Biased Brownian Motion in Confined Geometries

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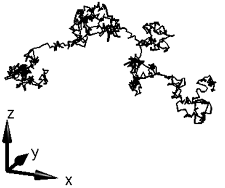
Free Brownian particle

- free Brownian particle subjected to external force $\mathbf{F} = (F, 0, 0)^T$ in x-direction

$$\eta \dot{\mathbf{q}}(t) = \mathbf{F} + \sqrt{2\eta\, k_B T} \xi(t)$$

- viscosity η, thermal energy $k_B T$,Gaussian white noise $\xi(t)$



- **transport quantities of interest**
  1. averaged velocity in the long time limit

$$\langle \dot{x} \rangle = \lim_{t\to\infty} \frac{\langle x(t) \rangle}{t}$$

  2. respectively, the mobility

$$\mu(F) = \langle \dot{x} \rangle / F$$

  3. effective diffusion coefficient D_{eff}

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

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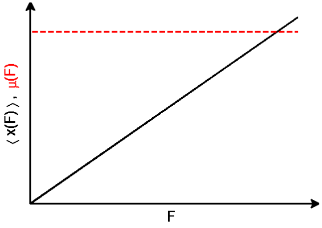
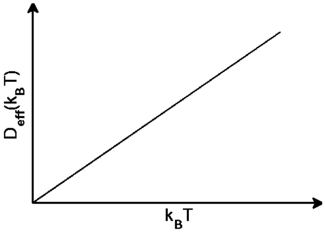




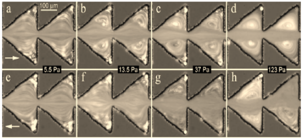
- averaged velocity $\langle \dot{x} \rangle = F/\eta$ is **independent** of thermal energy $k_B T$
- free mobility is given by $\mu = 1/\eta$

- effective diffusion coefficient $D_{\text{eff}} = k_B T/\eta$ is **independent** of external force magnitude F

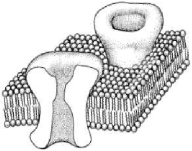
Sutherland-Einstein-relation $D_{\text{eff}} = \mu \, k_B T$

Brownian particle in confined geometries

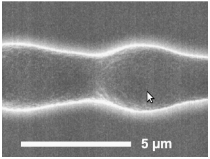
- interest in mass transport through confined structures such as microfluidic channels, irregular pores, and zeolites



A. Groismann et al., PRL 92, 094501 (2004)

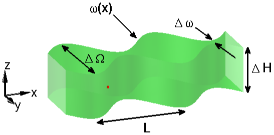


B. Hille, *Ion Channels of Excitable Membranes* (Sinauer, Sunderland, 2001)

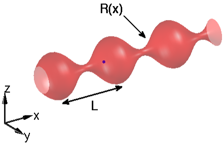


C. Kettner et al., PRE **61**,312 (2000)

- Brownian tracer particle evolves in 3D channel under the action of constant external force F in x-direction



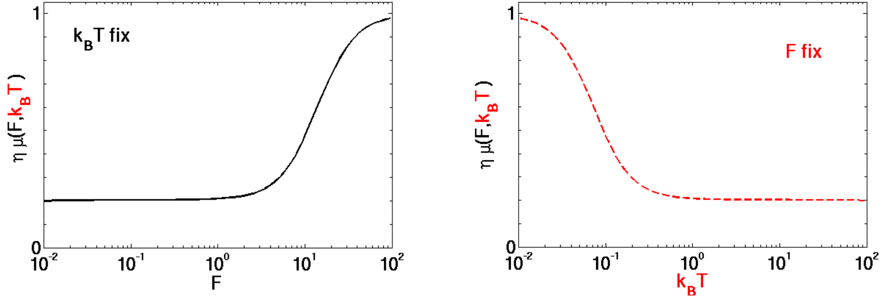
Planar 3D channel



3D tube with varying diameter

Qualitative differences to free diffusion

- numerical results for sinusoidal 3D planar channel with $\Delta\Omega = 0.1$ and $\Delta\omega = 0.01$
- viscosity η and period length L are set to 1



- mobility is a nonlinear function of F
- mobility decreases with thermal energy $k_B T$

