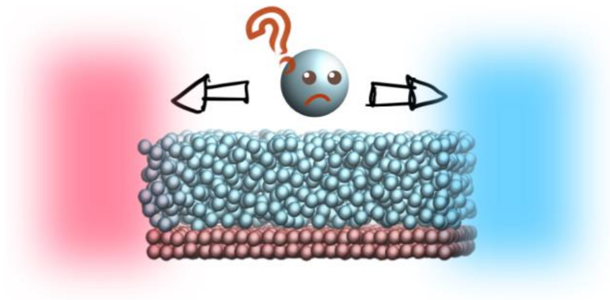
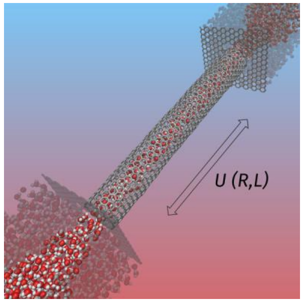




Molecular views on thermo-osmotic flows

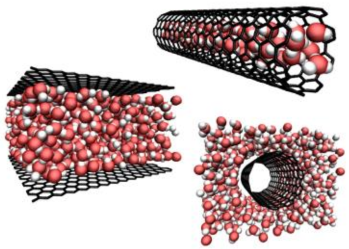
Li Fu, Samy Merabia, Laurent Joly

Univ Lyon, Université Claude Bernard Lyon 1, CNRS,
Institut Lumière Matière, F-69622, Villeurbanne, France

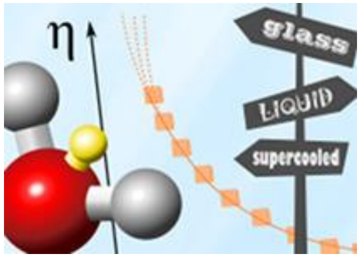
http://ilm-perso.univ-lyon1.fr/~ljoly/

Nanofluidics with LAMMPS

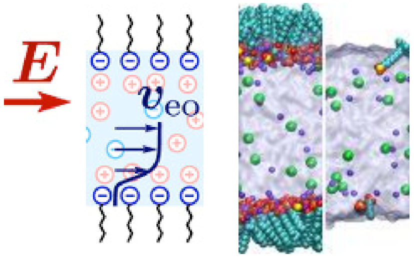
Micro/nanofluidic transport: from molecular mechanisms to applications



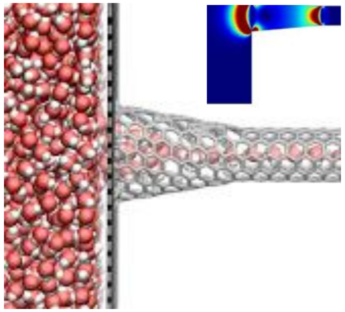
Interfacial hydrodynamics
Liquid/solid friction



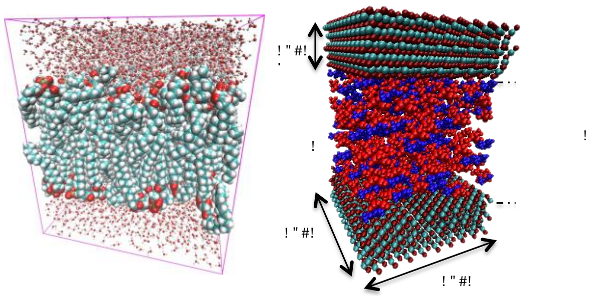
Understanding water



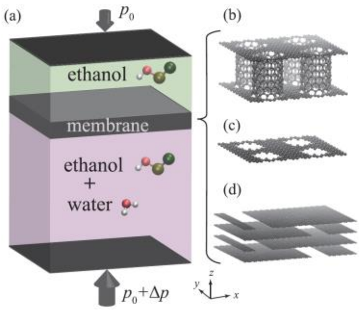
Energy conversion
Electrokinetic effects



Nanoscale flows



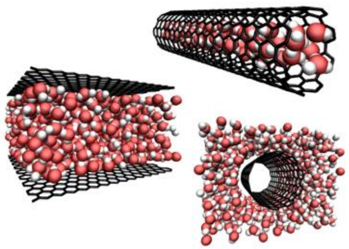
Lubrication



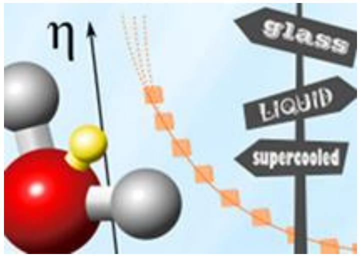
Devices

Nanofluidics with LAMMPS

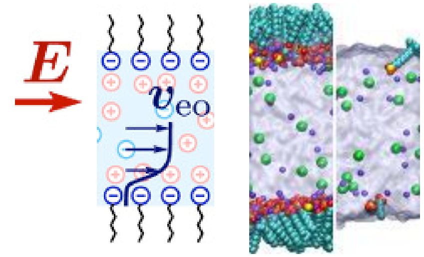
Micro/nanofluidic transport: from molecular mechanisms to applications



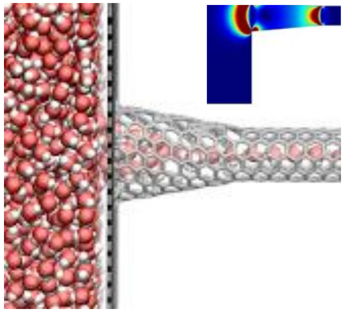
Interfacial hydrodynamics
Liquid/solid friction



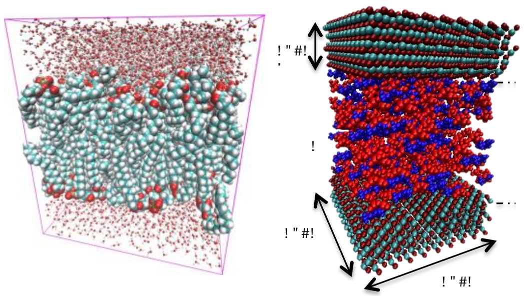
Understanding water



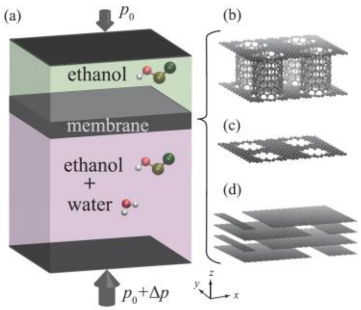
Energy conversion
Electrokinetic effects



