Theory of Electrokinetic Transport in Porous Media

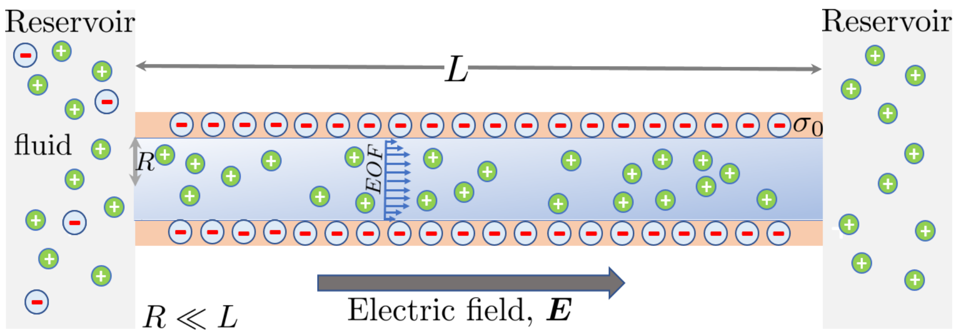
Mpumelelo Matse
(Dept. Physics, Simon Fraser University, Burnaby, BC, Canada)

Dr. Michael Eikerling
(Dept. Chemistry & Physics, Simon Fraser University, Burnaby, BC, Canada)

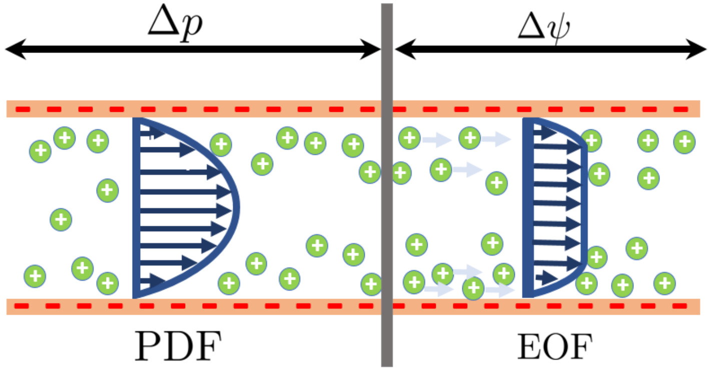
Dr. Peter Berg
(Dept. Science, University of Alberta, Edmonton, AB, Canada)

