Entropic transport - a step beyond Fick-Jacobs

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Motivation

We study the dynamics of point-size Brownian particles under the influence of a constant and uniform force field $\mathbf{F} = f\,\mathbf{e}_x$ ($f \equiv FL/k_BT$) in a planar 3D channel with smoothly varying periodic cross-section.

Our aim is to derive an analytic expression for the stationary probability density $P_{\text{st}}(\mathbf{q})$ in order to calculation the mean particle current $\langle \dot{x}(f) \rangle$ and the effective diffusion coefficient $D_{\text{eff}}(f)$ in force direction.

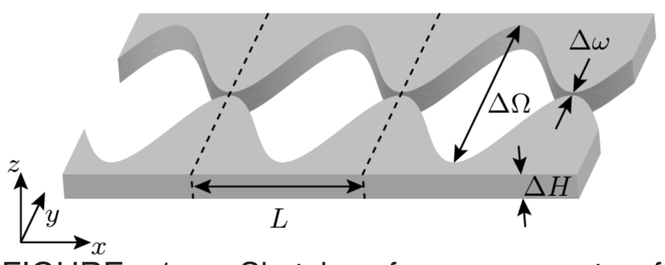


FIGURE 1: Sketch of a segment of a reflection-symmetric sinusoidally varying channel with periodicity L, constant height ΔH, minimal and maximal channel widths $\Delta\omega$ and $\Delta\Omega$, respectively.

- after scaling: $x = L\,\bar{x}$, $z = L\,\bar{z}$, and $y = \varepsilon\, L\,\bar{y}$
$$\varepsilon = \frac{\Delta\Omega - \Delta\omega}{L}$$
- dimensionless **boundary function**
$$\pm\, h(x) = \pm\,\omega(x)/\varepsilon L$$
- overdamped Langevin dynamics (in dimensionless units)
$$\dot{x} = f + \xi_x(t)\,,\quad \dot{y} = \frac{1}{\varepsilon}\,\xi_y(t)\,,\quad \dot{z} = \xi_z(t) \tag{1}$$
- Gaussian white noise with $\langle\, \xi(t) \,\rangle = 0$ and $\left\langle\, \xi_i(t), \xi_j(s) \,\right\rangle = \delta_{i,j}\,\delta(t-s)$ for $i, j = x, y, z$

The Smoluchowski-Equation

- in dimensionless units, the Smoluchowski equation reads:
$$\partial_t P\left(\mathbf{q}, t\right) + \nabla_{\mathbf{q}} \cdot \mathbf{J}\left(\mathbf{q}, t\right) = 0\,, \tag{2a}$$
with **no-flux boundary condition**
$$\mathbf{J}\left(\mathbf{q}, t\right) \cdot \mathbf{n} = 0\,, \quad \forall \mathbf{q} \in \text{channel wall}\,. \tag{2b}$$
- separation ansatz for stationary probability density
  1. dynamics in z-direction is decoupled from $x - y-$ dynamics
  2. shape of lower and upper boundary depends neither on x nor y
$$P_{\text{st}}(x, y, z) = p_{\text{st}}(x, y) \cdot \frac{L}{\Delta H}\,. \tag{3}$$
- reduction to 2D problem for stationary probability density
$$\varepsilon^2 \partial_x J^x_{\text{st}} + \partial_y J^y_{\text{st}} = 0\,. \tag{4a}$$
with no-flux boundary conditions
$$\pm\varepsilon^2 h'(x)\, J^x_{\text{st}} = J^y_{\text{st}}\,, \quad \forall y \in \pm h(x) \tag{4b}$$

