



Nanofluidics and electrokinetics

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Content

- 1) Introduction
- 2) Mass transport
- 3) Electrokinetics
- 4) Concentration gradients
- 5) Recent issues



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Nanofluidics:

fluid flows in channels with a least one nanometric dimension

(Here: fluid = water / nanometric dimension = 1 to 500 nm)





From soils...



SEM picture of the soil of a kaolin mine in middle Georgia. http://clay.uga.edu/courses/8550/DBK.html



Figure 9. SEM and secondary electron images. Matrix without fibers.

Gypsum





... to living cells.



 $\alpha\text{-h}\acute{e}molysine$



aquaporines



Mechanosensitive channels...





What is new?

• New synthetic systems: zeolites, imogolytes, nanotubes, nanofabrication

 New tools for study: optical and electronic microscopes, electrical detection, surface force apparatus, MD simulations.



1) Introduction





Gravelle S et al. The Journal of Chemical Physics 2014; 141: 18C526.

Patch-clamp Neher and Sakmann 1976

New applications



New applications

- Bio-analysis with single molecule resolution
- Specific hydrodynamic transport (super-lubricity)
- Specific ionic transport
- Applications in energy conversion





New applications

Filtering: Giant permeability CNT membranes



Holt et al Science 2006

Diagnosis: Concentration polarization



Kim et al., PRL 2007 Son et al., BioChip J. 2016

×	nanopo	prous junction —	
nd	¹ Handle Side	m	Cathodic side

Energy conversion



Straub et al., Nature Energy 2016



Non linear effects: nanofluidic diode



Limits of the macroscopic hydrodynamic description

#limit 1: Size of object / size of the pore



#limit 2: fluctuation and thermal relaxation timescale

- Observations (experiments and simulations):
 - Limits of viscosity definition: 1 nm for water...
 - Other transport coefficients (diffusion): larger...



#1 Polymers: entropical cost of confinement





Oûkhaled et al., PRL 2012



#2 Limits of the continuum description: fluctuations

N molecules : fluctuations expected of the order of



Reasonable experimental threshold 10% (100 molecules):

 $L \sim 1 nm$

Water



Is continuum hydrodynamics valid for water in a:

a) 1 μ m channel?

b) 1 nm channel?

c) 0.1 nm channel?





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Navier-Stokes equations for incompressible liquid

Momentum conservation

$$\rho \frac{\partial \vec{v}}{\partial t} + \rho \vec{v}. g \vec{radv} = \eta \Delta \vec{v} - g \vec{radP}$$

Mass conservation

 $div\vec{v} = 0$

MC Jullien's talk



Stokes equation for liquid at the nanoscale

Low Reynolds number, (quasi)-stationnary flows

$$0 = \eta \Delta \vec{v} - g \vec{radP}$$

$$div\vec{v} = 0$$

+ Boundary conditions





No-slip boundary condition : v_s=0







QUIZZ

The flow rate through a tube of radius R= 10 nm, length L=10 μm and under a pressure difference of 1 bar is:

a) 1 L/s
b) 1 μL/s (10⁻⁶ L/s)
c) 10 zL/s (10⁻²⁰L/s)



Measuring flow rate at the nanoscale: a difficult task!

#1 Direct measurement inside the channel

#2 Measurements of species transport at the exit of the channel

#3 Integrated measurements





Measuring flow rate at the nanoscale: a difficult task!

#1 Direct measurement inside the channel

• Diffusion/advection balance of dye repartition Q~50fL/min



Lee et al., PRL 2014

• Cross correlation spectroscopy Q~1pL/min



(*Mathwig et al. PRL 2012*) – no need of optical acess.



#2 Measurements of species transport at the exit of the channel

- Landau-squire jet
 - Punctual source, momentum conservation
- \circ Probed with optical tweezers : Q ~ 100 pL/min

(Laohakunakorn et al., Nanoletters 2013)-

 Fluorescent probe (Secchi et al., Nature 2016)

Particle translocation
 Zero mode wave guide
 (Auger et al. PRL 2014)









#3 Integrated measurements

• Coulter counting 100 fL/s Gadaleta et al., Nanotechnology 2015



• Capacitive flow rate sensor 100 fL/s *Sharma PhD Liphy 2017*





QUIZZ

1) Who wins?

