Biased and flow driven Brownian motion in confined geometries

S. Martens[1], A. Straube[1], G. Schmid[2], P. Hänggi[2], and L. Schimansky-Geier[1]

[1]Department of Physics, Humboldt-Universität zu Berlin
[2]Department of Physics, Universität Augsburg

23.02.2012

Free Brownian particle

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

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

- viscosity η, thermal energy $k_B T$, and Gaussian white noise $\boldsymbol{\xi}(t)$: $\langle \boldsymbol{\xi}(t) \rangle$ and $\langle \xi_i(t)\xi_j(s) \rangle = \delta_{i,j}\, \delta(t - s)$

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

Free Brownian particle

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

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

- viscosity η, thermal energy $k_B T$, and Gaussian white noise $\boldsymbol{\xi}(t)$: $\langle \boldsymbol{\xi}(t) \rangle$ and $\langle \xi_i(t)\xi_j(s)\rangle = \delta_{i,j}\,\delta(t-s)$

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

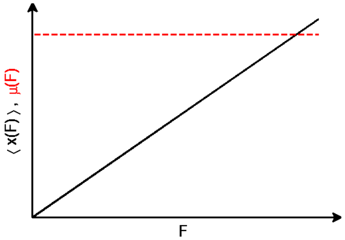
$$\langle \dot{x} \rangle = \lim_{t\to\infty} \frac{\langle x(t) \rangle}{t}$$

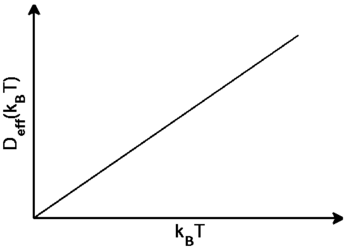
  2. respectively, the mobility

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

  3. effective diffusion coefficient D_{eff}

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



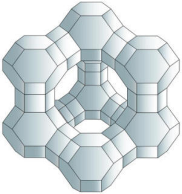


- averaged velocity $\langle \dot{x} \rangle = F/\eta$ is **independent** of thermal energy $k_B T$
- free mobility is given by $\mu_0 = 1/\eta$
- effective diffusion coefficient $D_{\text{eff}} = k_B T/\eta$ is **independent** of external force magnitude F

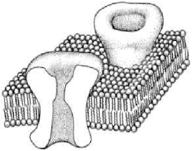
Sutherland-Einstein-relation $D_{\text{eff}} = \mu_0 \, k_B T$

Brownian particle in confined geometries

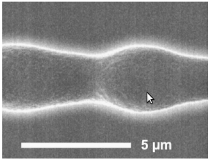
- interest in mass transport through confined structures such as porous media, zeolites, and irregular pores



http://www.explainthatstuff.com/zeolites.html



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



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

- *until now*: within the Fick-Jacobs approach [1] effective description of biased Brownian particles suspended in an **unmovable fluid** is possible [2] [3] [4]

[1] R. Zwanzig, J. Chem. Phys.,**96**,p. 3926-3930 (1992)
[2] D. Reguera et al., PRL,**96**,130603 (2006)
[3] P. S. Burada et al., BioSystems,**93**,16 (2008)
[4] P.S. Burada et al., Phil. Trans. R. Soc. A,**367**,3157 (2009)

Reminder: FJ approach [5]

- dimensionless Langevin equation for $V(x,y) = -f\,x$

$$\dot{x} = f + \sqrt{2}\xi_x(t)\,, \quad \dot{y} = \sqrt{2}\xi_y(t)$$

  where $f = FL/k_B T$
- assumption of fast equilibration in y
  $\hookrightarrow$ reduction to an effective 1D description

$$\dot{x} = -\partial_x A(x) + \sqrt{2}\xi_x(t)$$

„entropic“potential

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

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

Reminder: FJ approach [6]

„entropic“potential

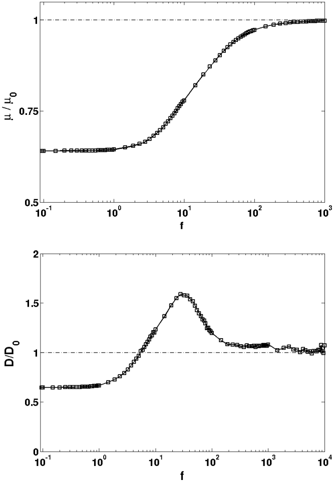
$$A(x) = -f\,x - \ln\left(W(x)\right)$$

$$\lim_{f\to 0} \mu/\mu_0 \leq 1 \approx \frac{1}{\langle W(x)\rangle \langle 1/W(x)\rangle}$$

