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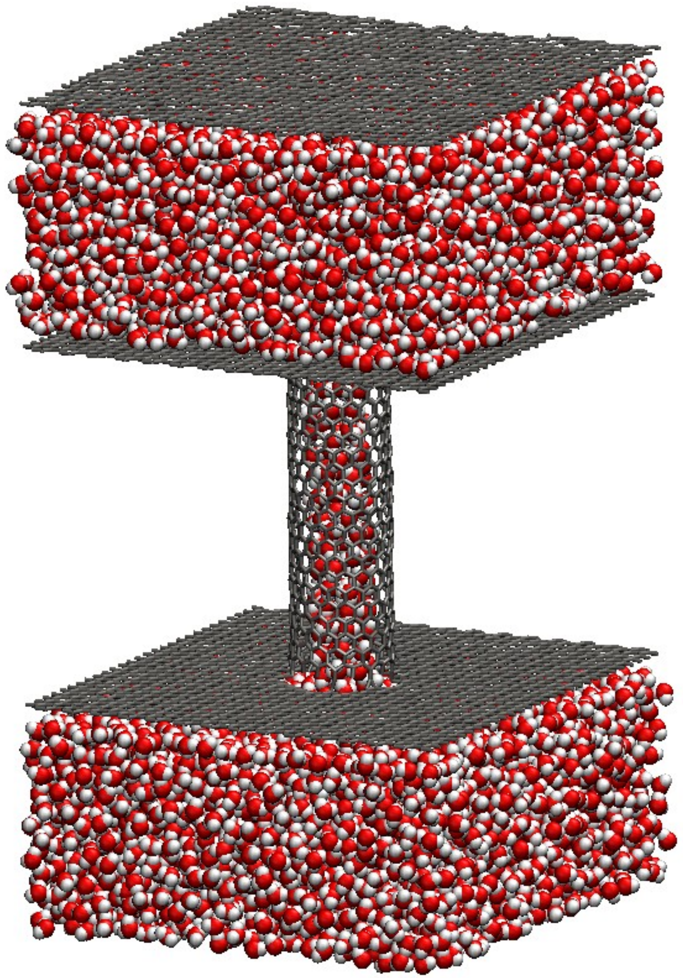
Pressure-driven water translocation through flexible carbon nanotubes

Thomas Brunner - Bachelor thesis presentation

Advisor: Prof. Douwe-Jan Bonthuis

Overview

- Research question
- Theory
  - Continuum mechanics
  - Molecular effects
- Methodology
  - Simulation setup
- Analysis
  - Velocity distribution
  - Slip length
  - Flow rate
  - Finite element model
- Literature

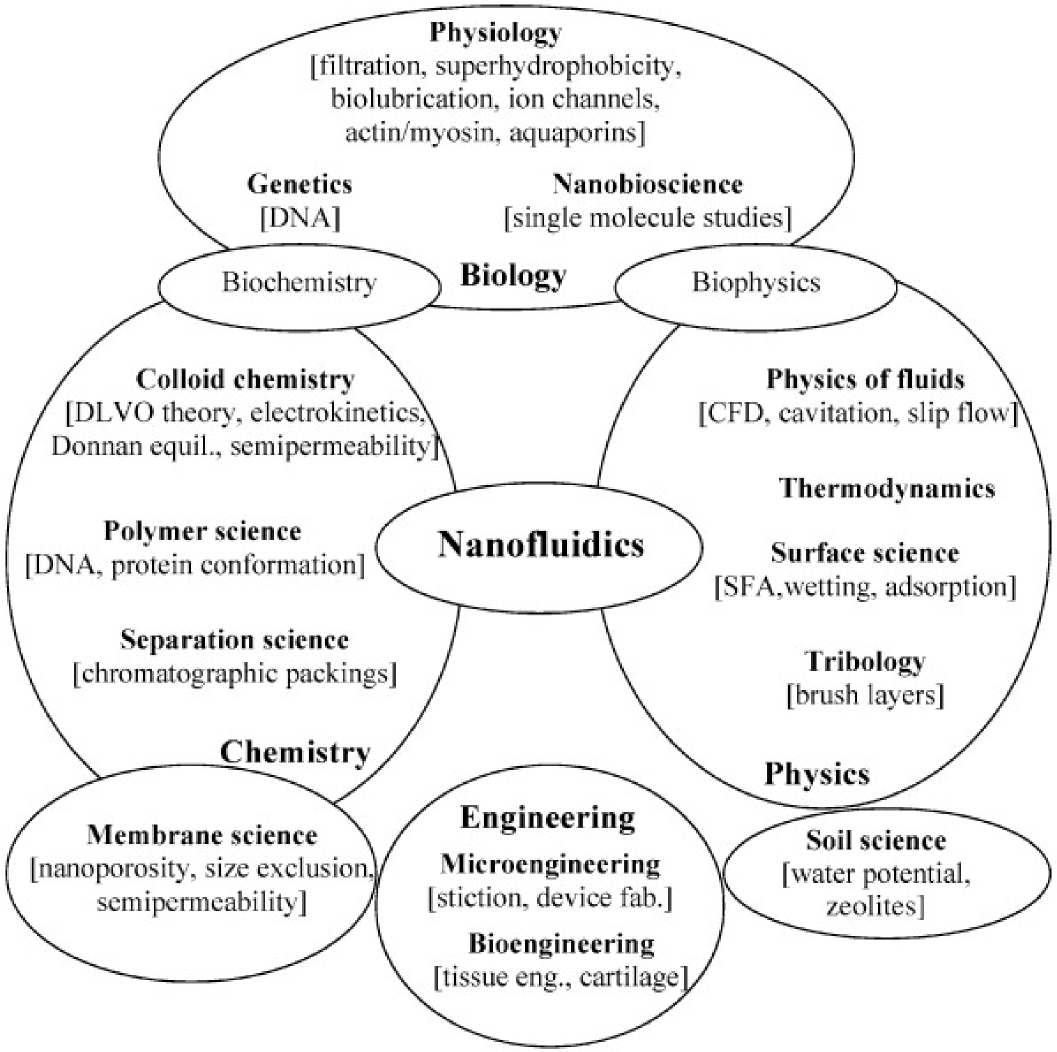


Research questions?

- Velocity behaviour at the interface (no-slip vs slip)?
- Hagen-Poiseuille law still usable?
- Any flow enhancement?
- CNTs as test bench for more flexible (bio-)channels?
- Comparison to the literature

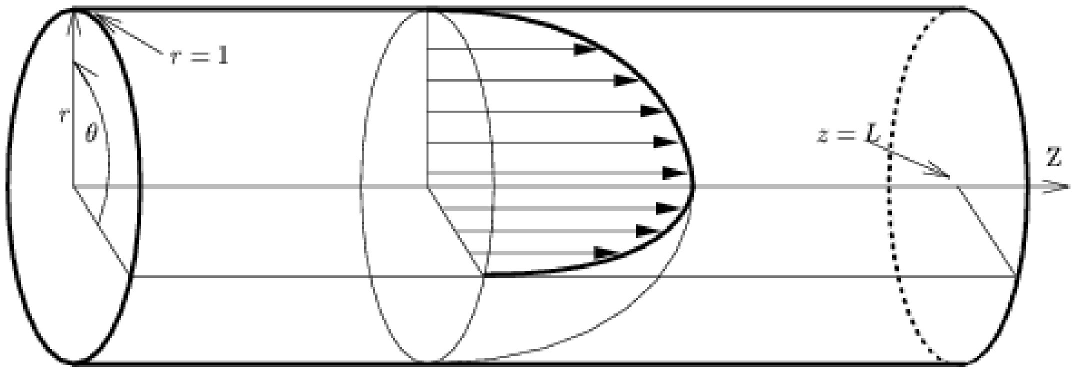
Research field - nanofluidics

- Description and modelling of flows on the scale of a few nanometers
- Intersection of many fields:
  - Physics
  - Biology
  - Chemistry
  - Engineering



Eijkel, J.C.T., Berg, A.v.d. Nanofluidics: what is it and what can we expect from it? Microfluid Nanofluid 1, 249–267 (2005)

Continuum theory – pipe flow



Andras Balogh: https://faculty.utrgv.edu/andras.balogh/pipe_mix.html

No-slip condition: $\mathbf{u}|_{r=\frac{d}{2}} = \mathbf{0}$

Velocity profile: $u_z(r) = \frac{\Delta p}{16\eta L}(d^2 - 4r^2)$

Hagen-Poiseuille law: $\Delta p = \frac{128\eta Q L}{\pi d^4}$

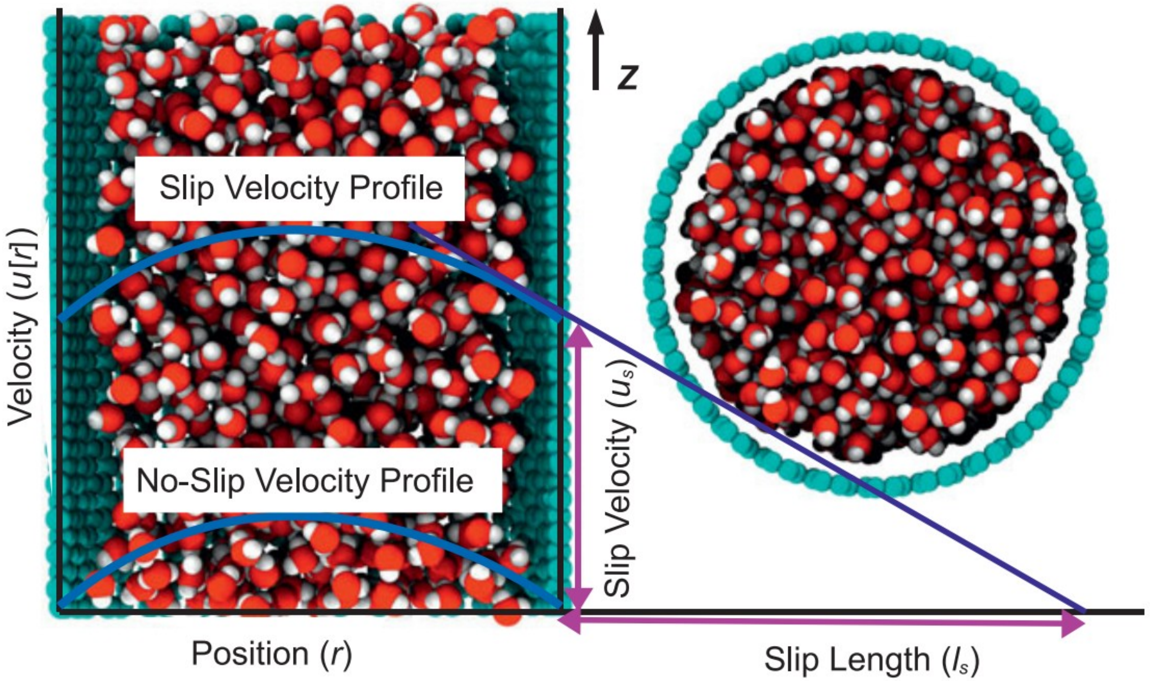
Continuum theory – slip boundary conditions

Slip condition:

$$-b\frac{\partial}{\partial r}u_z\big|_{r=\frac{d}{2}} = u_z\big|_{r=\frac{d}{2}}$$

Modified Hagen-Poiseuille law:

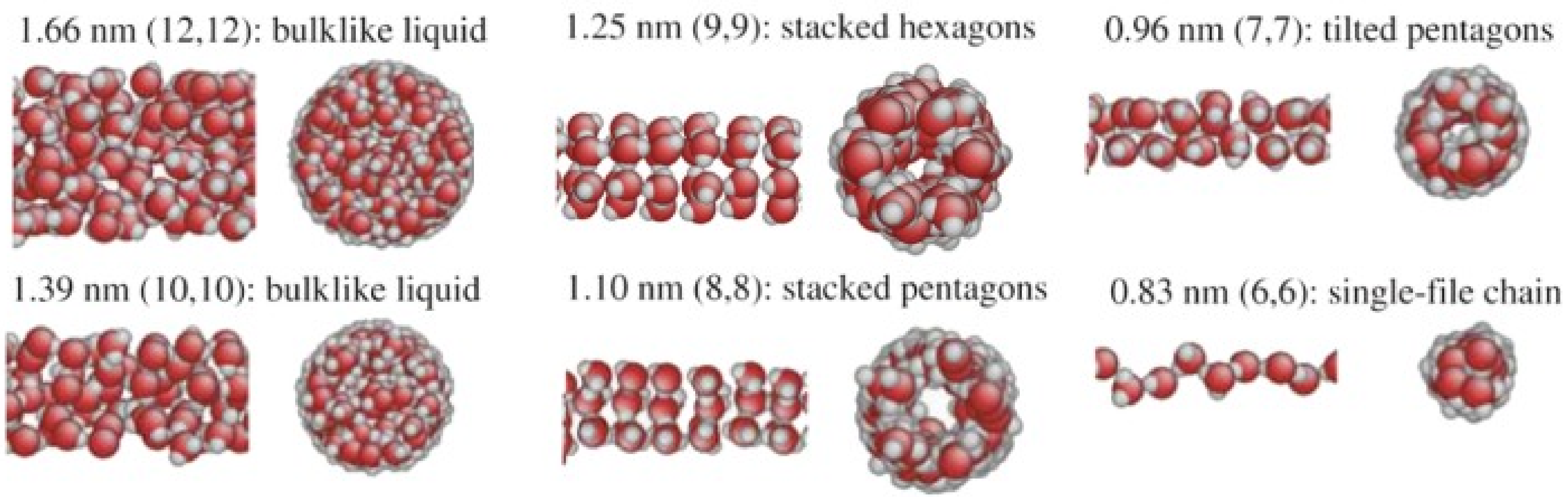
$$Q_{slip} = Q_{classical}(1 + \frac{8b}{d})$$