2) Who fits expectations?





Boundary condition: $v_s \neq 0$

Numerical observations



 $v(z=0) \neq v_0$

Huang et al.PRL 2008



Boundary condition: $v_s \neq 0$

Experimental observations

• Surface force apparatus: Cottin-Bizonne et al. (2005)



• Confined Brownian movement: Joly et al. (2006)





Formalism: friction coefficient and slip length

Viscous stress

$$-\lambda v_T = \eta \frac{\partial v}{\partial z}$$

$$b = \frac{\eta}{\lambda}$$

$$b\left(\frac{\partial v}{\partial z}\right)_{z=0} = v_t$$



Navier 1823



Formalism: slip length

Effect of wettability





Slip length b









Slip length on textures









The case of carbon nanotubes







The case of carbon nanotubes

Fast Mass Transport Through Sub–2-Nanometer Carbon Nanotubes

Jason K. Holt,^{1*} Hyung Gyu Park,^{1,2*} Yinmin Wang,¹ Michael Stadermann,¹ Alexander B. Artyukhin,¹ Costas P. Grigoropoulos,² Aleksandr Noy,¹ Olgica Bakajin¹†

Bakajin et al., Science 2006



Water, ...

Membrane	Pore diameter (nm)	Enhancement over no-slip, hydrodynamic flow† (minimum)	Calculated minimum slip length‡ (nm)
DWNT 1	1.3 to 2.0	1500 to 8400	380 to 1400
DWNT 2	1.3 to 2.0	680 to 3800	170 to 600
DWNT 3	1.3 to 2.0	560 to 3100	140 to 500
Polycarbonate	15	3.7	5.1



In one single tube



Secchi et al., Nature 2016



Commensurability and Mango effect





QUIZZ

Order of magnitude of the slip length – 1 or 100 nm. a) Near a smooth hydrophobic surface

b) In a nanometric carbon nanotube

2) Does the slip length depends on the fluid velocity? Viscosity?

3) For CNNT, which ones are the most slippery? The large one or the small ones?





Ultrathin membranes:

$$Q = \frac{a^3}{3\eta} \Delta P$$

$$Q = \left(\frac{\pi R^4}{8L} \left(1 + 4\frac{b}{R}\right) + \frac{a^3}{3}\right) \frac{\Delta P}{\eta}$$



Consequence 1: Coulter counter









R=85 nm L=50 nm 13.2 fL/mbar vs 13.9 fL/mbar


Consequence 2: the case of aquaporins





Consequence 2: the case of aquaporins



Gravelle et al., PNAS 2013



From one to many pores



PhD C. Sempere



From one to many pores, enhanced permeability



PhD C. Sempere



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Lengthscales in fluids





Coupling between *electrostatics* and fluid dynamics (*kinetics*)

• Charges at the liquid/solid interface, surface charge density noted $\boldsymbol{\sigma}$



$Si0H \to SiO^- + H^+$

 H^+ H^+ H^+ H^+ H^+ H^+



σ: number of charge per unit area,
 on the surface channel



Characteristic length 1

2*R* Number of bulk ions: $c_0 \pi R^2 L$ Number of surface ions: $\sigma 2\pi RL$

bulk dominates

 $R \gg \ell_{Du}$ $R \ll \ell_{Du}$

surface dominates

 ℓ_{Du} **Dukhin length**

From 0.1 nm to 10 μ m



Effect on channel conductivity



Saturation of the conductivity at low concentration



Effect on channel conductivity



$$I = \int_{S} e(c_{+}v_{+} - c_{-}v_{-})dS$$
$$v_{\pm} = v \pm e\mu_{\pm}\frac{\Delta V}{L}$$

$$I = e\left((\mu_{+} + \mu_{-})c + K_{surf}\right)h\frac{\Delta V}{L}$$

 $K_{surf} \sim K_{bulk} \times \frac{\ell_{Du}}{h}$

Surface contribtuion



Effect on channel conductivity



Karnik et al., Nanoletters 2007



Characteristic lengths 2-3

Between two ions in bulk: the Bjerrum length Electrostatic interaction / thermal agitation