Nanoscale flows



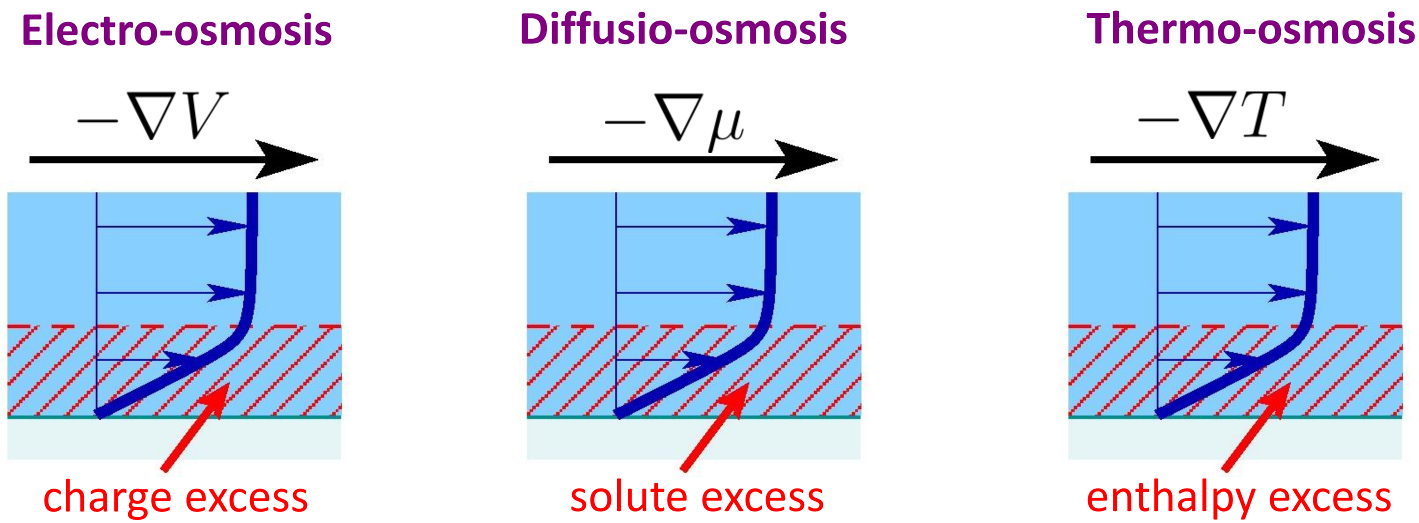
Lubrication



Devices

Osmotic flows

Surface-driven flows generated by non-hydrodynamic forcing



Micro/nanofluidics, sustainable energies (e.g. waste heat harvesting)

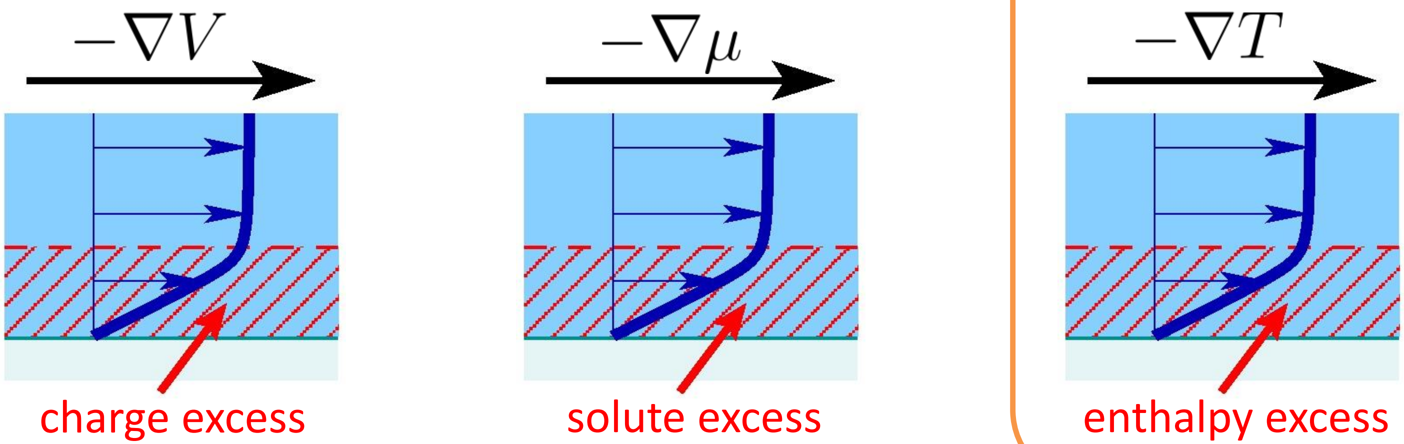
Originate in a nanometric interfacial layer

Nanoscale structure and dynamics

Osmotic flows

Surface-driven flows generated by non-hydrodynamic forcing

Electro-osmosis | **Diffusio-osmosis** | **Thermo-osmosis**



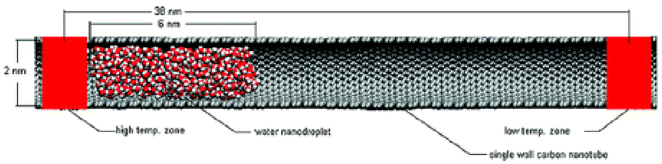
Micro/nanofluidics, sustainable energies (e.g. waste heat harvesting)

Originate in a nanometric interfacial layer

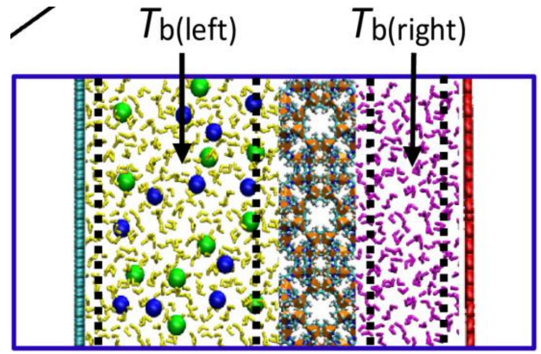
Nanoscale structure and dynamics

Nanofluidic systems under thermal gradients

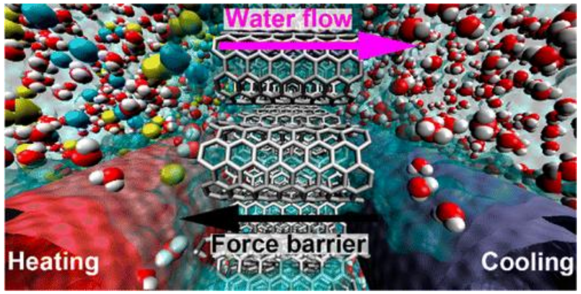
For applications



Zambrano et al. Nano Lett 2009

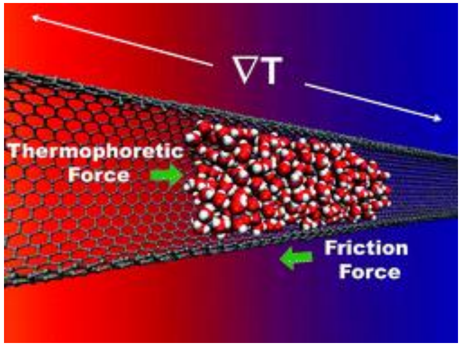


Gupta & Jiang ChemistrySelect 2017

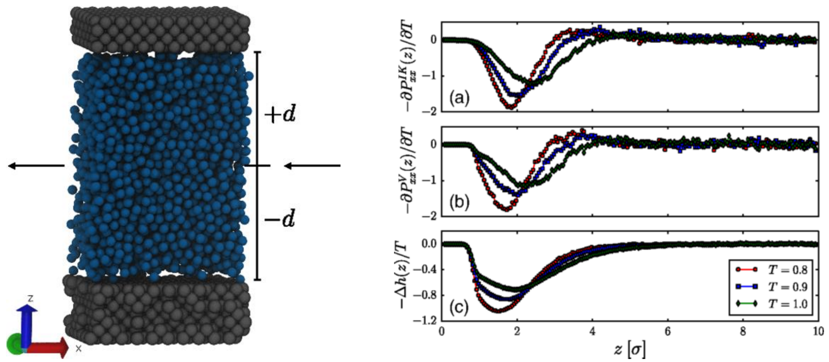


Zhao & Wu Nano Lett 2015

Molecular mechanisms?