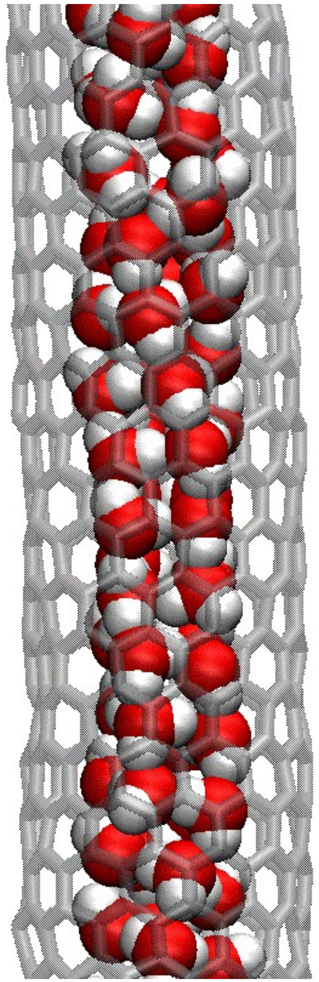
Sridhar Kannam. “Modeling slip and flow enhancement of water in carbon nanotubes
MRS Bulletin 42 (Apr. 2017)

Molecular effects - structuring

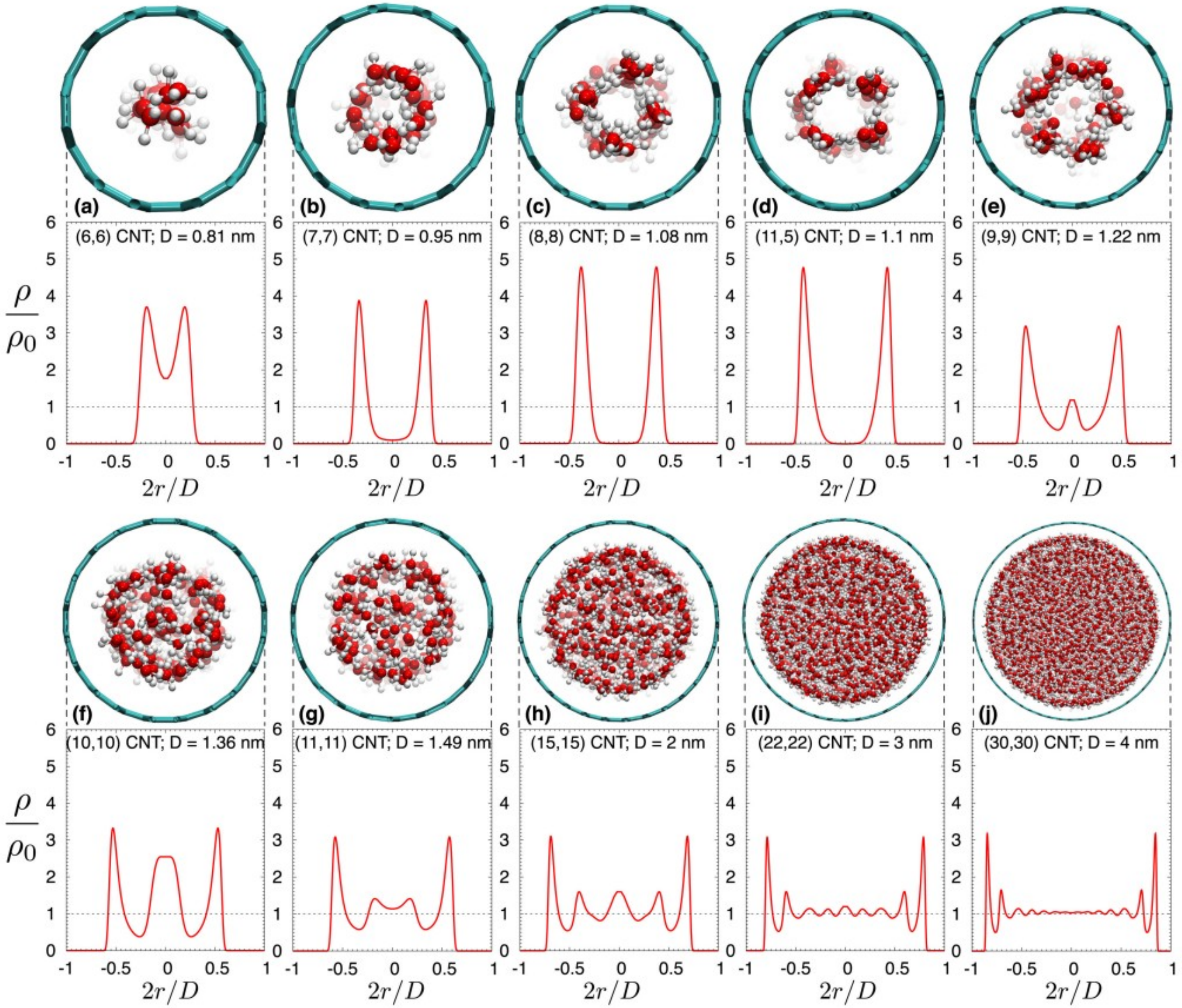
- Cause: Hydrogen bonds and repulsive VdW-force

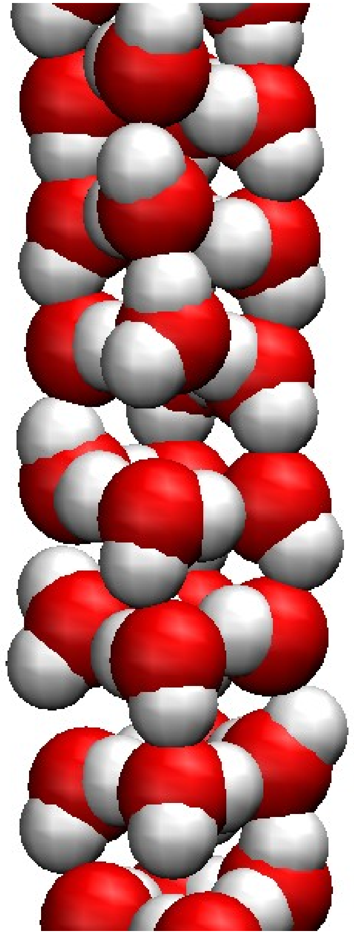


Nikita Kavokine, Roland Netz, and Lyderic Bocquet. “Fluids at the Nanoscale: from continuum to sub-continuum transport”



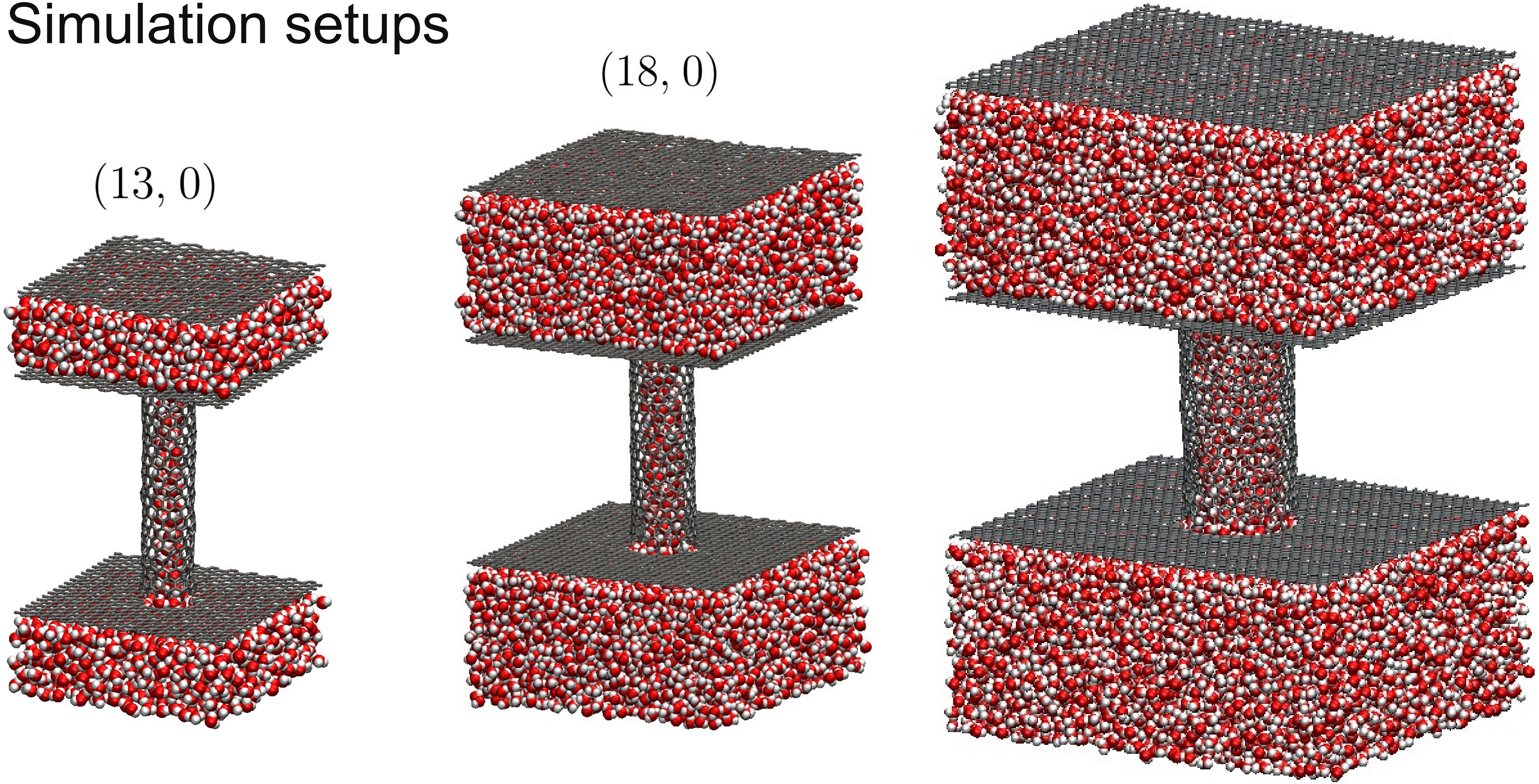
Molecular effects – density profiles





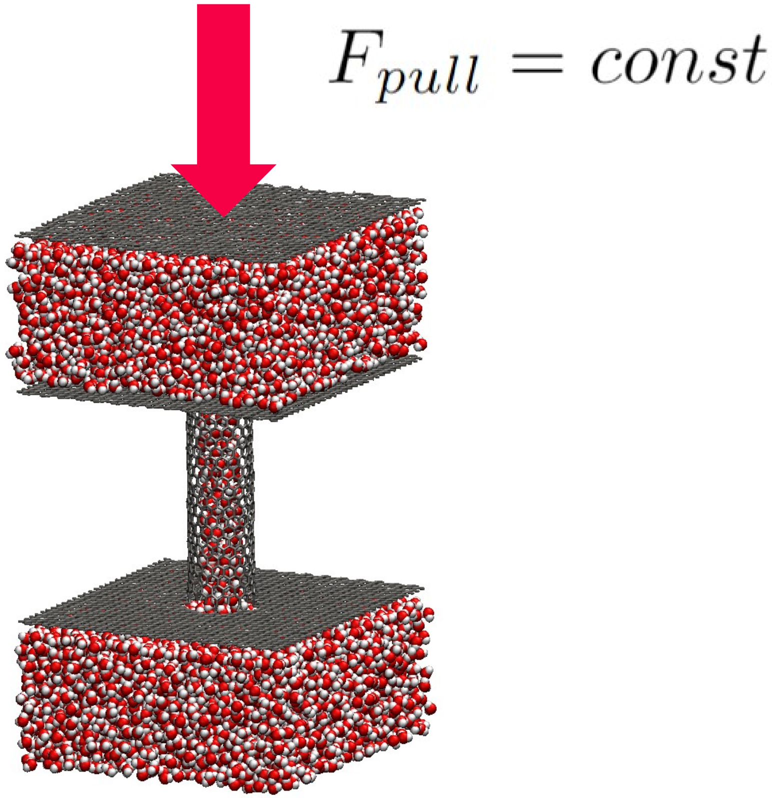
Aris Chatzichristos and Jamal Hassan. “Current Understanding of Water Properties inside Carbon Nanotubes”. Nanomaterials 12.1 (2022)