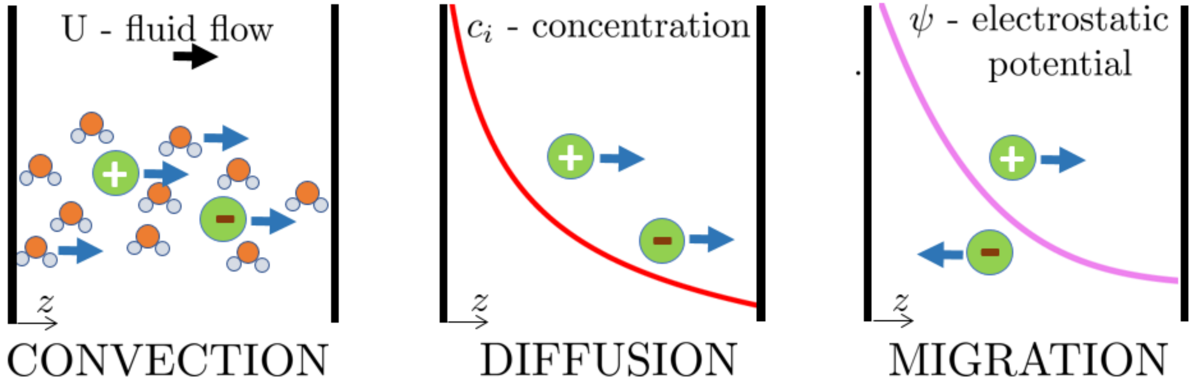
2019 CAP Congress, 03 June 2019

Introduction

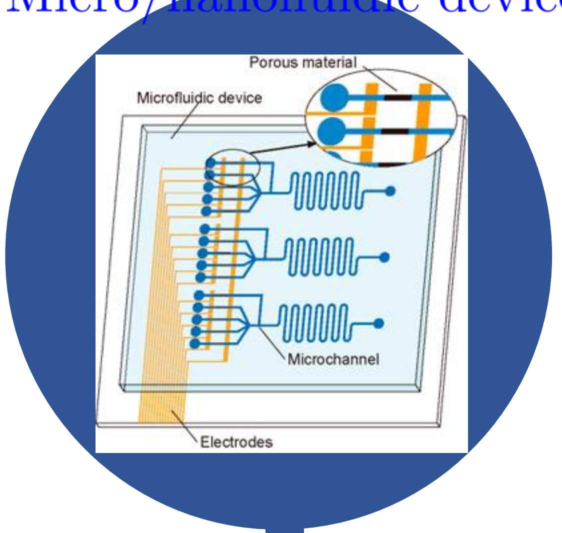


- electrokinetic flow of ions in a charged nanochannel with viscoelastic walls
- consider counterions-selective nanochannels with double-layer overlap
- driving forces for fluid flow:
  - pressure drop
  - electrostatic potential drop
- driving forces for ion flow:
  - fluid flow
  - chemical potential drop
  - electrostatic potential drop

