Biased and flow driven Brownian motion in confined geometries

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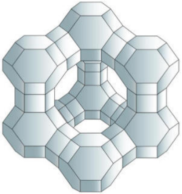
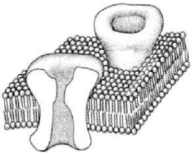
Brownian particle in confined geometries

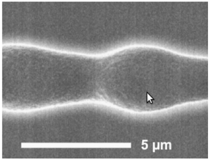
- interest in mass transport through confined structures such as porous media, zeolites, and irregular pores



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** [2] [3]
- experimentally relevant situation: **flow driven** separation of macro-molecules, colloids [4], and DNA [5]

[1] R. Zwanzig, J. Chem. Phys.,**96**,p. 3926-3930 (1992)
[2] P. S. Burada et al., BioSystems,**93**,16 (2008)
[3] P.S. Burada et al., Phil. Trans. R. Soc. A,**367**,3157 (2009)
[4] M. Balvin et al., PRL **103**, 078301 (2009)
[5] Lenshof et al., ChemSocRev **39**, 1203 (2010)

Entropic transport with solvent flow

- Langevin equation for point-size particles

$$\cancel{\ddot{\mathbf{q}}(t)} + \left(\dot{\mathbf{q}}(t) - \mathbf{u}(\mathbf{q}, t)\right) = \mathbf{f} + \sqrt{2}\boldsymbol{\xi}(t)$$

- solvent flow field $\mathbf{u}(\mathbf{q}, t)$, external bias $\mathbf{f} = \mathbf{F}\, L/k_B T$, Gaussian white noise $\boldsymbol{\xi}(t)$: $\langle \boldsymbol{\xi}(t) \rangle$ and $\langle \xi_i(t)\xi_j(s) \rangle = \delta_{i,j}\, \delta(t - s)$
- effective $2D$ problem
- evolution of volume element with flow velocity $\mathbf{u} = \left(u^x(\mathbf{q}, t), u^y(\mathbf{q}, t)\right)^T$

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

continuity equation

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

no-slip boundary condition

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

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Fokker-Planck equation

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

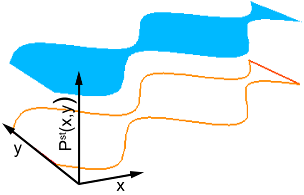
$$\partial_t P(\mathbf{q},t) + \nabla_{\mathbf{q}} \cdot \mathbf{J}(\mathbf{q},t) = 0\,,$$

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

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



PDF for $\Delta p = 100$ and $f = 0$. $\Delta\Omega = 1$ and $\Delta\omega = 0.1$.

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

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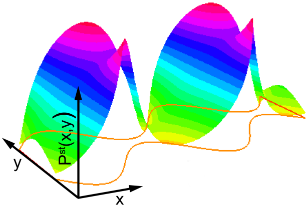

PDF for $\Delta p = 100$ and $f = 10.\Delta\Omega = 1$ and $\Delta\omega = 0.1$.

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

- periodicity condition $P(x + m, y, t) = P(x, y, t)\,, \forall m \in \mathbb{Z}$ and is normalized
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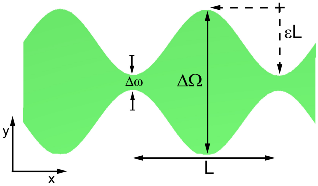
Long-wave analysis

- series expansion in the geometric parameter ε

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



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

$$\begin{aligned} u^x &= u_0^x + \varepsilon\, u_1^x + \dots\,, \\ u^y &= u_0^y + \varepsilon\, u_1^y + \dots\,, \\ \text{pressure}: \quad p &= \frac{1}{\varepsilon^2} p_0 + \frac{1}{\varepsilon}\, p_1 + \dots\,, \\ \text{prob.density}: \quad P^{\mathrm{st}} &= P_0^{\mathrm{st}} + \varepsilon^2\, P_1^{\mathrm{st}} + \dots\,, \end{aligned}$$

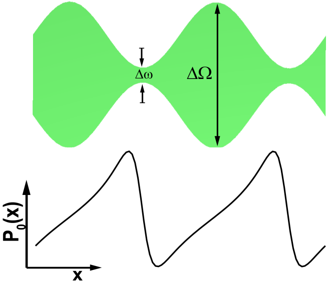
- exact solution for p_0, u_0^x, and u_0^y can be derived

Extension of Fick-Jacobs approach to solvent flows

- solution of the leading order

$$P_0^{\rm st}(x) = \int\limits_{h_-(x)}^{h_+(x)} P_0^{\rm st}(x,y)\,dy = \frac{e^{-\Psi(x)} \int\limits_x^{x+1} e^{\Psi(x')}dx'}{\int\limits_0^1 dx e^{-\Psi(x)} \int\limits_x^{x+1} e^{\Psi(x')}dx'}$$

$$\hookrightarrow \quad \dot{x}(t) = -\frac{d\,\Psi(x)}{d\,x} + \sqrt{2}\,\xi_x(t)$$



Marginal pdf for $f = 100$ and $\Delta p = 100$.