Characteristic lengths 4

 \succ Screening length: the Debye length λ_{D}

$$\lambda_D = \sqrt{\frac{\epsilon kT}{2e^2c_0}}$$

1 mol/L, 0.3 nm



From Hartkamp et al., 2018



Coupled transport

- Electro-osmosis
- Streaming current
- Streaming current: energy recovery efficiency





Electroosmosis



F. Reuss, Mémoires de la Société des naturalistes de Moscou, v. 2 (1809).

Applying a potential will induce a flow!



Electroosmosis



Audry 2010

3) Electrokinetics

Plug flow



(a)



(b)

J.G. Santiago Stanford Micro Fluidics Lab.

Electroosmosis



- Charges at interfaces (ionic surfactants)
 ➤ Counter-ions in the vicinity of the interface
 (Electrical Double Layer: λ_D)
 c(z) = c₀e^{- ψ(z)}/_{kT}
- Tangential electric field: force on the locally non-neutral liquid $f(z) = -(c_+(z) c_-(z))e\nabla V$
- Entrainment of the liquid: stationnary Stokes plug flow



Surface charge density Hydrodynamic boundary condition







Electroosmosis / Poiseuille flow







Taylor-Aris dispersion Cf. J.-B. Salmon's talk



Electroosmosis in soap films





Electroosmosis in soap films





 $\delta \propto R_c \left(\frac{\eta v_{EO}}{\gamma}\right)^{2/3}$ $v_{EO} = -\epsilon \frac{\zeta}{\eta} \nabla V \qquad \qquad \zeta=30 \text{ mV}$

(analogous to Landau-Levich film)

O. Bonhomme, O. Liot



Electroosmosis in soap films





QUIZZ

1) Is an electro-osmotic flow:

- a) Plug like?
- b) Parabolic like?

2) Is it affected by slippage?

3) By the surface potential?





Coupled transport

- Electro-osmosis
- Streaming current
- Streaming current: energy recovery efficiency





Streaming current



 $I = -S\frac{\Delta P}{\tau}\epsilon^{\frac{\zeta}{2}}$

- Velocity profile
 v(r) induced by a difference of pressure (Poiseuille)
- Ion distribtuion profile near a charged surface *c(r)* induced by a surface charge

$$I = \int_0^R e(c_+(r) - c_-(r))v(r)2\pi r dr \qquad \text{(tube geometry)}$$

Onsager reciprocity





Streaming current







Streaming current



Glass capillary: R=1µm, L=2cm



Streaming current and electroosmosis





Glass capillary: R=1µm, L=2cm





Streaming current - harvesting energy



Zhang et al., Nature Nanotechnology, dec 2018



Coupled transport

- Electro-osmosis
- Streaming current
- Streaming current: energy recovery efficiency





 $P_{in} = Q\Delta p$



$$\alpha = S_{str}^2 Z_{ch} R_{ch} \qquad \qquad k = \frac{R_L}{R_{ch}}$$

Van der Heyden et al., Nanoletter 2006 Van der Heyden et al., Nanoletter 2007

$$\epsilon = \frac{P_{out}}{P_{in}} = \frac{\alpha k}{(1+k)(1+k-\alpha k)}$$



Streaming current: Energy recovery efficiency

- Large surface charge density, large bulk concentration
- = a lot of ions, good output (S_{str} is large)
- Charges = dissipation by conductance, bad output
- (*R_{ch}* is small)... nanofluidic diodes?





Van der Heyden et al., Nanoletter 2006 Van der Heyden et al., Nanoletter 2007



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4) Concentration gradients

Back to basis: osmotic pressure

Osmotic energy $\omega \sigma \mu o \varsigma$: push

$\Delta G = -T\Delta S$

S = entropy in J/K it is always positive (second principle) !