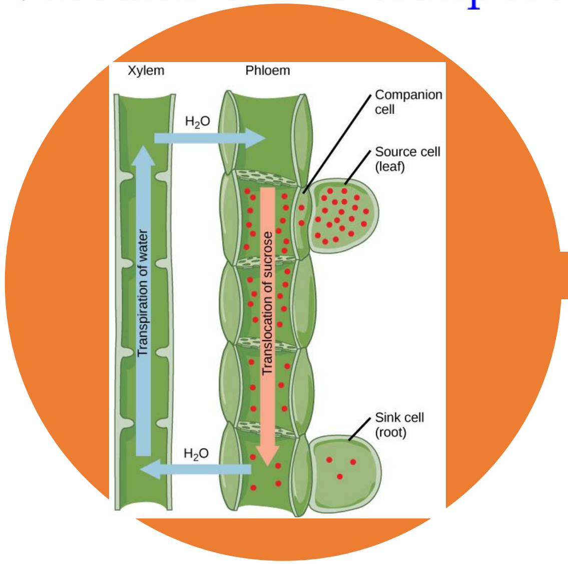




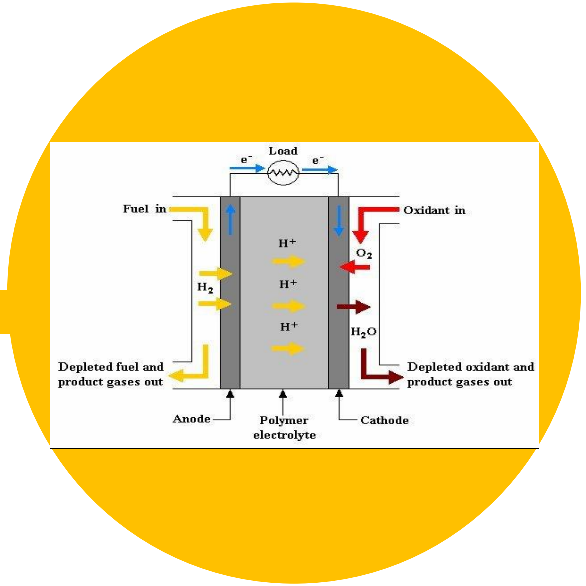
Micro/nanofluidic devices



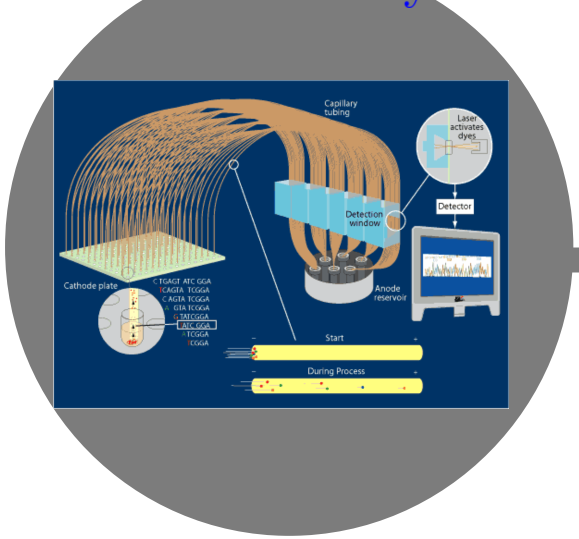
Vascular tissue tranport



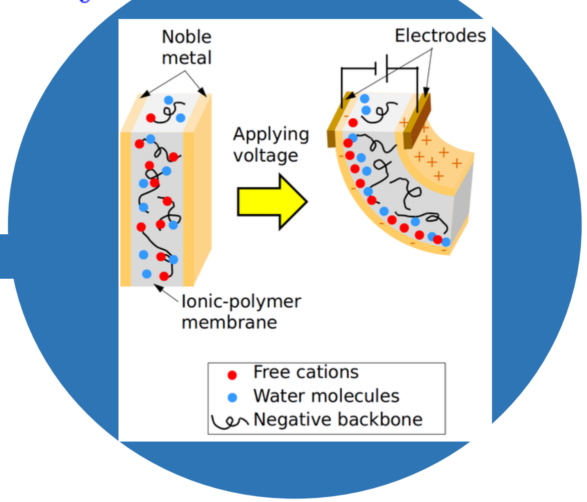
PEM fuel cells



Chemical analysis

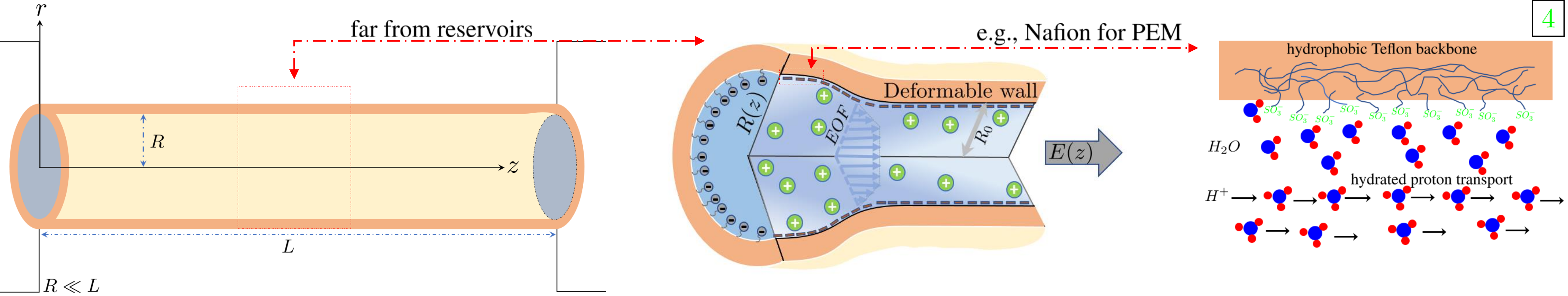


Polymer electro-actuators



http://www.geoengineer.com, http://www.boundless.com, http://www.microfluidics.iis.u-tokyo.ac.jp, http://simanaitissays.com, http://jgi.doe.gov/archived-educator-resources