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

potential of mean force

$$\Psi(x) = -\ln\left[\int_{h_-(x)}^{h_+(x)} e^{-V(x,y)} dy\right] - \int_0^x dx' \left[\int_{h_-(x')}^{h_+(x')} u_0^x(x',y) \frac{e^{-V(x',y)}}{\int_{h_-(x')}^{h_+(x')} e^{-V(x',y)} dy} dy\right]$$

potential of mean force

$$\Psi(x) = -\ln\left[\int\limits_{h_-(x)}^{h_+(x)} e^{-V(x,y)} dy\right] - \int\limits_0^x dx' \left[\int\limits_{h_-(x')}^{h_+(x')} u_0^x(x',y) \frac{e^{-V(x',y)}}{\int\limits_{h_-(x')}^{h_+(x')} e^{-V(x',y)} dy} dy\right]$$

$$\Downarrow$$

$$-\frac{d\,\Psi(x)}{d\,x} = \int\limits_{-\infty}^{\infty} f_x(x,y) P_{\mathrm{eq}}(y|x)\, dy \quad + \int\limits_{h_-(x)}^{h_+(x)} u_0^x(x,y) P_{\mathrm{eq}}(y|x)\, dy$$

potential of mean force

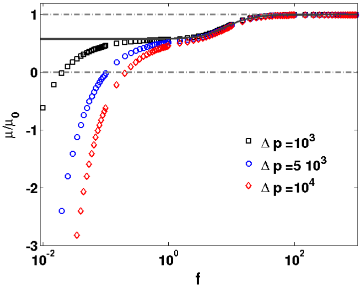
$$\Psi(x) = -\ln\left[\int_{h_-(x)}^{h_+(x)} e^{-V(x,y)} dy\right] - \int_0^x dx' \left[\int_{h_-(x')}^{h_+(x')} u_0^x(x',y) \frac{e^{-V(x',y)}}{\int_{h_-(x')}^{h_+(x')} e^{-V(x',y)} dy} dy\right]$$

$$\Downarrow$$

$$-\frac{d\,\Psi(x)}{d\,x} = \underbrace{\int_{-\infty}^{\infty} f_x(x,y) P_{\mathrm{eq}}(y|x)\, dy}_{\text{mean force by bias + particle-wall interaction}} + \underbrace{\int_{h_-(x)}^{h_+(x)} u_0^x(x,y) P_{\mathrm{eq}}(y|x)\, dy}_{\text{mean flow drag force}}$$

- Stratonovich formula [6]

$$\frac{\mu(f)}{\mu_0} = \frac{\langle \dot{x}(f)\rangle_0}{f} = \frac{1 - e^{\Delta\Psi}}{f \int\limits_0^1 dx\, e^{-\Psi(x)} \int\limits_x^{x+1} e^{\Psi(x')}\, dx'}, \text{ with } \Delta\Psi = \Psi(1) - \Psi(0)$$



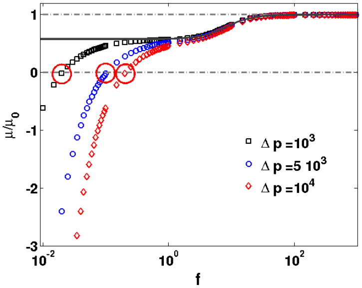
Particle mobility versus f. $\Delta\Omega = 0.1$, $\Delta\omega = 0.01$, and $Re = 0.1$

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

Numerical results - particle mobility μ

- Stratonovich formula [6]

$$\frac{\mu(f)}{\mu_0} = \frac{\langle \dot{x}(f)\rangle_0}{f} = \frac{1 - e^{\Delta\Psi}}{f \int\limits_0^1 dx\, e^{-\Psi(x)} \int\limits_x^{x+1} e^{\Psi(x')}\, dx'}\,, \text{ with } \Delta\Psi = \Psi(1) - \Psi(0)$$



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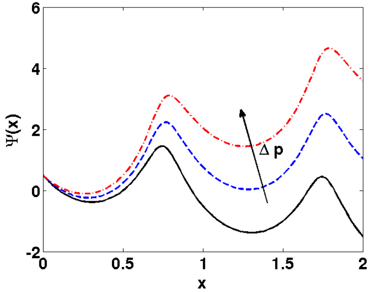


Effective potential $\Psi(x)$ for $f = 0.1$ and $\Delta p = 0, 5\,10^3, 10^4$ (from bottom to top). $\Delta\Omega = 1$, $\Delta\omega = 0.1$, and $Re = 0.1$.