Oyarzua, Walther & Zambrano, PCCP 2018



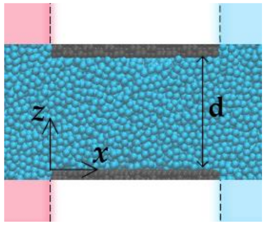
Ganti, Liu & Frenkel, PRL 2017

Effect of wetting and interfacial hydrodynamics?

Theory

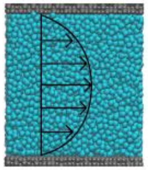
Thermo-osmosis

- flow induced by a thermal gradient: $v_s = M_{12}(-\frac{\nabla T}{T})$



Mechano-caloric effect

- heat flux induced by a pressure gradient: $j_h = M_{21}(-\nabla p)$



Standard prediction:

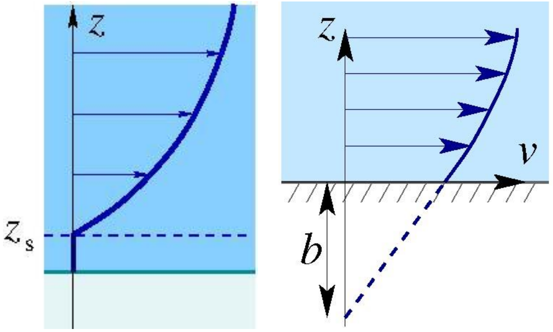
$$M_{12} = M_{21} = \frac{1}{\eta}\int_0^{+\infty} z\,\delta h(z)\,\mathrm{d}z$$

Derjaguin and Sidorenkov, 1941

enthalpy density excess

Interfacial hydrodynamics: stagnant layer (z_s), slip (b)…

$$M_{12} = M_{21} = \frac{1}{\eta}\int_{z_s}^{+\infty} (z - z_s + b)\,\delta h(z)\,\mathrm{d}z$$



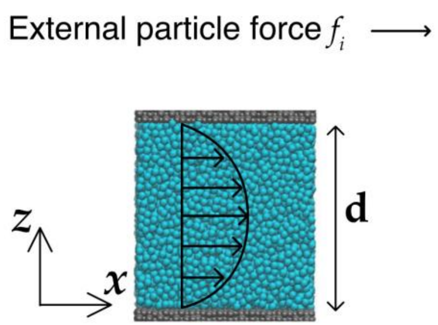
Following analogous treatment of electro-osmosis by Huang et al.

Fu, Merabia, Joly, PRL 2017

Molecular dynamics

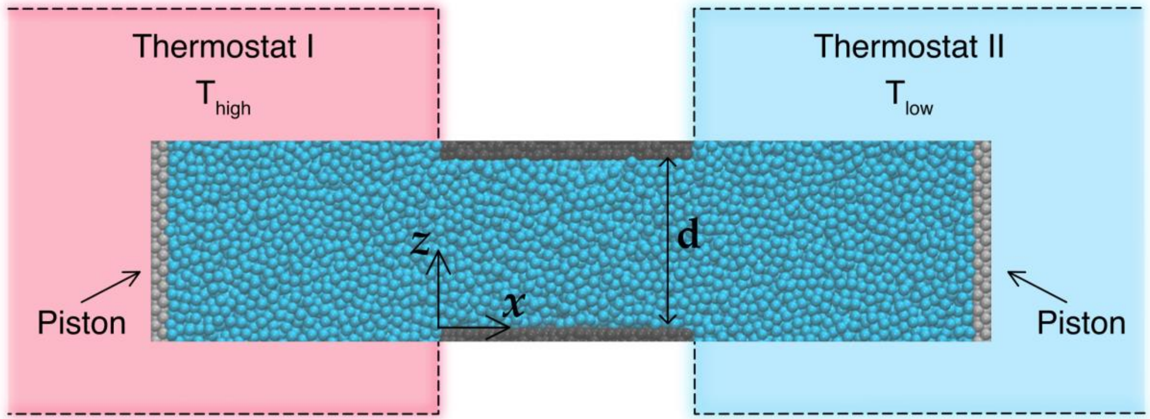
Generic Lennard-Jones interaction potential: $V(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$

(a) Mechano-caloric configuration



$$\delta j_h = M_{21}(-\nabla p)$$

(b) Thermo-osmotic configuration



$$v_s = M_{12}(-\frac{\nabla T}{T})$$

Effect of wetting?

Varying liquid-solid interaction energy ε_{ls}

Fu, Merabia, Joly, PRL 2017

Molecular dynamics

Measurements

$$j_h = M_{21}(-\nabla p)$$

$$j_h = \int \delta h(z) v_x(z) dz$$

$$-\nabla p = f_V = f_i N/V$$

$$v_s = M_{12}\left(-\frac{\nabla T}{T}\right)$$

from # of particles in reservoirs

from temperature profile in channel

Theoretical prediction

$$M_{12} = M_{21} = \frac{1}{\eta}\int_{z_s}^{+\infty} (z - z_s + b)\,\delta h(z)\,\mathrm{d}z$$

- hydrodynamics: from Poiseuille flow in mechano-caloric configuration
- thermodynamics: from equilibrium simulations

$$\delta h_{\mathrm{eq}}(r;T) = h_{\mathrm{eq}}(r;T) - h_{\mathrm{bulk}}(T)$$

$$h(r) = (u_i(r) + p_i^{zz}(r))\rho(r),$$

Fu, Merabia, Joly, PRL 2017

Molecular dynamics

Measurements

$$j_h = M_{21}(-\nabla p)$$

$$j_h = \int \delta h(z) v_x(z) dz$$

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- hydrodynamics: from Poiseuille flow in mechano-caloric configuration
- thermodynamics: from equilibrium simulations