Applications of surface charge and/or electric field induced transport of fluid and chemical species



problem

- consider pore with cylindrical symmetry and viscoelastic walls

- electric field in the fluid-ion sysytem is introduced by:
  - applied potential drop at reservoirs (vanishes far away from reservoirs for high-aspect-ratio pores)
  - counterions concentration gradients due to wall deformations

- let the undeformed state be characterized by reference radius R_0 and surface charge density σ_0

- intoduce an empirical power law model for z-dependent surface charge density,

$$\sigma_s(z) = \sigma_0 \times \left(\frac{R_0}{R(z)}\right)^{\alpha}, \quad 0 < \alpha \leq 1$$

- assume continuum mean field theories hold for conservation laws

Nonlinear coupling model between wall deformation and fluid-ion transport

◇ fluid conservation: Stokes equations

$$\nu \nabla^2 \mathbf{v}(\mathbf{r},t) - \nabla p(\mathbf{r},t) + qc(\mathbf{r},t)\mathbf{E}(\mathbf{r},t) = 0, \qquad \nabla \cdot \mathbf{v}(\mathbf{r},t) = 0$$

◇ proton conservation: Poisson-Nernst-Planck equation

$$\mathbf{j}(\mathbf{r},t) = c(\mathbf{r},t)\mathbf{v}(\mathbf{r},t) - D\nabla c(\mathbf{r},t) + \mu qc(\mathbf{r},t)\mathbf{E}(\mathbf{r},t), \quad \nabla \cdot \mathbf{j}(\mathbf{r},t) = 0$$

$$\nabla \cdot \mathbf{E}(\mathbf{r},t) = \frac{qc(\mathbf{r},t)}{\epsilon\epsilon_0}, \quad \mathbf{E}(\mathbf{r},t)\cdot\hat{\mathbf{n}}(\mathbf{r},t)\Big|_{r=R} = \frac{\sigma_s(\mathbf{r},t)}{\epsilon\epsilon_0}$$

◇ wall deformation:

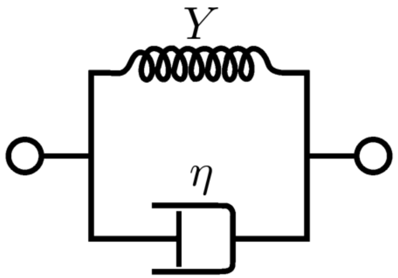
elasticity constant

$$\boldsymbol{\sigma} = Y\boldsymbol{\varepsilon} + \eta\frac{\partial \boldsymbol{\varepsilon}}{\partial t}$$

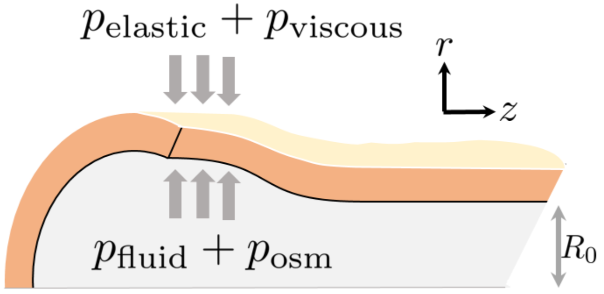
stress

strain

wall viscosity



Kelvin-Voigt Model



Pressure balance at wall

Advection-diffusion type model for elastic but non-viscous walls

- Set $\tilde{a} = (R/R_0)^2 \quad \Rightarrow \quad \boxed{\frac{\partial \tilde{a}}{\partial t} = \frac{\partial}{\partial z}\left[\mathcal{D}(\tilde{a}) \cdot \frac{\partial \tilde{a}}{\partial z}\right] - \frac{\partial}{\partial z}\left[\mathcal{G}(\tilde{a})\right]}$

where $\mathcal{D}(\tilde{a}) = \frac{\mathcal{K}_Y \tilde{a}^{\frac{1}{2}}}{2} + \mathcal{K}_{\mathrm{osm}}\left[(1+\alpha)\tilde{a}^{\frac{1-\alpha}{2}} + 4\alpha\kappa\tilde{a}^{1-\alpha}\right]$ & $\mathcal{G}(\tilde{a}) = 2(1-\xi_u)\tilde{a}^{\frac{1-\alpha}{2}}$

