Fluid transport at the molecular scale

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Laboratoire de Physique Statistique,
Ecole Normale Supérieure, CNRS

with T. Mouterde, E. Secchi, A Nigues and **L. Bocquet**

NanoSOFT

NANOFLUIDICS

Nanofluidics: field of physics studying the fluid behavior at the nanoscale

Challenges and benefices from the nano scales :

- ✓ **breakdown of bulk transport properties:** Navier-Stokes, thermal transport, …
- ✓ **surface to volume effects:** enhanced role of surface phenomena
- ✓ **fluctuations** of transport properties
- ✓ **new functionalities** from fluid behavior at smallest scale

What is new and why now?

- ✓ ability to build new and controlled nm channel!

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NANOFLUIDICS

Sensing :

single particle translocation

C. Dekker, **Nature Nanotechology** 2, 209 (2007);
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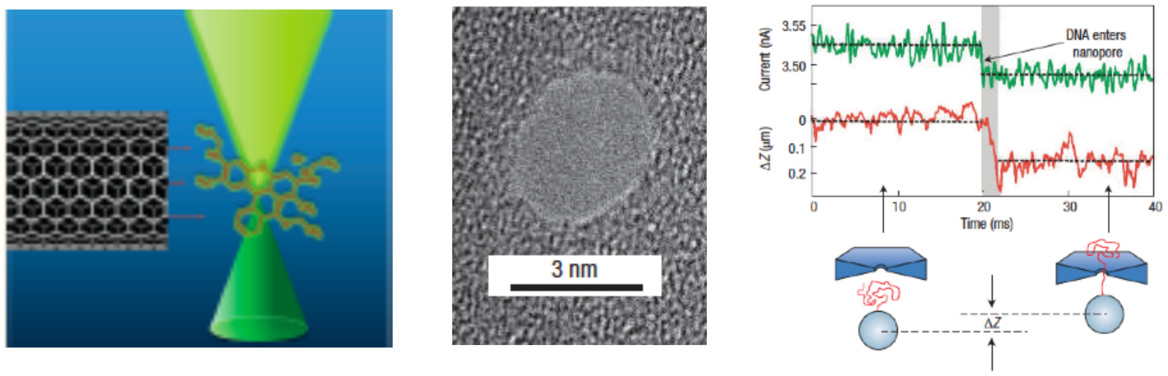

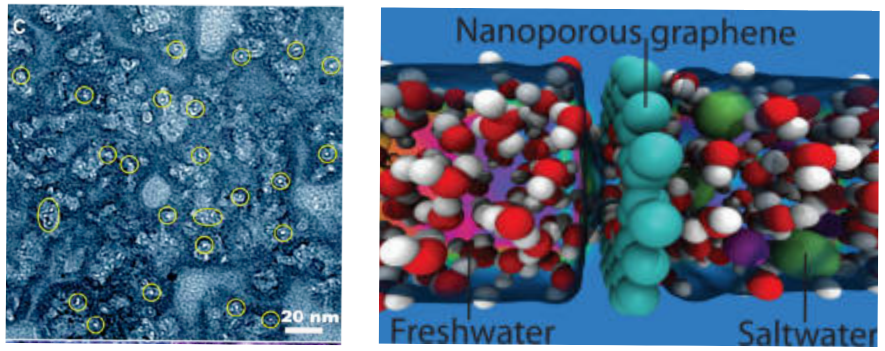

Ultrafiltration :

filter for **water desalination**

J. K. Holt et al. **Science** 312, 1034 (2006);
D. Cohen-Tanugi et al. **Nanoletters** 12, 3602 (2012);

Energy harvesting :

blue energy

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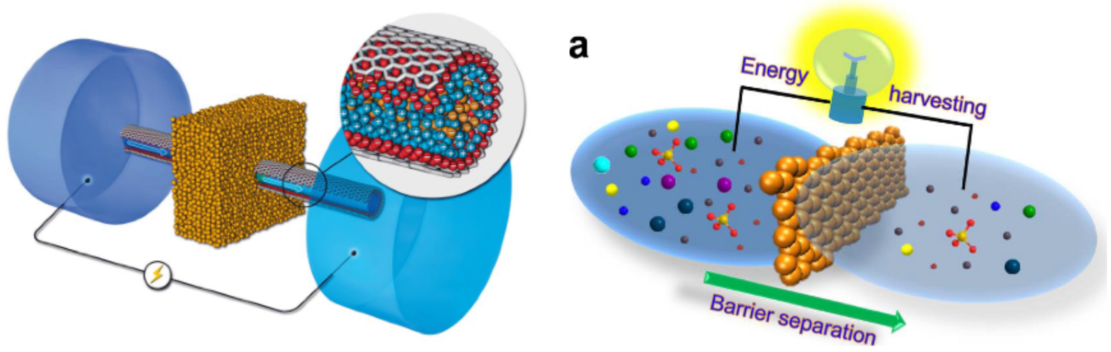

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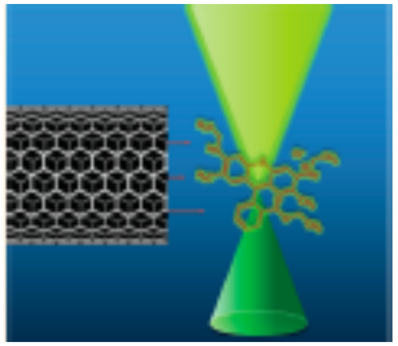

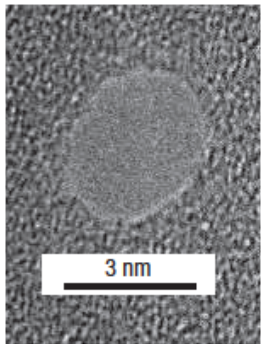

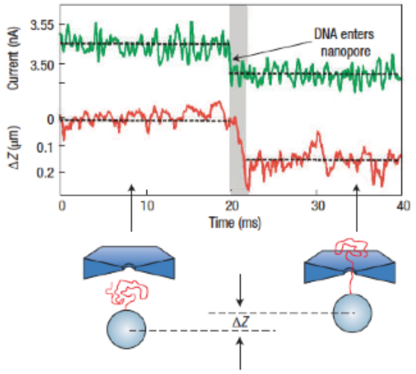

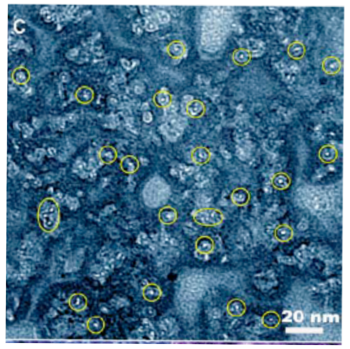

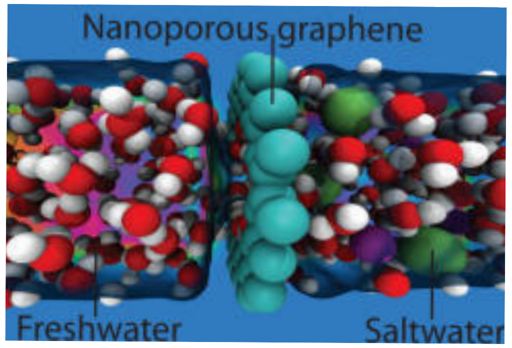

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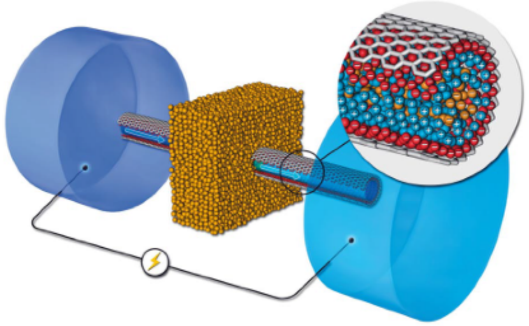
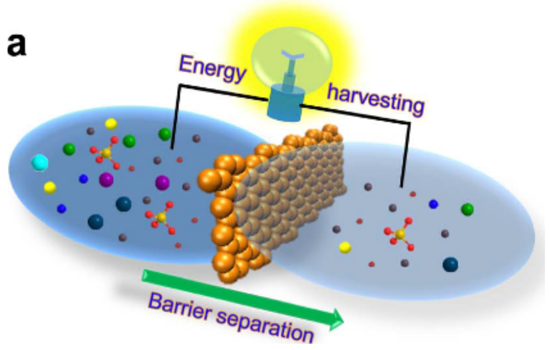
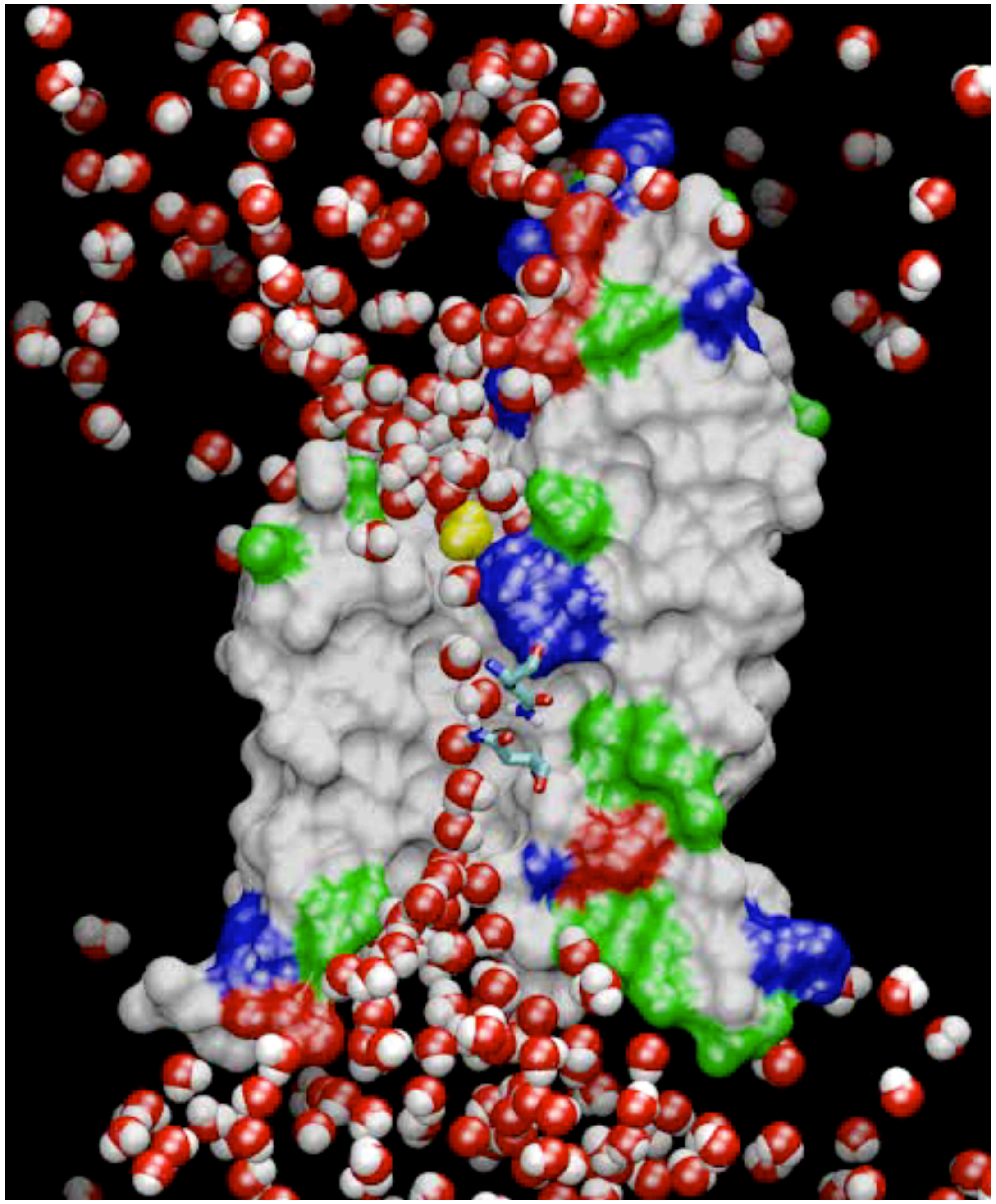




NANOFLUIDICS

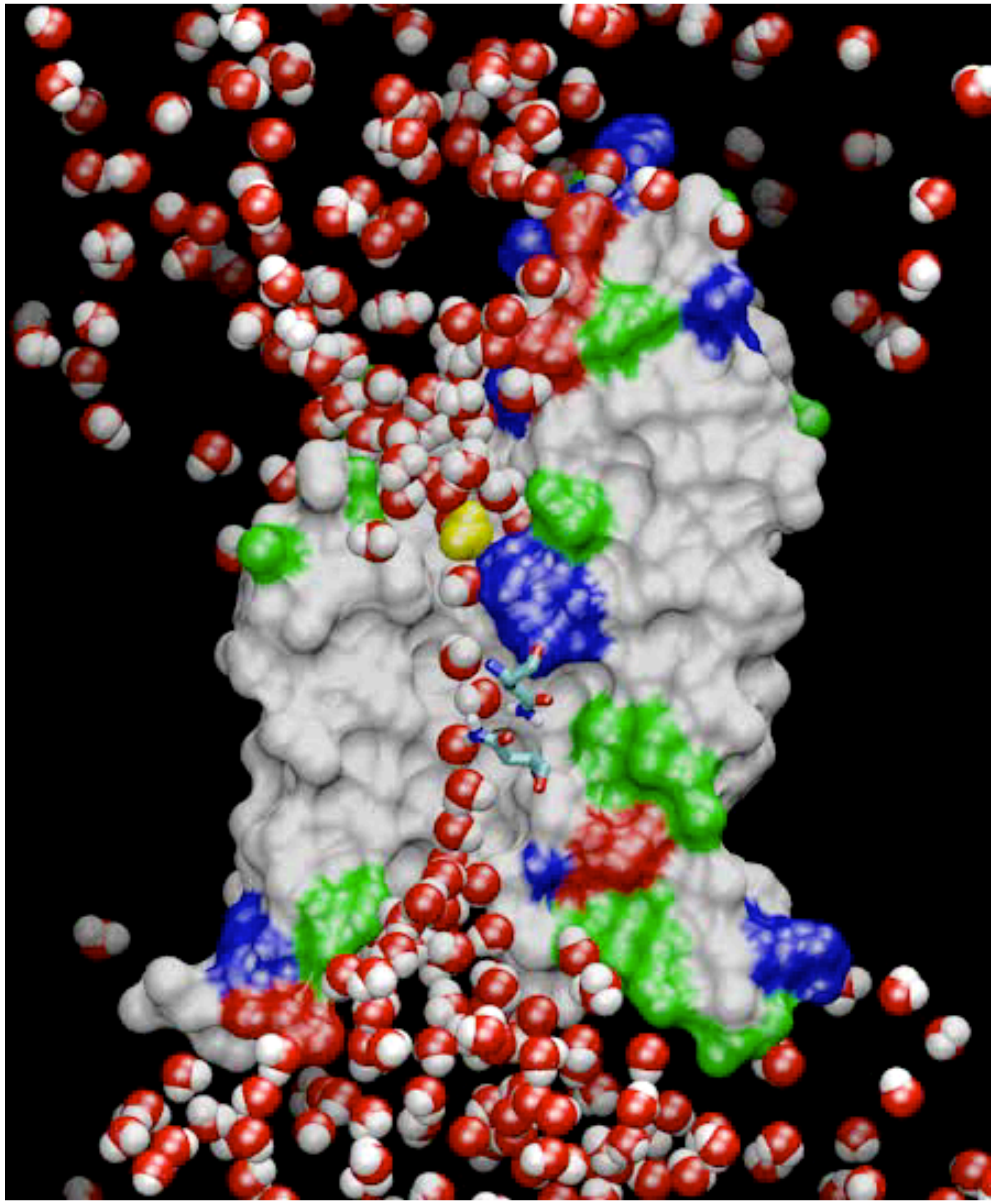


K. Schulten et al.

AQP-1

Bocquet-Charlaix, Chem Soc Rev (2010)

NANOFLUIDICS



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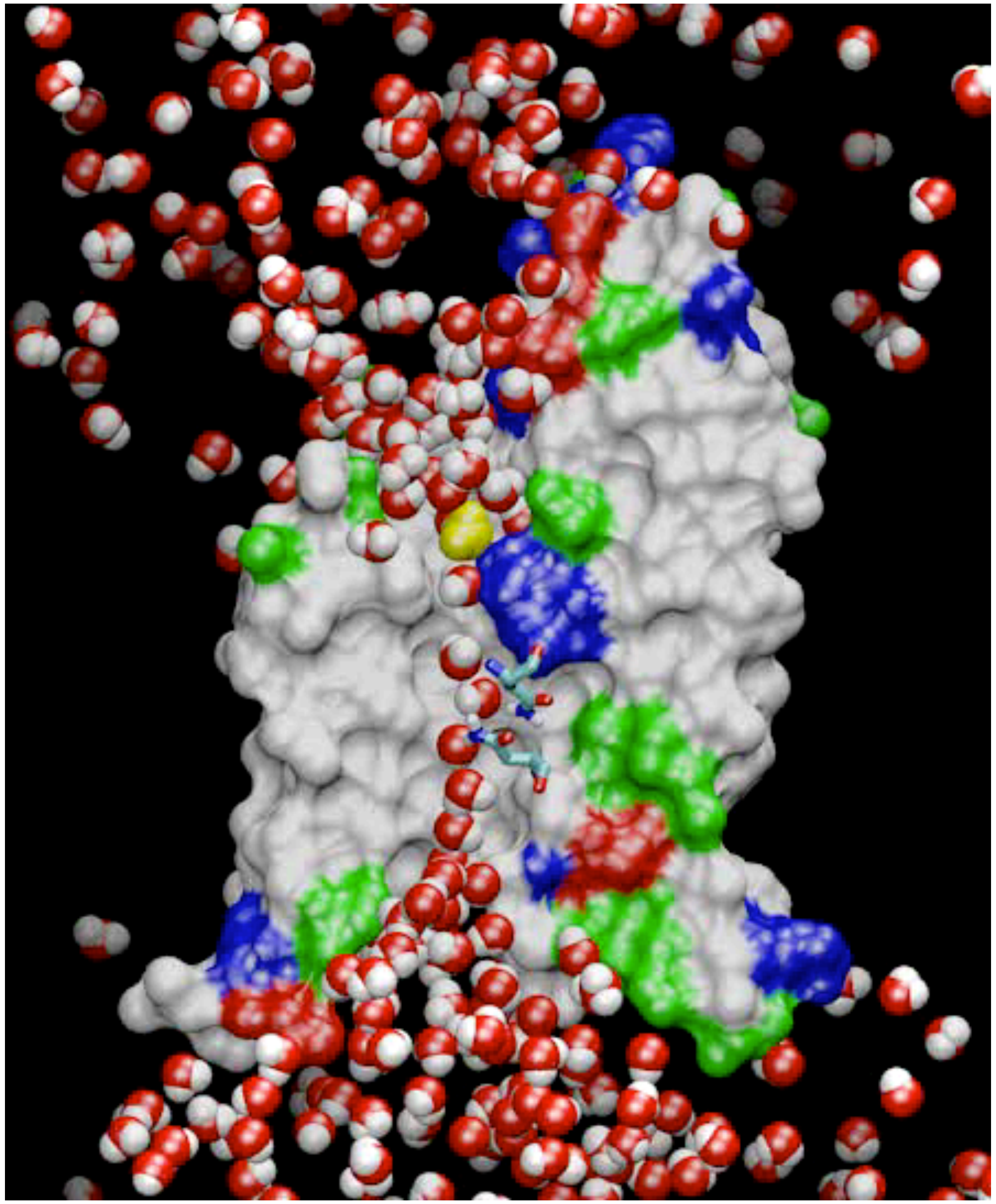

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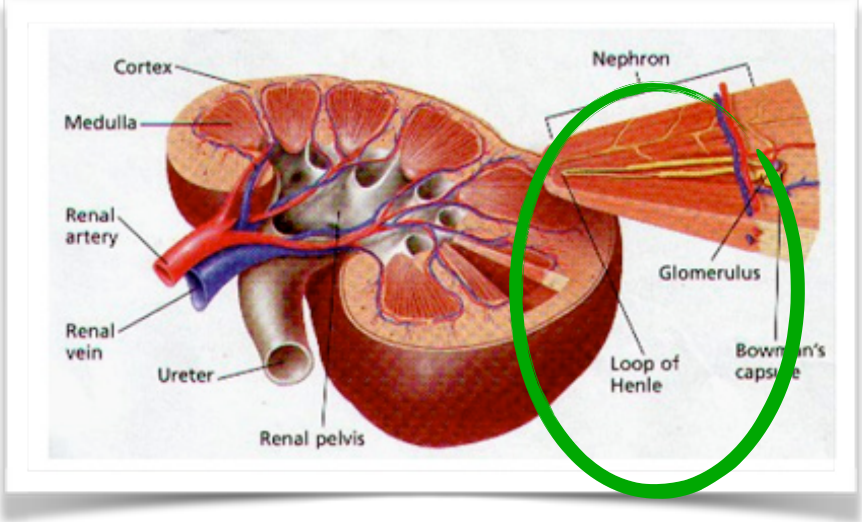
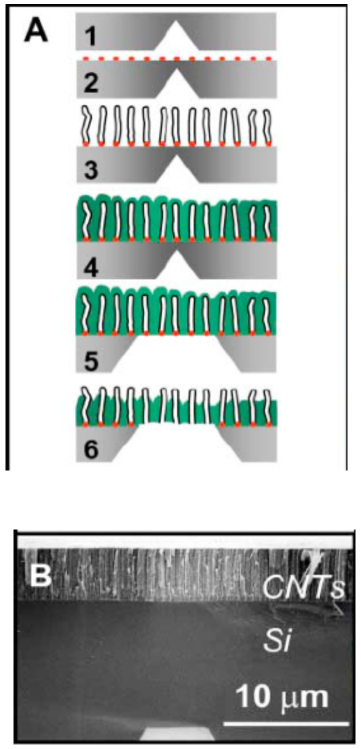