$$\delta h_{\mathrm{eq}}(r;T) = h_{\mathrm{eq}}(r;T) - h_{\mathrm{bulk}}(T)$$

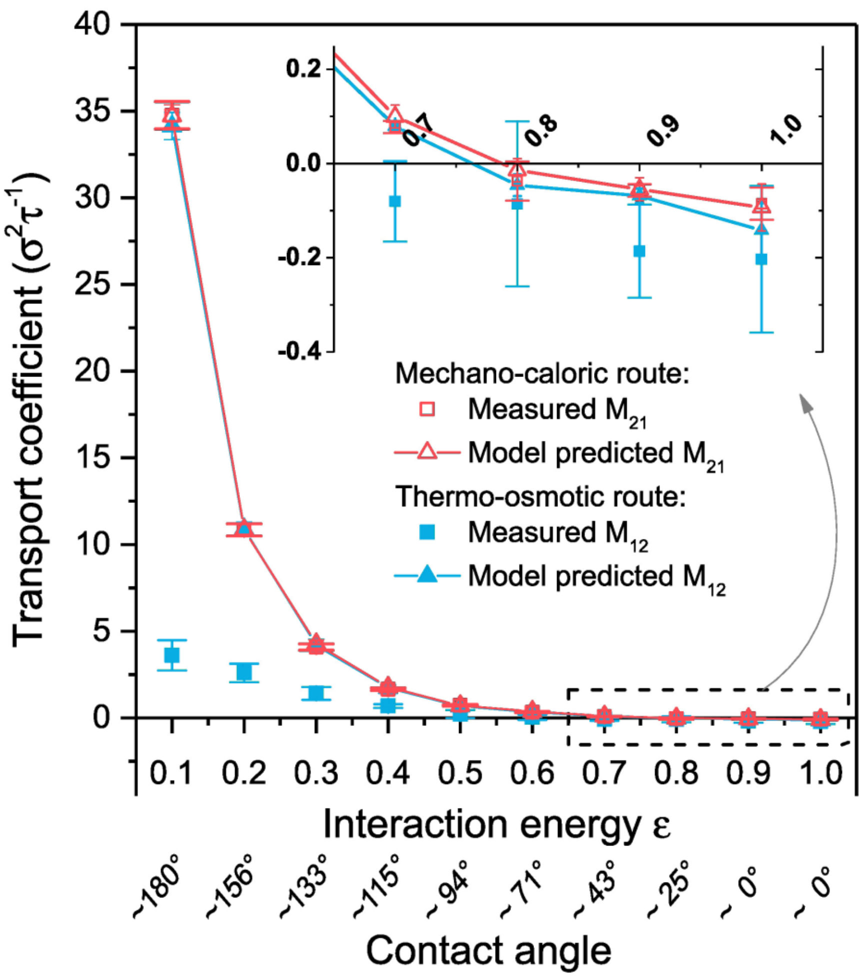
$$h(r) = (u_i(r) + p_i^{zz}(r))\rho(r),$$

compute stress/atom:

$$S_{ab} = -\Big[m v_a v_b + \frac{1}{2}\sum_{n=1}^{N_p}(r_{1_a}F_{1_b} + r_{2_a}F_{2_b}) + \frac{1}{2}\sum_{n=1}^{N_b}(r_{1_a}F_{1_b} + r_{2_a}F_{2_b}) + \frac{1}{3}\sum_{n=1}^{N_a}(r_{1_a}F_{1_b} + r_{2_a}F_{2_b} + r_{3_a}F_{3_b}) + \frac{1}{4}\sum_{n=1}^{N_d}(r_{1_a}F_{1_b} + r_{2_a}F_{2_b} + r_{3_a}F_{3_b} + r_{4_a}F_{4_b}) + \frac{1}{4}\sum_{n=1}^{N_i}(r_{1_a}F_{1_b} + r_{2_a}F_{2_b} + r_{3_a}F_{3_b} + r_{4_a}F_{4_b}) + \mathrm{Kspace}(r_{i_a}, F_{i_b}) + \sum_{n=1}^{N_f} r_{i_a}F_{i_b} \Big]$$

Fu, Merabia, Joly, PRL 2017

Results

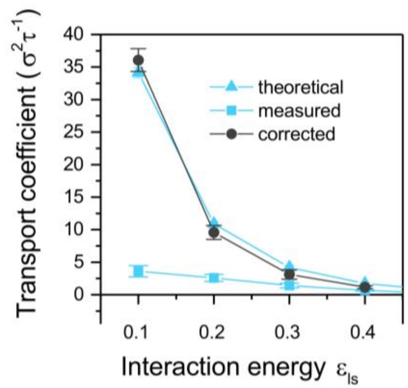


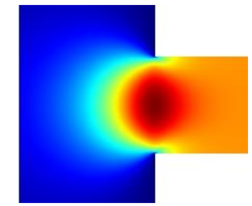
non-wetting wetting

Fu, Merabia, Joly, PRL 2017

Thermo-osmotic route

- viscous entrance effects





Wetting systems

- $|M_{21}| \sim 0.1\sigma^2/\tau \sim 10^{-8}\,\mathrm{m}^2/\mathrm{s}$
- cf. experiments ~ 10^{-10} to 10^{-9} m^2/s
- **change of sign**

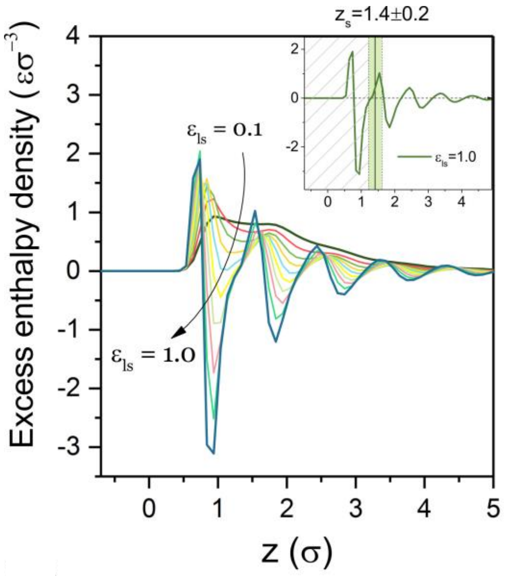
cf. Lüsebrink, Yang, Ripoll, JPCM 2012

Non-wetting systems

- **giant response**

up to $\sim 35\sigma^2/\tau \sim 4 \times 10^{-6}\,\mathrm{m}^2/\mathrm{s}$

Interfacial hydrodynamics

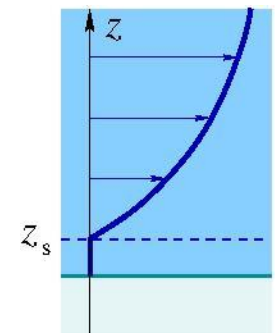


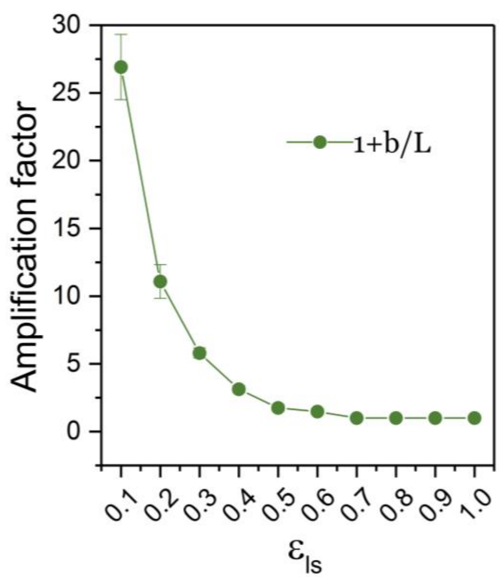
Wetting systems

Oscillations of the excess enthalpy

- crucial role of z_s

$$M_{12} = M_{21} = \frac{1}{\eta} \int_{z_s}^{+\infty} (z - z_s + b)\, \delta h(z)\, \mathrm{d}z$$

