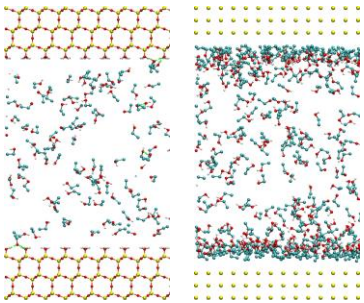
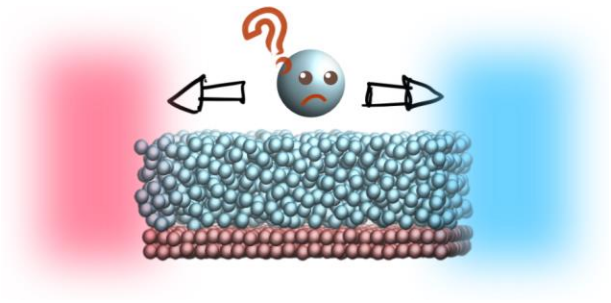
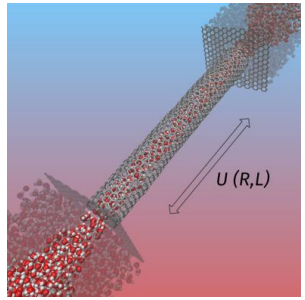





Molecular views on osmotic flows

Laurent Joly

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

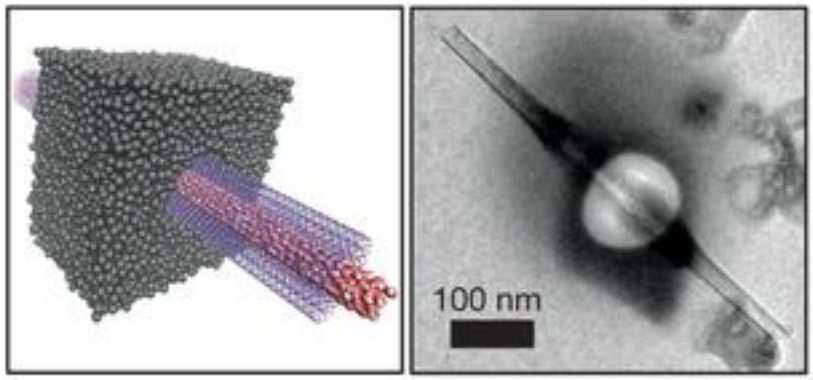
http://ilm-perso.univ-lyon1.fr/~ljoly/

Nanofluidics

Nanofluidics:
fluidic transport (hydrodynamic, electrical, ionic, thermal…) in nanoconfined fluids

Blue energy

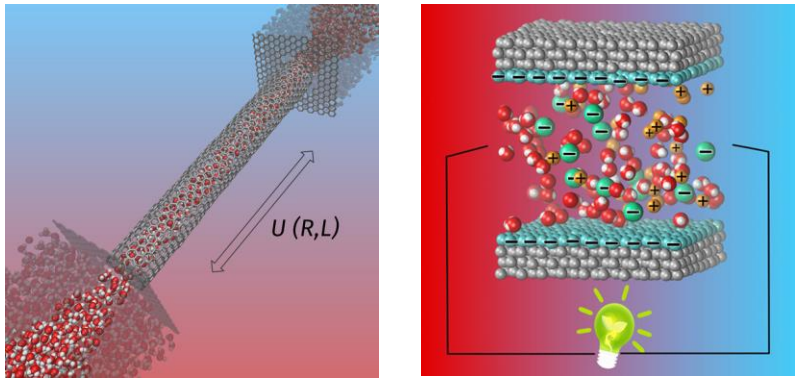
- Electricity from salinity gradients



Siria et al., Nature 2013

Waste heat harvesting

- Electricity from thermal gradients



Fu et al., PRL 2017, JPCL 2018, PRL 2019
Herrero et al. 2022, Ouadfel et al. 2023

surface effects

Siria, Bocquet, Bocquet, Nature Reviews Chemistry 2017
Kavokine, Netz & Bocquet, Annu. Rev. Fluid Mech., 2021
Herrero, Allemand, Merabia, Biance & Joly, arXiv:2204.13522

Electrokinetic effects

Coupling between different types of transport at surfaces:
hydrodynamic, electrical, compositional, thermal…