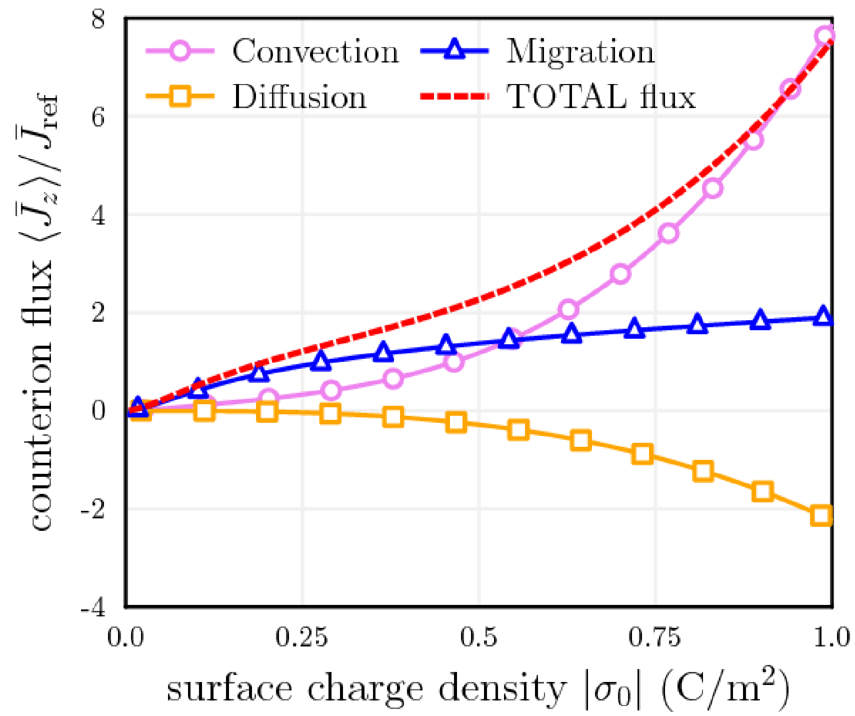
- For small deformations and fixed pressure jump between pore ends, linear perturbation and then[1]Laplace Transform give the analytical solution:

$$\tilde{a}(z,t) = 1 + \Delta\tilde{a}_i \exp(\lambda z)\left\{\frac{\sinh[\lambda(1-z)]}{\sinh(\lambda)} - 2\pi \times \sum_{n=1}^{\infty} \frac{n\sin(n\pi z)}{(\lambda^2 + n^2\pi^2)} \times \exp\left[-\left(\lambda^2 + n^2\pi^2\right)\mathcal{D}_0 t\right]\right\}$$

