, thus corroborating the Sutherland-Einstein relation. In addition, the Fick-Jacobs result, given by Eq. (44), and the higher order result, see Eq. (45), 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 Fick-Jacobs 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 fundamental ingredient for the validity of the Fick-Jacobs approximation is taking place. In virtue of Eq. (5), the slope parameter is defined by $\varepsilon = \delta \Omega - \delta \omega$. 

Figure 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) while the colored areas illustrate pairs of $(\delta \Omega, \delta \omega)$ where $\varepsilon \leq 0.1$ (blue, circles), $\varepsilon \leq 1$ (red, triangles), $\varepsilon \leq 5$ (green, dots), and $\varepsilon > 5$ (yellow, plus signs).

Figure 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 $\varepsilon$ 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 result, cf. Eq. (45). The zeroth order - Fick-Jacobs results given by Eq. (44) collapse to a single curve hidden by the solid line.
and hence the maximal value of \( \varepsilon \) equals \( \delta \Omega \), see Fig. 2. Consequently the influence of the higher expansion orders \( \varepsilon^{2n} \langle \partial^2 P_n(x, y) \rangle \) on the average velocity Eq. [31] 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. [41] overestimates the mobility \( \mu \) and the effective diffusion coefficient \( D_{\text{eff}} \). The higher order corrections need to be included and consequently provide a good agreement for a wide range of \( \varepsilon \)-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. 2. Upon 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-size Brownian particles under the influence of a constant and uniform force field through a three-dimensional 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 which 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 Fick-Jacobs formalism. Moreover, by using the higher order corrections we have derived an expression for the spatially dependent diffusion coefficient \( D(x) \) which substitutes the constant diffusion coefficient present in the common Fick-Jacobs equation. 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 Fick-Jacobs 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. In conclusion, the consideration of the higher order corrections leads to a substantial improvement of the Fick-Jacobs-approach, which corresponds to the zeroth order in our perturbation analysis, towards more winding side walls of the channel.

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