$$\lim_{f\to\infty} \mu/\mu_0 = 1$$

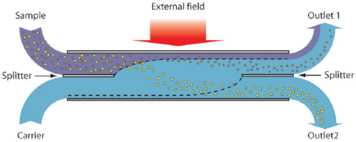
$$\lim_{f\to 0} D_{\rm eff}/D_0 = \lim_{f\to 0} \mu/\mu_0$$

$$\lim_{f\to\infty} D_{\rm eff}/D_0 = 1$$

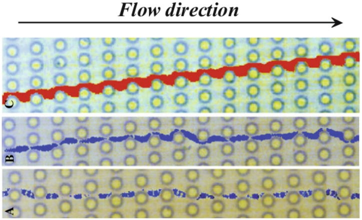


[6] R. Zwanzig, J. Chem. Phys., **96**, p. 3926-3930 (1992)

- experimentally relevant situation: **flow driven** separation of macro-molecules [7], colloids [8], and DNA [9]



A. Lenshof and T. Laurell, Chem. Soc. Rev. **39**, 1203 (2010),



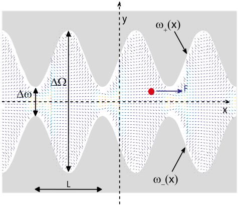
[7] Lenshof et al., ChemSocRev **39**, 1203 (2010)
[8] M. Balvin et al., PRL **103**, 078301 (2009)
[9] M. P. MacDonald et al., Nature **426**, 421 (2003)

The model

- particle dynamics described by

$$\cancel{m\ddot{\mathbf{q}}(t)} + \eta\left(\dot{\mathbf{q}}(t) - \mathbf{u}(\mathbf{q},t)\right) = -\vec{\nabla}V(\mathbf{q}) + \sqrt{2\eta\, k_B T}\boldsymbol{\xi}(t)$$

- solvent flow field $\mathbf{u}(\mathbf{q},t)$, external potential $V(\mathbf{q})$, viscosity η, thermal energy $k_B T$



  - passing to dimensionless quantities and set $m = L = \eta = k_B T = 1$

$$\mathbf{q}' \to \mathbf{q}/L\,,\; t' \to t\, k_B T/\eta L^2\,,\; \mathbf{u}' \to \mathbf{u}\,\eta L/k_B T\,,\; V' \to V/k_B T$$

  - yielding

$$\dot{\mathbf{q}} = \mathbf{u}(\mathbf{q},t) - \vec{\nabla}V(\mathbf{q}) + \sqrt{2}\boldsymbol{\xi}(t)$$

Fokker-Planck equation

- evolution of $P(\mathbf{q}, t)$ of finding the particle at $\mathbf{q} = (x, y)^T$ at time t

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

with no-flux boundary conditions

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

and probability flux

$$\mathbf{J}(\mathbf{q}, t) = \left(\mathbf{u}(\mathbf{q}, t) - \vec{\nabla} V(\mathbf{q})\right) P(\mathbf{q}, t) - \vec{\nabla} P(\mathbf{q}, t)$$

- obeys periodicity condition $P(x+m, y, t) = P(x, y, t)\,, \forall m \in \mathbb{Z}$ and is normalized
- focus on stationary probability density $P^{\mathrm{st}}(\mathbf{q})$

Navier-Stokes equation

- evolution of volume element with flow velocity $\mathbf{u} = (v(\mathbf{q},t), w(\mathbf{q},t))^T$

$$R_e \left[\partial_t \mathbf{u}(\mathbf{q},t) + \underbrace{\left(\mathbf{u}(\mathbf{q},t)\cdot\vec{\nabla}\right)\mathbf{u}(\mathbf{q},t)}_{\text{convection acceleration}}\right] = -\underbrace{\vec{\nabla} p(\mathbf{q},t)}_{\text{pressure drop}} + \underbrace{\triangle \mathbf{u}(\mathbf{q},t)}_{\text{viscosity}}$$

  with dimensionless quantities $R_e = \rho_f k_B T / \eta^2$ and $p \to p\, k_B T / L^3$