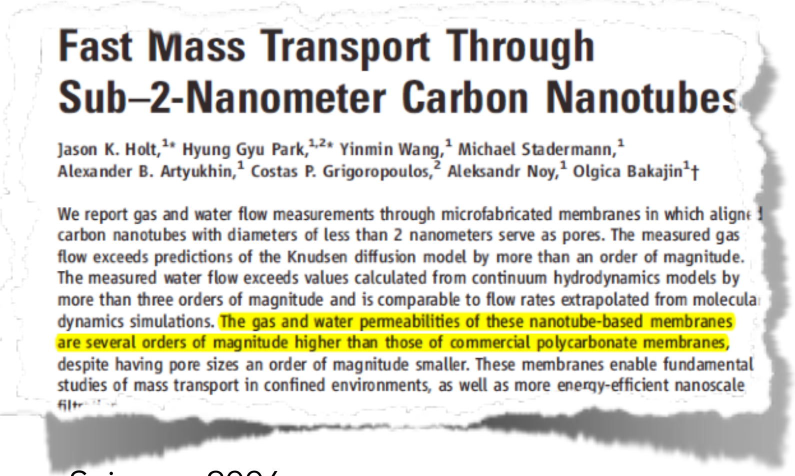
- 200 liter of water readsorbed/day
- 1.5kg NaCl

Bocquet-Charlaix, Chem Soc Rev (2010)

CARBON NANOCHANNELS

Intringuing results … fluidic transport in carbon materials





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 Bakajin[1]†

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Science 2006
also: Hinds et al., Whitby et al. Lindsay et al., Strano

MIRACULOUS CARBON WATER CHANNELS

CARBON NANOCHANNELS

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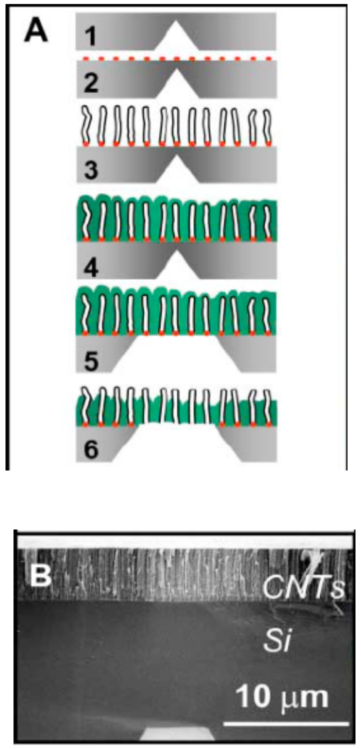

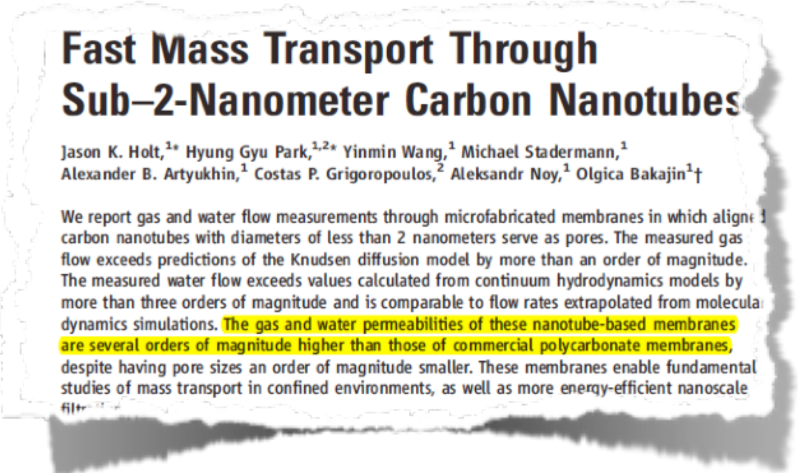

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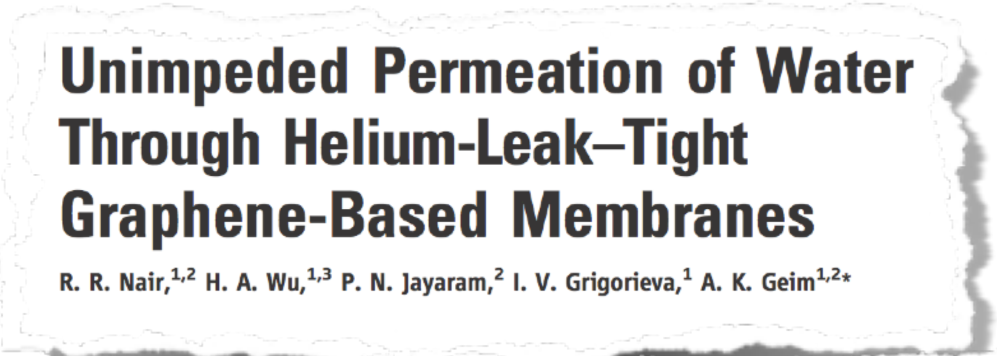
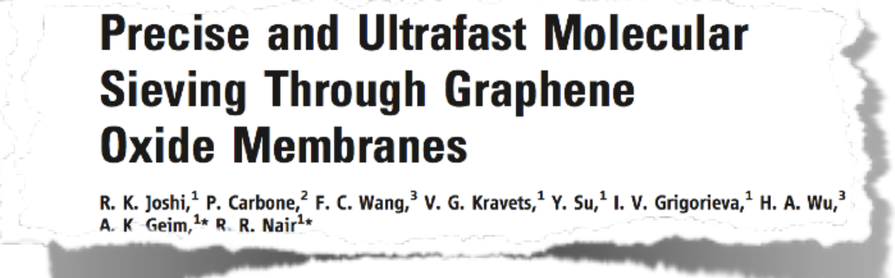
Membranes of graphene-like materials



Unimpeded Permeation of Water Through Helium-Leak–Tight Graphene-Based Membranes

R. R. Nair,[1,2] H. A. Wu,[1,3] P. N. Jayaram,[2] I. V. Grigorieva,[1] A. K. Geim[1,2*]

Science 2012



Precise and Ultrafast Molecular Sieving Through Graphene Oxide Membranes

R. K. Joshi,[1] P. Carbone,[2] F. C. Wang,[3] V. G. Kravets,[1] Y. Su,[1] I. V. Grigorieva,[1] H. A. Wu,[3] A. K. Geim,[1*] R. R. Nair[1*]

Science 2014

RESEARCH ARTICLE

NANOTECHNOLOGY

Ion transport in complex layered graphene-based membranes with tuneable interlayer spacing

Chi Cheng,[1*] Gengping Jiang,[1*] Christopher J. Garvey,[2] Yuanyuan Wang,[1] George P. Simon,[1,3] Jefferson Z. Liu,[3,4†] Dan Li[1,3†]

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10.1126/sciadv

Science Adv. 2016

MIRACULOUS CARBON WATER CHANNELS

FAST TRANSPORT IN CNTS ?

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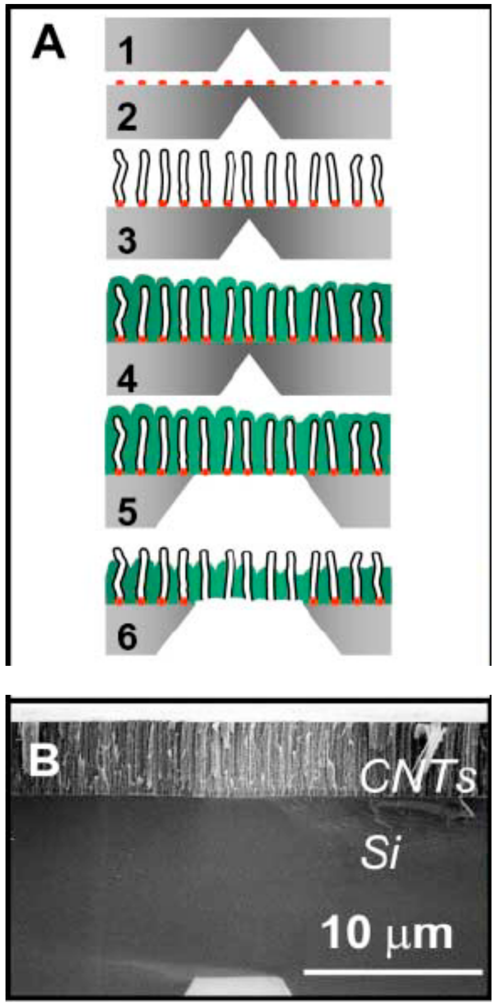

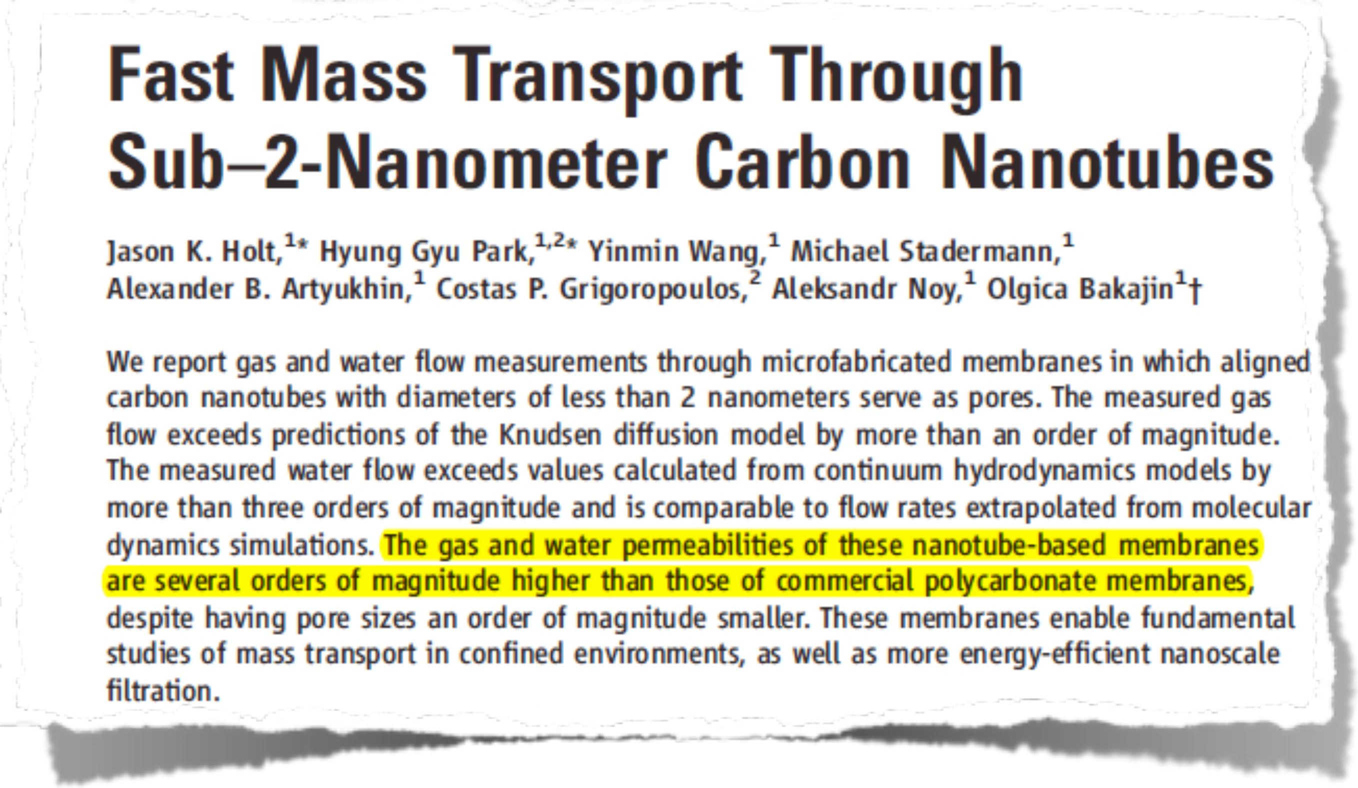

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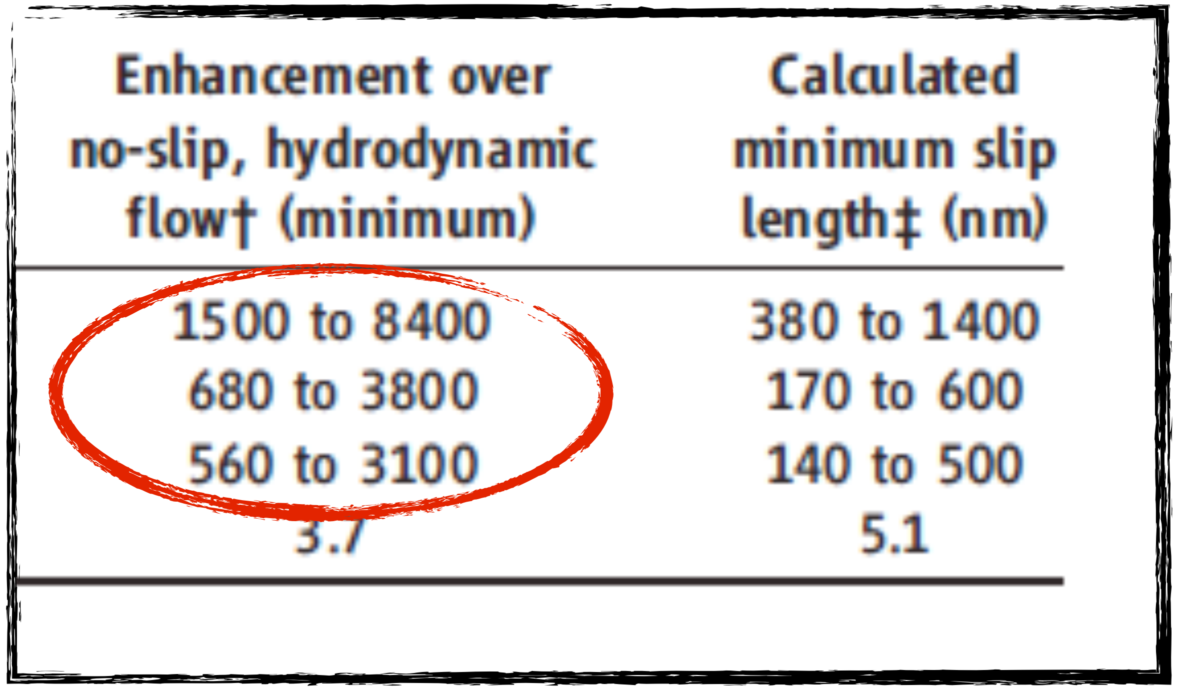
$$v_{flow} = \frac{k}{\eta}\frac{\Delta P}{L}$$

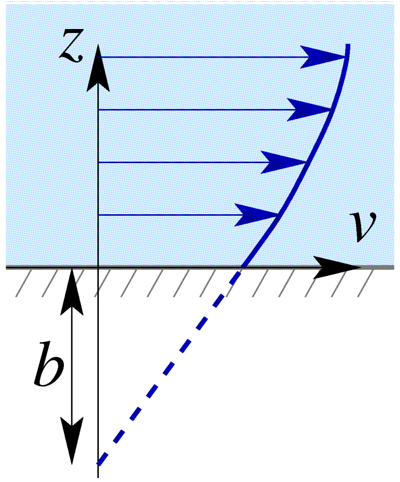


Enhancement over no-slip, hydrodynamic flow† (minimum)	Calculated minimum slip length‡ (nm)
1500 to 8400	380 to 1400
680 to 3800	170 to 600
560 to 3100	140 to 500
3.7	5.1

BREAKDOWN OF NO-SLIP BOUNDARY CONDITIONS

Solid-liquid slippage at surfaces

$$v_{\text{wall}} = b \frac{\partial v}{\partial z}\bigg|_{\text{wall}}$$



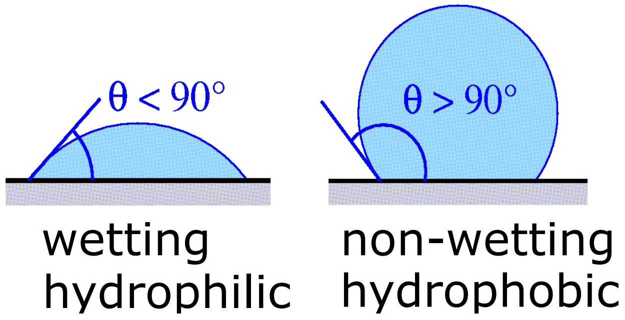
large slippage = *low solid-liquid friction*

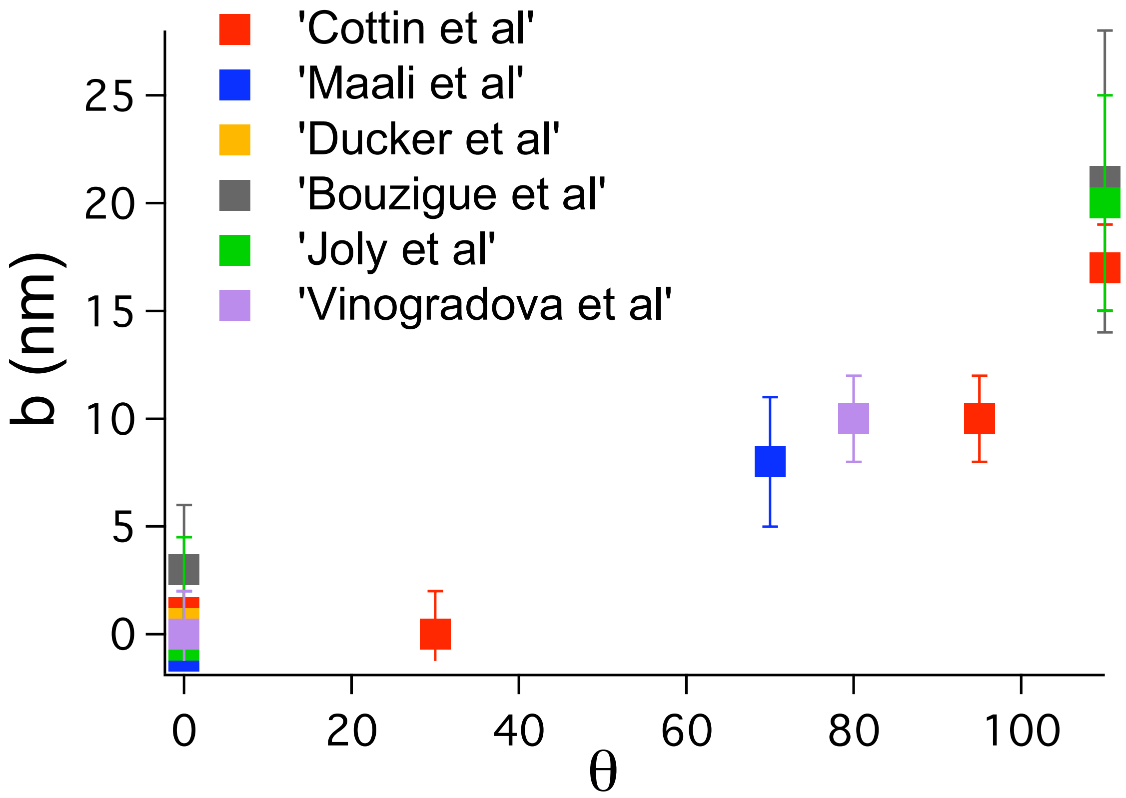
$$F = -\lambda S V_g$$

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

AFTER MORE THAN TEN YEARS OF WORK...

Water slippage versus wettability



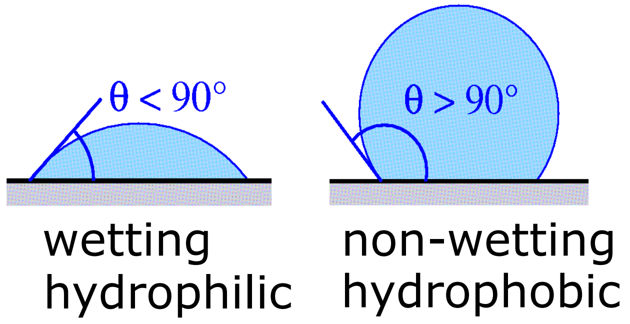


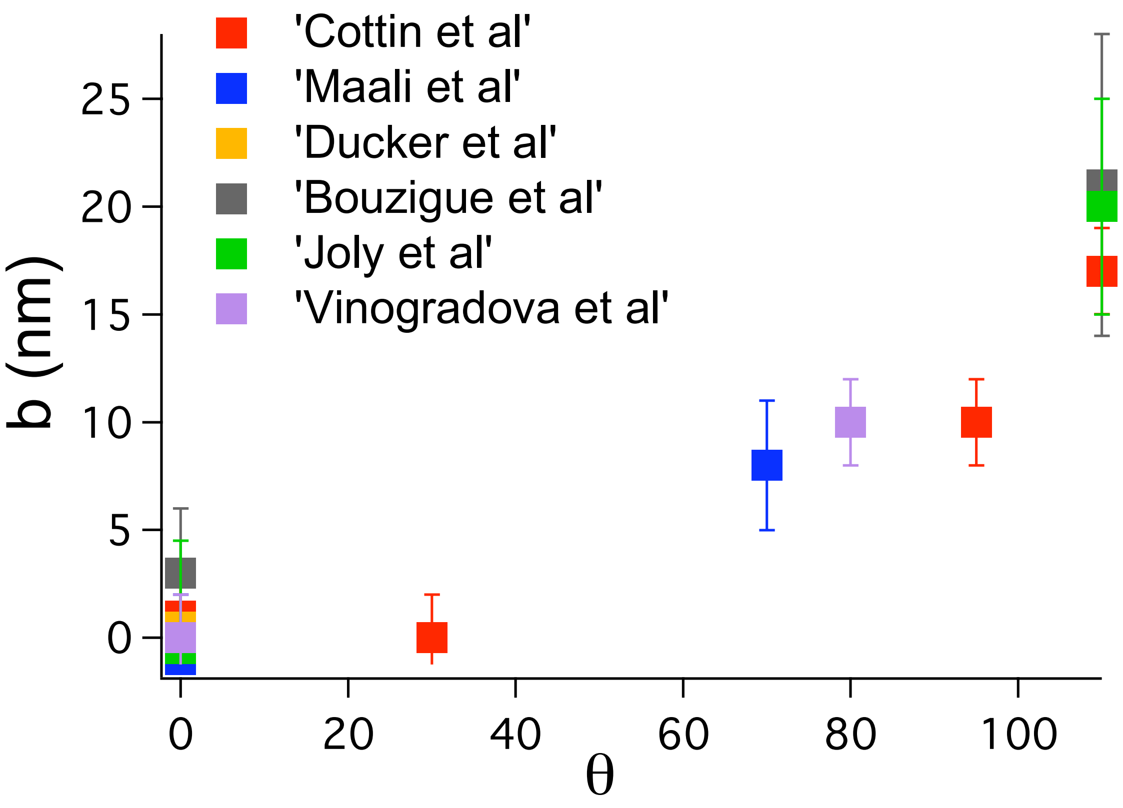
Experiments

HYDROPHOBICITY DECREASES WATER-SOLID FRICTION (LARGER SLIP)

AFTER MORE THAN TEN YEARS OF WORK...