Simulation setups



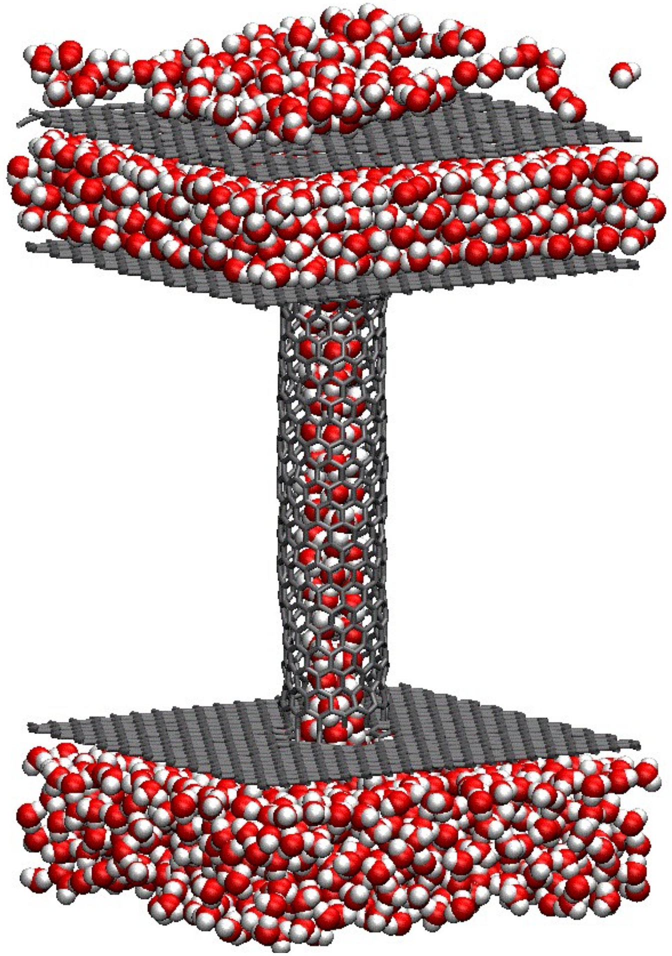
Molecular dynamics simulations

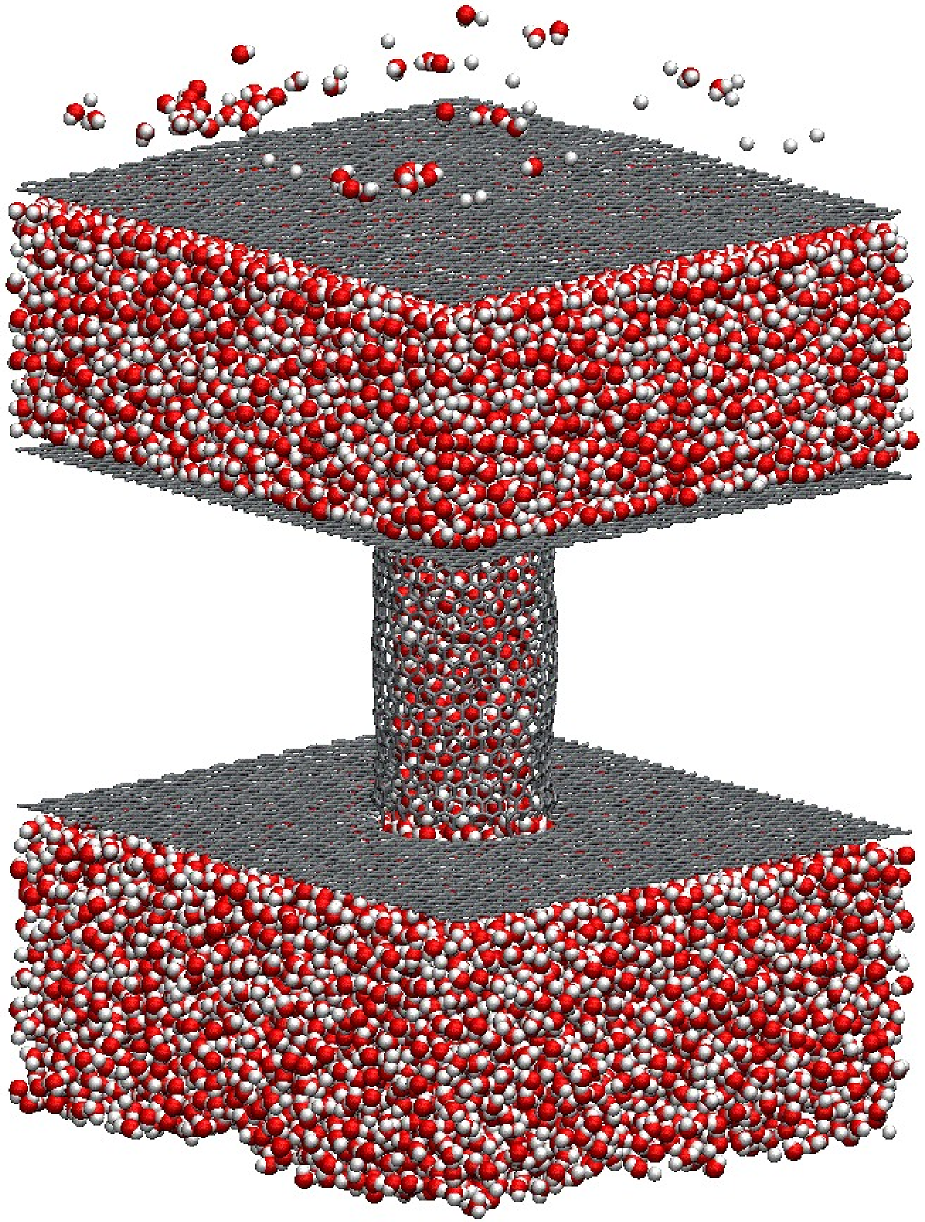
- Equilibriation:
  - Energy minimization
  - NVT – step
  - NPT – step



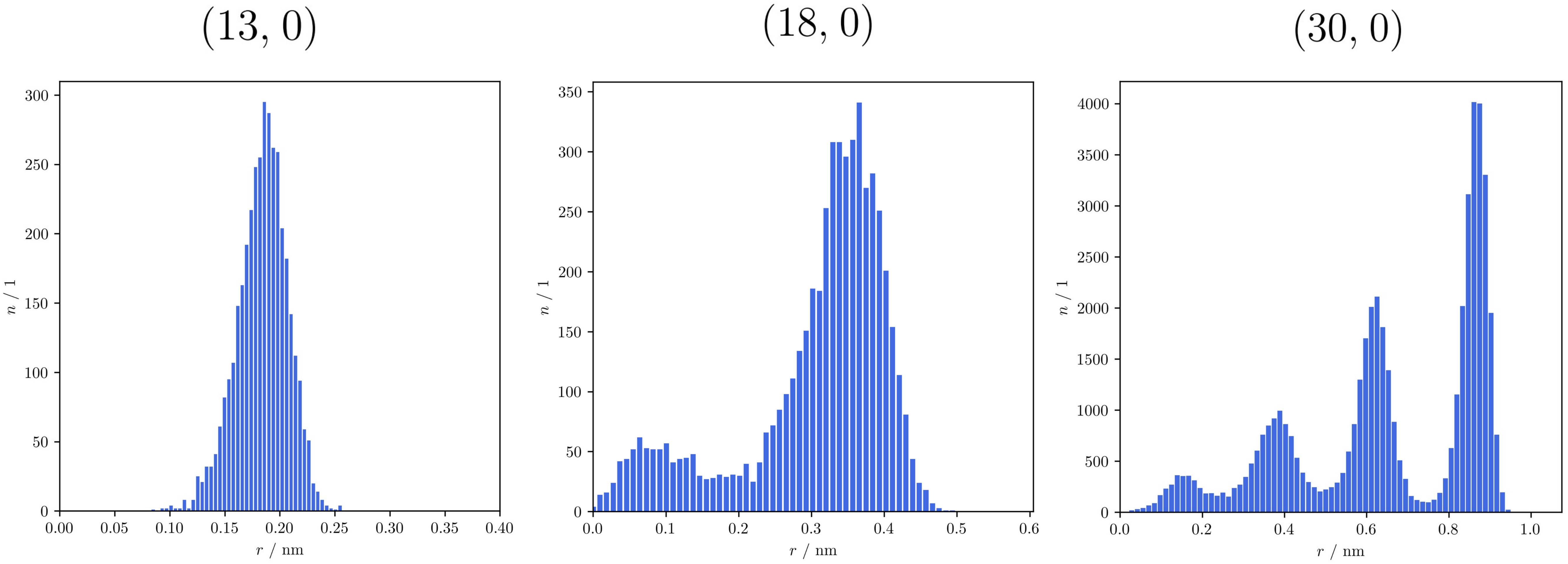
- NVT with pull code
  - generating pressure by constant force on graphene sheet