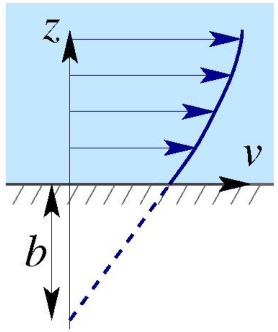




Non-wetting systems

Molecular thickness of the interaction layer

- large amplification by slip

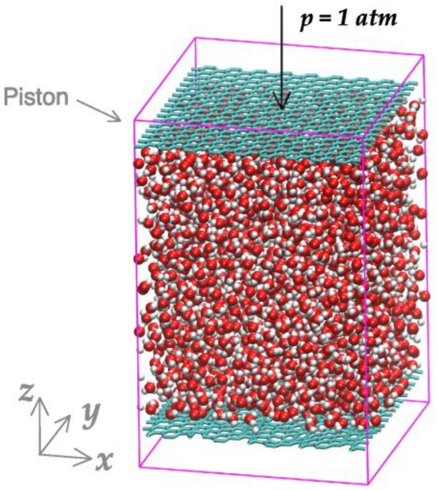


cf.

electro-osmosis: Joly et al. PRL 2004, JCP 2006
Joly et al. PRL 2014, Barbosa De Lima & Joly 2017
diffusio-osmosis: Ajdari & Bocquet, PRL 2006
thermo-phoresis: Morthomas, Würger, JPCM 2009

Fu, Merabia, Joly, PRL 2017

Water-graphene interface

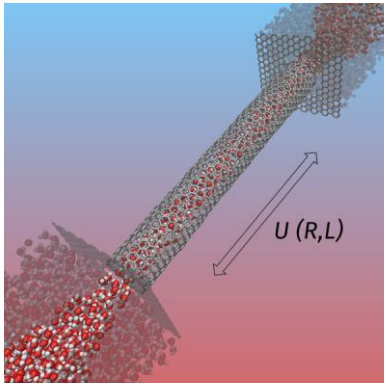


Giant thermo-osmotic response:

$$M_{21} = (2.5 \pm 0.3) \times 10^{-6}\,\mathrm{m}^2/\mathrm{s}$$

Waste heat harvesting with graphitic membranes?

- entrance pressure drop
- thermal short-circuit by walls
- desalination applications: ultra-confinement



Fu, Merabia, Joly, PRL 2017

Carbon nanotube membranes

Analytical model coupling thermodynamics and hydrodynamics

$$U = \frac{R\,\overline{\delta h}}{2\lambda L + \pi C \eta} \times \frac{\Delta T}{T_{\text{avg}}} \times \left(1 - \frac{T_{\text{avg}}\,\Delta\Pi}{\Delta T\,\overline{\delta h}}\right)$$

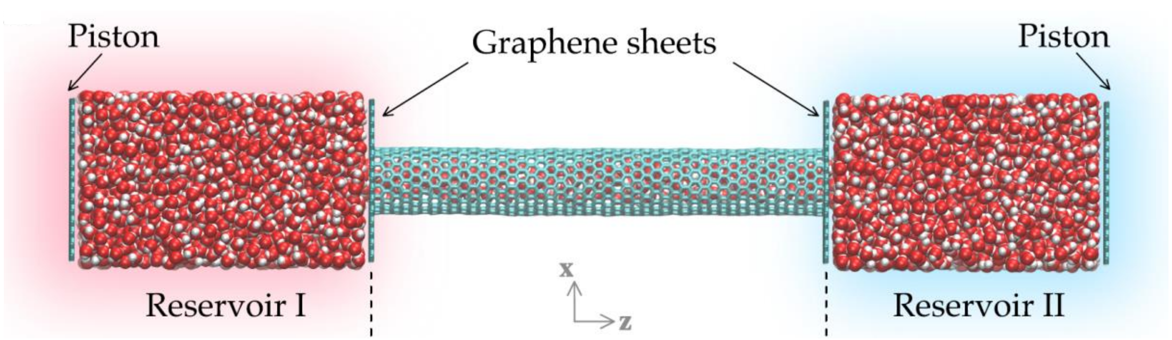
$\overline{\delta h}$: average enthalpy excess density over the section of the tube

λ : friction coefficient

C : numerical constant depending on the geometry and the hydrodynamic boundary condition => entrance effects

$\Delta\Pi$: osmotic pressure

MD simulations

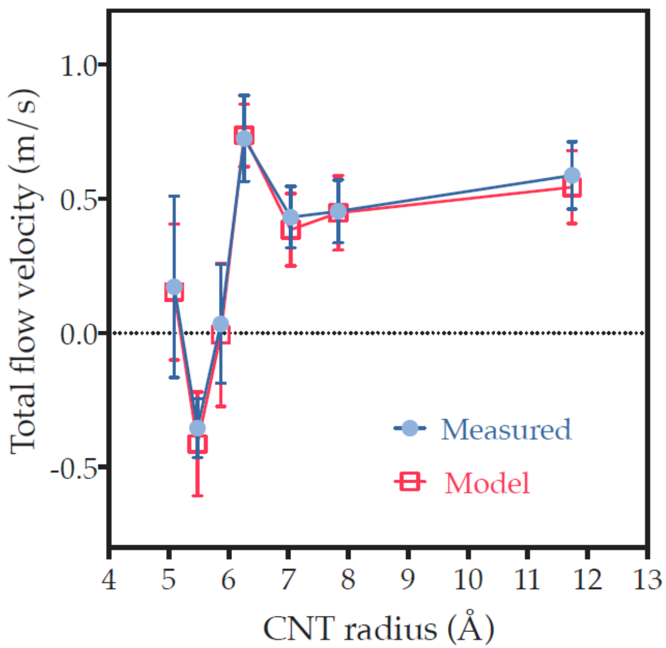


Fu, Merabia, Joly, J. Phys. Chem. Lett. 2018

Carbon nanotube membranes

Pumping ($\Delta\Pi = 0$)

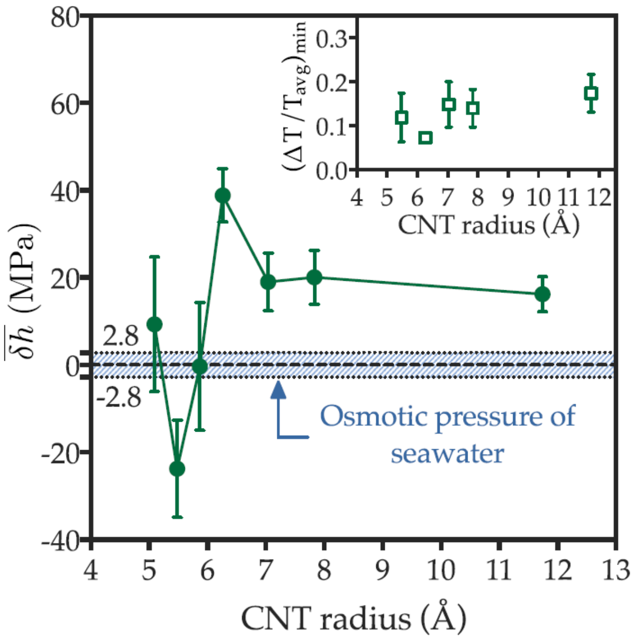
$$U = \frac{R\,\overline{\delta h}}{2\lambda L + \pi C\eta} \times \frac{\Delta T}{T_{avg}}$$



Desalination / overcoming a pressure difference

$$\Delta\Pi_{max} = \overline{\delta h} \times \Delta T / T_{avg}.$$

cf. Dariel & Kedem J. Phys. Chem. 1975



- **Model validated by MD results -> can help searching for other innovative membranes**
- **Fast and robust flows (even when extrapolated to experimental parameters)**