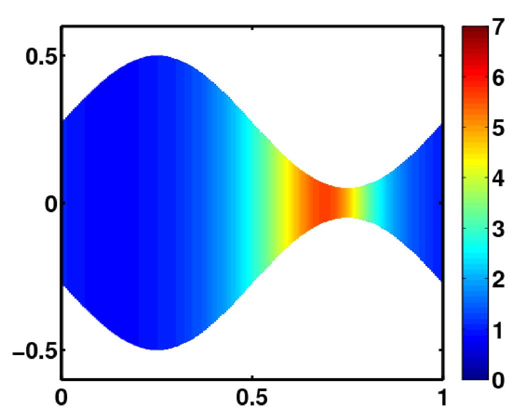
Asymptotic analysis

- apply the asymptotic analysis [1] to the stat. problem Eq. (4) (index *st* will be omitted):
$$p(x, y) = \sum_{n=0}^{\infty} \varepsilon^{2n} p_n(x, y)$$
Substituting the latter into Eqs. (4)
$$0 = \partial_y J^y_0(x, y) + \sum_{n=1}^{\infty} \varepsilon^{2n} \left\{ \partial_x J^x_{n-1}(x, y) + \partial_y J^y_n(x, y) \right\}\,, \tag{5a}$$
the no-flux boundary condition at the channel walls $y = \pm h(x)$ turns into
$$0 = -\,J^y_0(x, y) + \sum_{n=1}^{\infty} \varepsilon^{2n} \left\{ \pm h'(x) J^x_{n-1}(x, y) - J^y_n(x, y) \right\}\,. \tag{5b}$$
- in addition, **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 each value of ε

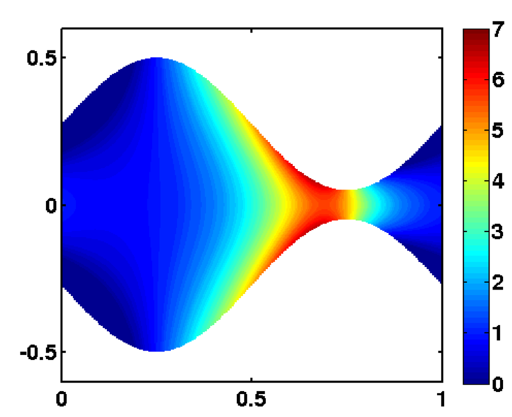
- upon **recursively** solving, we obtain

zeroth-order (**Fick-Jacobs approach**):
$$p_0(x, y) = N^{-1}\, e^{-V(x,y)} \int_x^{x+1} e^{A(x')} dx' \tag{6}$$
with the effective potential
$$A(x) = -\,f\,x - \ln\left(2\,h(x)\right) \tag{7}$$
first order correction:
$$p_1(x, y) = -\,\frac{\langle \dot{x} \rangle_0}{2} \left(\frac{h'(x)}{h^2(x)} \right) \frac{y^2}{2!} \tag{8}$$
higher order corrections:
$$p_n(x, y) = \mathfrak{L}^n p_0(x, y) \frac{y^{2n}}{2n!} + d_{n,2} + \sum_{k=1}^{n} \mathfrak{L}^{n-k} d_{k,1}(x) \frac{|y|^{2(n-k)+1}}{(2(n-k)+1)!}\,, \tag{9}$$
where $\mathfrak{L} = \left(f\partial_x - \partial_x^2 \right)$ and
$$d_{n,1}(x) = -\,\partial_x \left(\int_0^{h(x)} dy\, J^x_{n-1}\left(x, y\right) \right) \tag{10}$$

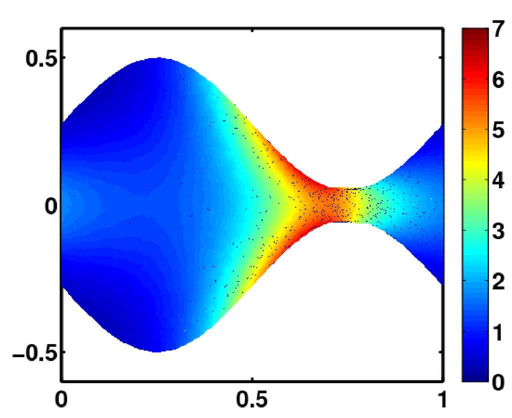
- each order $p_n(x, y)$ is a reflection symmetric function in y-direction
- $p_n(x, y)$ is proportional the averaged current within the Fick-Jacobs approach $\langle\, \dot{x} \,\rangle_0$
$\hookrightarrow p(x, y) = p_0(x, y) = const$ for $f = 0$



Visualization of $p_0(x, y)$ for $\Delta\Omega = 1$, $\Delta\omega = 0.1$, and $f = 10$.