Example simulations

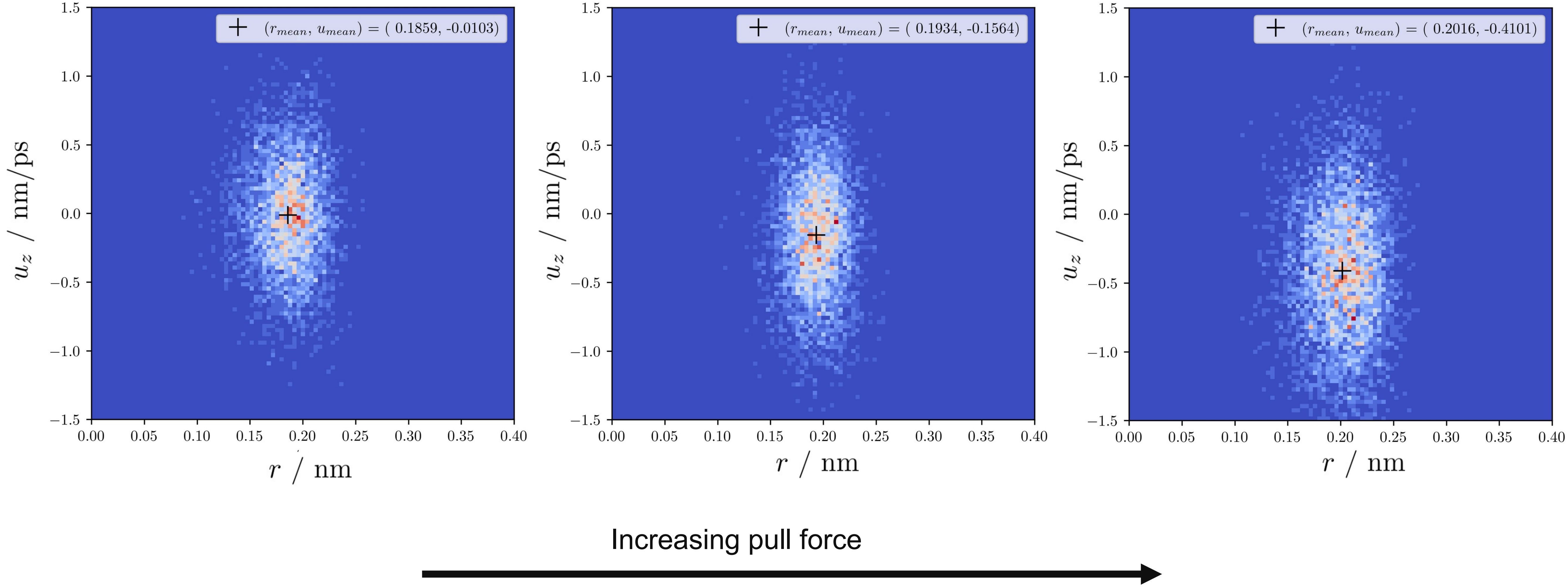




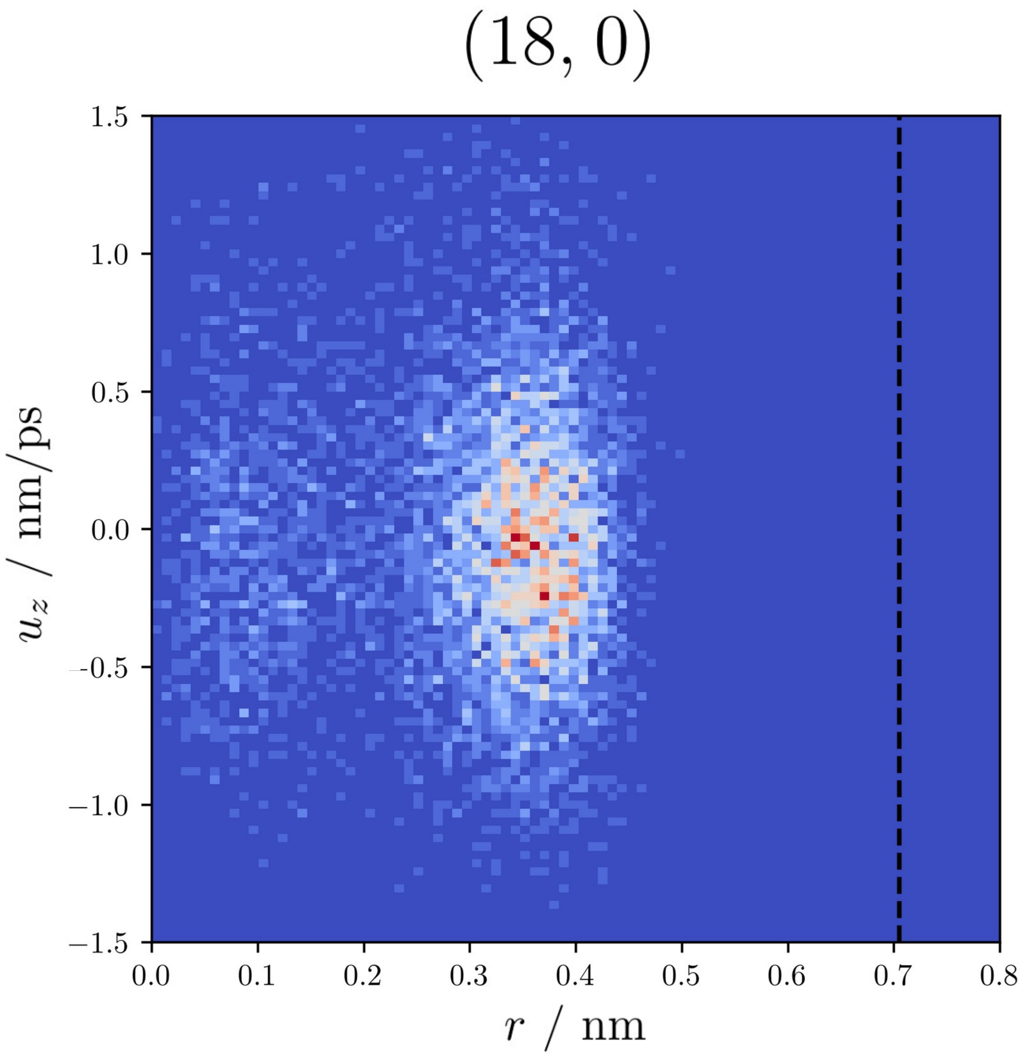
Density distributions

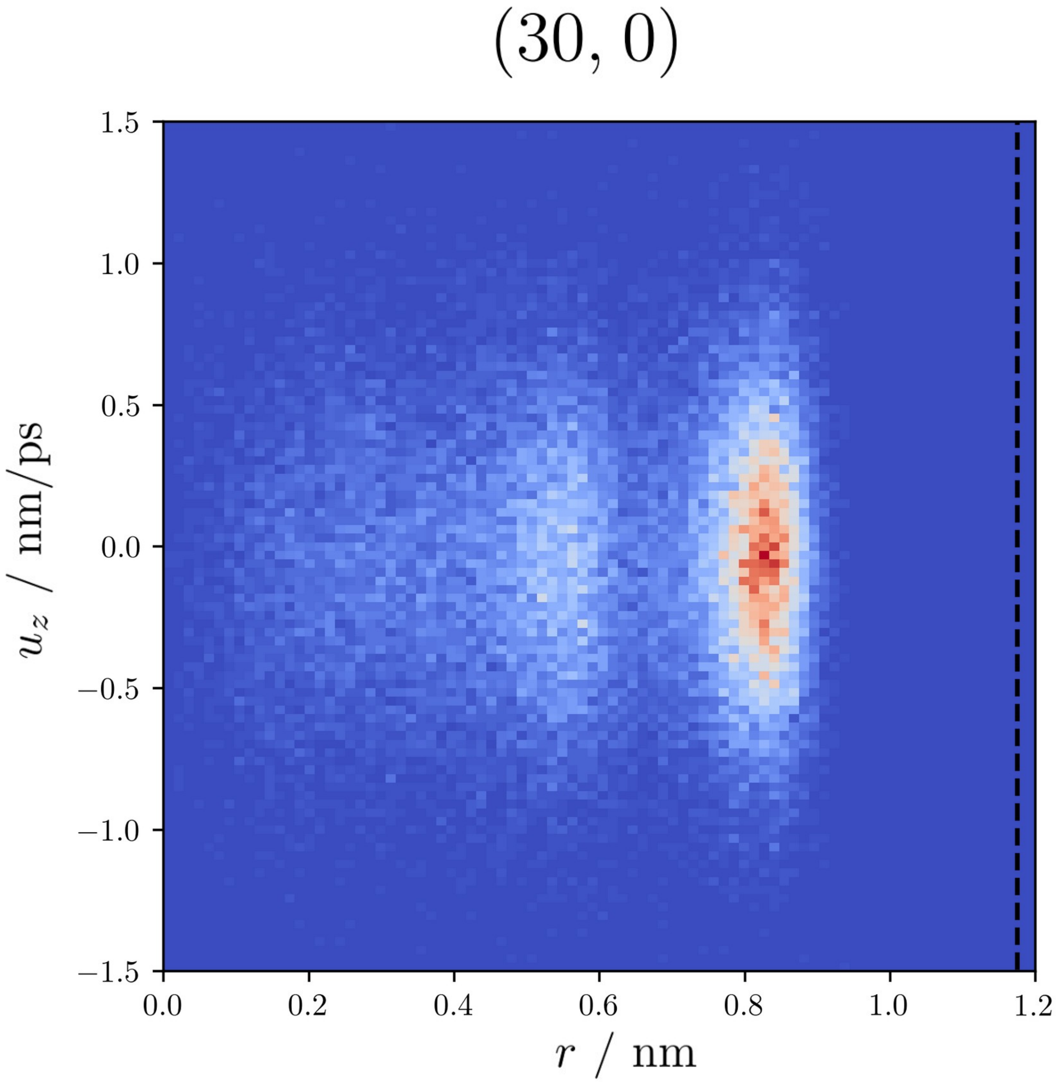


Velocity distributions – smallest $(13, 0)$ system



Velocity distributions – bigger systems





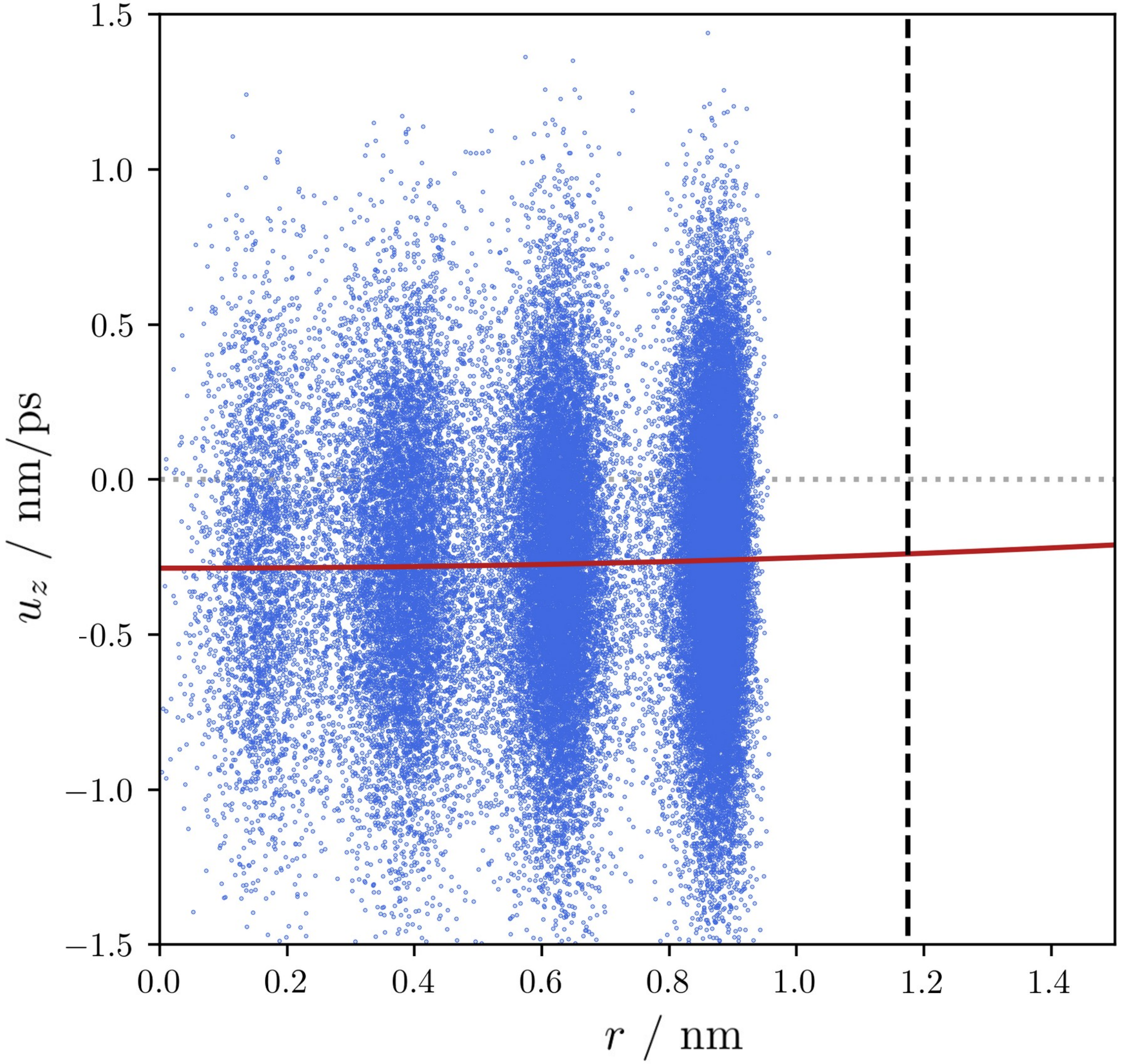
Fitting parabolic velocity profiles

Fit function:

$$u_z(r) = ar^2 + c$$

Extracted slip length:

$$b \approx 3 \text{ nm}$$



Does Hagen-Poiseuille hold?

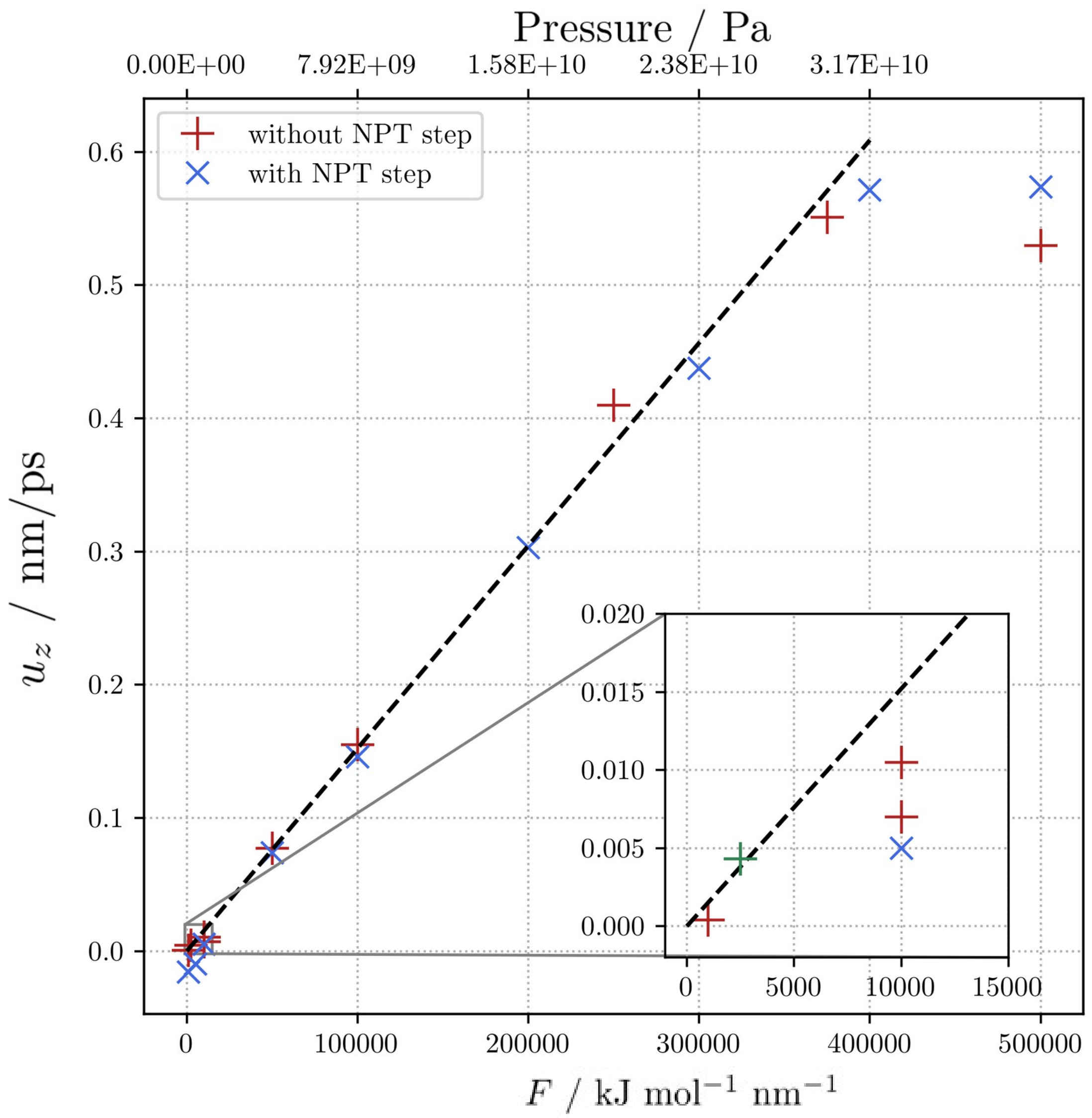
Assumption:

$$u_z(r) = u_\mu$$

$$Q \approx u_\mu A_{CNT}$$

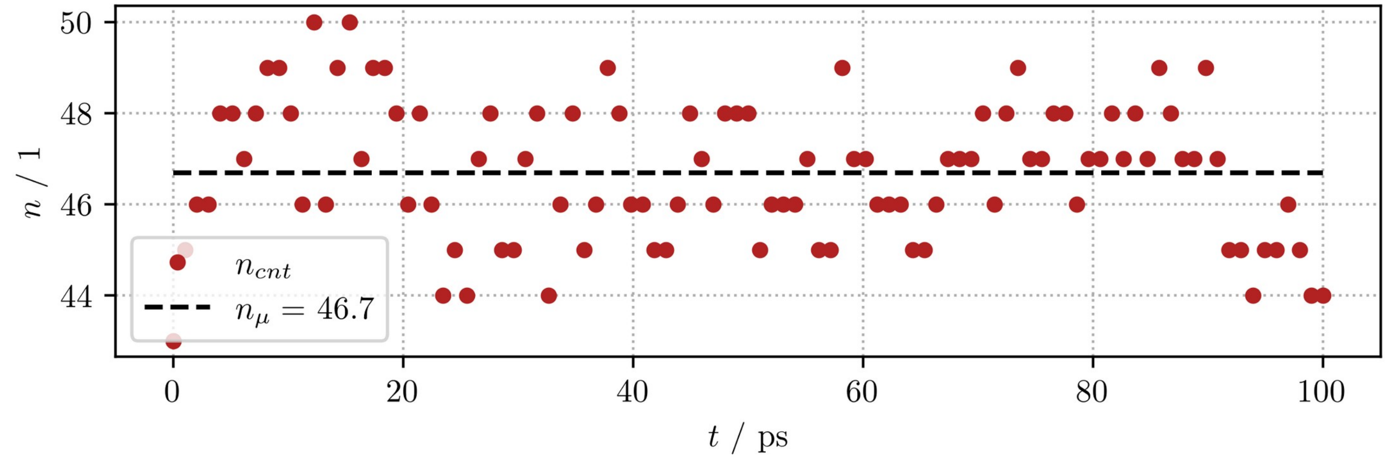
Calculated slip length:

$$b = 0.25 \text{ nm}$$

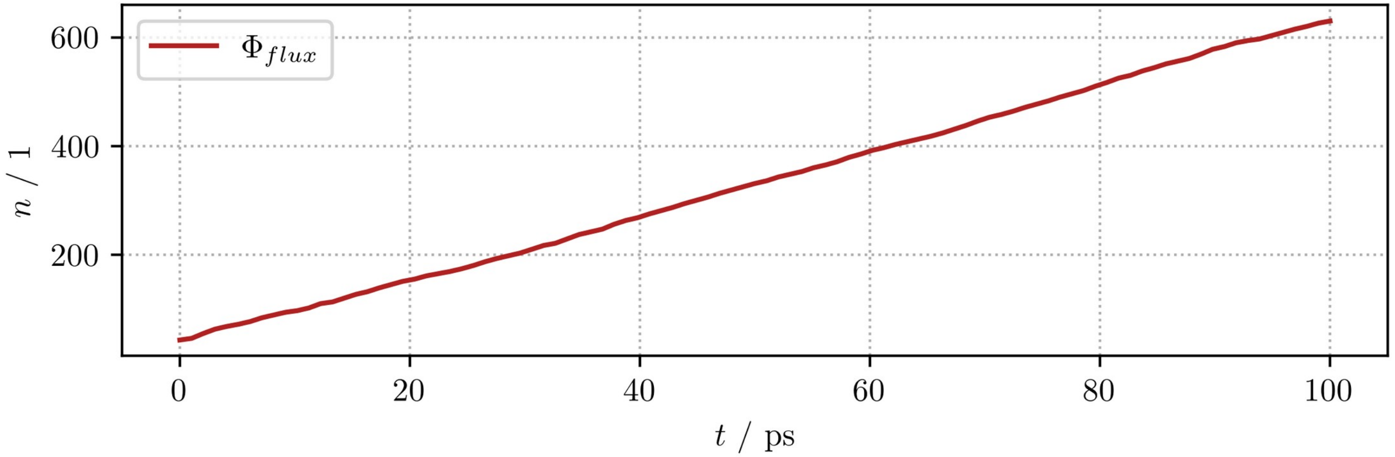


Simulated volume flux

Mean number of particles in CNT:



Cumulative particle flux:



$$Q \approx const$$

Enhanced flow rates?

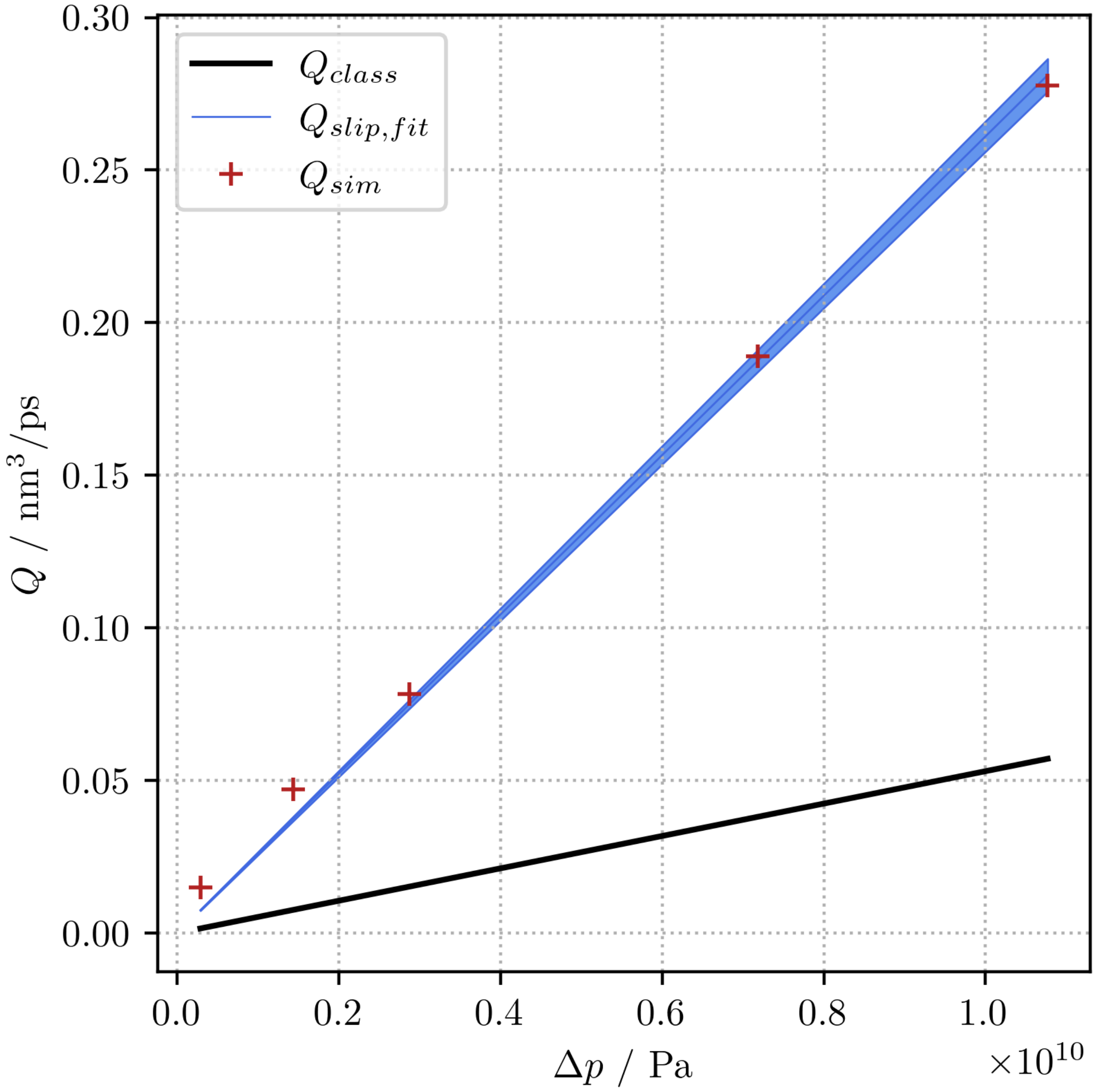
Comparison:

- classical & modified Hagen-Poiseuille flow
- simulation data flow rates

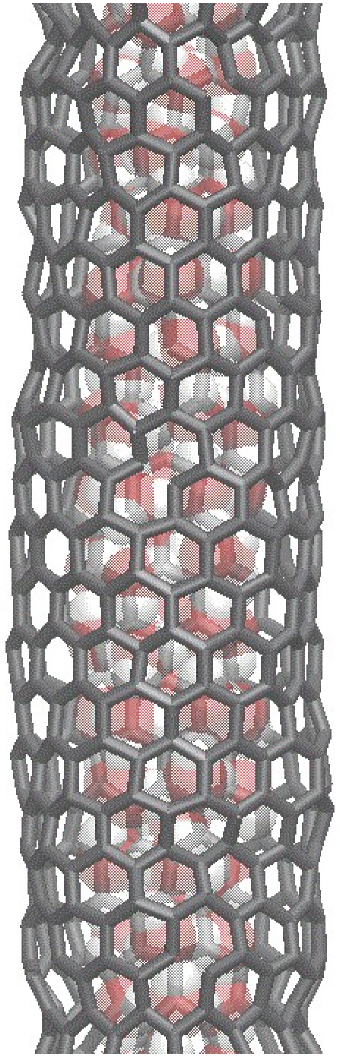
$$Q_{sim} = \frac{\Phi_{flux}}{D}$$

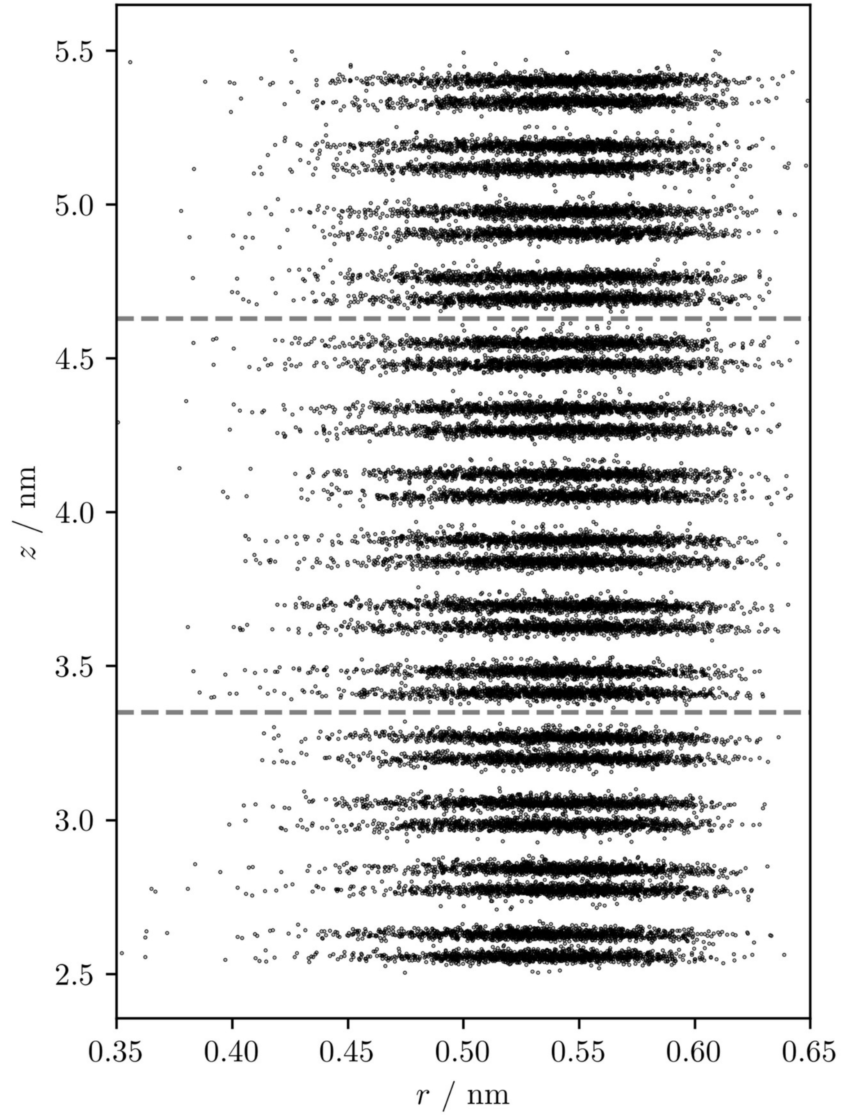
Flow enhancement factor:

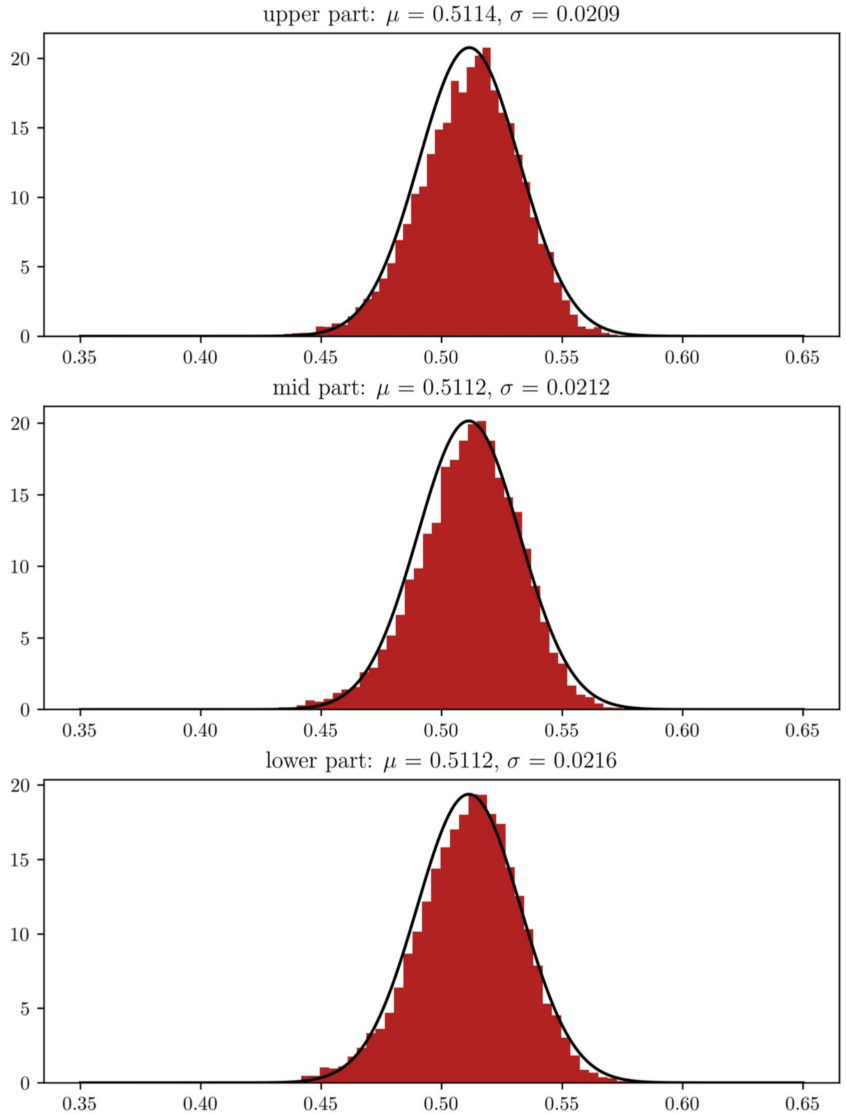
$$\mathrm{EF} = \frac{Q_{slip}}{Q_{continuum}}$$



CNTs as a test-bench for more flexible (bio-)channels?

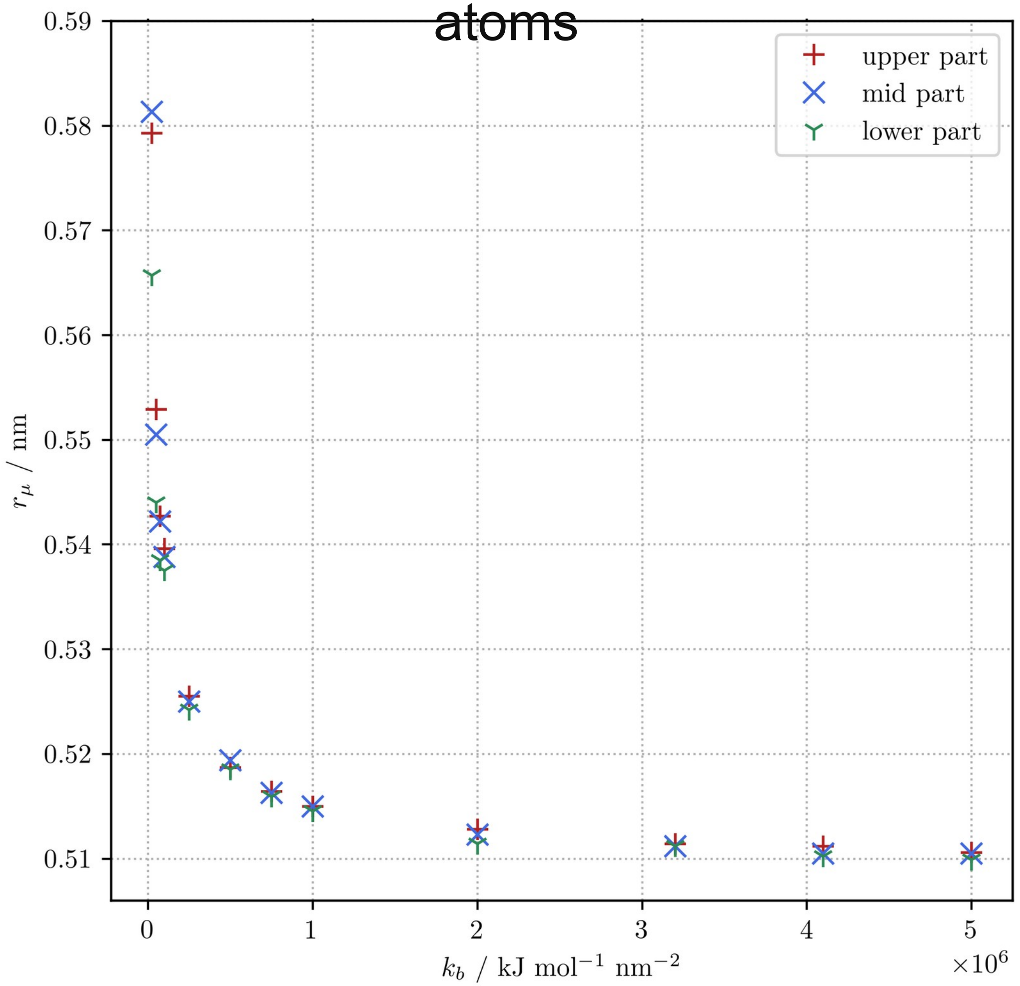




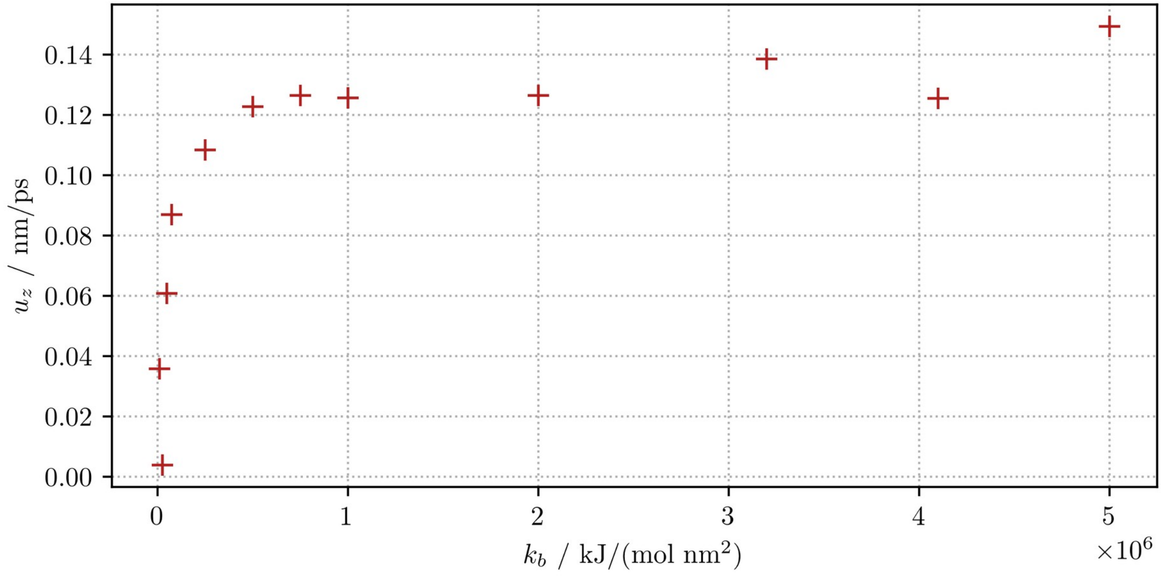


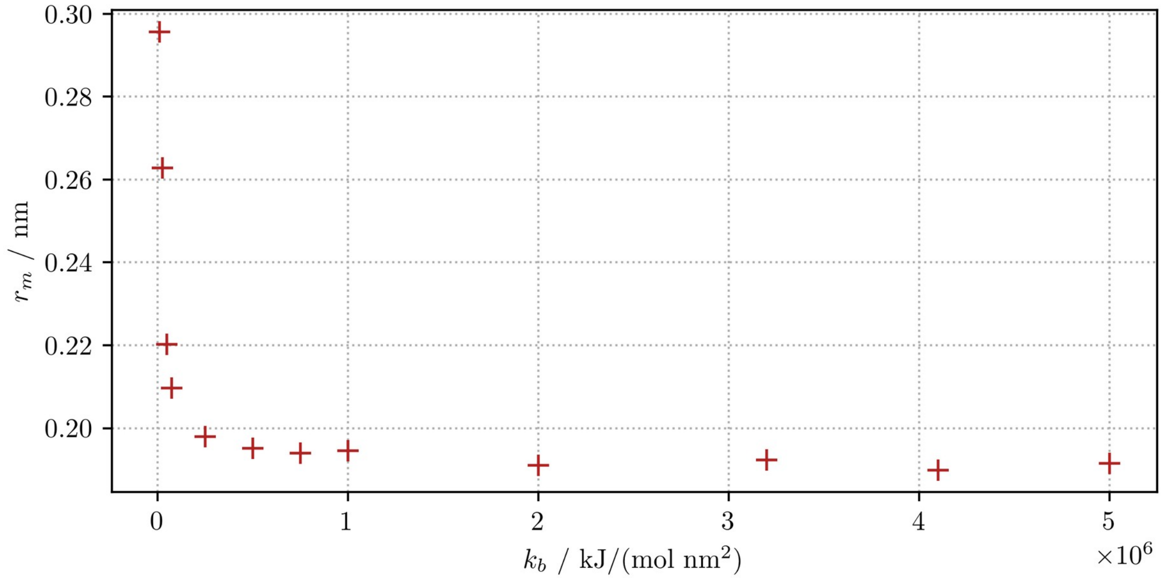
Changes of the CNT/flow?