- continuity equation for an incompressible flow

$$\vec{\nabla}\cdot\mathbf{u}(\mathbf{q},t) = 0$$

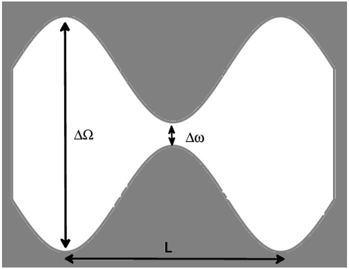
- no-slip boundary condition

$$\mathbf{u}(\mathbf{q},t) = 0 \quad , \forall \mathbf{q} \in \text{wall}.$$

Long-wave analysis

- series expansion in the geometric parameter ε

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



- new scaling $y \to y/\varepsilon$, $w \to w/\varepsilon$, and $\omega_\pm(x) \to \varepsilon\, h_\pm(x)$
- perturbation series in the geometric parameter ε

$$v = v_0 + \varepsilon\, v_1 + \ldots\,,$$

$$w = w_0 + \varepsilon\, w_1 + \ldots\,,$$

$$\text{pressure}: \quad p = \frac{1}{\varepsilon^2} p_0 + \frac{1}{\varepsilon} p_1 + \ldots\,,$$

$$\text{prob.density}: \quad P^{\text{st}} = P_0^{\text{st}} + \varepsilon^2\, P_1^{\text{st}} + \ldots\,,$$

Navier-Stokes equation: Zeroth order

- time derivative and convection acceleration are proportional to $\mathbf{R_e}\varepsilon^2$

leading order

$$p_0(x,y) = p_0(0,y) + \Delta p \int_0^x dx\, 1/W(x)^3 \Big/ \int_0^1 dx\, 1/W(x)^3\,,$$

$$v_0(x,y) = -\frac{p_0'(x)}{2}\,(h_+(x) - y)\,(y - h_-(x))\,,$$

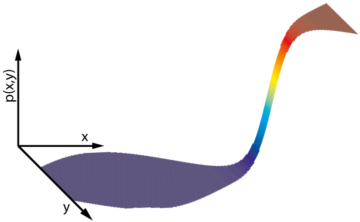
$$w_0(x,y) = -\frac{1}{12}\partial_x\left[p_0'(x)\,(y - h_-(x))^2\,(3h_+(x) - h_-(x) - 2y)\right]$$

- pressure drop over period $\Delta p = p(x+1,y) - p(x,y)$
- local channel width $W(x) = h_+(x) - h_-(x)$

- exemplarily taken boundary function

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

with $\delta = \Delta\omega / \Delta\Omega$



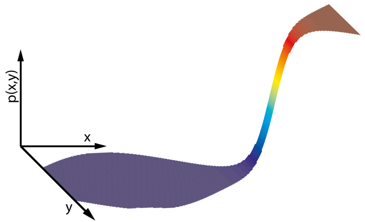
Pressure profile $p(x, y)$ for $\Delta p > 0$.

$\Delta\Omega = 1, \Delta\omega = 0.1$, and $Re = 0.1$

- exemplarily taken boundary function

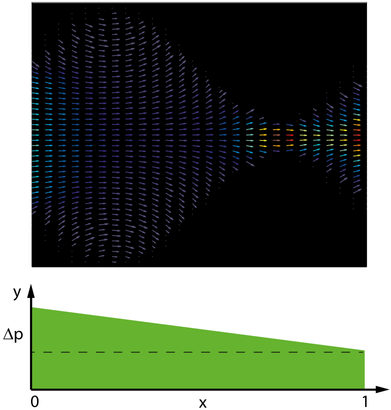
$$h_{\pm}(x) = \pm h(x) = \pm\frac{1}{4}\left(\frac{1+\delta}{1-\delta} + \sin(2\pi x)\right)$$

with $\delta = \Delta\omega/\Delta\Omega$



Pressure profile $p(x, y)$ for $\Delta p > 0$.

$\Delta\Omega = 1, \Delta\omega = 0.1$, and $Re = 0.1$



Solvent velocity $\mathbf{u}(\mathbf{q})$.

$\Delta\Omega = 1, \Delta\omega = 0.1, \Delta p = -10^3$, and $Re = 0.1$

Extension of FJ-approach to solvent flows

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

"generalized" Fick-Jacobs equation

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

"generalized" effective potential

$$\Psi(x) = A(x) - \int_0^x dx' \left[\int_{h_-(x')}^{h_+(x')} v_0(x',y) e^{-V(x',y)} dy \Big/ \int_{h_-(x')}^{h_+(x')} e^{-V(x',y)} dy \right]$$

"generalized" effective potential

- concept of mean force

$$\frac{d\,\Psi(x)}{d\,x} = -\partial_x \ln \left[\int\limits_{h_-(x)}^{h_+(x)} e^{-V(\mathbf{q})} dy \right] - \int\limits_{h_-(x)}^{h_+(x)} v_0(x,y) \frac{e^{-V(\mathbf{q})}}{\int_{h_-(x)}^{h_+(x)} e^{-V(\mathbf{q})} dy} dy$$