Back to basis: osmotic pressure



S=k ln(Ω), Ω = numbers of states in a system

4) Concentration gradients



Leçons de physique expérimentale, Abbé Nollet, 1770



4) Concentration gradients

 $\Delta \Pi = R T \, \Delta C_{\rm sel}$

membrane semi-imperméable

Osmotic pressure \rightarrow mechanical pressure



Reversing osmosis for desalination

Selective membrane

concentrée

diluée

280 m water fall


Osmotic pressure \rightarrow mechanical pressure



$$\Delta (P - \Pi)$$
$$\Delta \Pi = 2k_B T \Delta c$$
$$P_{out} = Q \Delta \Pi \quad Q \sim R^4 !!!$$

Applications: PRO (Pressure Retarded Osmosis)

- ► Pore size: <0.6nm
 - Power density:
 - Maximal expected power: 7
- 1-2.7 W/m² 7-8 W/m²



Osmotic pressure Selective membranes: new strategies



Lee et al. Nature Nanotechnology 2014

1000 larger than for semipermeable membranes!



Osmotic pressure <u>Non-selective membranes</u>: interactions with surfaces



Anderson, Ann. Rev of Fluid Mech., (1989)





Osmotic pressure Non-selective membranes: interactions with surfaces





Diffusio-osmosis



Plug flow outside the Debye layer



Diffusioosmosis



Prepare concentration step





C. Lee, R. Fulcrand, P. Joseph, C. Cottin-Bizonne, C. Ybert



Non-selective $h > \lambda_D$

Diffusioosmosis





Diffusioosmotic current

$$I = \int_{h} e(c_{+}(z) - c_{-}(z))v(z)dz$$

$$I_{osm} = 2\pi R \sigma \frac{kT}{2\pi\ell_B} \left(1 - \frac{\ell_{GC}}{\lambda_D} sinh^{-1} \frac{\lambda_D}{\ell_{GC}} \right) \frac{\partial c}{c\partial x}$$





Expected power density with BN nanotubes: 1kW/m²



Comparison diffusioosmosis -electroosmosis

Streaming current

Osmotic current

$$I_{streaming} = -\pi R^2 \frac{\Delta P}{L} \epsilon \frac{\zeta}{\eta} \qquad I_{osm} = 2\pi R \sigma \frac{kT}{2\pi \ell_B} \left(1 - \frac{\ell_{GC}}{\lambda_D} sinh^{-1} \frac{\lambda_D}{\ell_{GC}} \right) \frac{\partial c}{c\partial x}$$

$$\frac{I_{osm}}{I_{str}} \simeq \frac{kT\Delta c}{\Delta P} \frac{\lambda_D}{R}$$

kT Δ c=50 bars !! >> Δ P



Comparison diffusioosmosis -electroosmosis

Streaming current

$I_{str} \sim S \sim R^{2}$	$_r\sim \lambda$	$\tilde{r} \sim$	R^2
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Osmotic current

 $I_{osm} \sim R$

Channel density $N \sim A/S$

 $I_{str,tot} \sim A/S \times S \sim A$

$$I_{osm,tot} \sim A/S \times R \sim A/R$$

Interesting for small devices!



QUIZZ

1) Do we need selective membrane to see effects of salinity difference?

2) What is the most efficient: diffusioosmosis or electroosmosis?

3) Do you think that the two can be coupled?





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4) Recent issues

Nanofluidic diodes



Nanofluidic osmotic diode Picallo et al., PRL 2013



Non-symmetric Joule heating



Jubin et al., PNAS 2016



4) Recent issues

Thermoosmosis

Giant Thermoelectric Response of Nanofluidic Systems Driven by Water Excess Enthalpy

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(Received 21 April 2019; revised manuscript received 11 July 2019; published 24 September 2019)





Miralles et al., PRL 2014







NECTAR Project

THANK YOU





QUIZZ: who's who? Laurent Joly Cécile Cottin-Bizonne Christophe Ybert Oriane Bonhomme