Water slippage versus wettability





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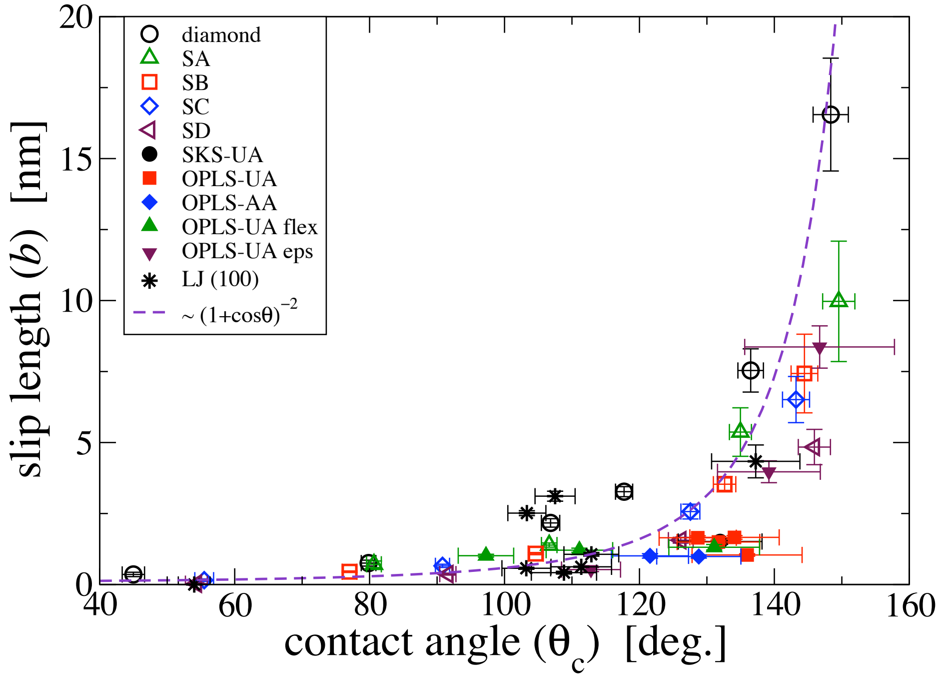

Theory

(Huang et al. PRL 2008)

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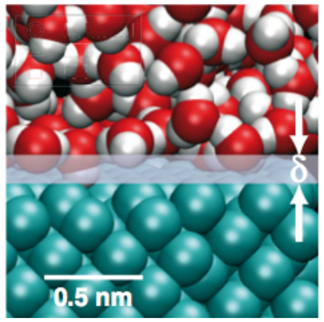


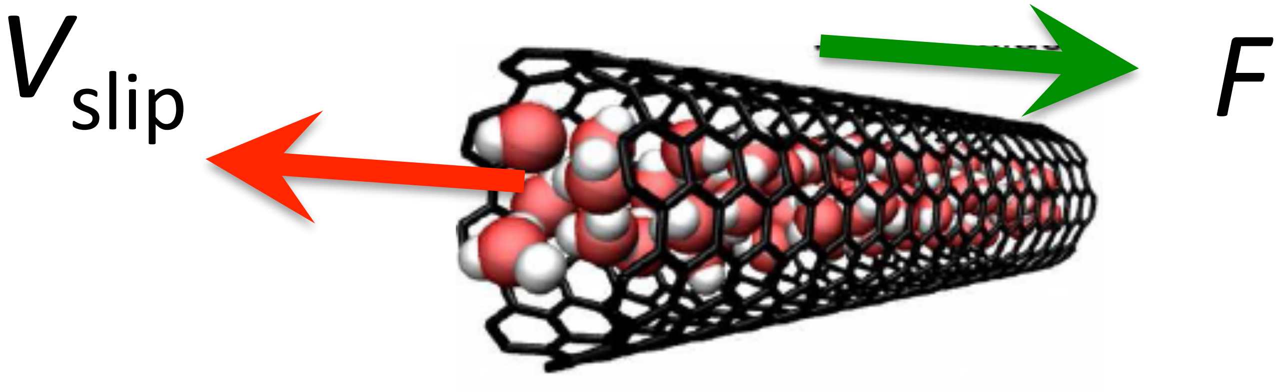
$$b \propto (1 + \cos\theta)^{-2}$$

SLIPPAGE AND WATER FRICTION AT CNT

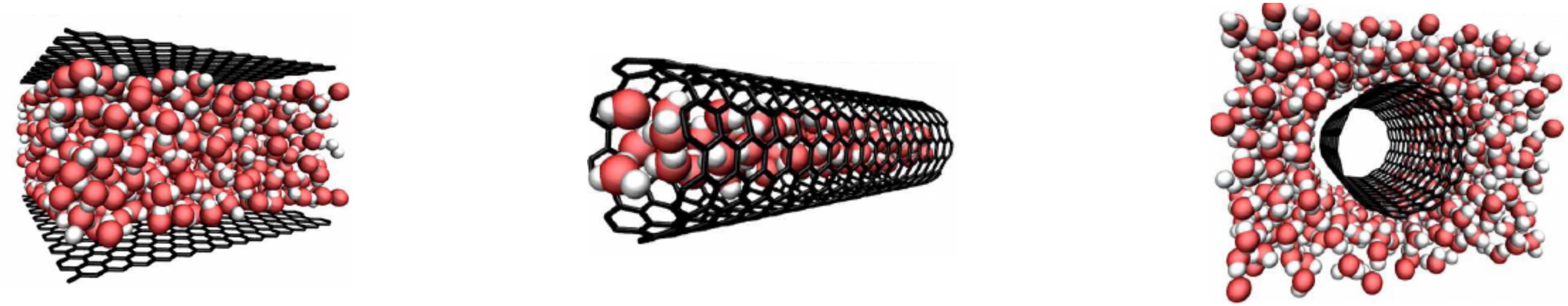
Molecular Dynamics simulations

with R. Netz

$$F = -\lambda \mathcal{A} \times V_{\mathrm{slip}}$$



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



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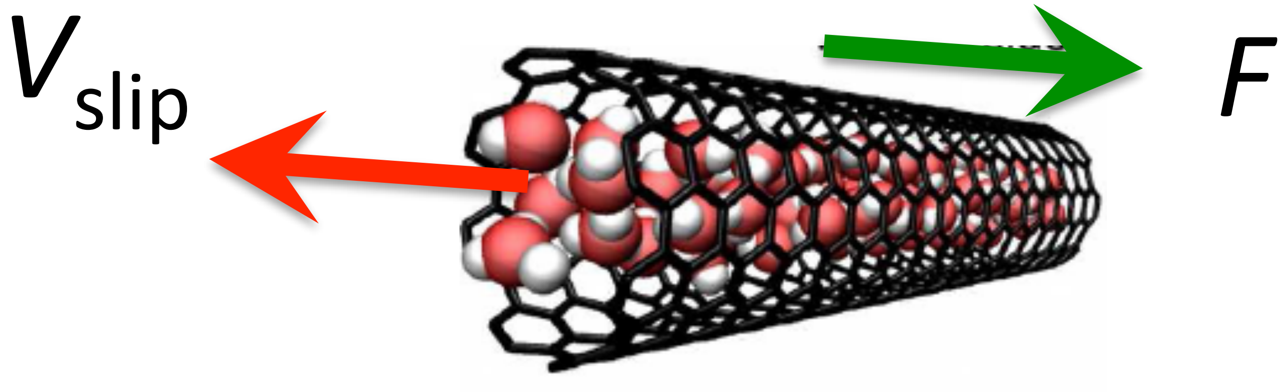

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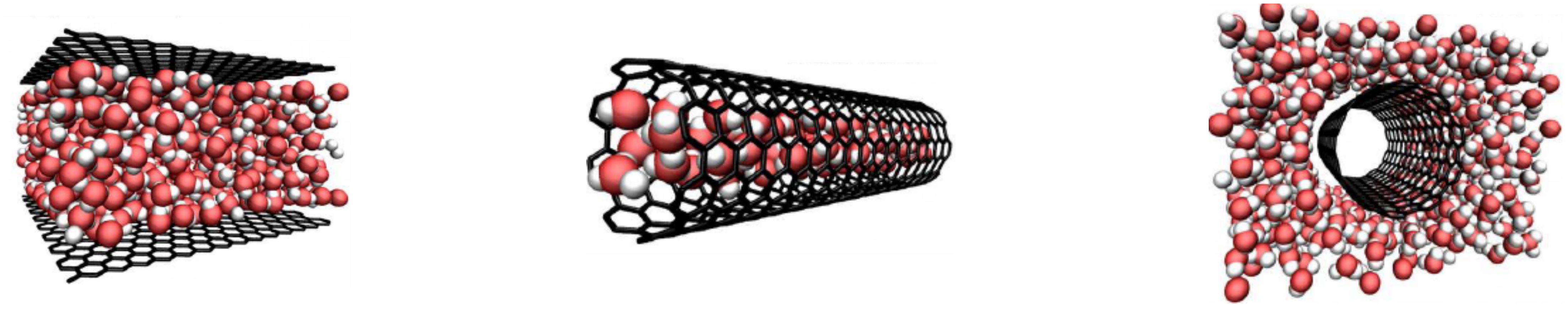
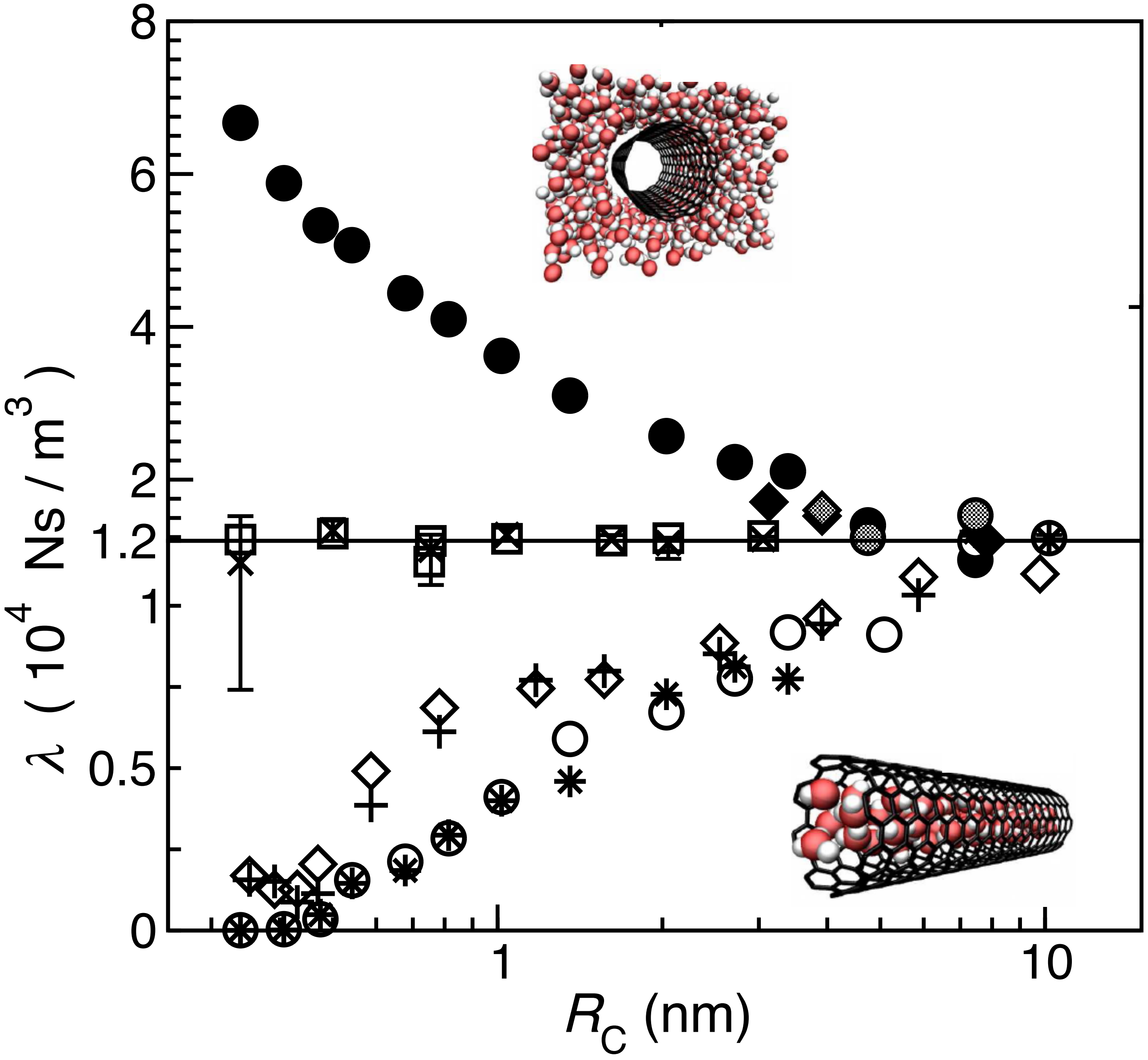
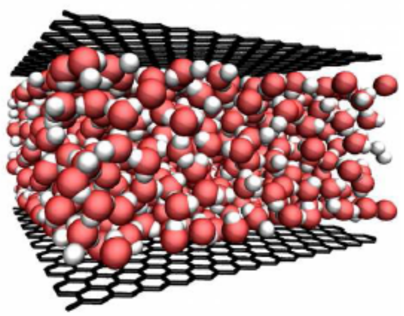


NOW, WATER-CNT FRICTION ?

Molecular Dynamics simulations

Friction coefficient





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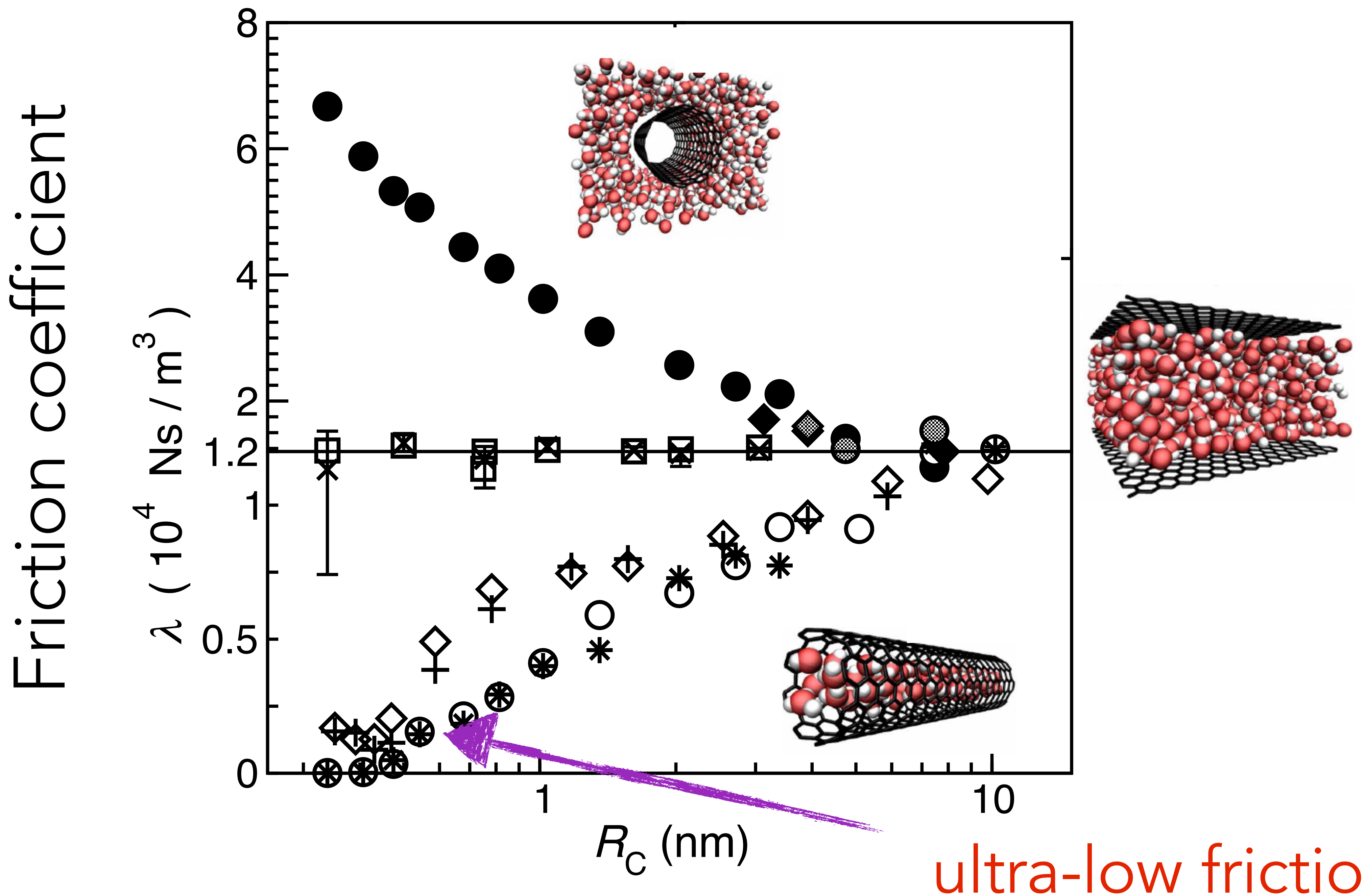

ultra-low friction

permeability increase by 10^4

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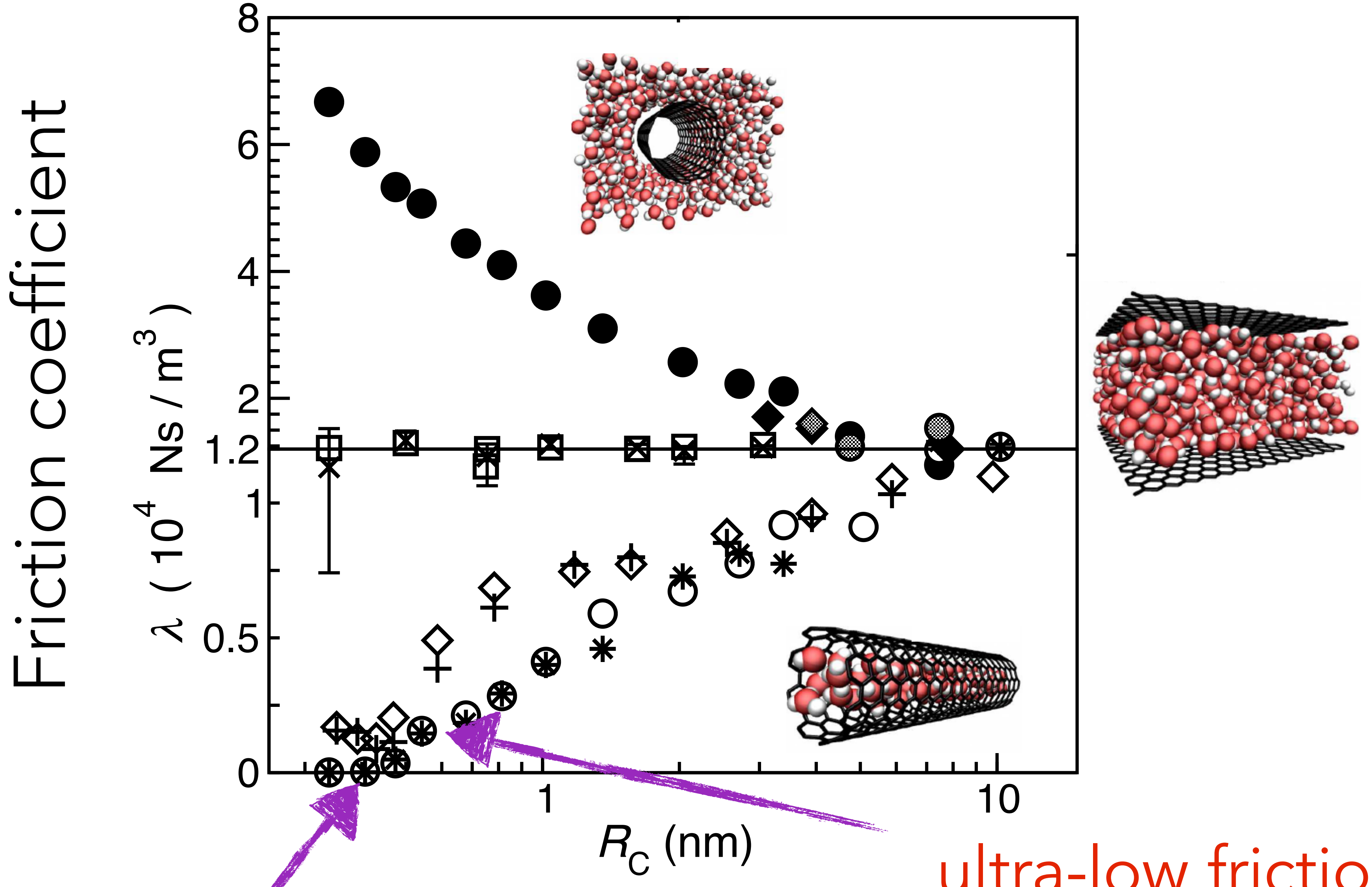
Molecular Dynamics simulations



ultra-low friction

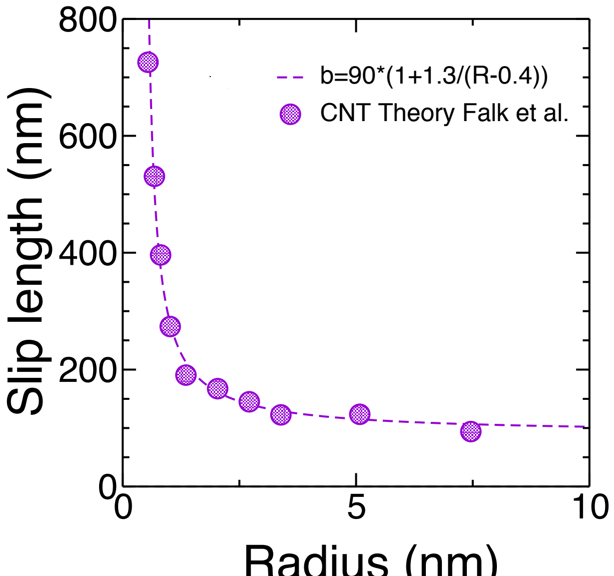
permeability increase by 10^4

Transition to superlubricity

ALTOGETHER

✔ water superlubricity in CNT at nanoscales

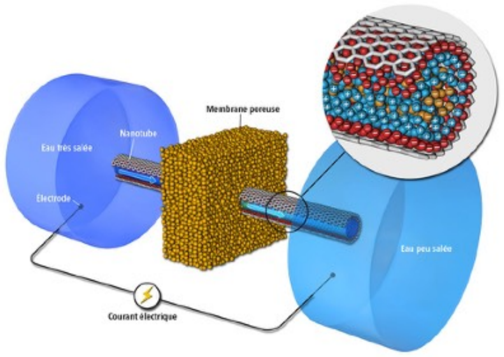
- A nanoscale effect
- A key ingredient of CNT: perfect crystallographic structure
- MD simulations: similar behavior for CNT and BNNT
- Lacks of experimental systematic investigation (!!)