Carbon atoms



Water molecules





A finite element model for CNT flows

Stokes equation:

$$\mu \Delta \mathbf{u} - \nabla p + \mathbf{f} = 0 \text{ in } \Omega$$
$$\nabla \cdot \mathbf{u} = 0 \text{ in } \Omega$$
$$\mathbf{u} = \mathbf{u}_D \text{ in } \partial\Omega$$

⋮

Weak form

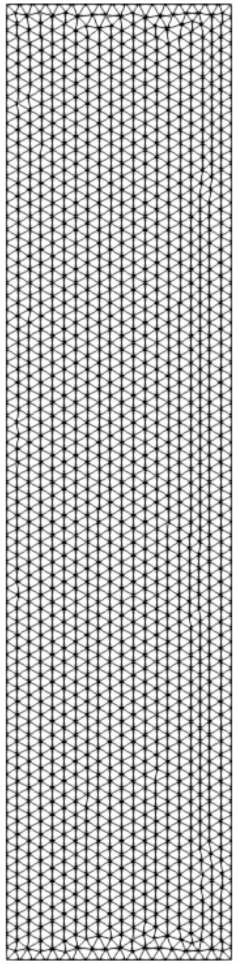
Mixed FE formulation

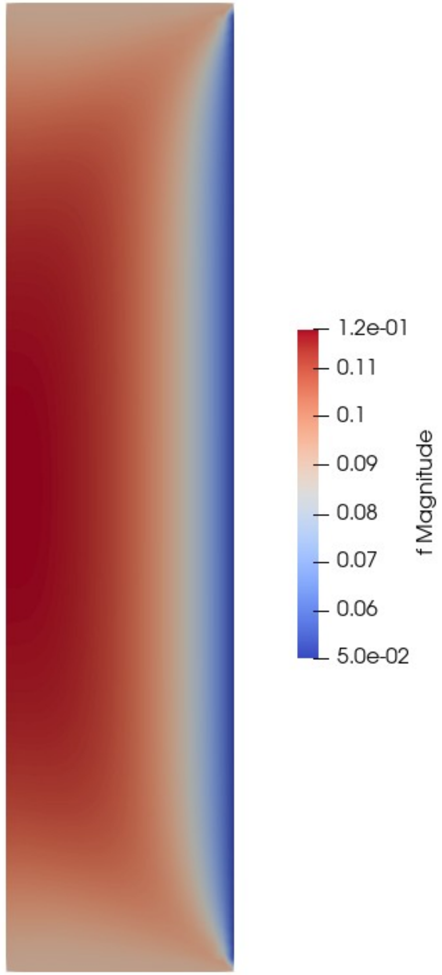
Taylor-Hood elements

$$\begin{pmatrix} a(u_h, v) + b(v, p_h) = l(v) \quad \forall v \in V_h \\ b(u_h, q) = 0 \quad \forall q \in P_h \end{pmatrix}$$

Model problem:

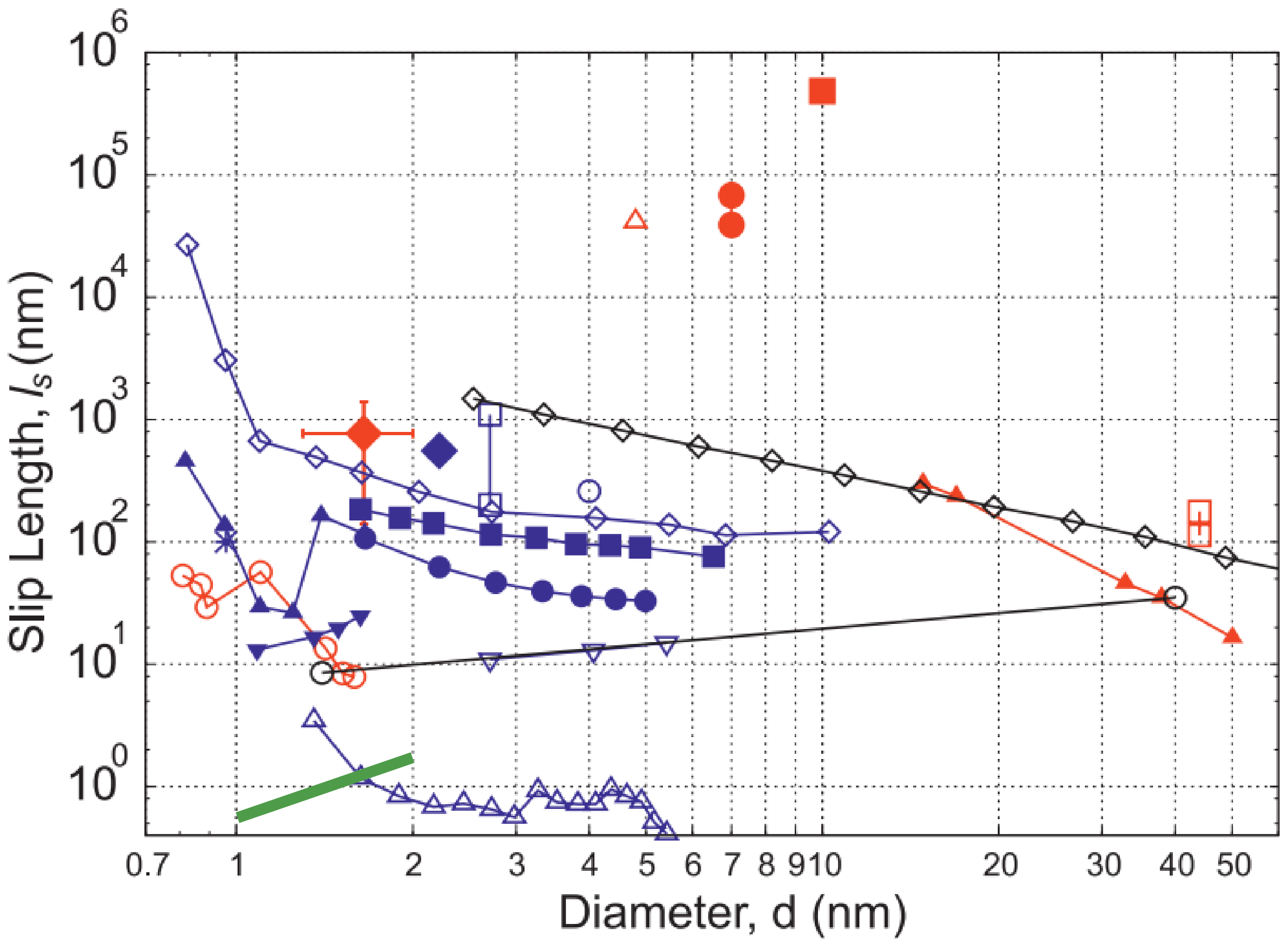
parameter	value
d_{CNT}	2,35 nm
l_{CNT}	5 nm
η_{WAT}	1 mPa s
v_{slip}	0,05 nm/ps
v_{inflow}	0,09 nm/ps
$v_{outflow}$	0,09 nm/ps





Comparison to the literature

- Black – Theory
- Blue – Simulations
- Red – Experiments
- Green – This work



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Conclusion

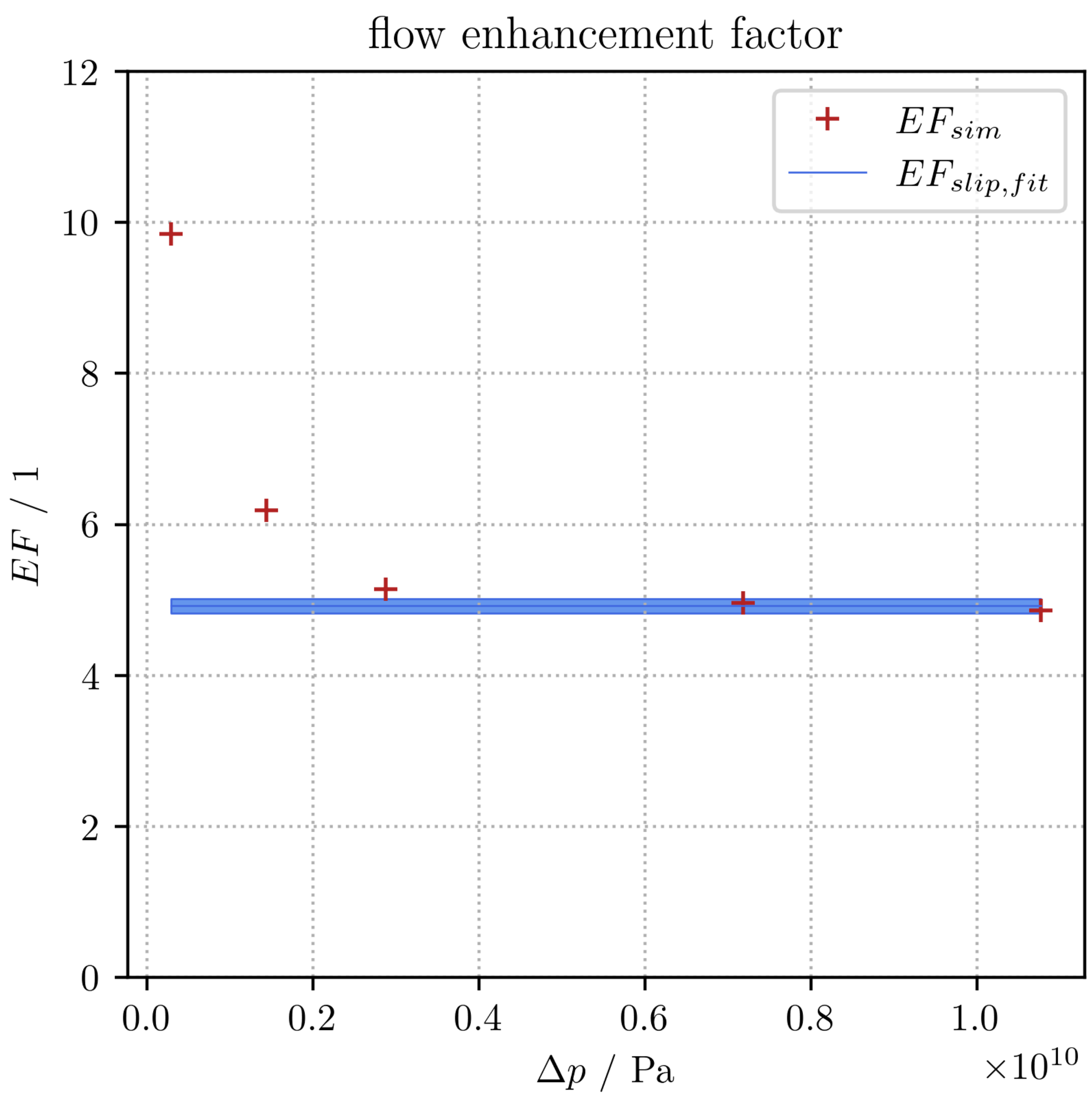
- Obtained slip lengths appear smaller than in other works
- Modified Hagen-Poseuille law holds very far
- Flexibility expands the tubes radius but decreases flux
  - ➢ Water-CNT interaction
- Simulation results vary alot
  - ➢ Difficult to compare due to differences in setup
- More experimental studies needed

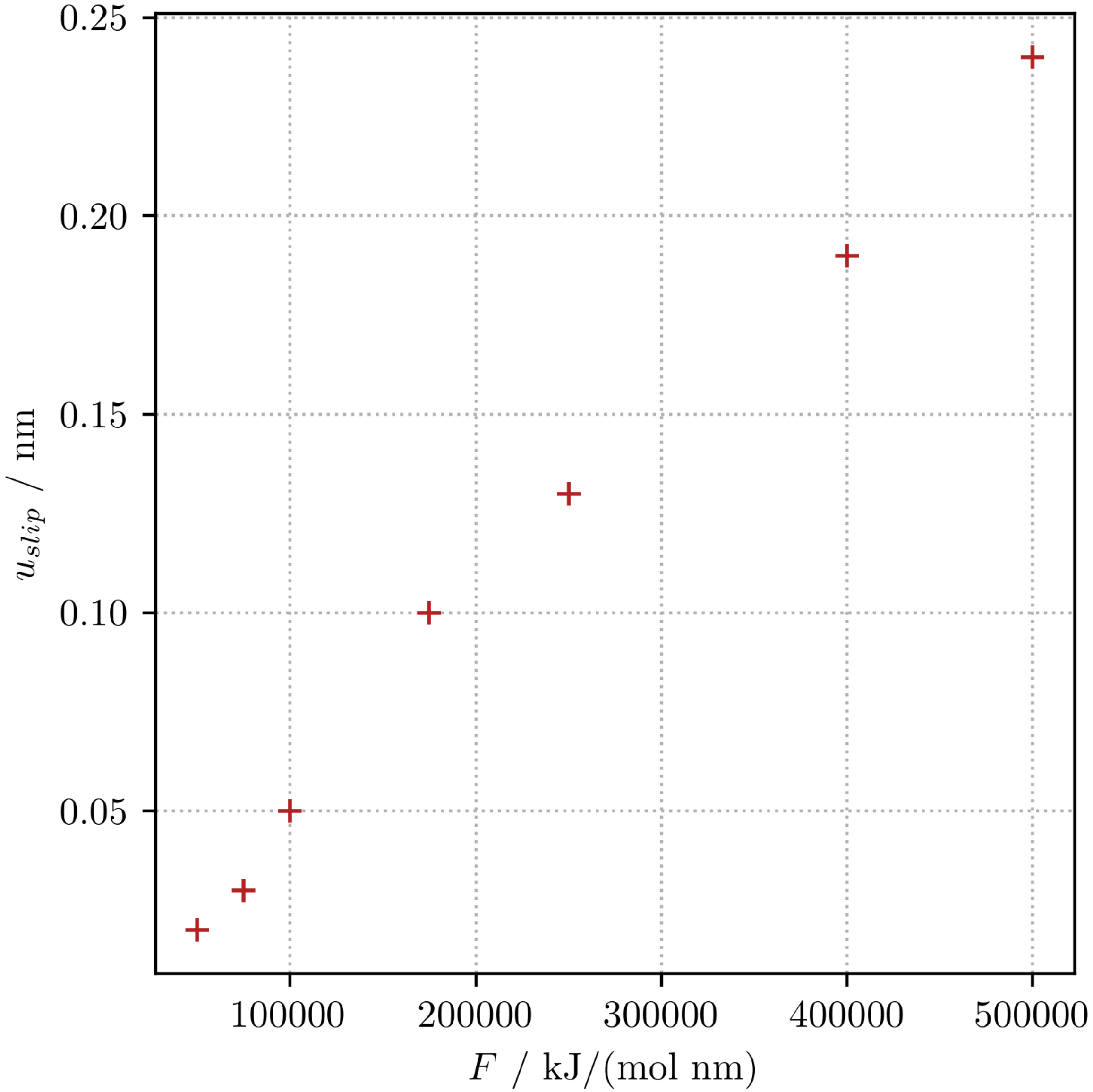
Table 1: SPC/E water model parameters [15] [16]