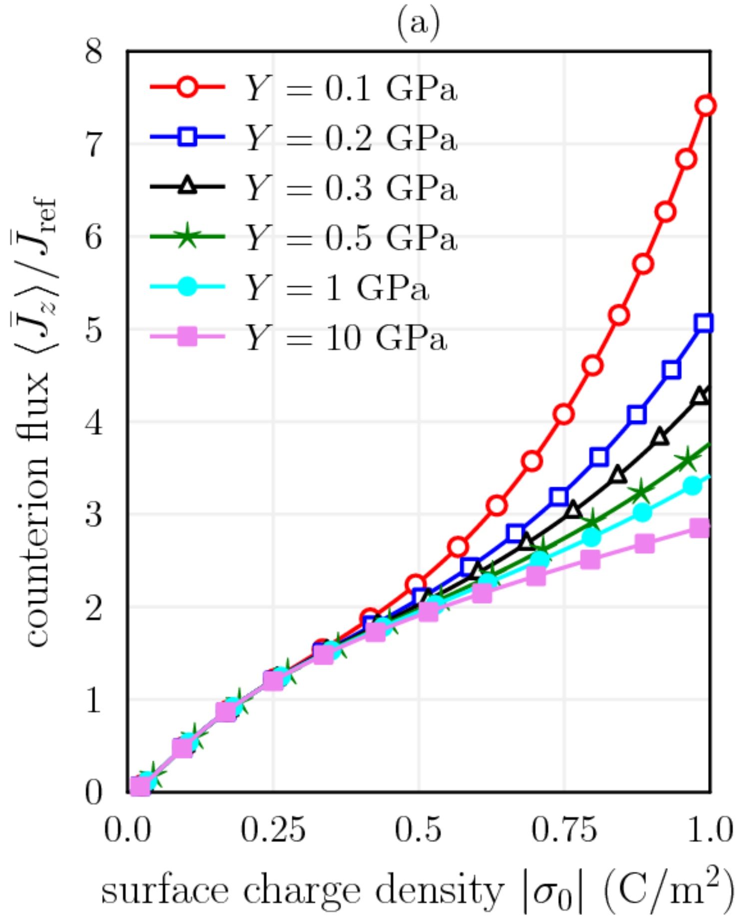
[1]G. B. Davis, Appl. Math. Model. **9**, 69–71 (1985).

where $\Delta a_i \equiv$ initial entrance deformation, $\lambda = \mathcal{V}_0/2\mathcal{D}_0$, $\mathcal{V}_0 = \mathcal{G}'(1)$, $D_0 = \mathcal{D}(1)$

Strong coupling between elasticity and surface charges at high σ_0



$\Longrightarrow$



- interior of infinite elastic pore under weak deformations considered
- anlytical solutions for counterion flux found by a projection of 3-D equations to 1-D equations via cross-sectional averaging