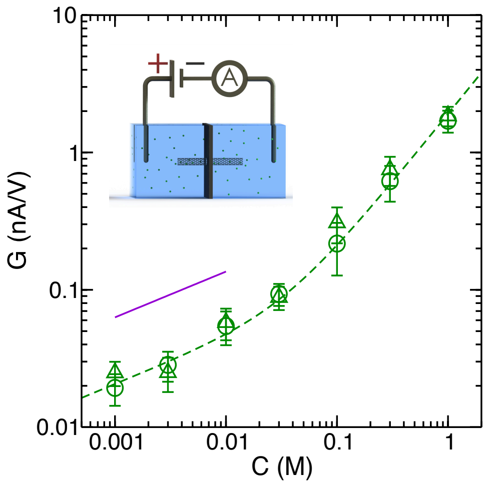


cf reviews:
Whitby-Quirke Nat. Nano (2007)
Bocquet-Charlaix Chem Com Rev (2010)
Forniasero et al. Adv. Mat. (2015)

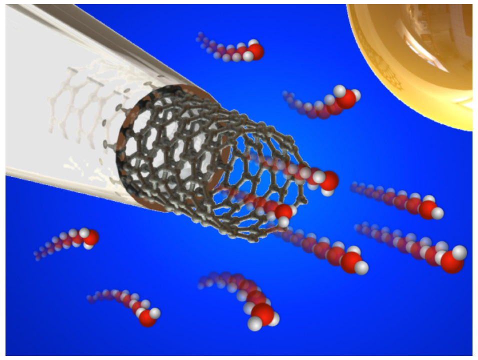
Fluidics in nanotubes and nanochannels

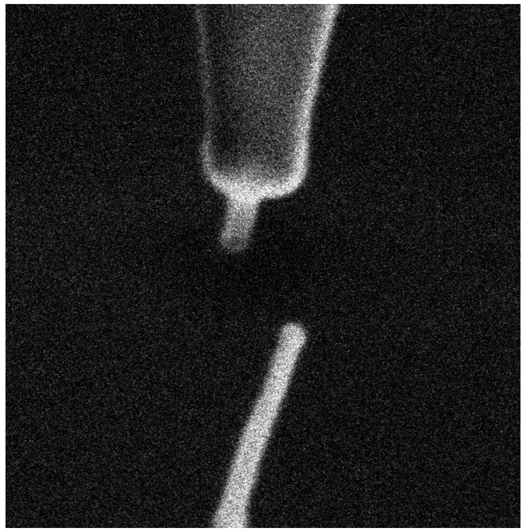
Ionic transport



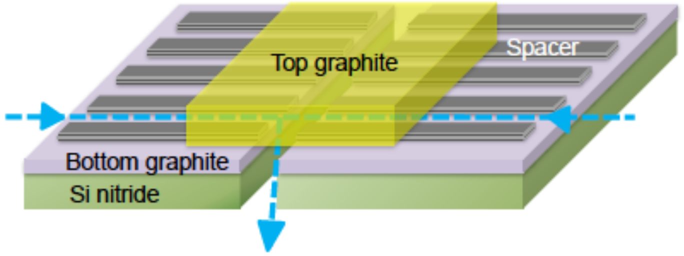


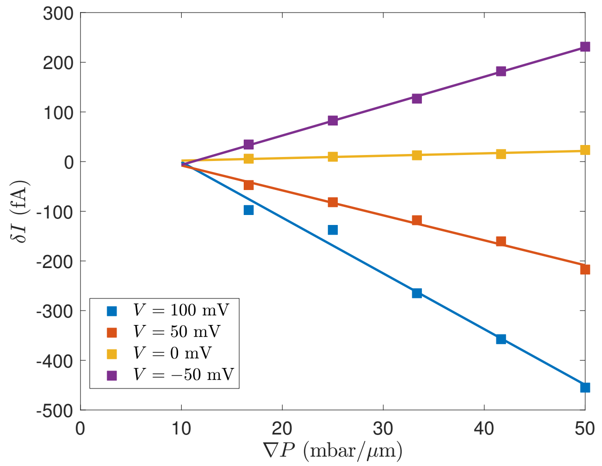
Mass transport and interfacial properties





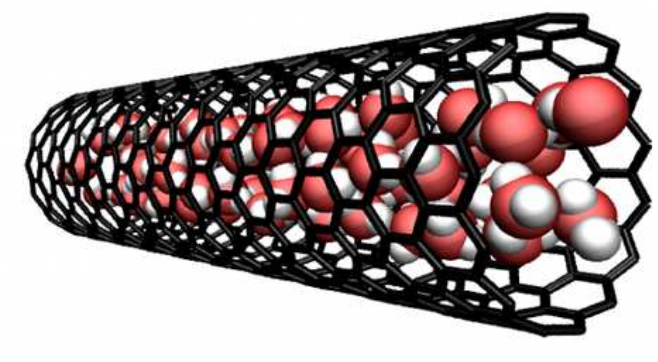
Nonlinear transport

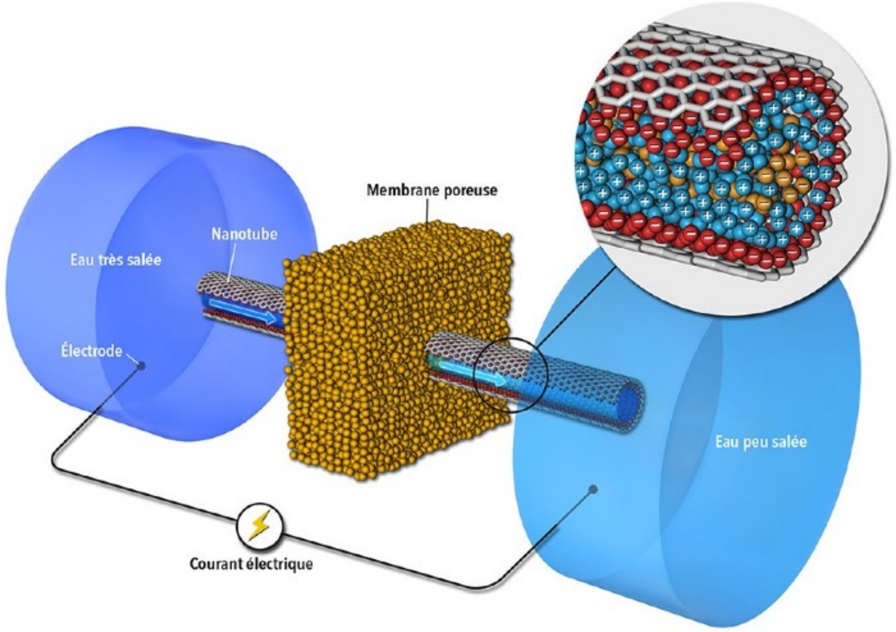




TOWARDS SINGLE NANOTUBES

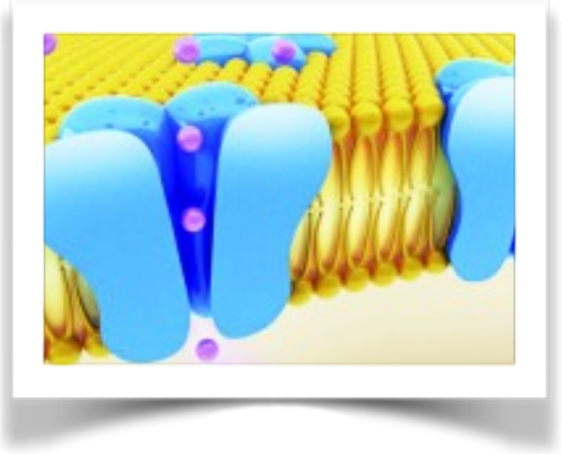
assess fundamentals of transport in **single nanotubes**

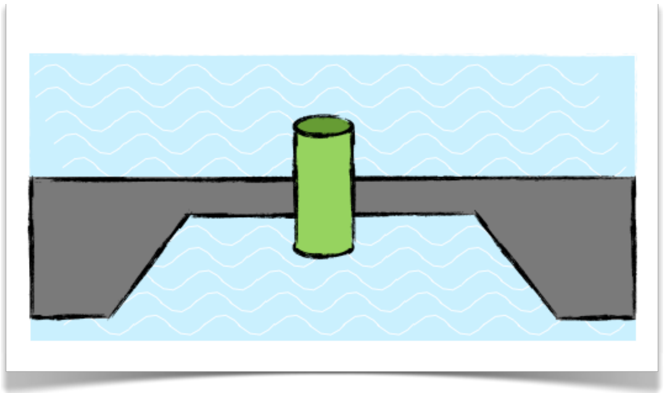




transport in nano-channels for a better fundamental understanding

NANO TOOLBOX





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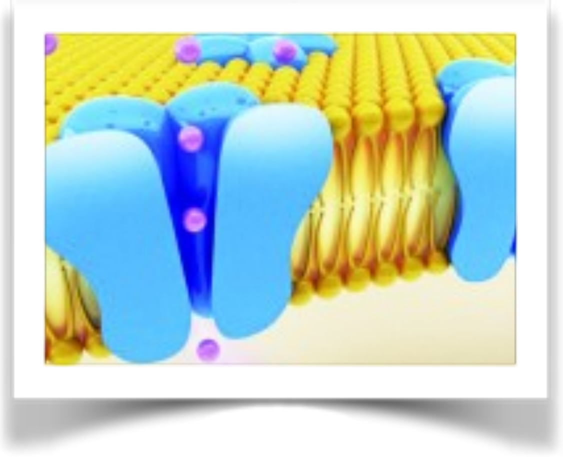
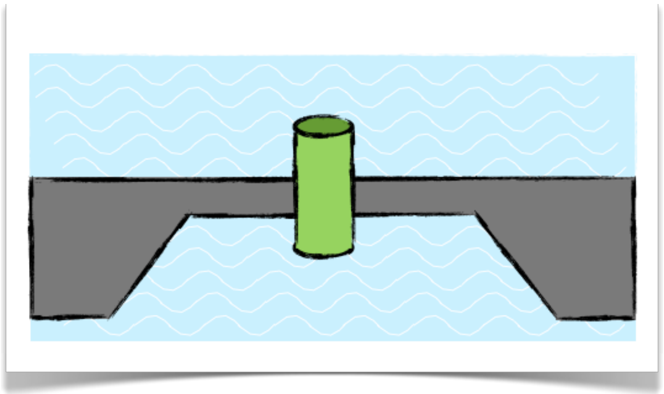
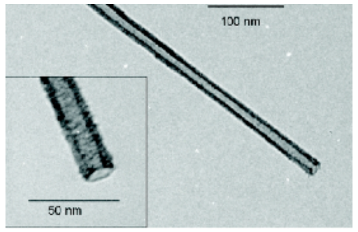