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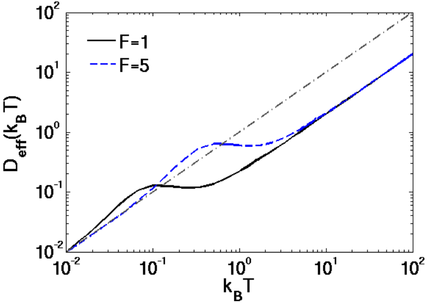
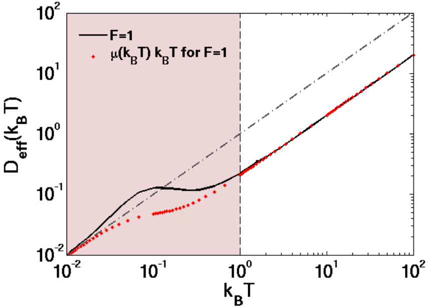
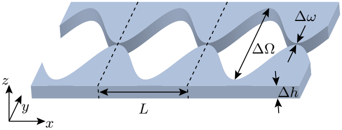




- effective diffusion coefficient depends on force magnitude F
- broad excess peak of $D_{\rm eff}$ above free diffusion limiting
- violation of Sutherland-Einstein relation for small k_BT



- evolution of probability density

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

with no-flux boundary conditions

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

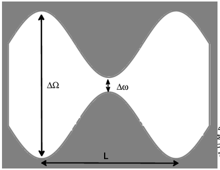
- probability flux

$$\mathbf{J}(\mathbf{q}, t) = F\,\mathbf{e}_x P(\mathbf{q}, t) - \nabla P(\mathbf{q}, t)$$

- obeys periodicity condition $P(x+m, y, z, t) = P(x, y, z, t)\,,\ \forall m \in \mathbb{Z}$ and is normalized $\int_{unit-cell} d^3 q P(\mathbf{q}, t) = 1$

- focus on stationary probability density $p_{\rm st}(\mathbf{q})$
- geometric parameter

$$\varepsilon = \frac{\Delta\Omega - \Delta\omega}{L}$$



[1] Martens et al., PRE **83**,051135 (2011)

3D planar channel geometry [1]

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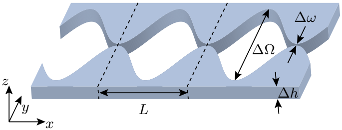

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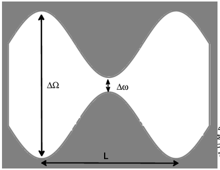

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Long-wave analysis

- pass to dimensionless quantities, e.g., $x = L\,\bar{x}, y = \varepsilon\,L\,\bar{y}, \omega(x) = \varepsilon\,L\,h(x)$, and

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

- reduction to 2D stationary Smoluchowski equation

$$\Longrightarrow \quad \varepsilon^2 \partial_x J^x_{\mathrm{st}}(x,y) + \partial_y J^y_{\mathrm{st}}(x,y) = 0\,,$$

  with boundary conditions

$$\varepsilon^2 h'_{\pm}(x)\, J^x_{\mathrm{st}}(x,y) = J^y_{\mathrm{st}}(x,y)\,, \quad \forall y \in \text{wall}\,.$$

- series expansion in the geometric parameter ε (st will be omitted)

$$p(x,y) = \sum_{n=0}^{\infty} \varepsilon^{2n} p_n(x,y) \quad \text{and} \quad \mathbf{J}(x,y) = \sum_{n=0}^{\infty} \varepsilon^{2n} \mathbf{J}_n(x,y)$$

Zeroth order - Fick-Jacobs equation

- zero-th order: $0 = \partial_y \left[e^{-V}\partial_y \left(e^{V} p_0(x,y)\right)\right] \quad \hookrightarrow \quad p_0(x,y) = g(x)\, e^{-V(x,y)}$

- integrating $O(\varepsilon^2)$ balance equation over cross section in y and taking no-flux boundary conditions into account, one gets

Fick-Jacobs equation

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

- with the effective „entropic“potential [2]

$$A(x) = -f\,x - \ln\left(2\,h(x)\right)$$

- reduction of 2D problem with reflecting boundary conditions to 1D coordinate evolving in effective periodic potential

[2] R. Zwanzig, J. Chem. Phys.,**96**,p. 3926-3930 (1992)

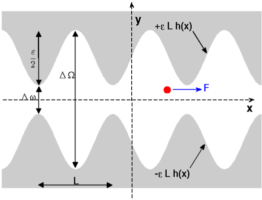
Sinusoidal channel - particle mobility

- exemplarily taken boundary function

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

where $b = \left(1 + \frac{\Delta\omega}{\Delta\Omega}\right) / \left(1 - \frac{\Delta\omega}{\Delta\Omega}\right)$