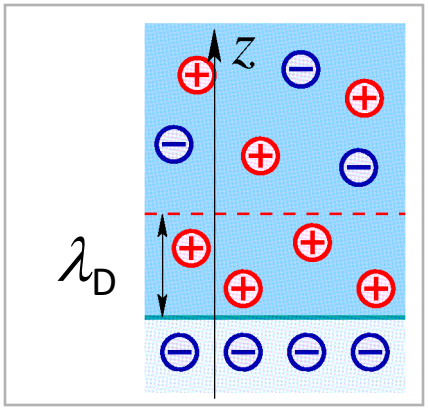
Response matrix

$$\begin{pmatrix} q \\ j_e \\ j_n \\ j_h \\ \vdots \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} & \cdots & & \\ M_{21} & M_{22} & \cdots & & \\ \vdots & \ddots & M_{33} & & \\ & & & M_{44} & \\ & & & & \ddots \end{pmatrix} \begin{pmatrix} -\nabla p \\ -\nabla V \\ -k_B T \nabla c/c \\ -\nabla T/T \\ \vdots \end{pmatrix}$$

Onsager reciprocal relations:

$$M_{ij} = M_{ji}$$





Interaction layer → surface excesses

e.g. electrical double layer (EDL)

Debye length λ_D ~ 0.3 to 30 nm

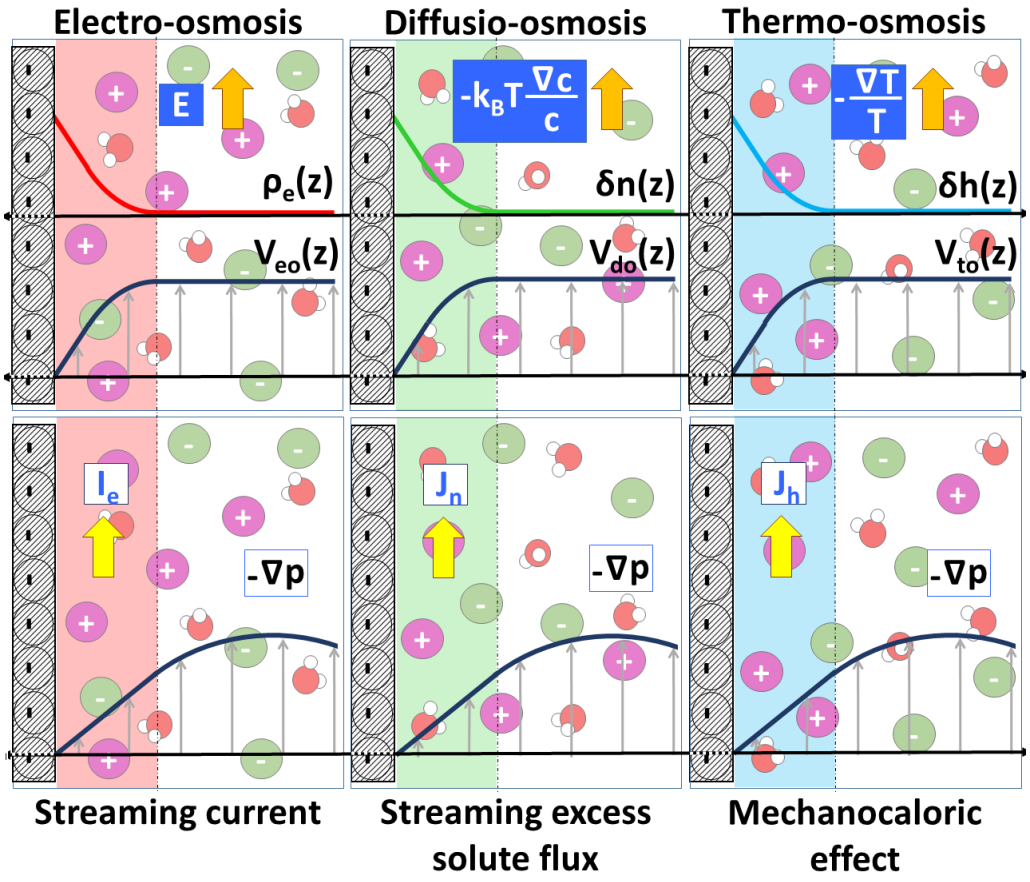
in aqueous electrolytes at room temperature