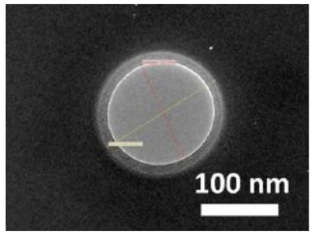
nanostructure building blocks

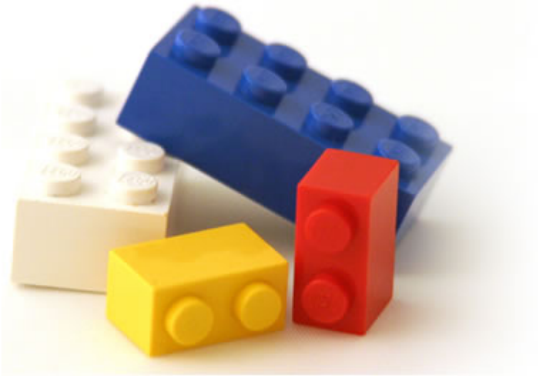
Open nanotube



+

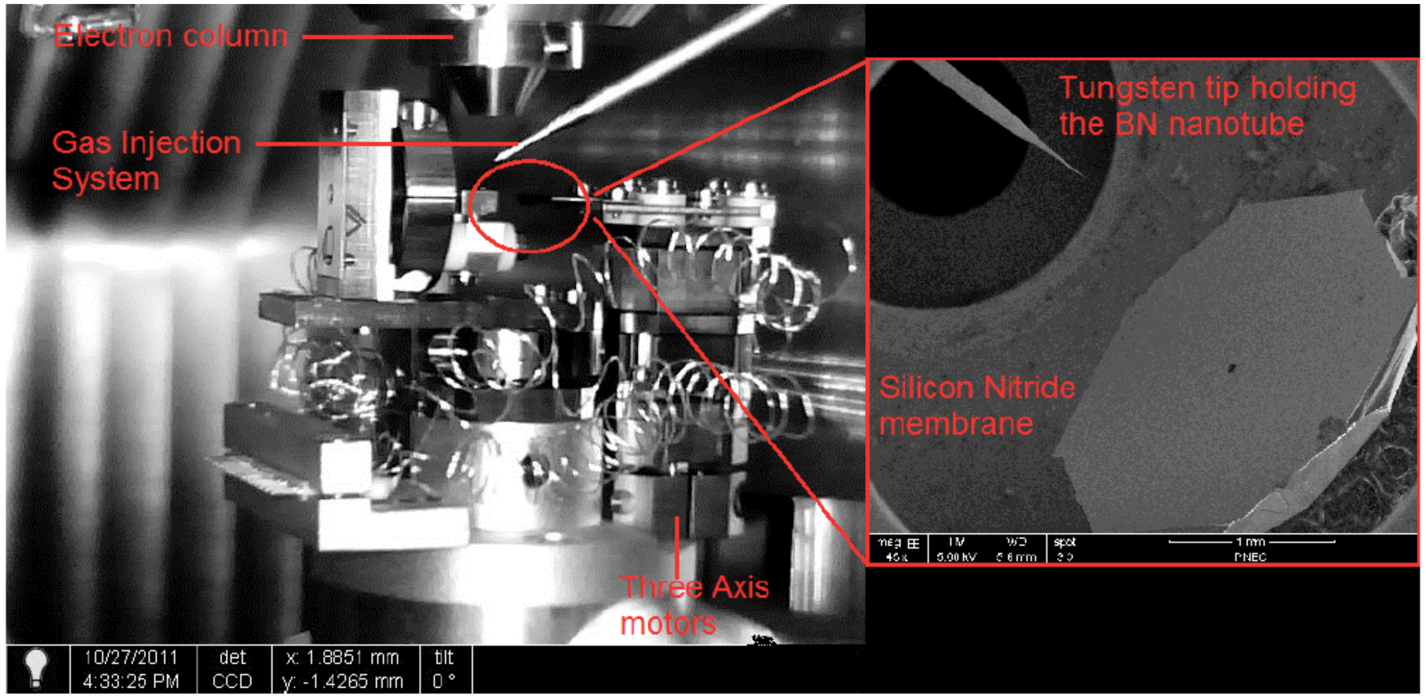
Drilled membrane





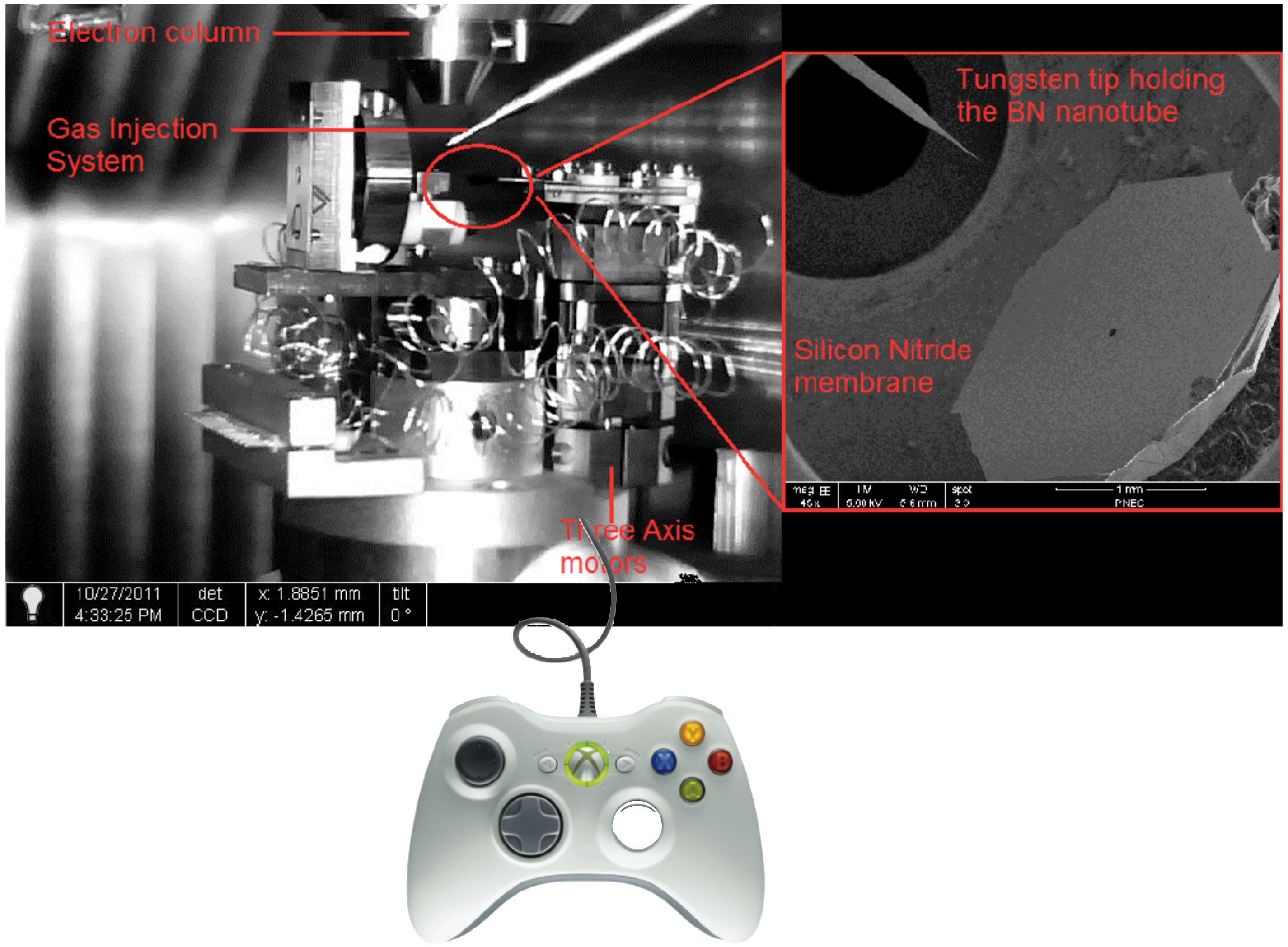
with Alessandro Siria since 2011

Scanning Electron Microscope in situ manipulation



PSL★
RESEARCH
UNIVERSITY

Scanning Electron Microscope in situ manipulation



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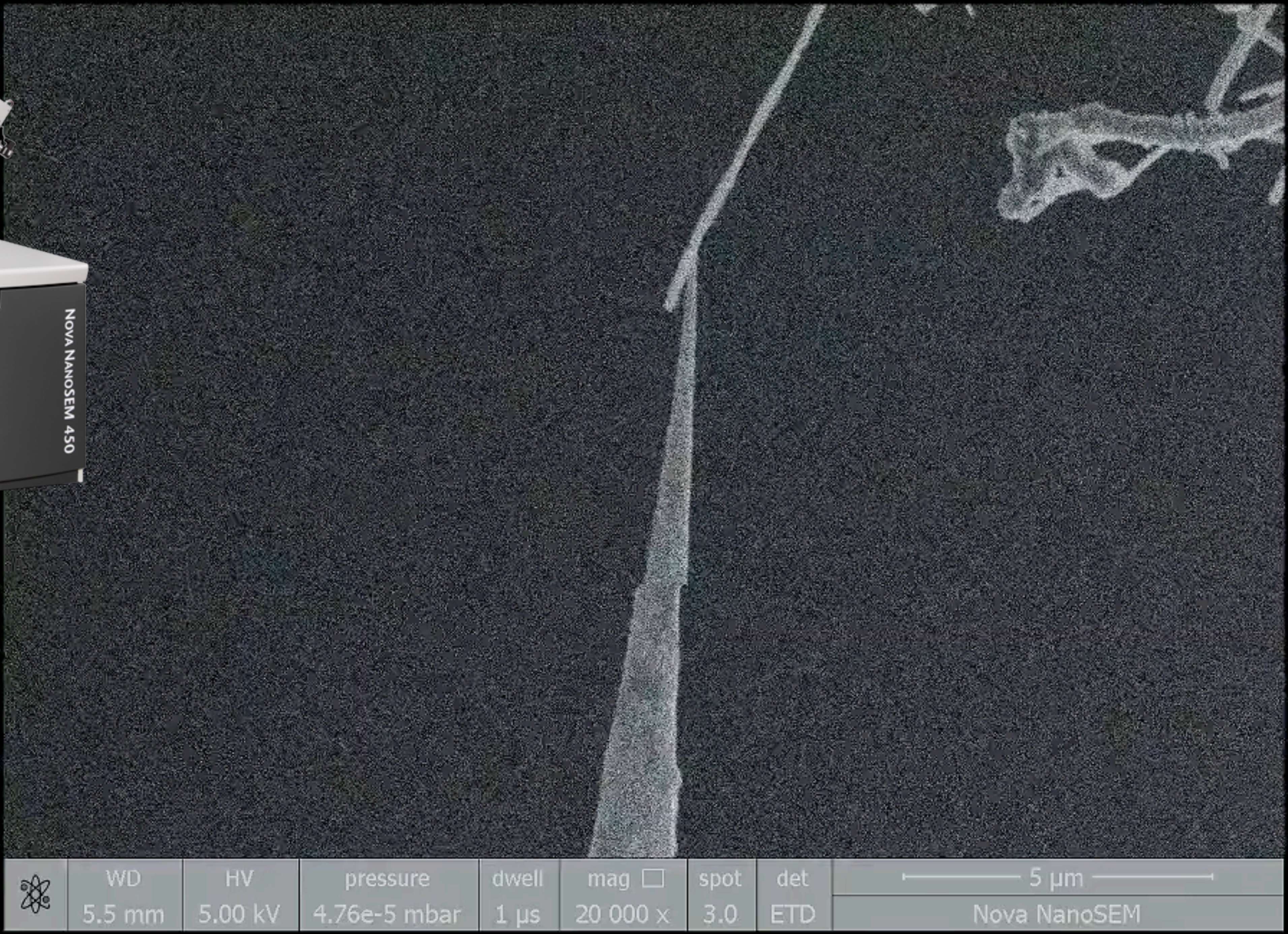
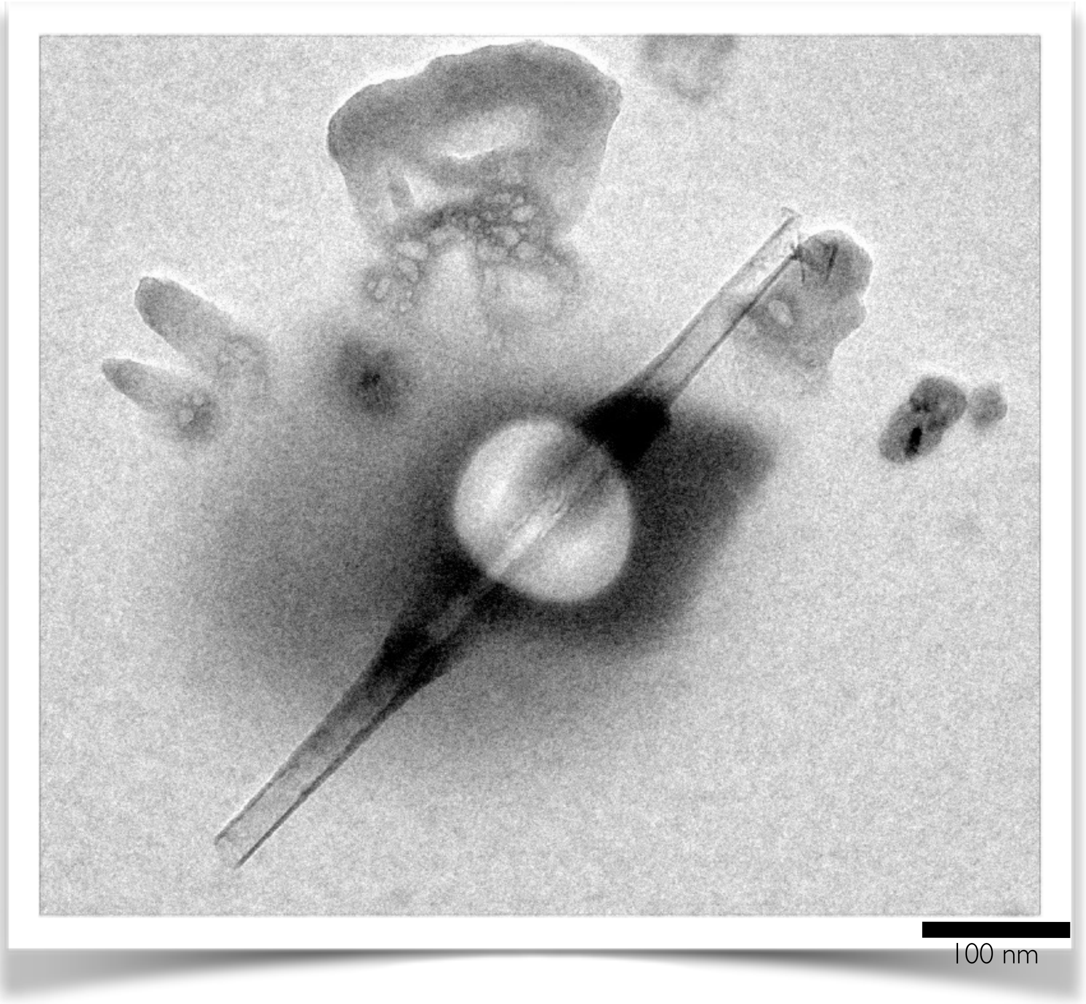
Nova NanoSEM 450

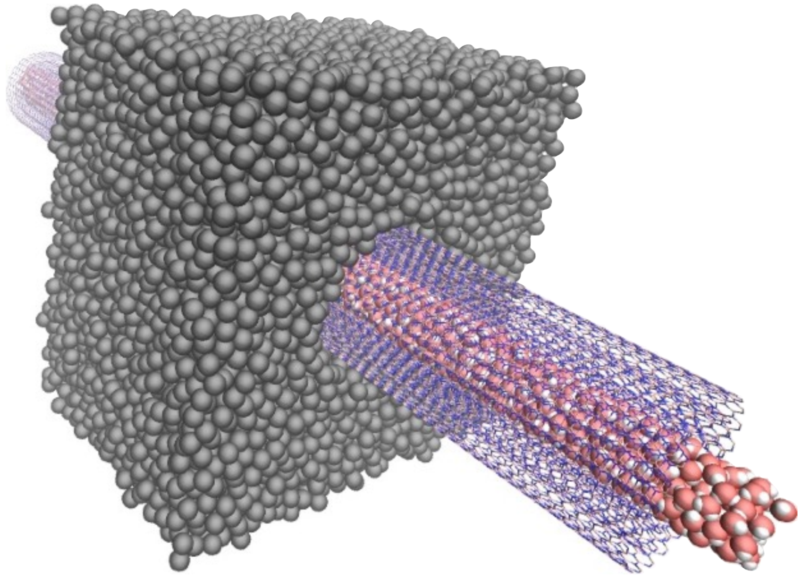

WD
5.5 mm
HV
5.00 kV
pressure
4.76e-5 mbar
dwell
1 µs
mag ☐
20 000 x
spot
3.0
det
ETD
5 µm
Nova NanoSEM

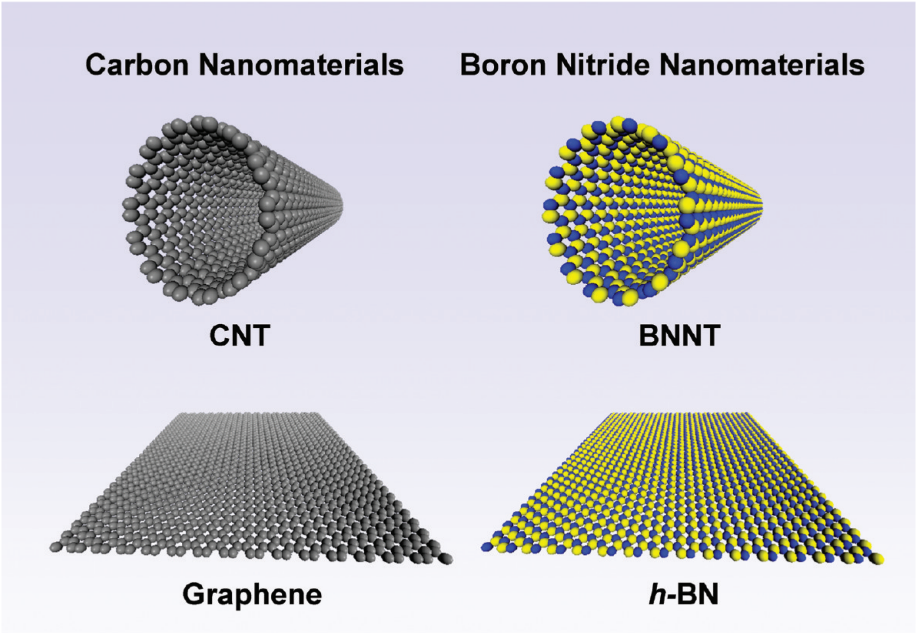
PSL
RESEARCH UNIVERSITY

TRANSMEMBRANE NANOTUBE



Here nanotubes:
multiwall Boron-Nitride nanotube
and Carbon nanotubes





3.WATER FLOW IN SINGLE CNT

Now, back to fundamentals:

are carbon materials specific to transport ?

and why ?

➡ superlubricity of carbon nanotubes ?

requires some fundamentals insight into transport across carbon materials

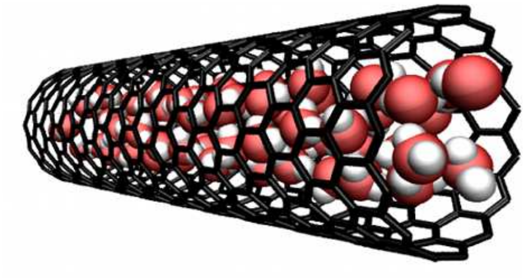
experimental challenge…

FLOW THROUGH SINGLE NANOTUBE

Fast flows through single CNT vs BNNT ?

Question: permeability of single nanotubes ?

$$v_{flow} = \frac{\boxed{k}}{\eta}\frac{\Delta P}{L}$$



Challenge: flow through single nanotubes is too small to be measured using standard techniques

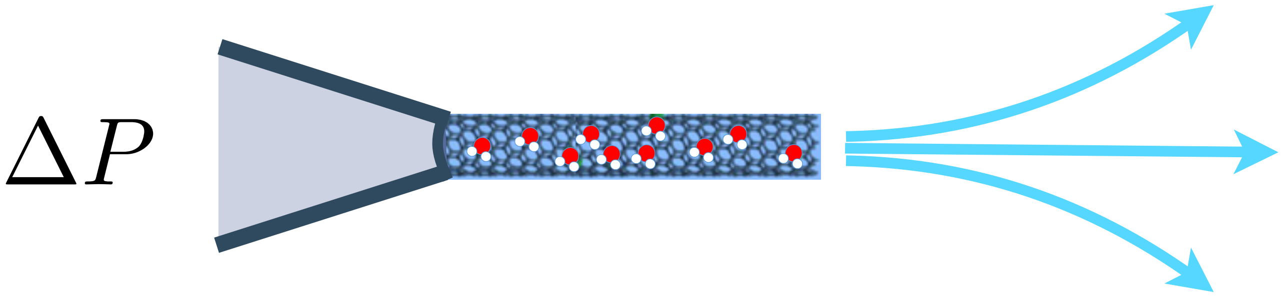
requires resolution below femto-L/s, presently at most pico-L/s

ROUTE TO MEASURE FLOW

a water nano-jet emerging from a single nanotube

the peculiarity of the flow allows for a dye free flow measurement, with unprecedented sensitivity

CNT inserted in a pipette



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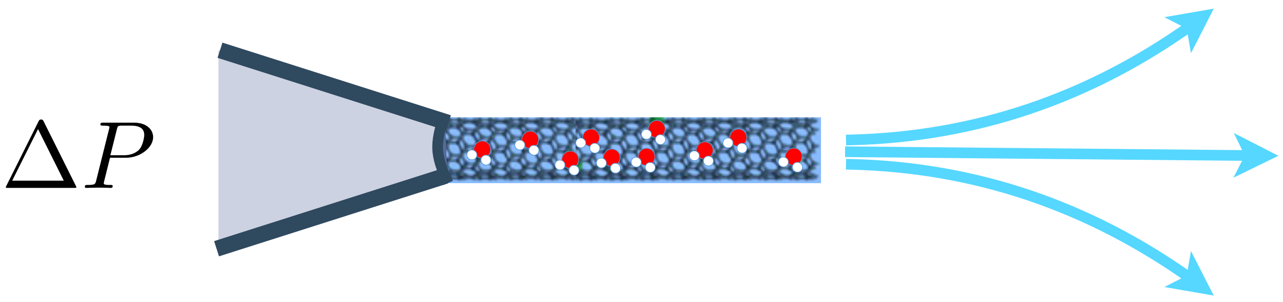
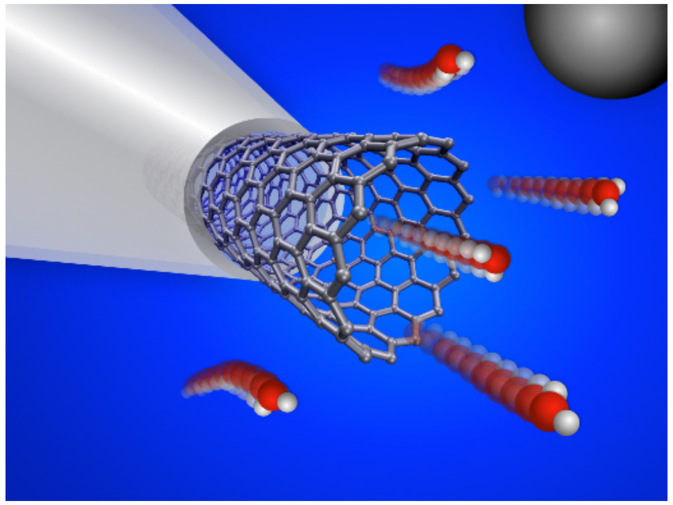
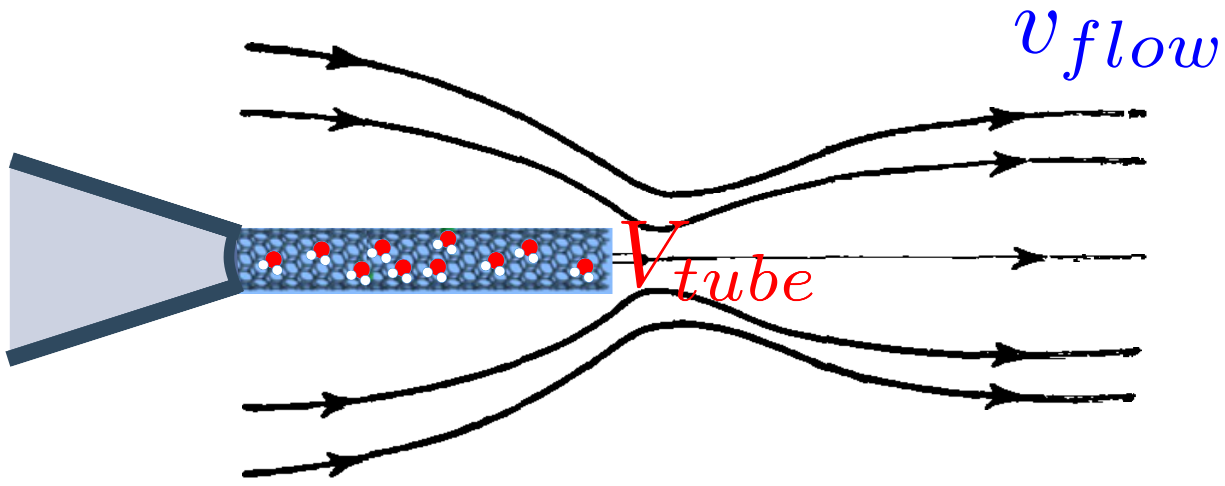


CNT inserted in a pipette



FLOW THROUGH SINGLE NANOTUBE

Harvest the specificities of the Landau-Squire **jet flow**



Landau, Fluid dynamics

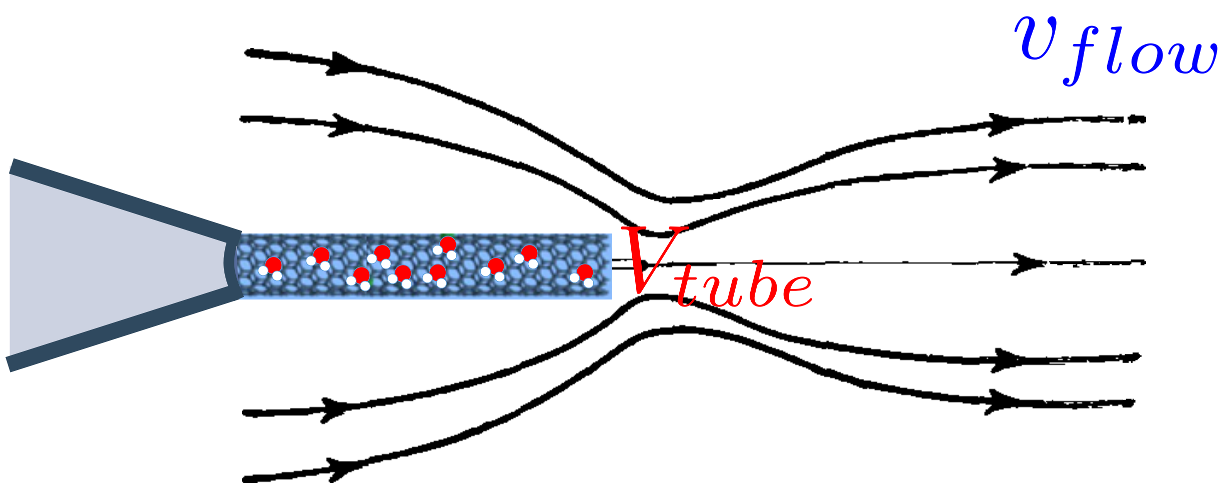
Flow generated from a semi-infinite pipe towards a reservoir

$$v_{flow} \sim \frac{F_p}{4\pi\eta} \times \frac{1}{r}$$

MEASURE A FORCE, NOT A FLUX

FLOW THROUGH SINGLE NANOTUBE

Harvest the specificities of the Landau-Squire **jet flow**



Landau, Fluid dynamics

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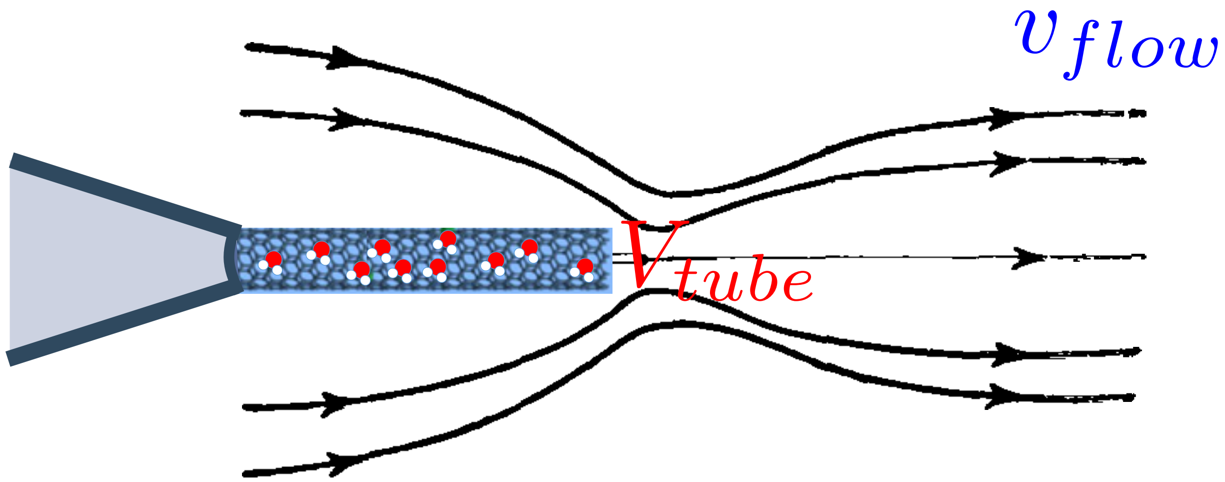
Scalings (tube radius R): $F_P \sim \eta\, R\, V_{tube}$ $Q \sim R^2\, V_{tube}$