Visualization of $p_0(x, y) + \varepsilon^2 p_1(x, y)$ for $\Delta\Omega = 1$, $\Delta\omega = 0.1$, and $f = 10$.



FreeFem simulation for $\Delta\Omega = 1$, $\Delta\omega = 0.1$, and $f = 10$.

Spatially dependent diffusion coefficient $D(x, f)$

- Fick-Jacobs approach: projection of highly dimensional dynamics onto a single coordinate $\Longrightarrow$ valid only for narrow channels $\varepsilon \ll 1$
- **idea**: introduction of position dependent temperature/diffusion coefficient in order take the relaxation dynamics in transverse direction into account [2]
- determining equation for $D(x, f)$
$$D(x, f) = \frac{\int_{-h(x)}^{h(x)} dy\, \left(-f + \partial_x\right) p(x, y)}{A'(x)\, p(x) + \partial_x p(x)} \tag{11}$$
- marginal probability density
$$p(x) = \int_{-h(x)}^{+h(x)} dy \int_0^{\Delta H/L} dz\, P(x, y, z)\,. \tag{12}$$
- **force dominated regime** $f \gg 1$
$$\lim_{f \to \infty} D(x, f) = 1 \tag{13}$$
- **diffusion dominated regime** $f \ll 1$ and neglect of higher derivatives $h^{(m)}(x)$, $m \geq 2$
$$\lim_{f \to 0} D(x, f) \simeq \frac{\arctan\left(\varepsilon\, h'(x)\right)}{\varepsilon\, h'(x)} + O\left(h''(x)\right) \tag{14}$$
- averaged particle velocity and effective diffusion coefficient are **proportional to the expectation value of D(x, f)**
$$\lim_{f \ll 1} \frac{\langle\, \dot{x}(f) \,\rangle}{\langle\, \dot{x}(f) \,\rangle_0} = \frac{\mu(f)}{\mu_0(f)} = \frac{D_{\text{eff}}(f)}{D_{\text{eff}}(f)_0} = \int_0^1 dx\, \lim_{f \to 0} D(x, f) + O(h''(x), \mathbf{f^2}) \tag{15}$$

An example - Sinusoidal channel

- dimensionless boundary function [3]
$$h(x) = \pm\frac{1}{4}\left(\frac{1+\delta}{1-\delta} + \sin\left(2\pi x\right) \right) \quad \text{with aspect ratio} \quad \delta = \Delta\omega/\Delta\Omega$$
- FJ result for the mobility in units of its free value $1/\eta$
$$\eta\mu_0\left(f\right) = \frac{\langle \dot{x}(f) \rangle_0}{f} = \frac{f^2 + (2\pi)^2}{f^2 + \frac{(2\pi)^2}{2}\left\{ \sqrt{\delta} + \sqrt{1/\delta} \right\}} \tag{16}$$
- the mobility possesses the following properties:
$$(i)\quad \mu_0(-f) = \mu_0(f)\,, \qquad (ii)\quad \lim_{f \to 0} \eta\,\mu_0(f) = \frac{2\sqrt{\delta}}{1+\delta}\,, \qquad (iii)\quad \lim_{f \to \infty} \eta\,\mu_0(f) = 1.$$

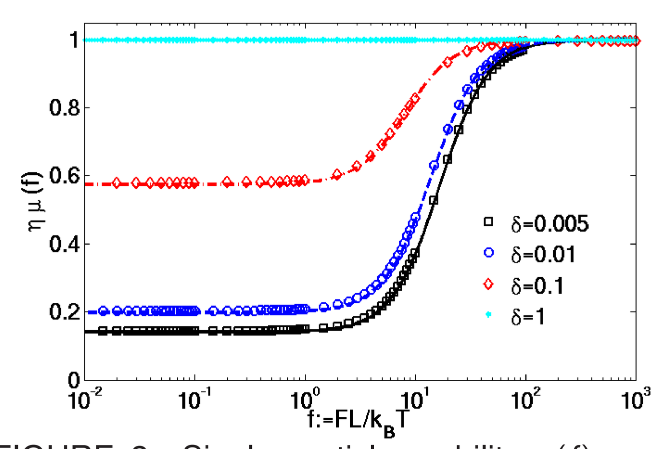


FIGURE 2: Single particle mobility $\mu(f)$ versus driving force f for different aspect ratios δ. The maximum width is fixed $\varepsilon \propto \Delta\Omega = 0.1$. The lines correspond to Eq. (16).