Fu, Merabia, Joly, J. Phys. Chem. Lett. 2018

Conclusion

Osmotic flows generated in the nanometric vicinity of interfaces

- Molecular **structure** and **dynamics**
- *Interfacial hydrodynamics can control amplitude and sign of the response!*

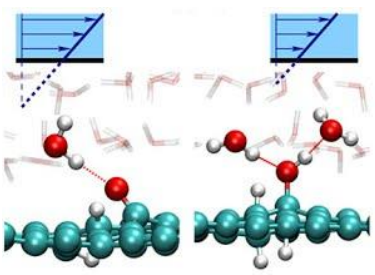
➡ **Molecular dynamics simulations**

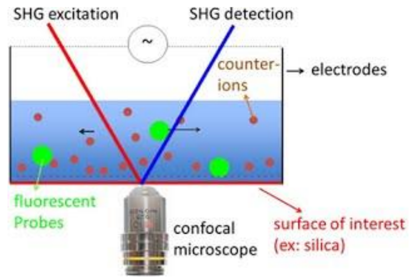
However:

- Numerical investigations limited to classical molecular dynamics

→ reactivity?
see e.g. Joly et al., J. Phys. Chem. Lett. 2016

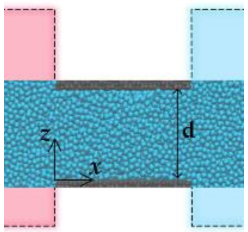
➡ **NECtAR project: Nanofluidic Energy Conversion using reActive suRfaces**
https://sites.google.com/site/anrnectar/





Bonhomme, Blanc, Joly, Ybert, Biance, Adv. Colloid Interface Sci. 2017
Hartkamp, Biance, Fu, Dufrêche, Bonhomme, Joly, submitted to Curr. Opin. Colloid Interface Sci

Thank you



Li Fu
Samy Merabia

- French National Research Agency, project NECtAR
- Institut Universitaire de France

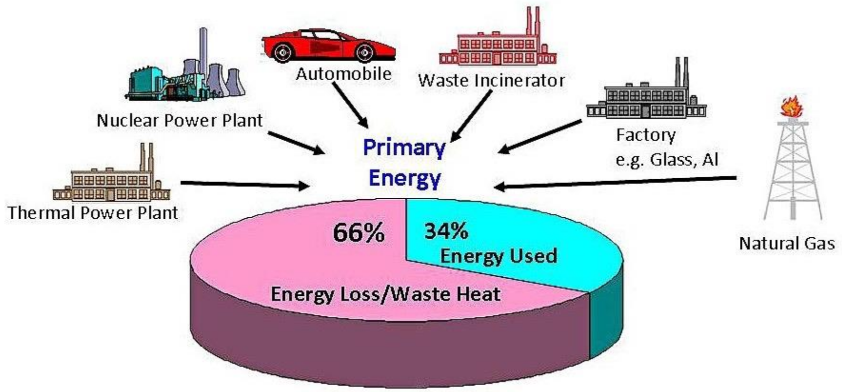
Joly, Detcheverry, Biance, PRL 2014
Barbosa De Lima, Joly, Soft Matter 2017
Lee, Cottin-Bizonne, Fulcrand, Joly, Ybert, J. Phys. Chem. Lett. 2017
Fu, Merabia, Joly, PRL 2017
Fu, Merabia, Joly, J. Phys. Chem. Lett. 2018

http://ilm-perso.univ-lyon1.fr/~ljoly/

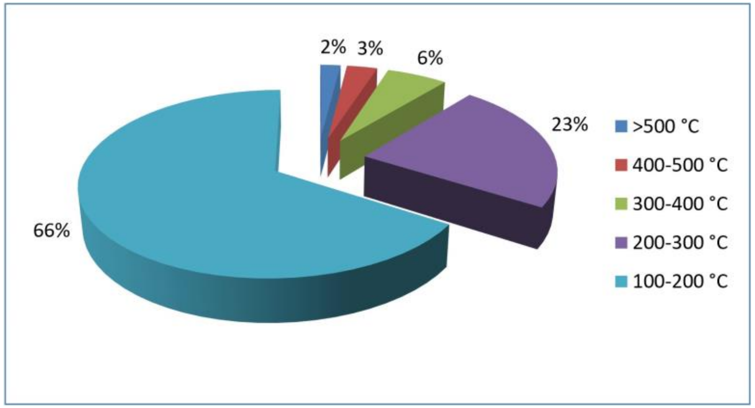
Thermo-osmosis: waste heat

Heat management: a crucial challenge

- Waste heat produced by industry and energy conversion
- Large fraction of low grade waste heat



Energy loss through waste heat (Penn State University)



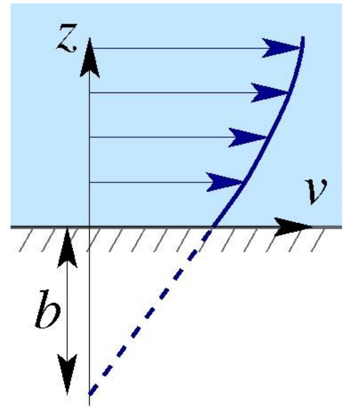
Distribution of waste heat in industry

Could nanofluidic systems be used for (low grade) waste heat harvesting?

Interfacial hydrodynamics

Hydrodynamic slip

$$v_{\text{slip}} = b \left.\frac{\partial v}{\partial z}\right|_{\text{wall}}$$



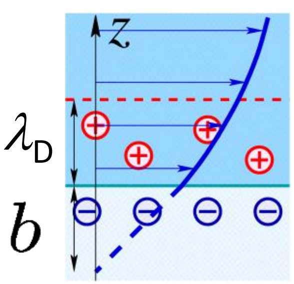
Slip length

b ~ tens of nm

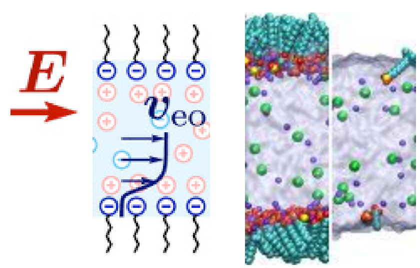
Flow amplification factor: $$1 + \frac{b}{L}$$

interfacial layer thickness

Electro-osmosis

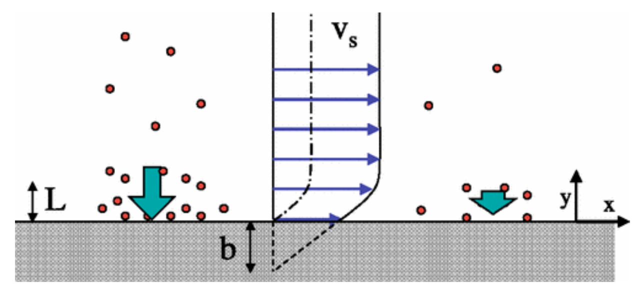


Joly et al., PRL 2004, JCP 2006



Joly et al., PRL 2014
Barbosa De Lima & Joly 2017

Diffusio-osmosis



Ajdari & Bocquet, PRL 2006

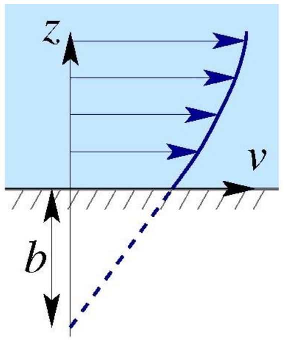
A more general model

Continuum hydrodynamics (cst η), partial slip BC

$$\frac{\mathrm{d}^2 v_x}{\mathrm{d}z^2} = -\frac{E_x}{\eta}\rho_\mathrm{e}(z) \quad \text{with} \quad v_x(z_\mathrm{w}) = b\,\frac{\mathrm{d}v_x}{\mathrm{d}z}\bigg|_{z=z_\mathrm{w}}$$