FLOW THROUGH SINGLE NANOTUBE

Harvest the specificities of the Landau-Squire **jet flow**



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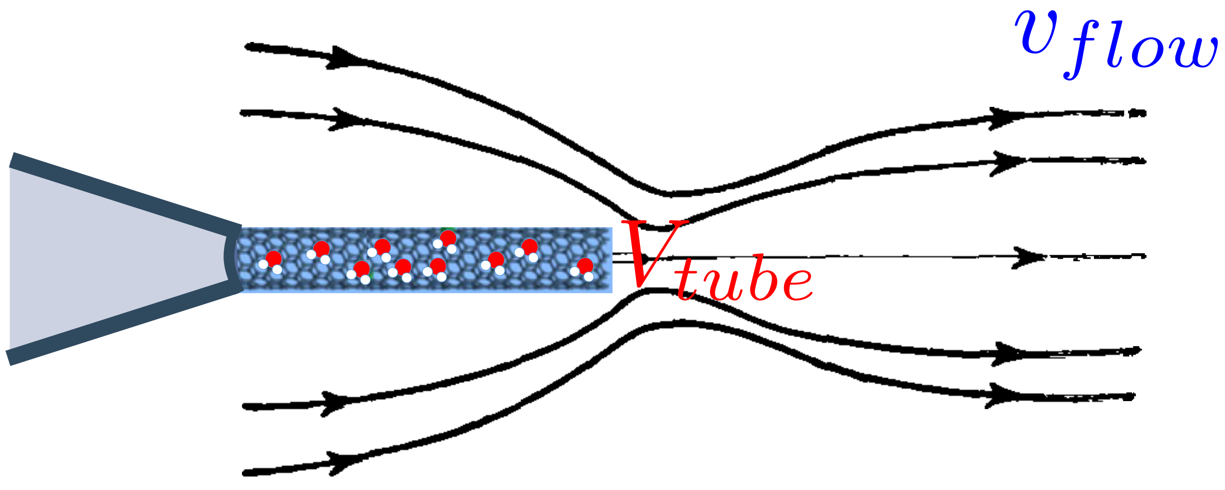

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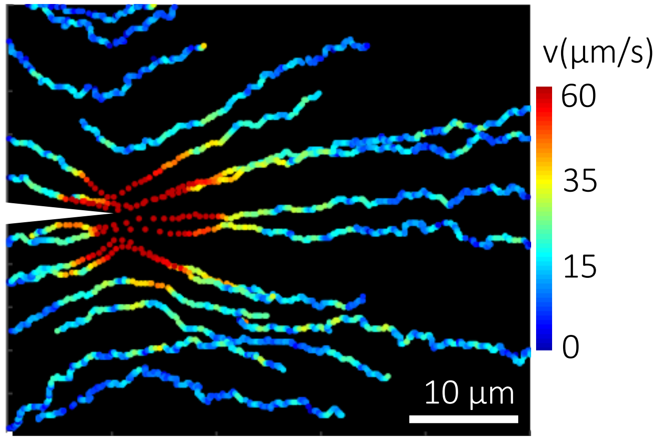
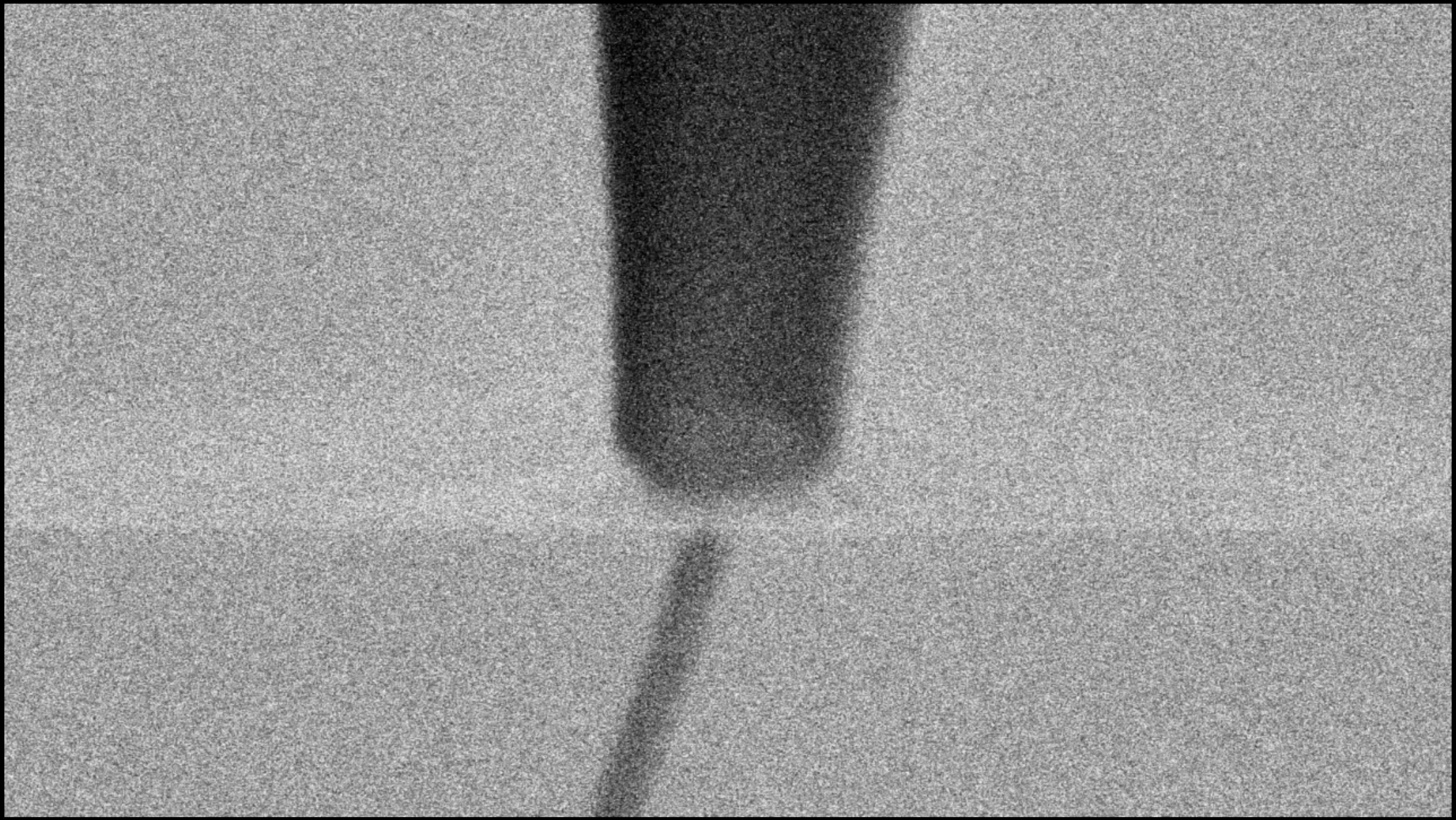
A nanotube creates a measurable flow !

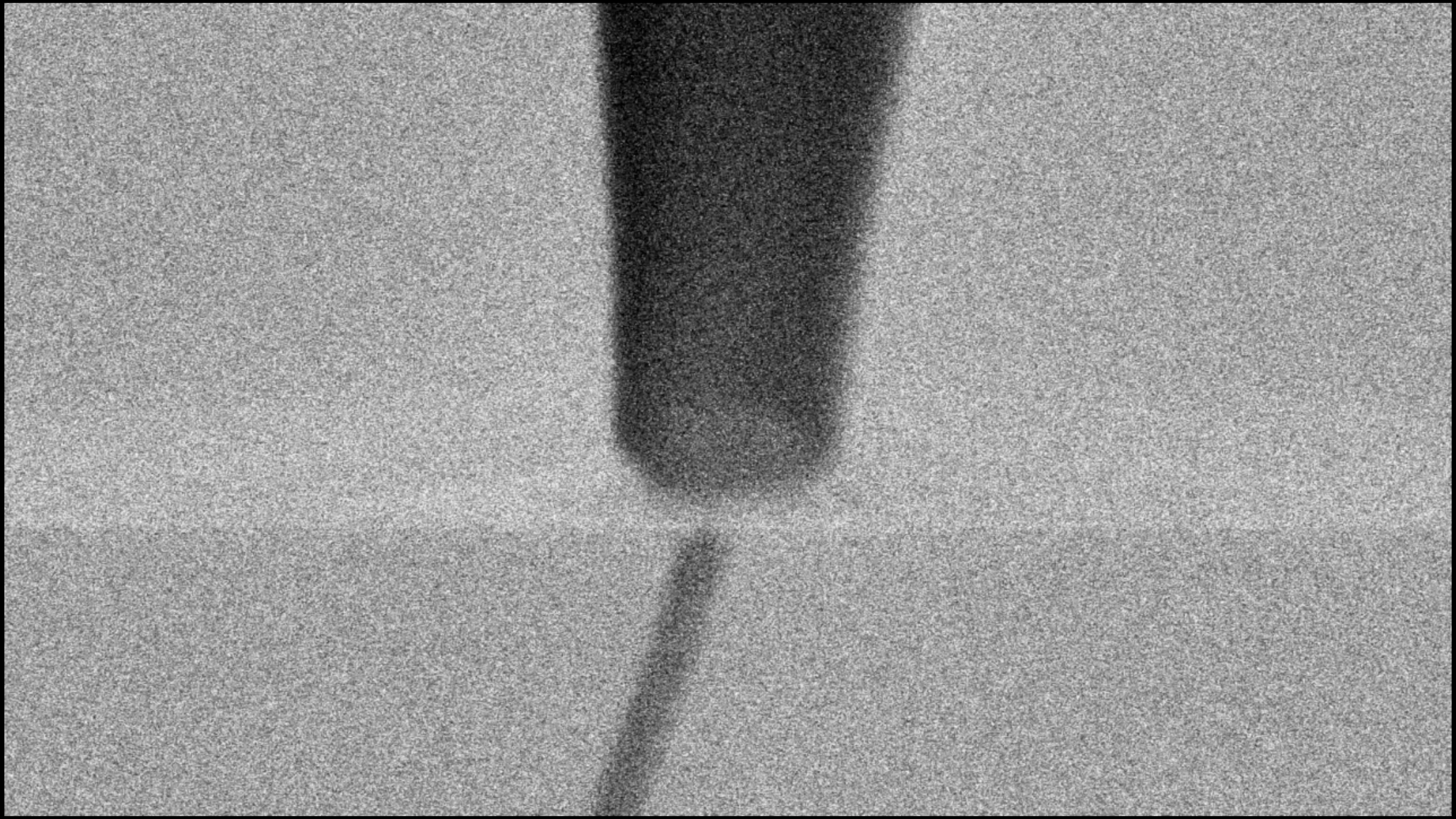


33nm CNT

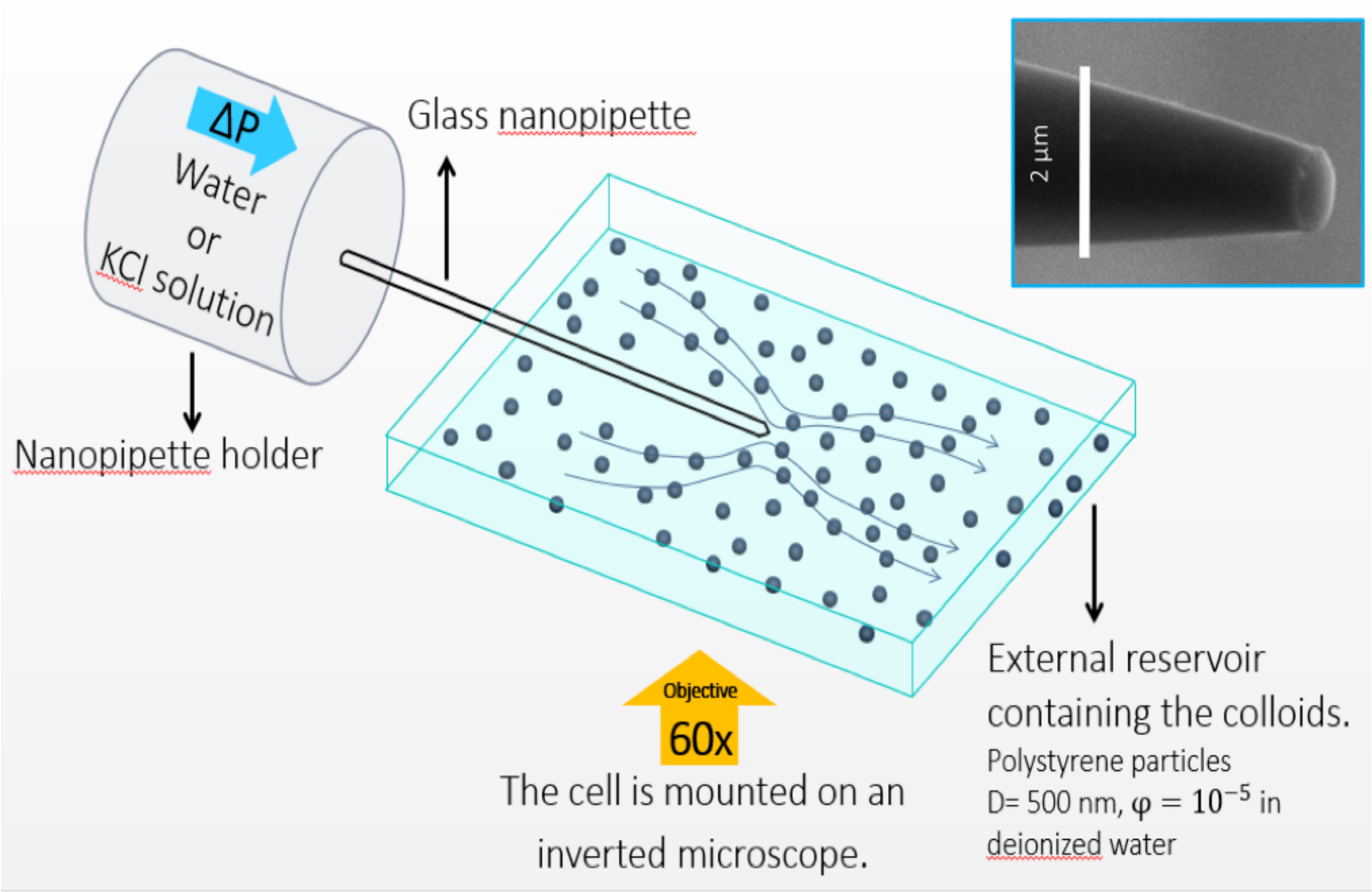

NOVA NANOSEM 450
FEI




Nova NanoSEM 450



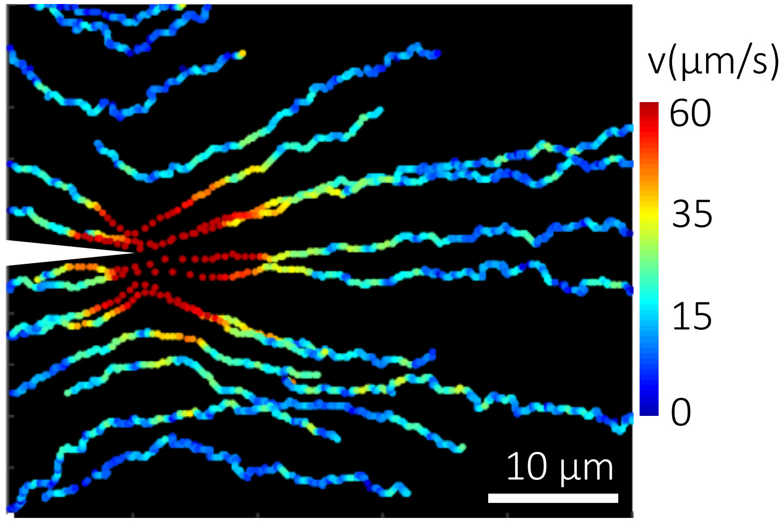
NANOJET FLOWS



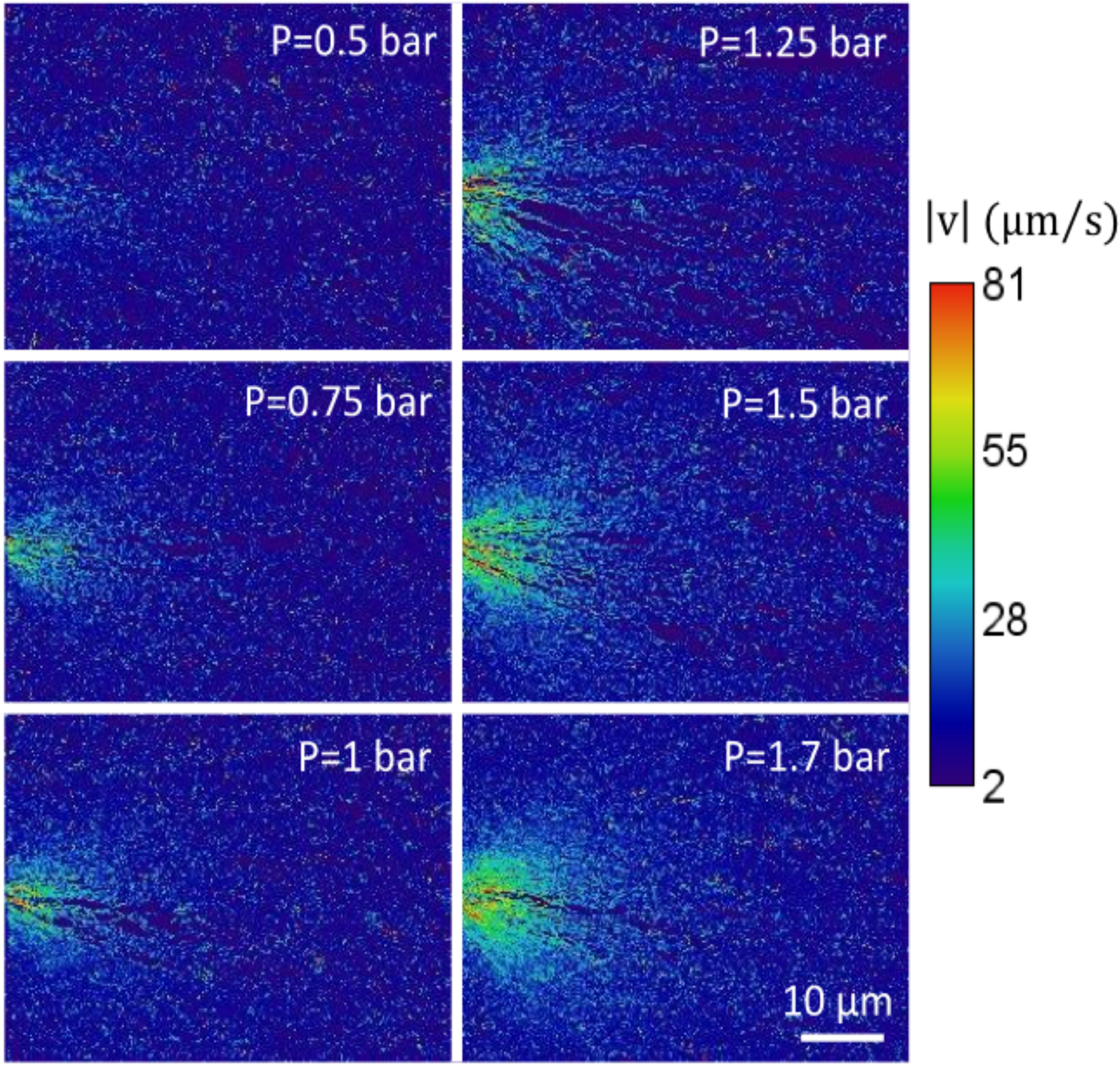
Strategy:

1. measure the flow induced in the reservoir
2. deduce the mean velocity inside the nanotube