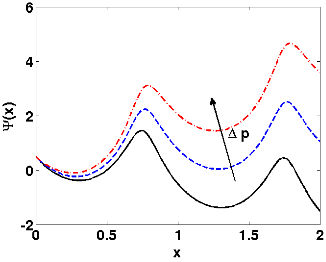
[6] R. L. Stratonovich, Radiotekh. Elektron. (Moscow),**3**, 497 (1958)

Competition between external bias and solvent flow

- mean particle current vanishes if

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

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



Potential of mean force $\Psi(x)$

- for sinusoidal channel $h(x)$

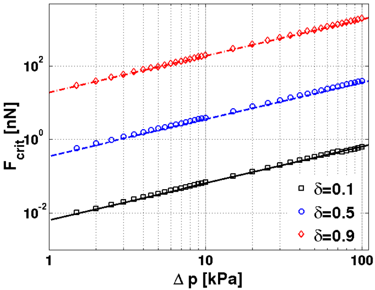
$$\left(\frac{F}{\Delta p}\right)_{\mathrm{crit}} = \frac{\pi d_p\,(\Delta\Omega)^2}{2\,L}\,\frac{\delta^2}{(3+2\delta+3\delta^2)}$$

Polystyrene beads:

- density $\rho_p = 2g/cm^2$
- diameter $d_p = 0.1 - 1\mu m$
- charge $q = 10^4|e|$, $E = 10^4\,V/m$
  $\hookrightarrow$ $F = 0.1nN$
- $k_B T = 4\,fN\,\mu m$ $[T = 20^\circ$ C$]$

Channel geometry:

- period $L = 200\mu m$
- $\Delta\Omega = 40\,\mu m$



Critical force magnitude versus pressure drop Δp

Summary

- present expansion of Navier-Stokes equation and Fokker-Planck equation in geometric parameter ε $\hookrightarrow$ calculate leading order of $\mathbf{u}(\mathbf{q})$ and $P(\mathbf{q})$

1. purely biased driven transport [7]
2. 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
3. combined biased and flow driven transport
   - effective description where particle evolve in potential of mean force

$$\Psi(x) = A(x) - \int_0^x \left[\int_{h_-(x)}^{h_+(x)} u_0^x(x,y) P_{\mathrm{eq}}(y|x) \right]$$

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

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

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

Thank You very much for your attention !

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Publications:

1. S. Martens et al. PRE **83**, 051135 (2011)
2. S. Martens et al. Chaos **21**, 047518 (2011)
3. P.K. Ghosh et al. PRE **85**, 011101 (2012)
4. S. Martens et al. JCP Communication, accepted (2012)
5. S. Martens et al., in preparation (2012)

Navier-Stokes equation: Zeroth order

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

leading order

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

$$u_0^x(x,y) = -\frac{p_0'(x)}{2}\,(h_+(x) - y)\,(y - h_-(x))\,,$$

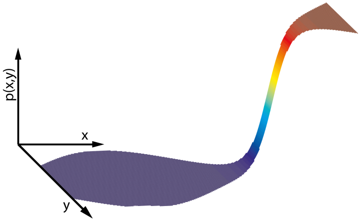
$$u_0^y(x,y) = -\frac{1}{12}\partial_x\left[p_0'(x)\,(y - h_-(x))^2\,(3h_+(x) - h_-(x) - 2y)\right]$$

- 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

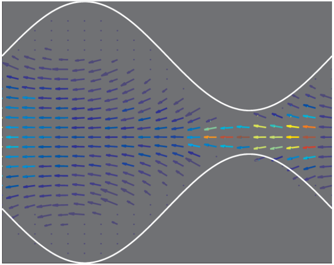
$$h_{\pm}(x) = \pm h(x) = \pm\frac{1}{4}\left(\frac{\Delta\Omega+\Delta\omega}{\Delta\Omega-\Delta\omega} + \sin(2\pi x)\right)$$

width aspect ratio $\delta = \Delta\omega/\Delta\Omega$



Pressure profile $p(x, y)$ for $\Delta p = 10^3$.

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



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

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