The interaction layer couples different types of transport

Herrero, Allemand, Merabia, Biance, Joly, arXiv preprint 2022

Osmotic flows

with **C. Herrero**, A. Allemand, S. Merabia, A.-L. Biance



$$\begin{pmatrix} M_{11} & M_{12} & \cdots \\ M_{21} & M_{22} & \cdots \\ \vdots & \cdots & M_{33} \\ & & & M_{44} \\ & & & & \ddots \end{pmatrix}$$

$$\begin{pmatrix} M_{11} & M_{12} & \cdots \\ M_{21} & M_{22} & \cdots \\ \vdots & \cdots & M_{33} \\ & & & M_{44} \\ & & & & \ddots \end{pmatrix}$$

$$M_{ij} = M_{ji}$$



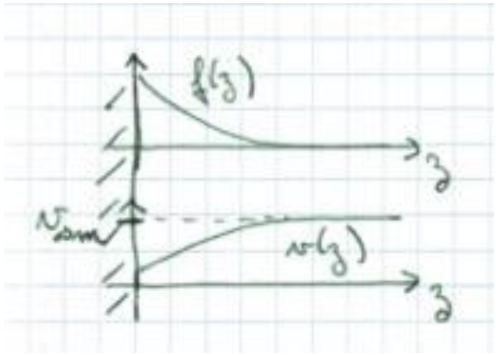
Generic framework?

Osmotic velocity over a planar wall

Low-Reynolds hydrodynamics: Stokes equation

Newtonian incompressible liquid with homogeneous viscosity

Force density $f(z)$ close to the wall (e.g. electric force for EO)



$$-\eta \frac{\mathrm{d}^2 v}{\mathrm{d}z^2} = f(z)$$

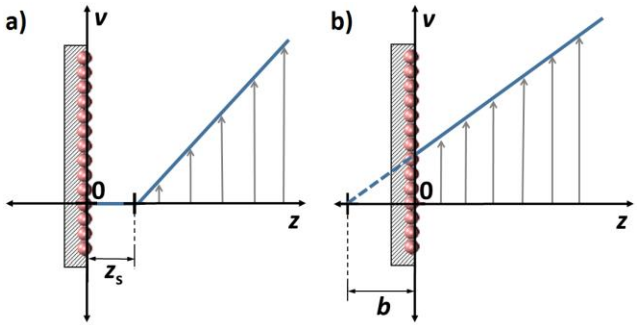
Hydrodynamic boundary condition:

stagnant layer

$$v(z_\mathrm{s}) = 0$$

slip

$$v_\mathrm{slip} = v(0) = b \left.\frac{\mathrm{d}v}{\mathrm{d}z}\right|_{z=0}$$



Velocity far from the wall:

stagnant layer

$$v_\mathrm{osm} = \frac{1}{\eta} \int_{z_\mathrm{s}}^{\infty} \mathrm{d}z\, (z - z_\mathrm{s}) f(z)$$

slip

$$v_\mathrm{osm} = \frac{1}{\eta} \int_{0}^{\infty} \mathrm{d}z\, (z + b) f(z)$$

From now on: focus on slipping surfaces

Derjaguin, Churaev, Muller, in Surface Forces

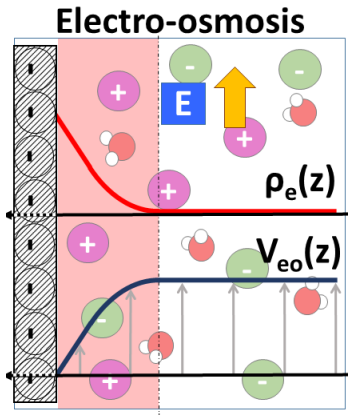
Anderson, Annu. Rev. Fluid Mech. 1989

Electro-osmosis

Force density: $f(z) = \rho_e(z)E$ with ρ_e the free charge density

$$\Rightarrow \quad \frac{v_{osm}}{E} = \frac{1}{\eta}\int_0^\infty dz\,(z+b)\rho_e(z)$$

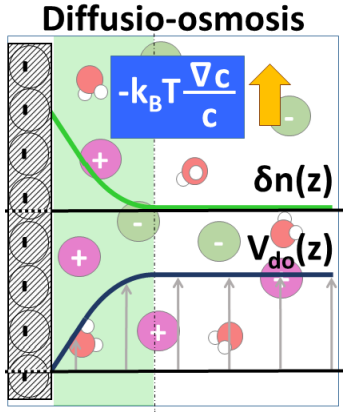
with $\rho_e = q(n_+ - n_-)$ ⇒ atomistic simulations