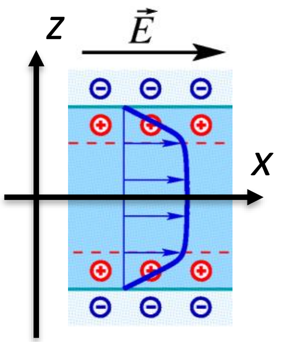
Stokes equation

Partial slip BC at $z = z_\mathrm{w}$



$$\zeta = \frac{\eta v_\mathrm{eo}}{\varepsilon E_x} = \frac{\eta v_x(0)}{\varepsilon E_x} = \frac{1}{\varepsilon}\int_{z_\mathrm{w}}^{0} \mathrm{d}z\,(z - z_\mathrm{w} + b)\rho_\mathrm{e}(z)$$

ε = bulk permittivity, no assumption on $\varepsilon(z)$ close to the surface



Uncharged surfaces: $$\int_{z_\mathrm{w}}^{0} \mathrm{d}z\,\rho_\mathrm{e}(z) = 0$$

$$\zeta = \frac{1}{\varepsilon}\int_{z_\mathrm{w}}^{0} \mathrm{d}z\,z\rho_\mathrm{e}(z)$$

- **independent of *b***
(i.e. of friction)

Huang et al., PRL 2007, Langmuir 2008

Model (1)

Thermal gradient → thermodynamic force density

$$f_{\mathrm{thermo}} \approx \delta h_{\mathrm{eq}}(r;T_{\mathrm{avg}})\,\frac{\nabla T(z)}{T_{\mathrm{avg}}},$$

with

$$\delta h_{\mathrm{eq}}(r;T) = h_{\mathrm{eq}}(r;T) - h_{\mathrm{bulk}}(T)$$
$$h(r) = \ (u_i(r) + p_i^{zz}(r))\rho(r),$$

Fluid friction on the wall: $F_{\mathrm{friction}} = 2\pi R L \lambda v_{\mathrm{osm}}$

- **Bare thermo-osmotic velocity in the tube (large slip limit)**

$$v_{\mathrm{osm}} = \frac{R\,\overline{\delta h}}{2\lambda L} \times \frac{\Delta T}{T_{\mathrm{avg}}}.$$

with

$$\overline{\delta h} = \frac{1}{\pi R^2}\int_0^R \mathrm{d}r\, 2\pi r\, \delta h_{\mathrm{eq}}(r;T_{\mathrm{avg}}),$$

- **General hydrodynamic boundary condition**

$$v_{\mathrm{osm}} = \frac{R^2}{4\eta L}\left(1 + \frac{2b}{R}\right) \times \overline{\delta h} \times \frac{\Delta T}{T_{\mathrm{avg}}}.$$

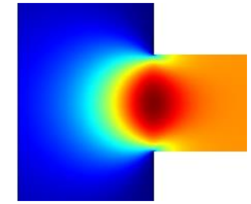
with

$$\overline{\delta h} = \frac{1}{\pi R^2}\int_0^R \mathrm{d}r\, 2\pi r\, \delta h\, \left(1 - \frac{r^2}{R^2 + 2bR}\right),$$

Model (2)

Backflow due to:

- viscous entrance pressure drop $\Delta p_{\text{in}} = (\pi C\eta/R) \times U$
- pressure difference between reservoirs $\Delta\Pi$



Sampson, 1891

- **Total velocity through the membrane (large slip limit)**

$$U = \frac{R\,\overline{\delta h}}{2\lambda L + \pi C\eta} \times \frac{\Delta T}{T_{\text{avg}}} \times \left(1 - \frac{T_{\text{avg}}\,\Delta\Pi}{\Delta T\,\overline{\delta h}}\right).$$

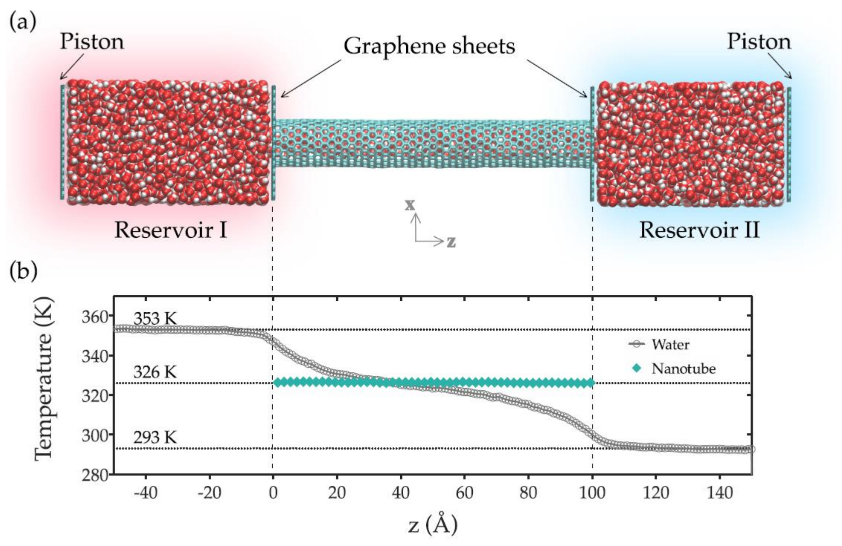
$$\Delta\Pi_{\text{max}} = \overline{\delta h} \times \Delta T / T_{\text{avg}}.$$

cf. Dariel & Kedem J. Phys. Chem. 1975

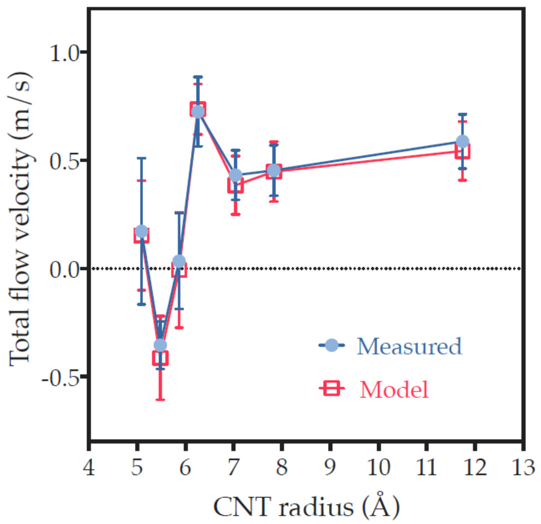
- **General hydrodynamic boundary condition**

$$U = \frac{R^2\left(1+\frac{2b}{R}\right) \times \overline{\delta h} \times (\Delta T/T_{\text{avg}})}{4\eta L + \frac{\pi C\eta R}{2}\left(1+\frac{4b}{R}\right)} \times \left(1 - \frac{\left(1+\frac{4b}{R}\right)}{2\left(1+\frac{2b}{R}\right)} \times \frac{T_{\text{avg}}\,\Delta\Pi}{\Delta T\,\overline{\delta h}}\right).$$