- mobility within the FJ approximation

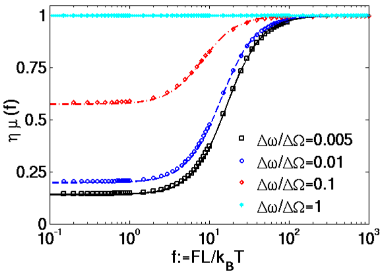


$$\mu_0(f) = \frac{\langle \dot{x}(f) \rangle_0}{f} = \frac{1 - e^{-f}}{f} \frac{1}{\int_0^1 dx\, e^{A(x)} \int_{x-1}^{x} dx'\, e^{-A(x')}}$$

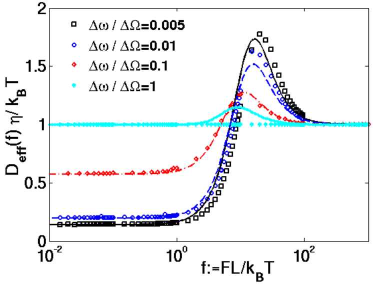
Sinusoidal channel - particle mobility

$$\mu_0(f) = \frac{f^2 + (2\pi)^2}{f^2 + \frac{(2\pi)^2}{2}\left\{\sqrt{\frac{\Delta\Omega}{\Delta\omega}} + \sqrt{\frac{\Delta\omega}{\Delta\Omega}}\right\}}$$

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



Mobility versus f for fixed maximum width $\Delta\Omega = 0.1$.

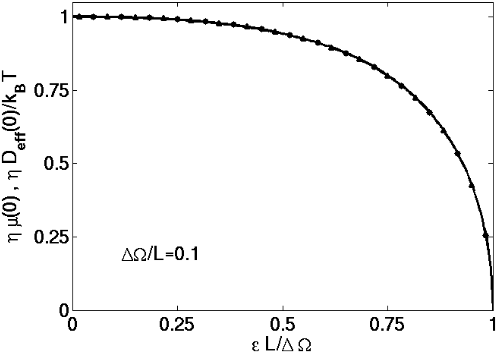


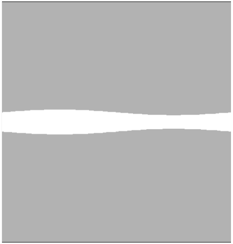
Effective diffusion coefficient versus f for fixed maximum width $\Delta\Omega = 0.1$.

Higher order corrections in ε

higher order corrections to mobility and effective diffusion coefficient

$$\lim_{f\to 0}\eta\mu(f) = \lim_{f\to 0}\eta D_{\mathrm{eff}}(f)/k_B T \simeq \frac{2\sqrt{1-\varepsilon L/\Delta\Omega}}{2-\varepsilon L/\Delta\Omega}\,\frac{\mathrm{asinh}\,(\pi\,\varepsilon/2)}{\pi\,\varepsilon/2} + O\left(h''(x)\right) \quad (*)$$





Left: Mobility and D_{eff} versus ε (FJ: solid line, (*): dash-dotted line). Maximum width $\Delta\Omega = 0.1$ and $f = 10^{-3}$.

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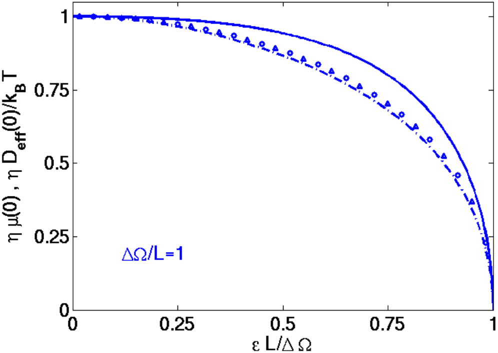

Left: Mobility and D_{eff} versus ε (FJ: solid line, (*): dash-dotted line). Maximum width $\Delta\Omega = 1$ and $f = 10^{-3}$.

higher order corrections to mobility and effective diffusion coefficient

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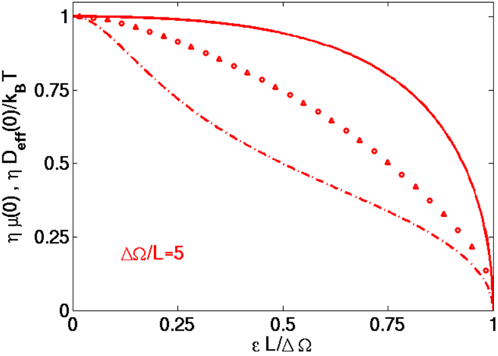

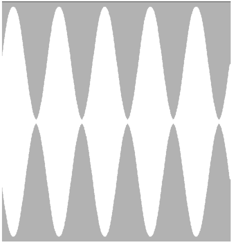

Left: Mobility and $D_{\rm eff}$ versus ε (FJ: solid line, (*): dash-dotted line). Maximum width $\Delta\Omega = 5$ and $f = 10^{-3}$.