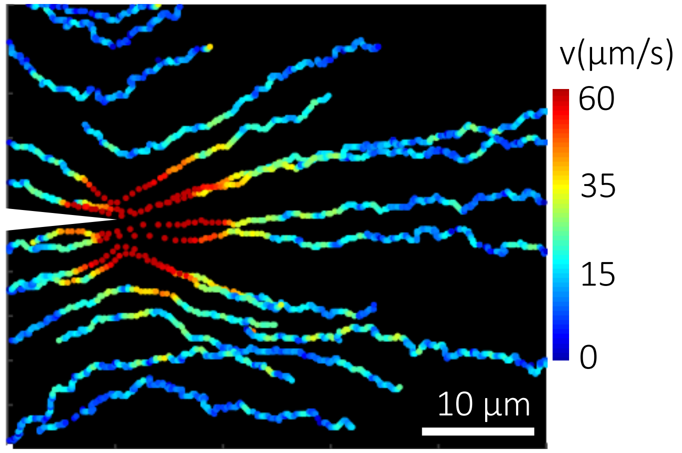
PROBE FLOW THROUGH A ***SINGLE CNT***



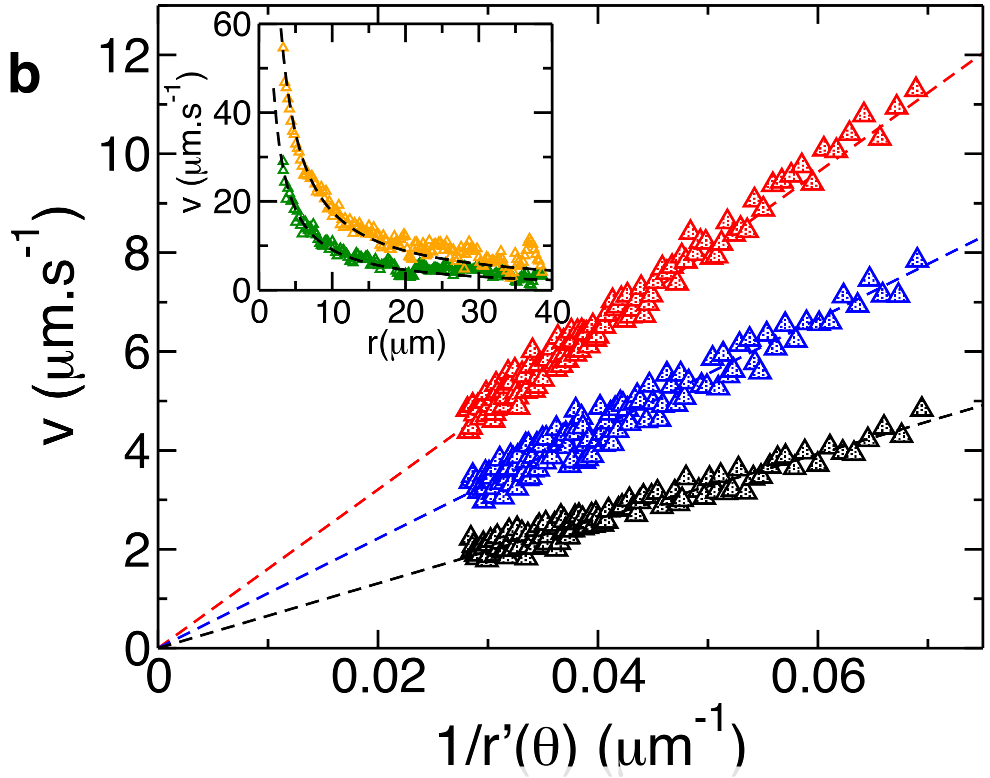
CNT 33nm

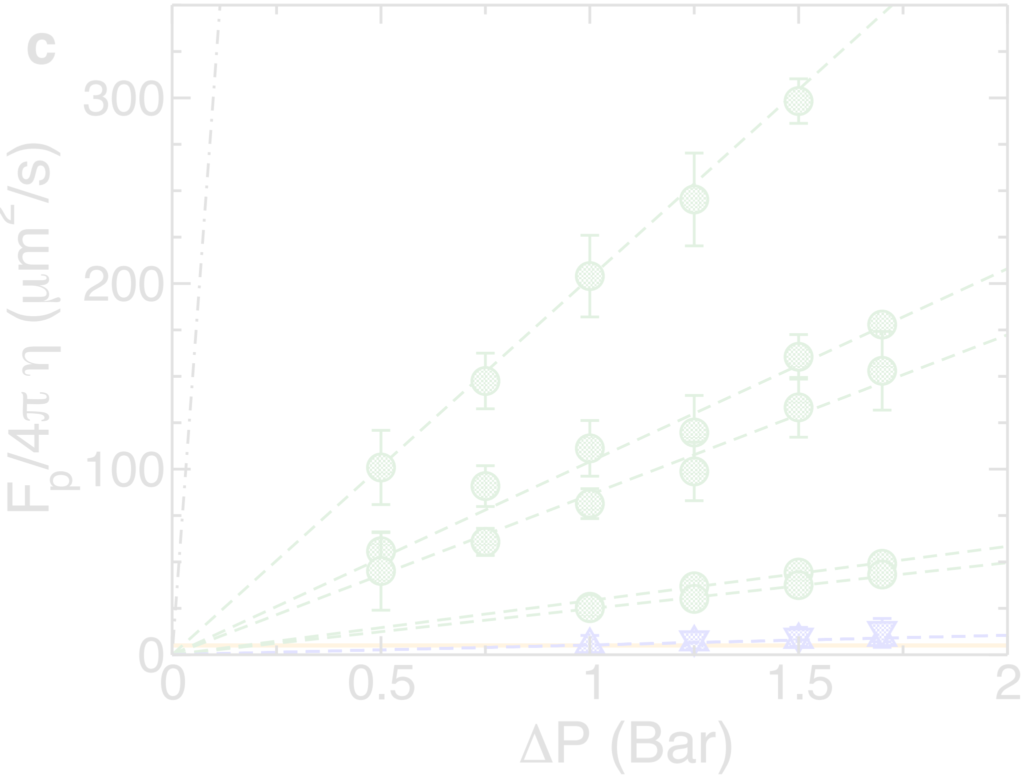


MORE QUANTITATIVELY

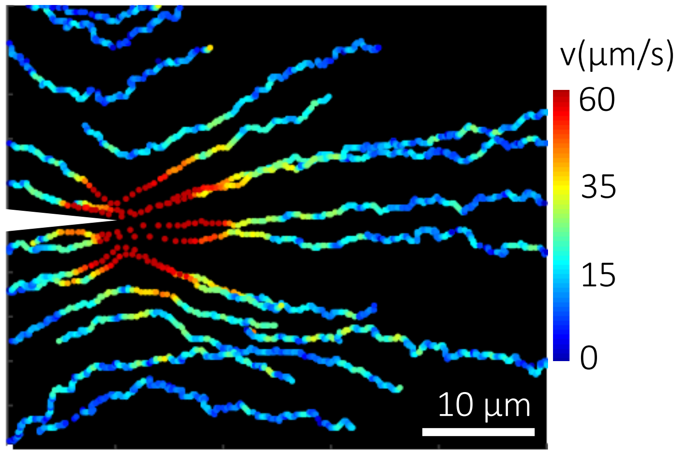


$$v_{flow} \sim \frac{F_P}{4\pi\eta} \times \frac{1}{r}$$





MORE QUANTITATIVELY

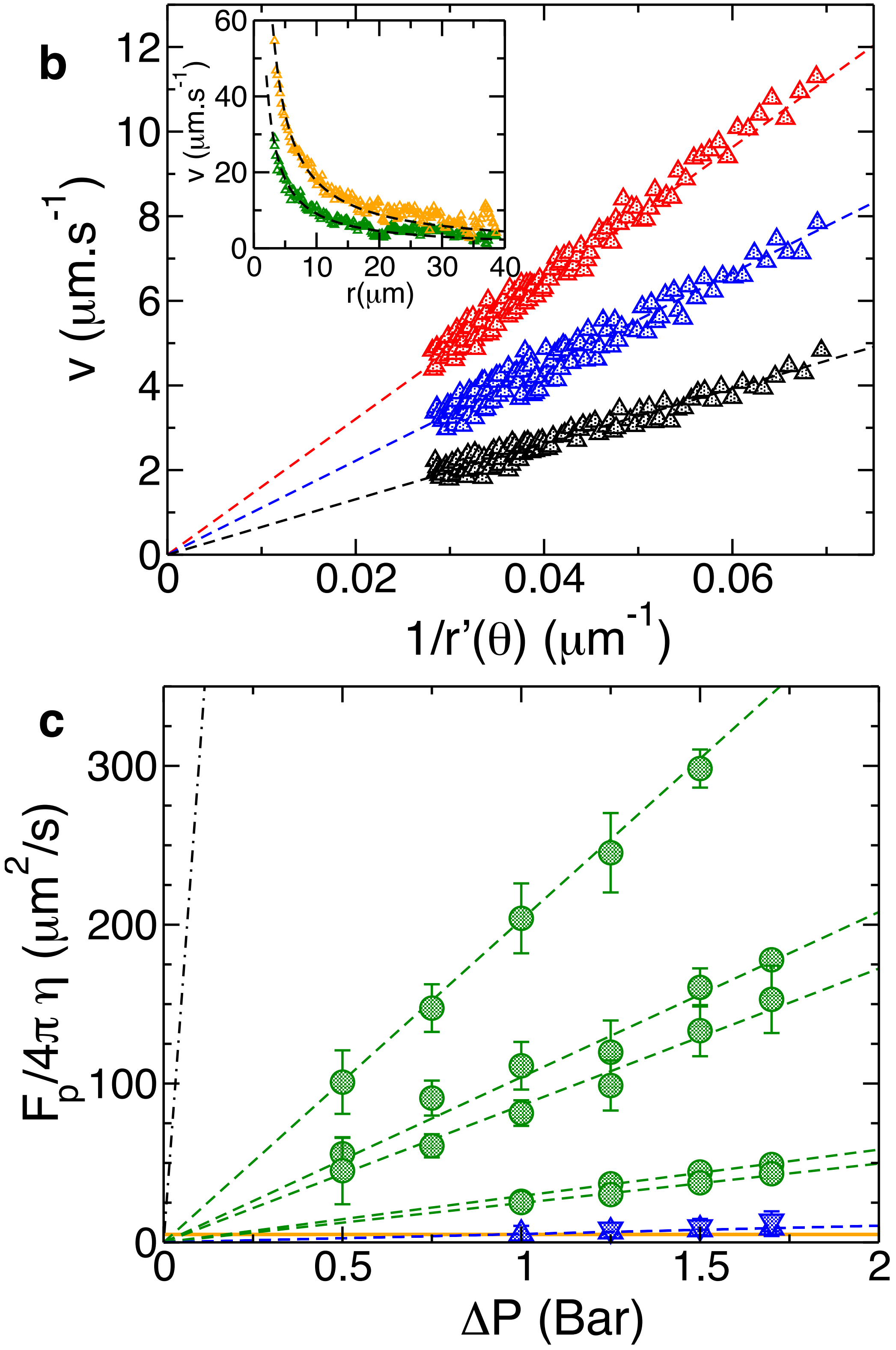


$$v_{flow} \sim \frac{F_P}{4\pi\eta} \times \frac{1}{r}$$

$$F_P = \alpha\,\eta\,R \times V_{tube}$$

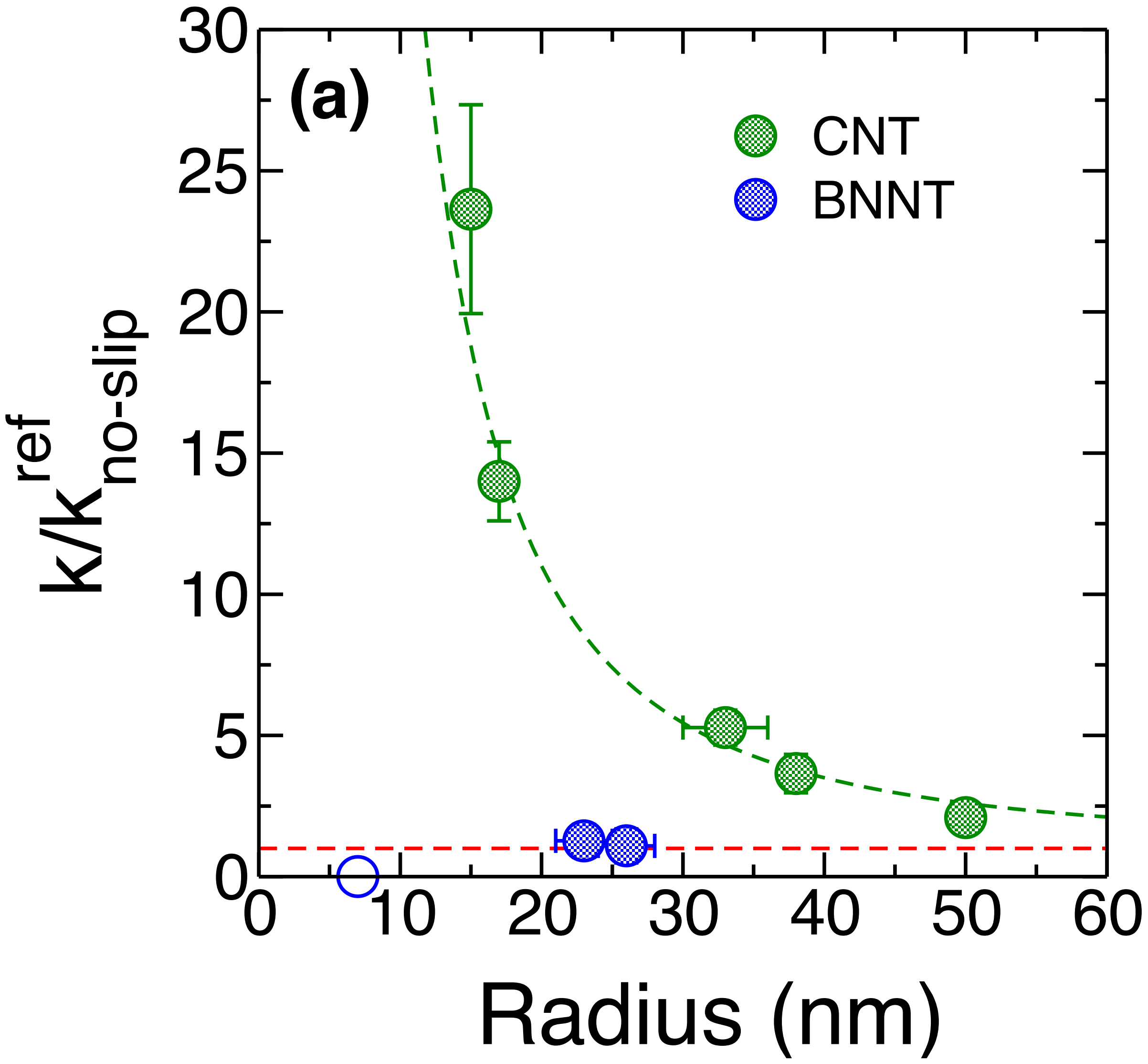
$$V_{tube} = \frac{k}{\eta}\,\frac{\Delta P}{L}$$

$$F_p = \frac{\alpha\,R\,k}{L} \times \Delta P$$



STRONGLY INCREASED PERMEABILITY IN CNTS… NOT IN BNNTS

Permeability



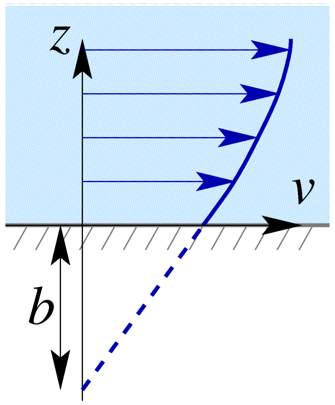
$$V_{tube} = \frac{k}{\eta}\frac{\Delta P}{L}$$

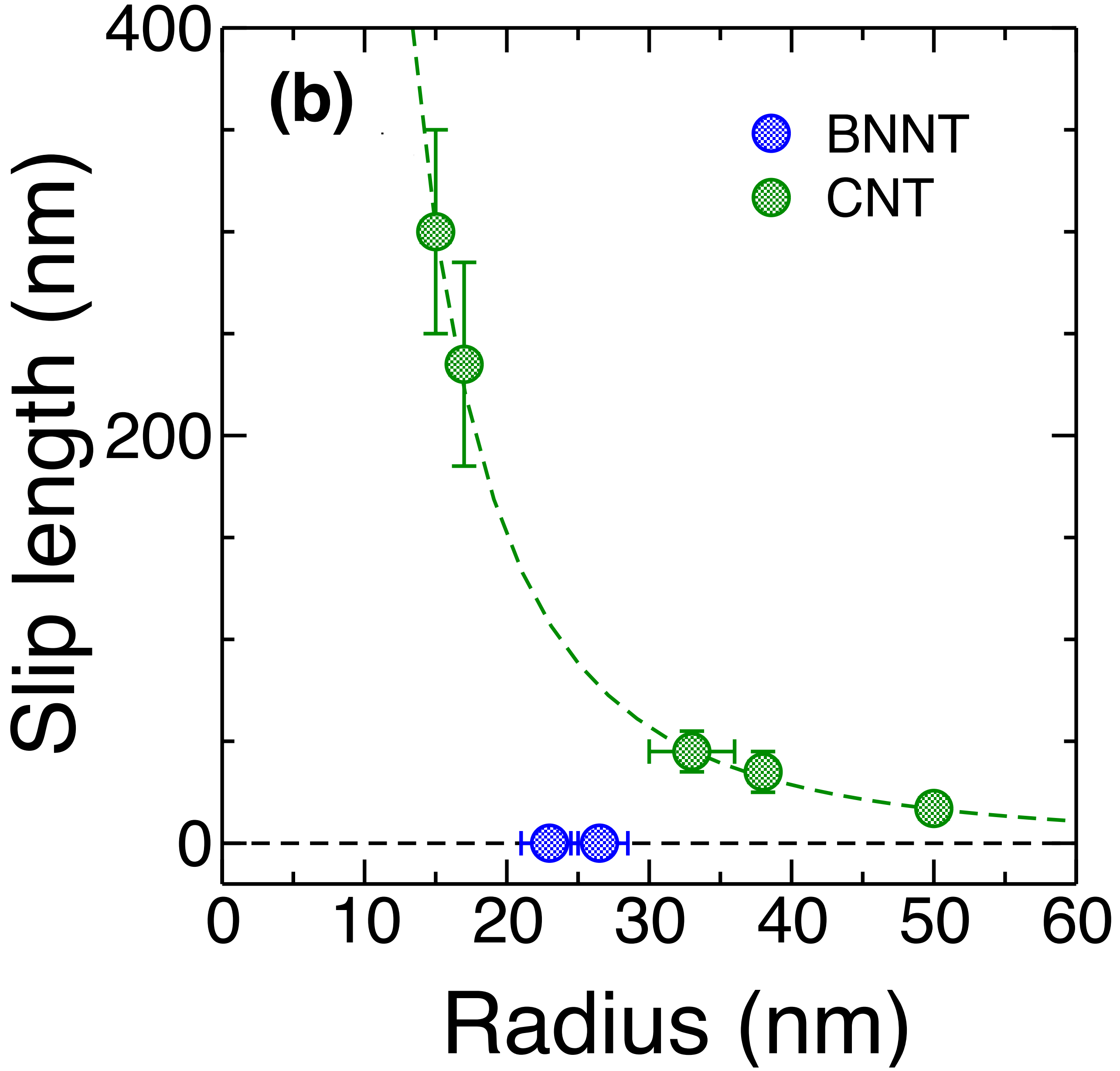
$$k_{\mathrm{no-slip}} = \frac{R^2}{8}$$

Secchi, Marbach, Niguès, Stein, Siria, Bocquet, **Nature** 537 (7619), 210-213 (2016)

Secchi, Marbach, Niguès, Siria, Bocquet, **JFM** (2017)

RADIUS DEPENDENT SLIPPAGE IN CNTS





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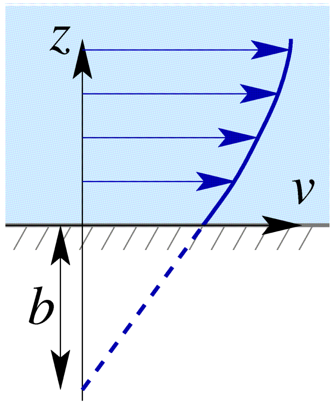
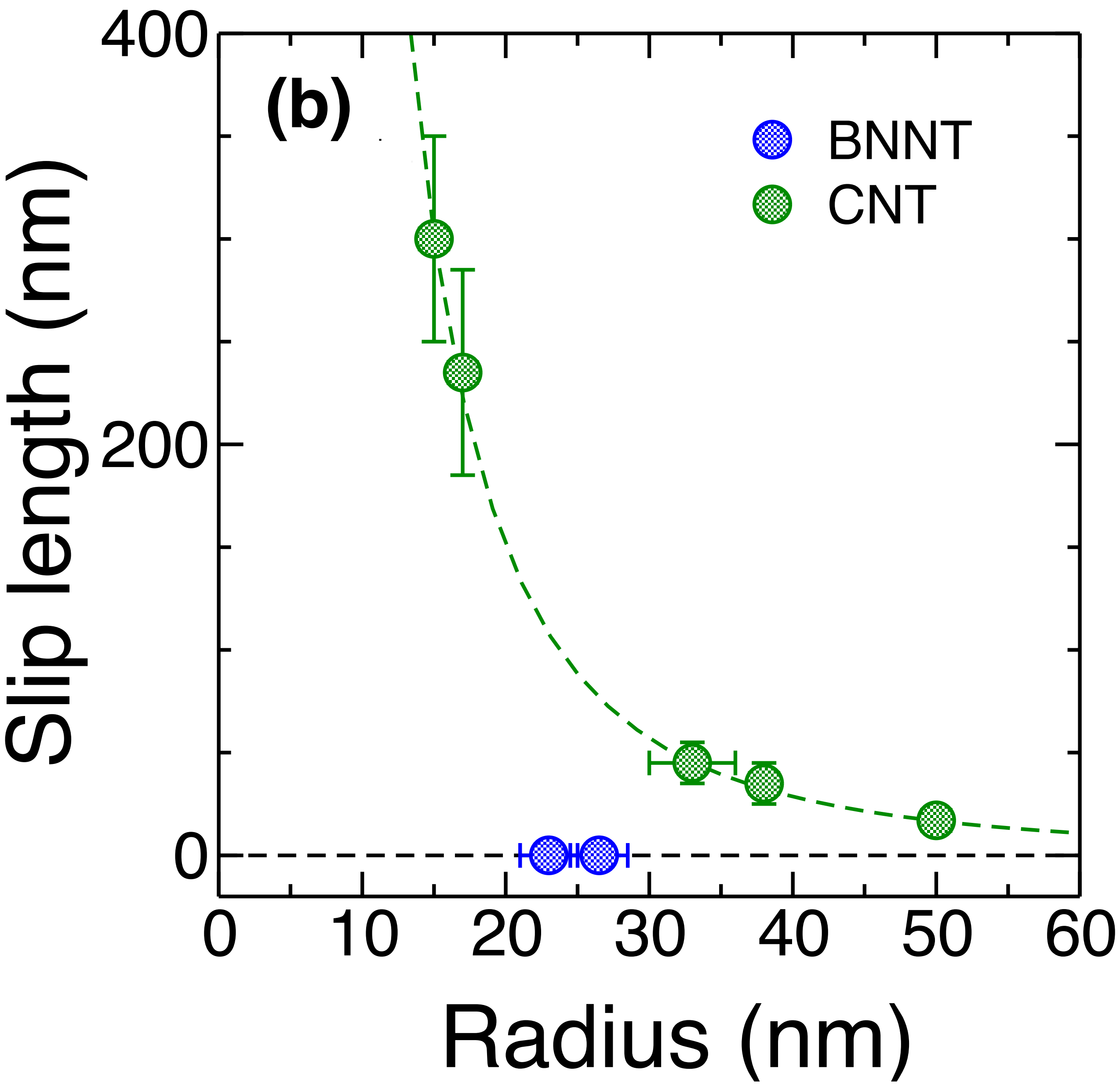
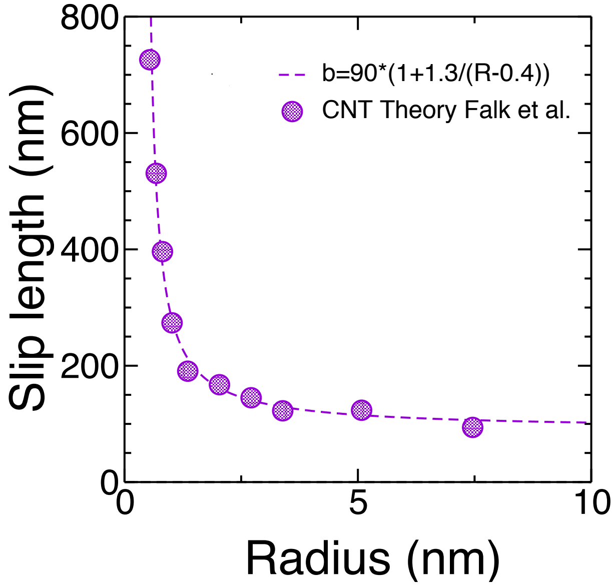