Molecular dynamics



Model ($\Delta\Pi = 0$): $U = \dfrac{R\,\overline{\delta h}}{2\lambda L + \pi C \eta} \times \dfrac{\Delta T}{T_{\text{avg}}}$



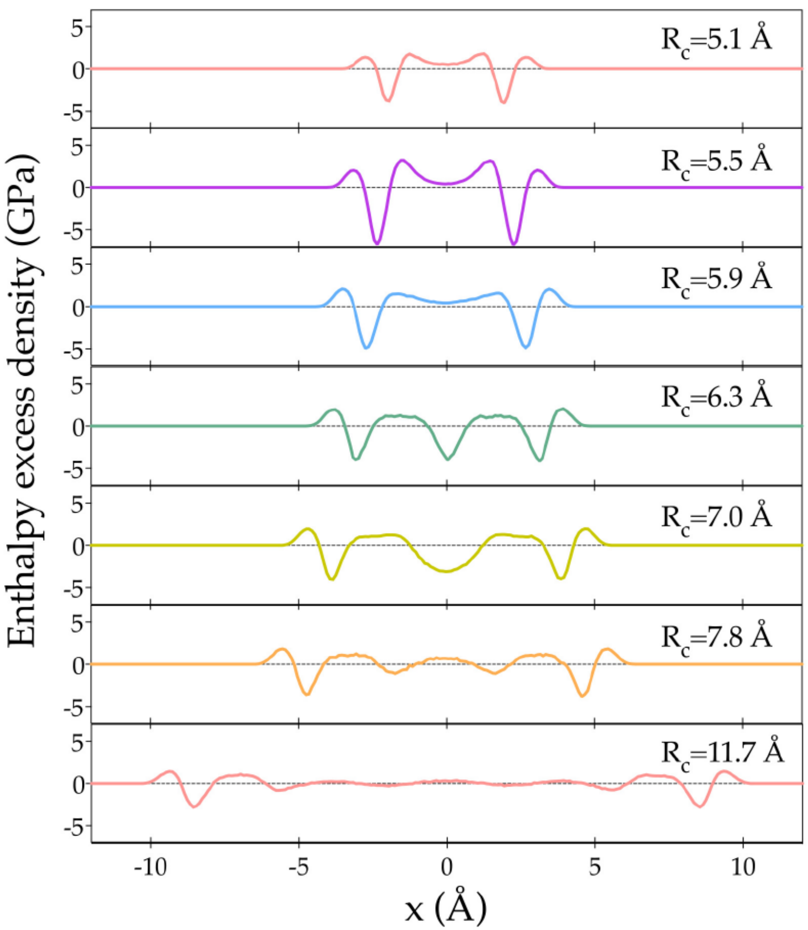
Quantitative match between model and MD results

- Crucial role of hydrodynamics
- The MD-validated model can predict velocity in experimental situations

Giant velocities, despite entrance effects and thermal short-circuit mechanism

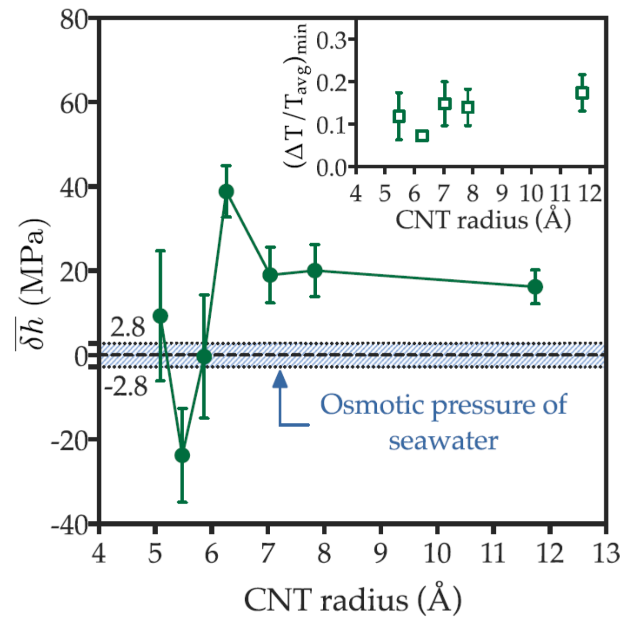
- Reaching a plateau ~ 0.5 m/s for large radii
- Complex dependency on *R* for small radii

Enthalpy profiles



Model ($\Delta\Pi = 0$): $$U = \frac{R\,\overline{\delta h}}{2\lambda L + \pi C\eta} \times \frac{\Delta T}{T_{\rm avg}}$$

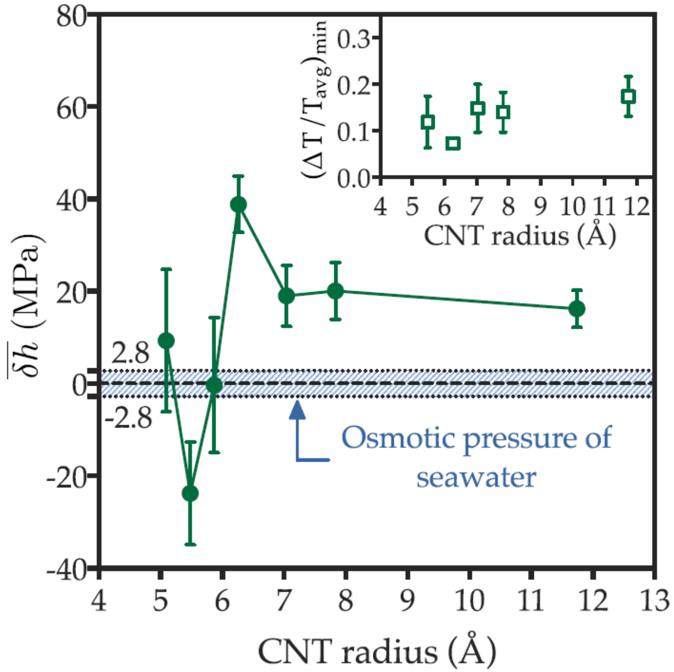
$$\overline{\delta h} = \frac{1}{\pi R^2}\int_0^R \mathrm{d}r\; 2\pi r\; \delta h_{\rm eq}(r; T_{\rm avg}),$$



- Weak confinement: model predicts $\overline{\delta h}$ varies as $1/R$. → **constant velocity**
- Strong confinement: overlap of the interaction layers → complex evolution of $\overline{\delta h}$

Overcoming a pressure difference

$$\Delta\Pi_{\max} = \overline{\delta h} \times \Delta T/T_{\text{avg}}.$$



- **Desalination possible!**
- MD simulation with $\Delta\Pi = 2.8\,\text{MPa}$ → $U = 0.38 \pm 0.18\,\text{m/s}$

(model: $U = 0.44 \pm 0.06\,\text{m/s}$)