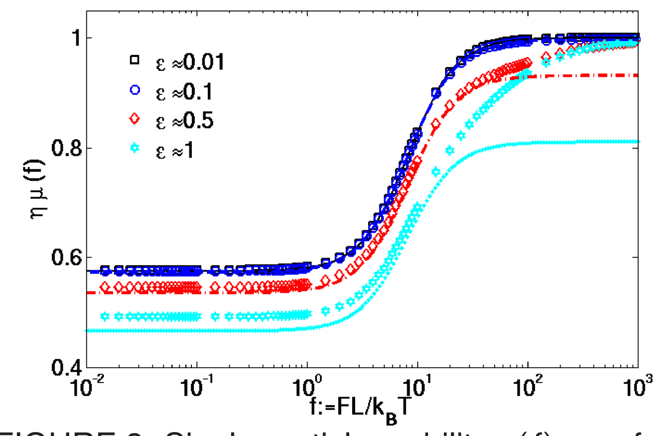


FIGURE 3: Single particle mobility $\mu(f)$ as a function of the driving force f at various values of the slope parameter ε. The aspect ratio is set to $\delta = 0.1$. The lines show the analytic estimate Eq. (15).

- diffusion dominated regime $f \ll 1$
$$\lim_{f \to 0} \eta\mu(f) = \lim_{f \to 0} \frac{\eta D_{\text{eff}}(f)}{k_B T} = \frac{4\sqrt{1 - \varepsilon/\delta\Omega}\, \operatorname{asinh}\left(\pi\varepsilon/2\right)}{2 - \varepsilon/\delta\Omega \quad\quad \pi\,\varepsilon} + O(h''(x)) \tag{17}$$

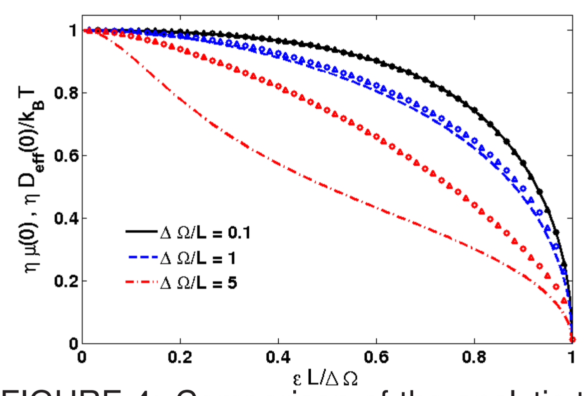


FIGURE 4: Comparison of the analytic theory versus precise numerics (in dimensionless units): The mobility and the effective diffusion constant are depicted as function of ε and maximal channel width $\Delta\Omega/L$ for different values $\Delta\Omega/L = 0.1, 1, 2, 5$ and bias $f = 10^{-3}$. The lines correspond to analytic higher order result, cf. Eq. (17).

- very good agreement for more winding structures
- **Fick-Jacobs** result **overestimates** for $\varepsilon \gg 0.1$
- higher order corrections tend to **underestimate** $\Longrightarrow$ caused by the neglect of higher derivatives

Conclusion

- exact series expansion for the stationary probability density $p(x, y)$ for arbitrary reflection symmetric 3D channels [4]
- verification of the result for $D(x)$ previously derived by [5]
- analytic result for the mobility $\mu_0(f)$ within the FJ approach
- estimate for the effective diffusion coefficient $D_{\text{eff}}(f)_0$ (not presented)
- consideration of higher order corrections lead to a substantial improvement of the FJ result towards more windwing structures

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