M. Matse, P. Berg, and M. Eikerling, Phys. Rev. E **98**, 053101 (2018).

Onsager coefficients

hydaulic conductance

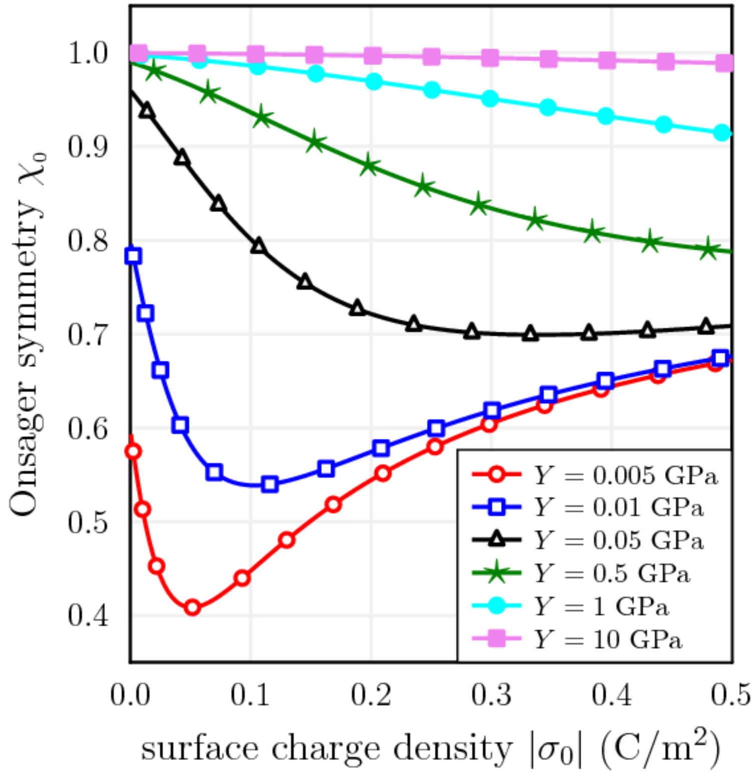
electroosmotic coefficient

$$\begin{pmatrix}\text{fluid}\\ \text{flux}\\ \\ \text{ion}\\ \text{flux}\end{pmatrix} = \begin{pmatrix}\mu_{\text{hyd}} & \mu_{\text{osm}}\\ \mu_{\text{str}} & \mu_{\text{ele}}\end{pmatrix}\begin{pmatrix}\text{pressure}\\ \text{drop}\\ \\ \text{potential}\\ \text{drop}\end{pmatrix}$$

$\longleftarrow$ Absence of concentration gradients

electric conductance

streaming potential coefficient

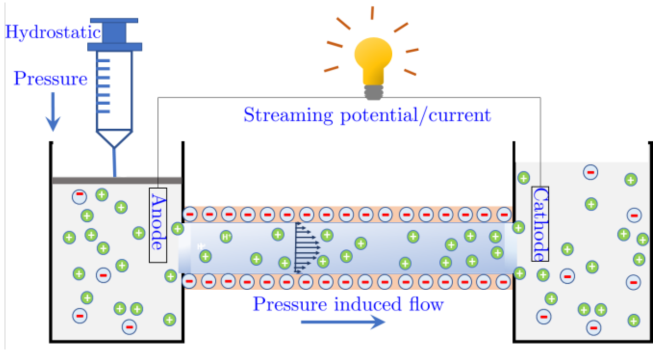


- ◇ Onsager reciprocal relation : $\mu_{\text{osm}} = \mu_{\text{str}}$
- ◇ a pore of radius $R_0 = 2\text{nm}$, with $\alpha = 0.5$ is considered
- ◇ Onsager symmetry coefficient $\chi_0 = \mu_{\text{str}}/\mu_{\text{osm}}$ is introduced and investigated
- ◇ soft pores do not comply with Onsager symmetry condition, particularly in the weakly charged regime