"generalized" effective potential

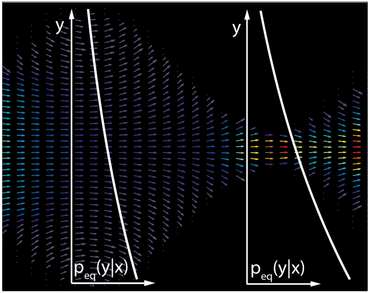
- concept of mean force

$$\frac{d\,\Psi(x)}{d\,x} = -\partial_x \ln\left[\int\limits_{h_-(x)}^{h_+(x)} e^{-V(\mathbf{q})}\,dy\right] - \int\limits_{h_-(x)}^{h_+(x)} dy\; v_0(x,y)\,\underbrace{\frac{e^{-V(\mathbf{q})}}{\int_{h_-(x)}^{h_+(x)} e^{-V(\mathbf{q})}\,dy}}_{p_{\mathrm{eq}}(y|x)}\,dy$$

"generalized" effective potential

- concept of mean force

$$-\frac{d\,\Psi(x)}{d\,x} = -\int_{h_-(x)}^{h_+(x)} \partial_x V(\mathbf{q}) p_{\mathrm{eq}}(y|x)\,dy + \int_{h_-(x)}^{h_+(x)} v_0(x,y) p_{\mathrm{eq}}(y|x)\,dy$$

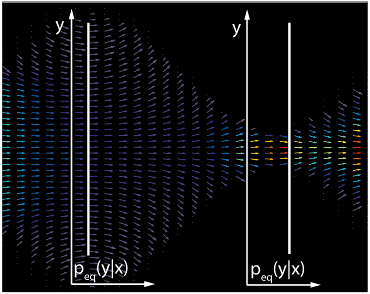


$p_{\mathrm{eq}}(y|x)$ for $V(\mathbf{q}) = -f\,x - g\,y$.

"generalized" effective potential

- for only longitudinal forcing $V(\mathbf{q}) = -f\,x$

$$-\frac{d\,\Psi(x)}{d\,x} = \underbrace{f + \frac{W'(x)}{W(x)}}_{\text{mean force originated by bias}} - \underbrace{\frac{\Delta p}{12\int\limits_0^1 dx 1/W^3(x)}\,\frac{1}{W(x)}}_{\text{mean force originated by solvent flow}}$$



$p_{\mathrm{eq}}(y|x)$ for $V(\mathbf{q}) = -f\,x$.

mean particle velocity

- solution of "generalized" Fick-Jacobs equation

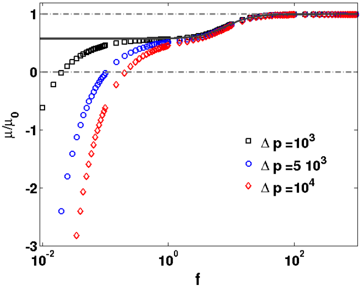
$$p_0(x) = e^{-\Psi(x)} \int\limits_{x}^{x+1} e^{\Psi(x')} dx' \Bigg/ \left[\int\limits_{0}^{1} dx e^{-\Psi(x)} \int\limits_{x}^{x+1} e^{\Psi(x')} dx' \right]$$

- Stratonovich formula [10]

$$\frac{\mu(f)}{\mu_0} = \frac{\langle \dot{x}(f) \rangle_0}{f} = \frac{1 - e^{\Delta\Psi}}{f \int\limits_0^1 dx\, e^{-\Psi(x)} \int\limits_x^{x+1} e^{\Psi(x')}\, dx'}$$

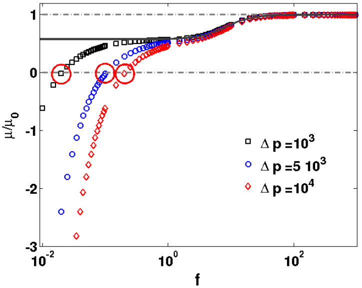
with $\Delta\Psi = \Psi(1) - \Psi(0)$

[10] R. L. Stratonovich, Radiotekh. Elektron. (Moscow),**3**, 497 (1958)

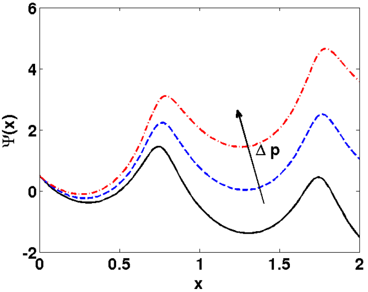


Particle mobility versus f. $\Delta\Omega = 0.1$, $\Delta\omega = 0.01$, and $Re = 0.1$

Particle mobility μ



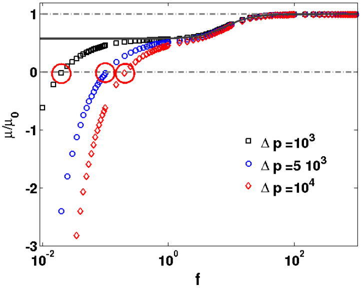
Particle mobility versus f. $\Delta\Omega = 0.1$, $\Delta\omega = 0.01$, and $Re = 0.1$.