Theory

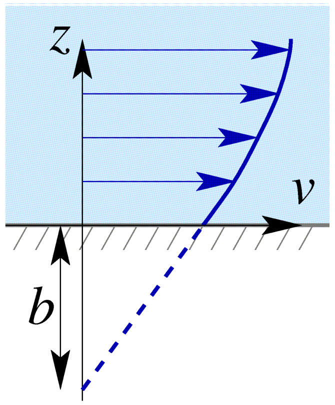


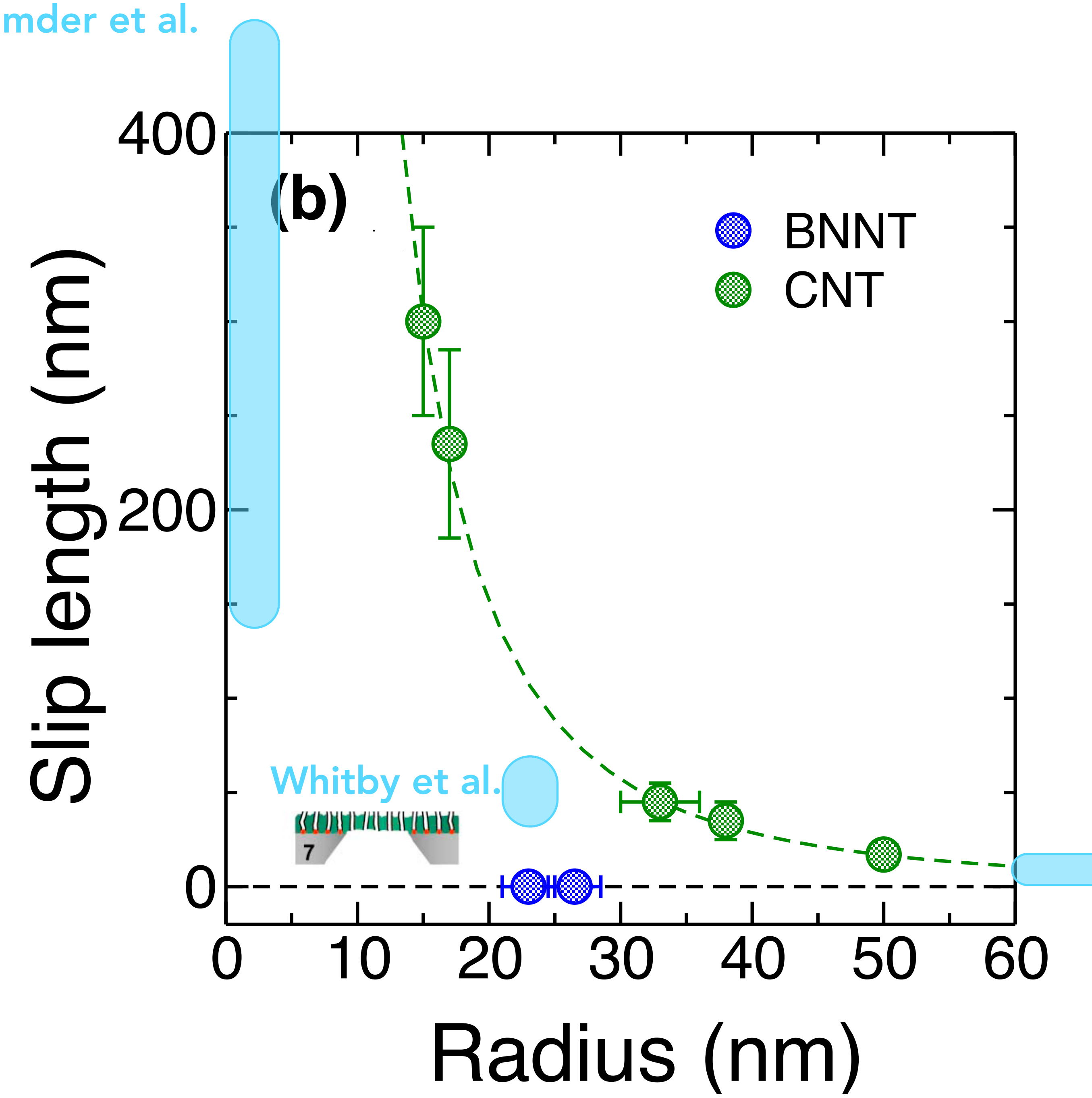
Falk et al. NanoLett (2010)

Secchi, Marbach, Niguès, Stein, Siria, Bocquet, **Nature** 537 (7619), 210-213(2016)

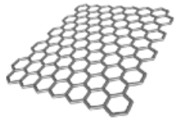
RADIUS DEPENDENT SLIPPAGE IN CNTS

Bakajin et al., Majumder et al.

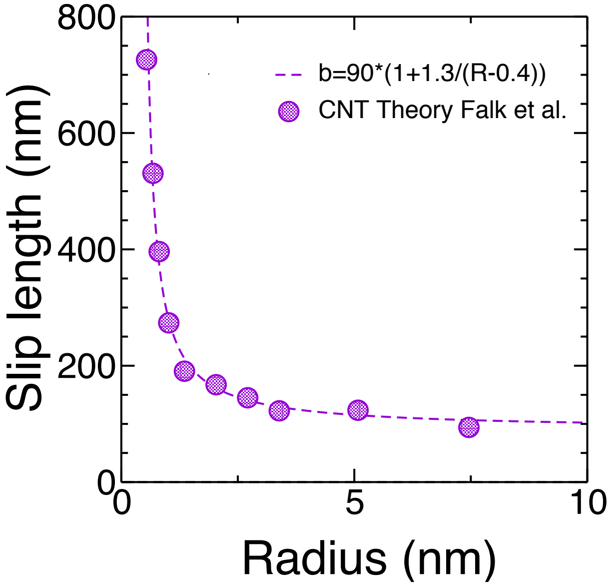




Maali et al.



Theory



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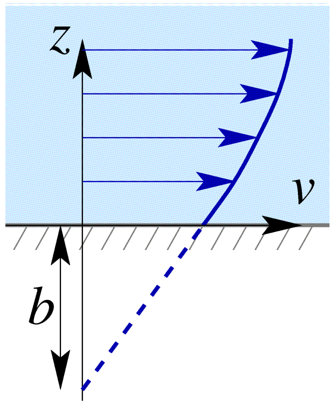
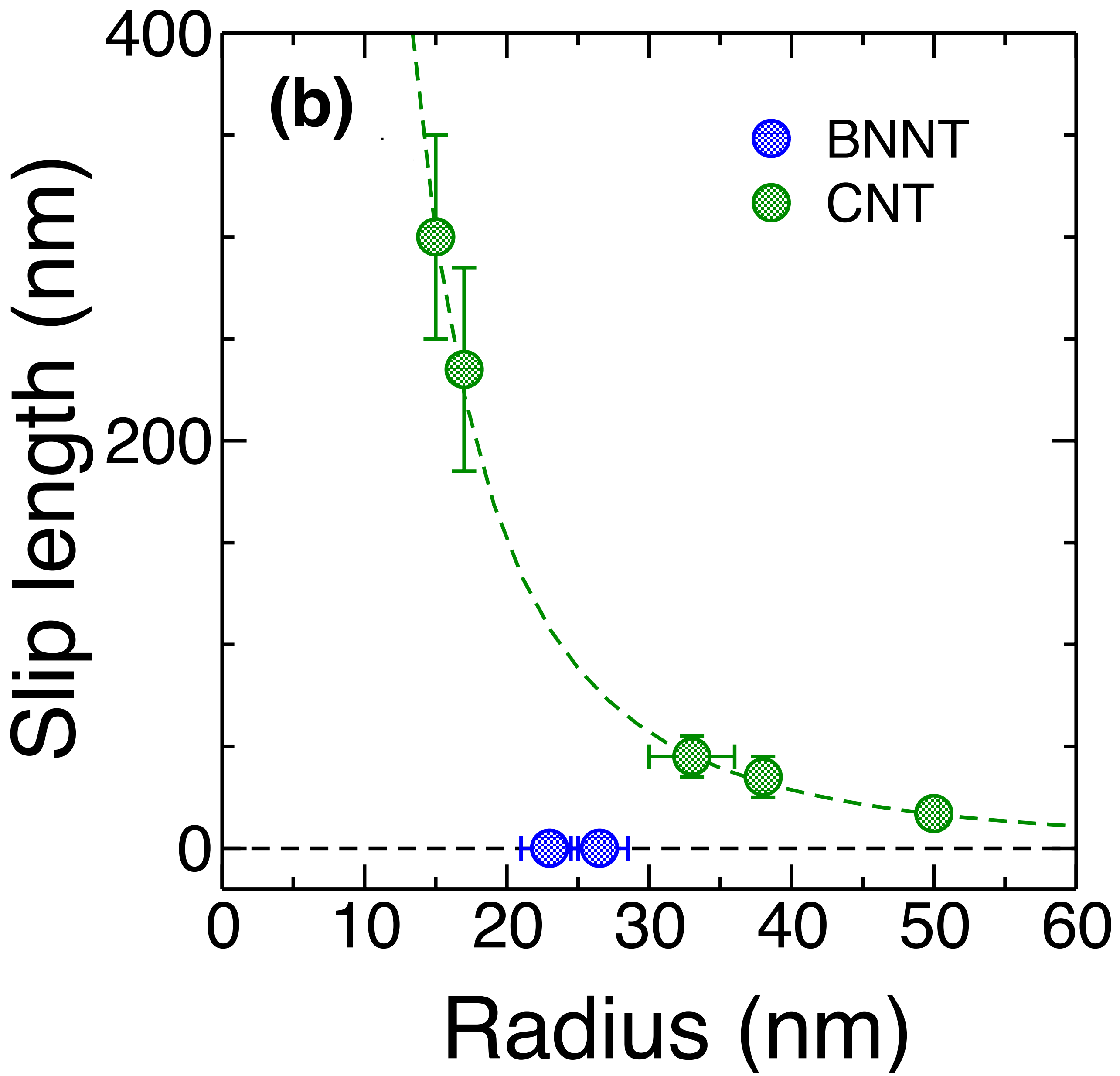
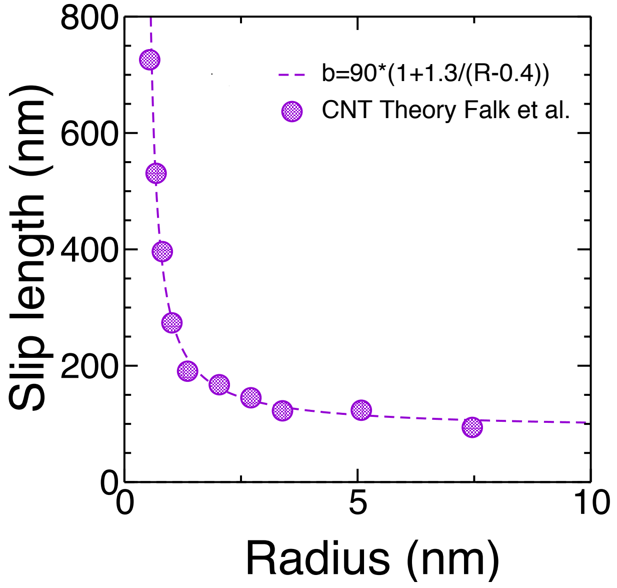




Theory



Falk et al. NanoLett (2010)

HUGE DIFFERENCE CNT/BNNT, WHILE SAME CRYSTALLOGRAPHY

Secchi, Marbach, Nigues, Stein, Siria, Bocquet, **Nature** 537 (7619), 210-213(2016)

CARBON VS BN NANOFLUIDICS

first mass flow measurements in single nanotubes

- radius dependent superlubricity of CNTs
  (qualitative *but not quantitative* agreement with theory)

- subtle (sub-)molecular origin: BN vs C
  cf not predicted by classical MD
  but by *ab initio* simulations: Tocci, Joly, Michaelides, Nanoletters 2014

- couple hydrodynamics with the electronic nature of the confining material (semi-metallic carbon vs insulating BN)

cross-road between soft and hard condensed matter

much to understand

CARBON VS BN NANOFLUIDICS

- subtle (sub-)molecular origin: BN vs C
- couple **hydrodynamics** with the **electronic** nature of the confining material (semi-metallic carbon vs insulating BN)
- many-body like fluidic transport: analogy with electronic transport

  gating, fluidic transistor, coulomb blockade

cross-road between soft and hard condensed matter

much to understand

COLLABORATORS

Micromégas team, Ecole Normale Supérieure

http://www.lps.ens.fr/-MICROMEGAS-?lang=en

ERC StG *NanoSoft*

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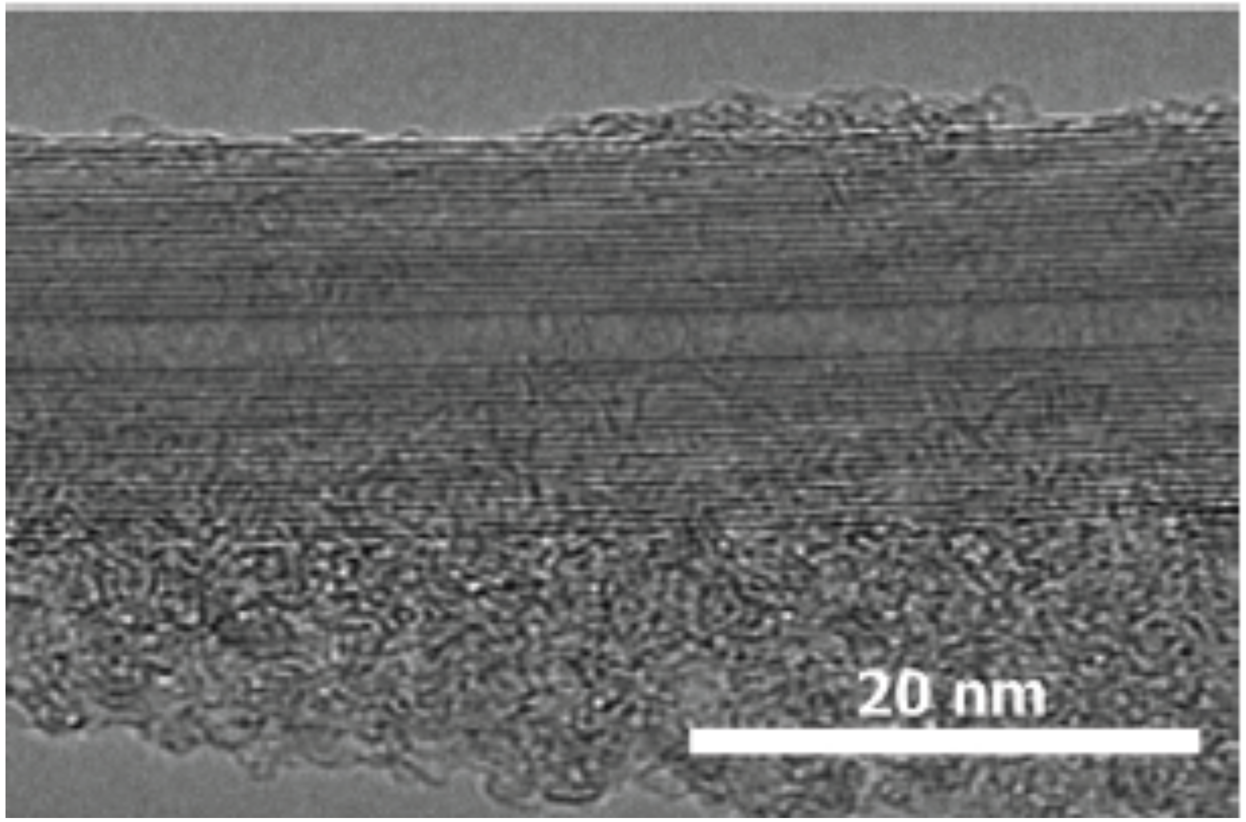
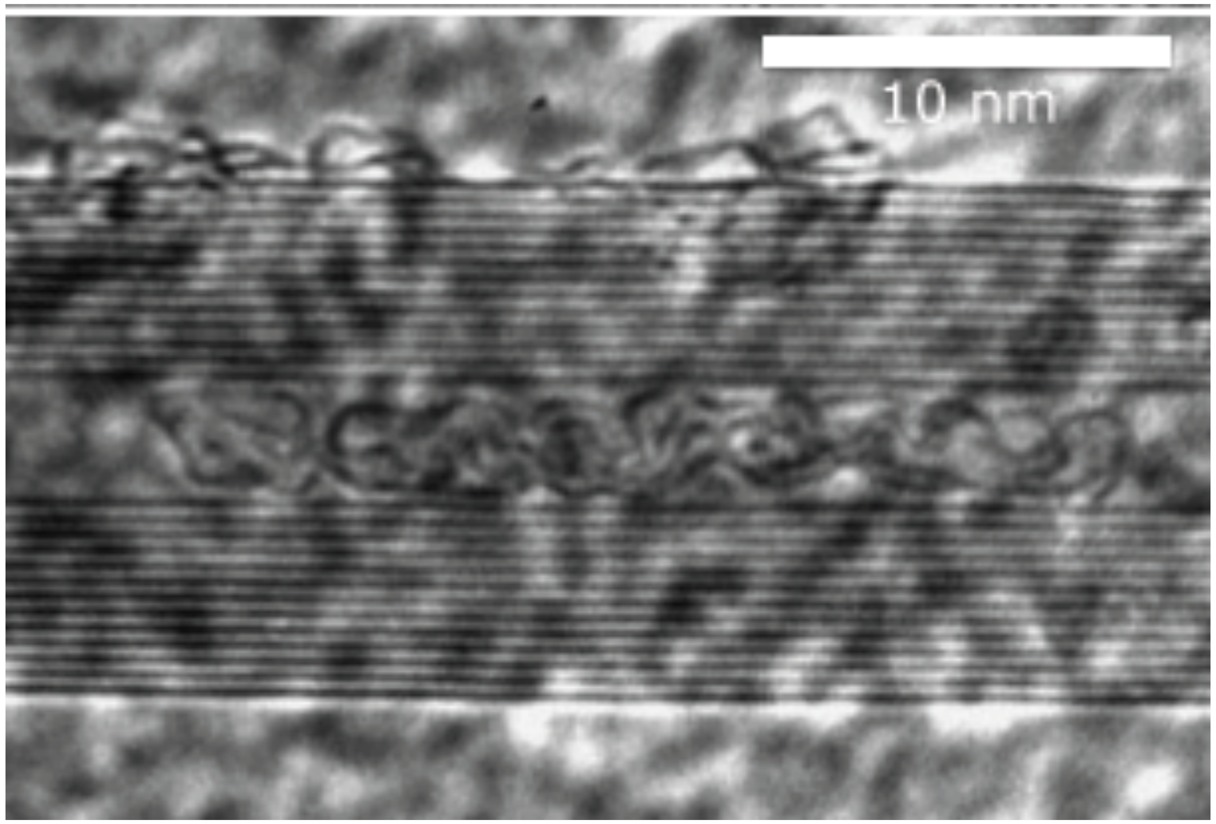
ERC StG *NanoSoft*

Nanotubes under study



Arc discharge
Carbon nanotubes



CVD Boron Nitride
nanotubes