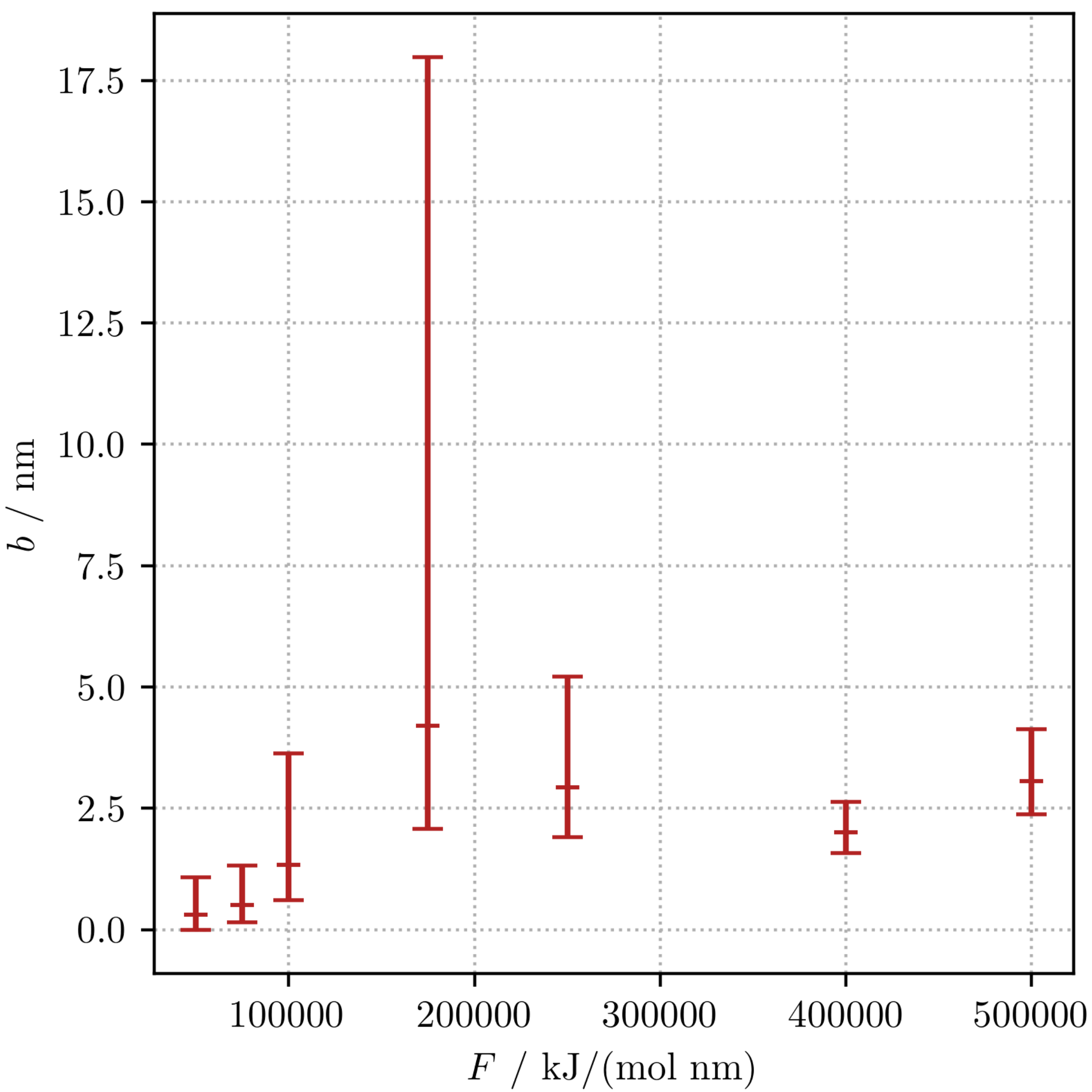
parameter	value	unit
σ	3,166	Å
ϵ	0,65	kJ/mol
r_{OH}	1	Å
θ_{HOH}	109,47	$\circ$
q_O	-0,847	e
q_H	$-q_O/2$	e

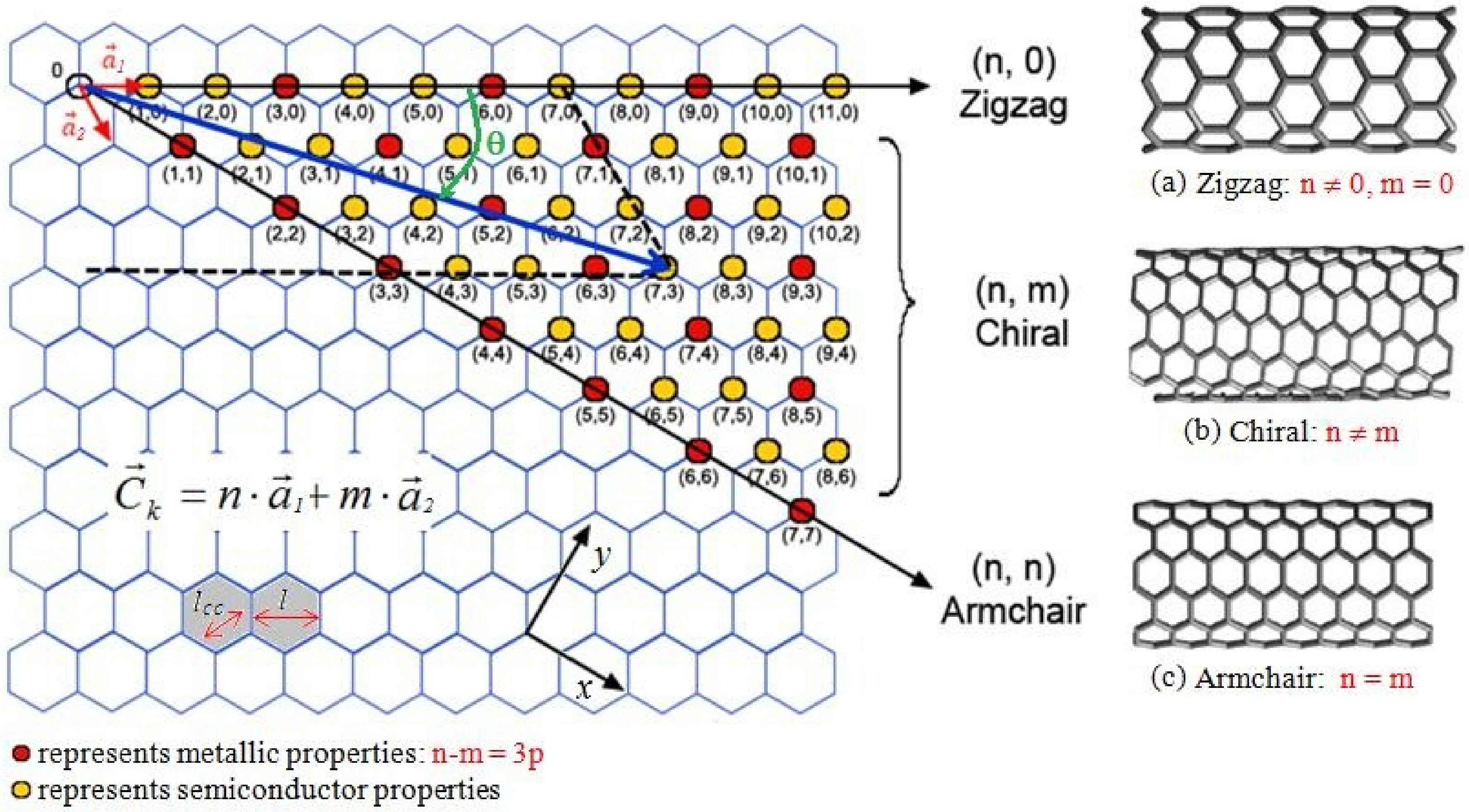
Table 2: Carbon parameters

parameter	value	unit
σ	3,581	Å
ϵ	0,2775	kJ/mol
r_{CC}	1,421	Å
θ_{CCC}	120	$\circ$
q_C	0	e

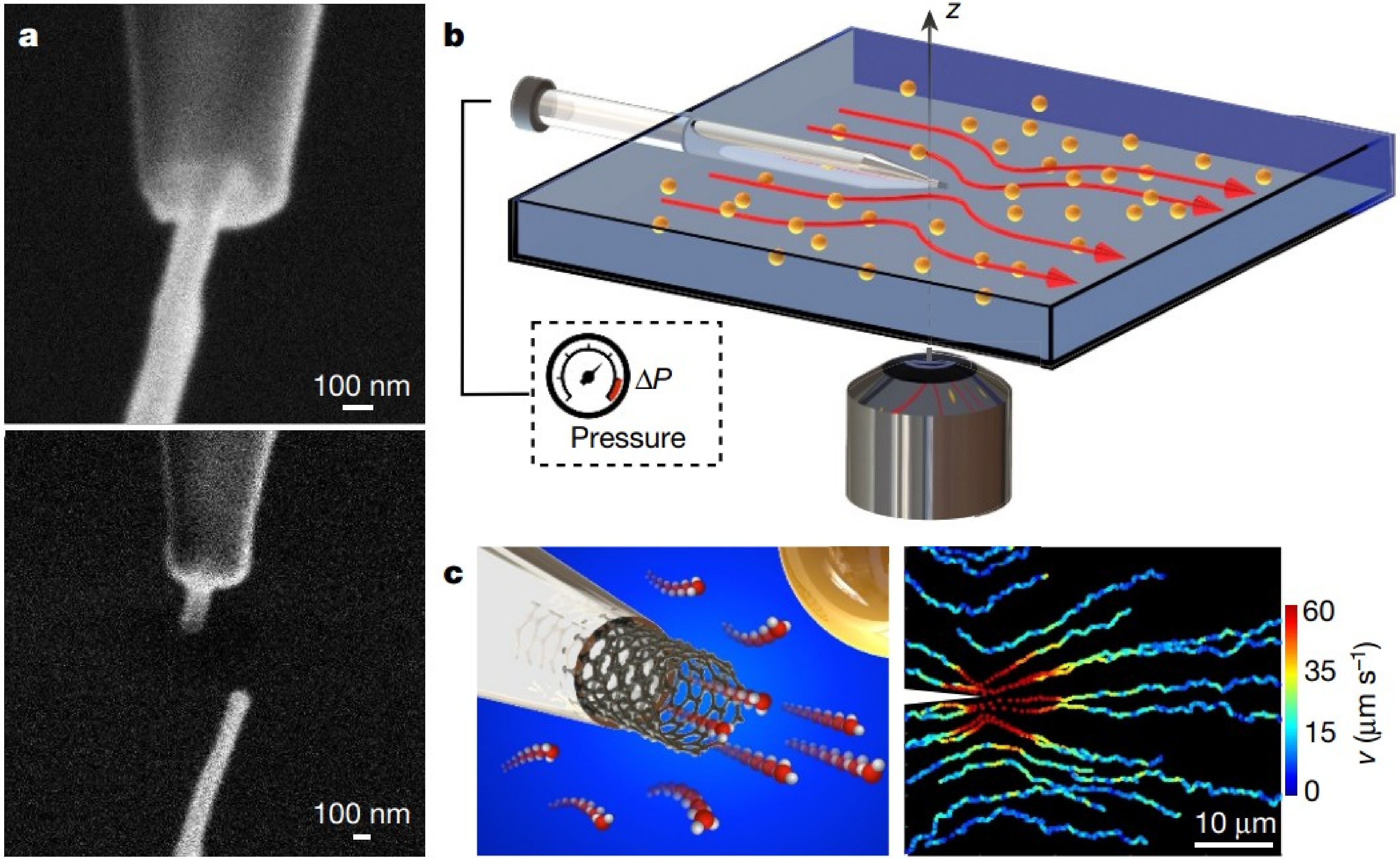

flow enhancement factor
EF_{sim}
$EF_{slip,fit}$
EF / 1
Δp / Pa
$\times 10^{10}$
0
2
4
6
8
10
12
0.0
0.2
0.4
0.6
0.8
1.0


0.25
0.20
0.15
0.10
0.05
u_{slip} / nm
100000
200000
300000
400000
500000
F / kJ/(mol nm)


17.5
15.0
12.5
10.0
7.5
5.0
2.5
0.0
b / nm
100000
200000
300000
400000
500000
F / kJ/(mol nm)



Attaf, Brahim. (2015). An Eco-Approach to Boost the Sustainability of Carbon Nanotube-Based Composite Products.



Secchi, E., Marbach, S., Niguès, A. et al. Massive radius-dependent flow slippage in carbon nanotubes. Nature 537, 210–213 (2016).