1-D model violates Onsager symmetry principle

M. Matse, P. Berg, and M. Eikerling, Phys. Rev. E **98**, 053101 (2018).

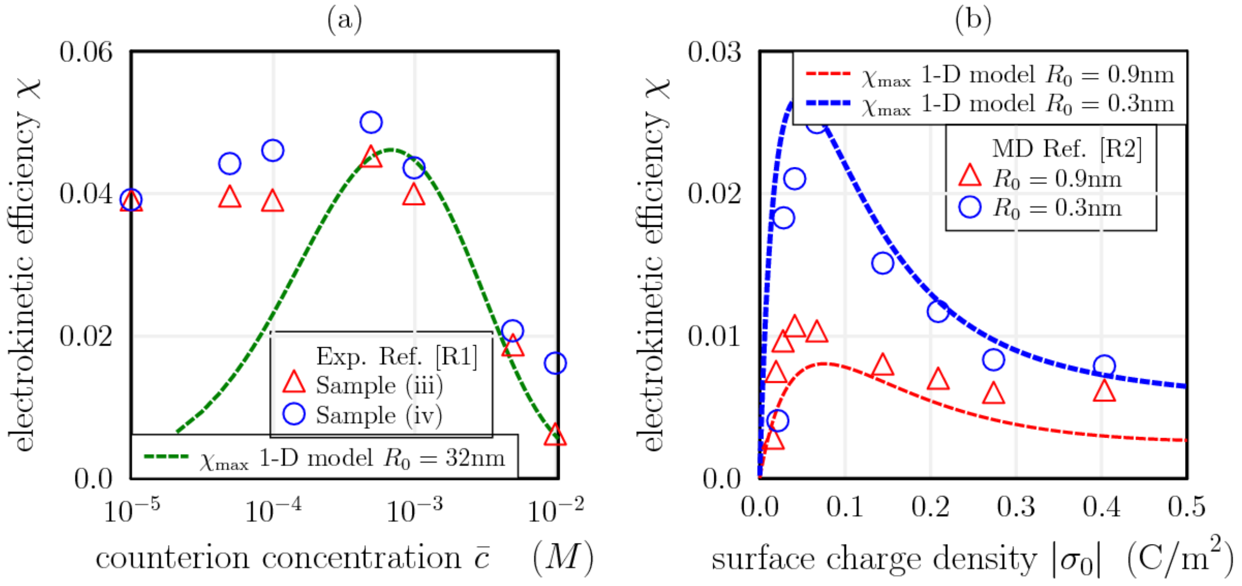
Electrokinetic energy conversion

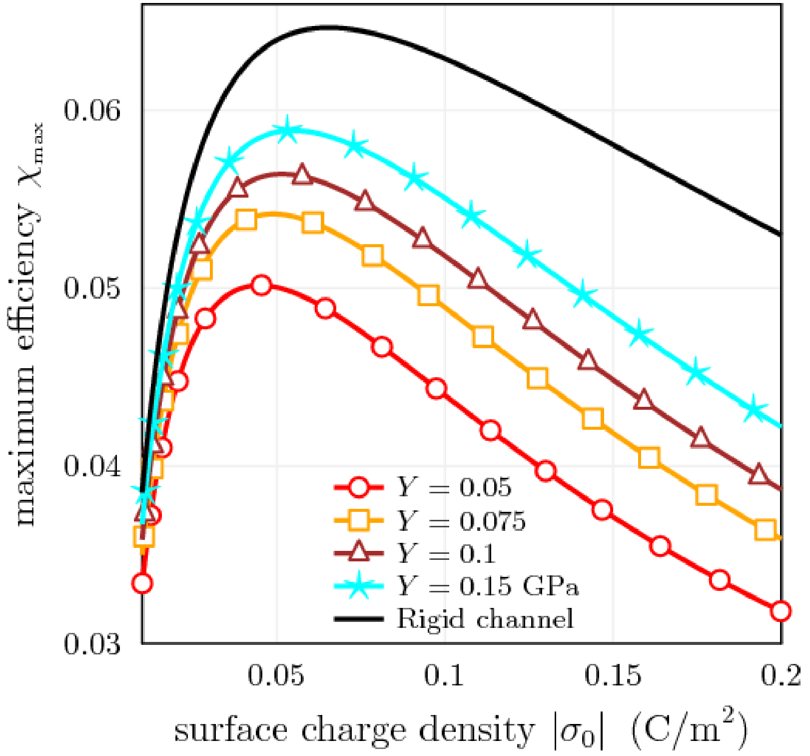


◇ define energy conversion efficiency

$$\chi = \frac{\text{output power}}{\text{input power}} = \begin{cases} \dfrac{I\bar{E}_z}{Q\nabla\bar{p}}, & \text{electrical power generation mode.} \\[2ex] \dfrac{Q\nabla\bar{p}}{I\bar{E}_z}, & \text{pumping mode.} \end{cases}$$

◇ efficiency gets amplified and peaks over a narrow regime at low σ_0





◇ softness of channel walls diminishes the efficiency

R1: Y. Xie, X. Wang, J. Jin, K. Chen, and Y. Wang, Appl. Phys. Lett. **93**, 163116 (2008).

R2: C. Bakli and S. Chakraborty, Electrophoresis **36**, 675–681 (2015).

Conclusions

- we developed a 1-D continuum model that describes nonlinear coupling between wall deformation and fluid and counterion flows in a charged, deformable nanochannel

- results unveil a rich coupling between the elasticity and charge distribution of the channel walls, which vanishes in the limit of weakly charged channels

- the reduction of the model to 1-D leads to a violation of the Onsager reciprocity principle when the channel is deformed

- the proposed model predicts that softness of channel walls diminishes the energy conversion efficiency compared to their rigid counterparts