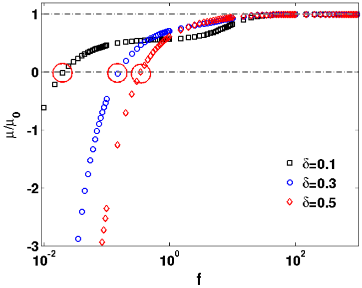
Effective potential $\Psi(x)$ for $f = 0.1$ and $\Delta p = 0, 5\,10^3, 10^4$ (from bottom to top).

$\Delta\Omega = 1$, $\Delta\omega = 0.1$, and $Re = 0.1$

Particle mobility μ



Particle mobility versus f. $\Delta\Omega = 0.1$, $\Delta\omega = 0.01$, and $Re = 0.1$.

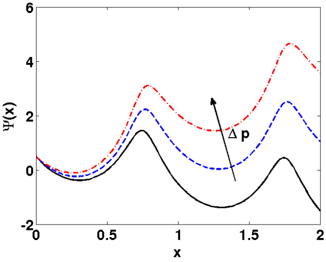


Particle mobility versus f. $\Delta\Omega = 0.1$, $\Delta p = 10^3$, and $Re = 0.1$.

Competition between external bias and solvent flow

- mean particle current vanishes if

$$0 = \Delta\Psi = -f - \frac{\Delta p}{12} \frac{\int_0^1 1/W(x)dx}{\int_0^1 1/W(x)^3 dx}$$

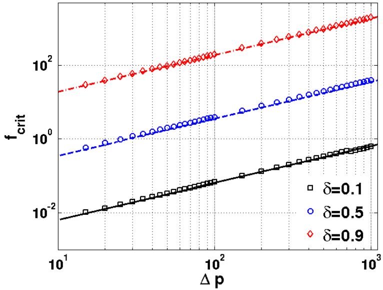


Potential of mean force $\Psi(x)$

$$\hookrightarrow \left(\frac{f}{\Delta p}\right)_{\mathrm{crit}} = -\frac{\int_0^1 1/W(x)dx}{12 \int_0^1 1/W(x)^3 dx}$$

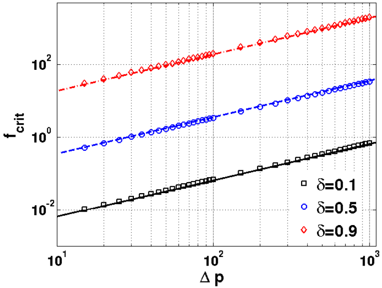
- for sinusoidal channel $h(x)$

$$\left(\frac{f}{\Delta p}\right)_{\mathrm{crit}} = \frac{\delta^2}{6\,(1-\delta)^2\,\left(3+2\delta+3\delta^2\right)}$$



Critical force magnitude versus pressure drop Δp.

$\Delta\Omega = 0.1$ and $Re = 0.1$.



Critical force magnitude versus pressure drop Δp.

$\Delta\Omega = 1$ and $Re = 0.1$.

Summary

- present expansion of NSE and FPE in geometric parameter ε
  $\hookrightarrow$ calculate leading order of $\mathbf{u}(\mathbf{q})$ and $P(\mathbf{q})$

1. purely flow driven transport
   - obtain $P(\mathbf{q}) = 1/A_{\mathrm{unit-cell}}$ and analytic expression for $\langle \dot{x} \rangle_0$ and D_{eff}/D_0
2. combined biased and flow driven transport
   - present extension of Fick-Jacobs approach to experimentally relevant situation of moving solvent
   - effective description where particle evolve in potential of mean force

$$\Psi(x) = A(x) - \int_0^x \left[\int_{h_-(x)}^{h_+(x)} v_0(x,y) p_{\mathrm{eq}}(y|x) \right]$$

   - it exist critical ratio $(f/\Delta p)_{\mathrm{crit}}$ where both drag forces anihilate each other

- numerics show that results are also valid for $\varepsilon \simeq 1$