Huang et al., PRL 2007, Langmuir 2008

Herrero, Allemand, Merabia, Biance, Joly, arXiv preprint 2022

Diffusio-osmosis

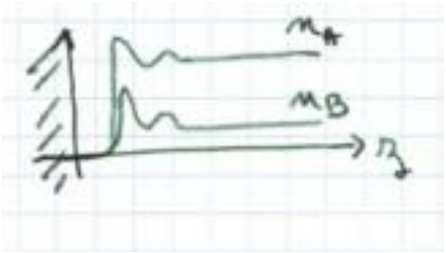


Force density: Local thermal equilibrium -> Gibbs-Duhem relation

$$V\,\mathrm{d}P - S\,\mathrm{d}T = \sum_{i=1}^{N} n_i\,\mathrm{d}\mu_i$$

E.g.: solution of B in A

$$f(z) = -k_\mathrm{B}T\frac{\nabla n_\mathrm{B}^\mathrm{b}}{n_\mathrm{B}^\mathrm{b}}\left(n_\mathrm{B}(z) - n_\mathrm{B}^\mathrm{b}\frac{n_\mathrm{A}(z)}{n_\mathrm{A}^\mathrm{b}}\right)$$



Liu, Ganti, Frenkel, J. Phys. Cond. Mat. 2018
Herrero, Allemand, Merabia, Biance, Joly, arXiv preprint 2022

Example of application:

predicting D_{DO} of NaI on graphene and BN from ab initio MD

$$D_\mathrm{do} = \frac{v_\mathrm{osm}}{-\nabla n_\mathrm{s}/n_\mathrm{s}} = \frac{k_\mathrm{B}T}{\eta}\int_0^\infty (z+b)\left(n_+(z) + n_-(z) - 2n_\mathrm{s}\frac{n_\mathrm{water}(z)}{n_\mathrm{water}^\mathrm{b}}\right)\mathrm{d}z$$

Joly, Meißner, Iannuzzi, Tocci, ACS Nano 2021

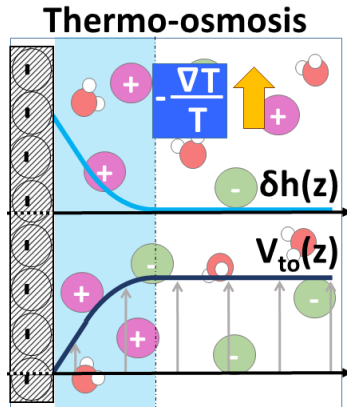
Thermo-osmosis

with **L. Fu**, **C. Herrero**, M. De San Féliciano, **M. Ouadfel**, S. Merabia

Local thermal equilibrium: Gibbs-Duhem relation

$$\frac{\partial P}{\partial x} = \left(\sum_{i=1}^{n} \rho_i \frac{\partial \mu_i}{\partial T} + \frac{S}{V} \right) \frac{\partial T}{\partial x}$$

$$f(z) = -\partial_x P = \delta s(z) \times (-\partial_x T) = \frac{\delta h(z)}{T} \times (-\partial_x T)$$



δs entropy excess density
δh enthalpy excess density

Ganti, Liu, Frenkel, PRL 2017, PRL 2018

Thermo-osmotic coefficient

$$M_{\mathrm{to}} = \frac{v_{\mathrm{osm}}}{-\partial_x T/T} = \frac{1}{\eta} \int_0^\infty \mathrm{d}z \, (z+b) \delta h(z)$$

Derjaguin, Churaev, Muller, in Surface Forces
Fu, Merabia, Joly, PRL 2017

Thermo-osmosis: aqueous electrolyte

Standard description:

Water contribution neglected, ion contribution purely from ES origin, ion distribution from Poisson-Boltzmann framework

Derjaguin, Churaev, Muller, in Surface Forces

Herrero, Joly, Poisson-Boltzmann formulary, arXiv:2105.00720

NOW WITH: thermodynamics of the EDL, osmotic flows in the PB framework…

MD simulations:

$$\delta h = \delta h^{0}_{\text{water}} + \delta h^{\text{dipole}}_{\text{water}} + \delta h^{0}_{\text{ions}} + \underbrace{\delta h^{\text{ES}}_{\text{ions}} + \delta h^{\text{mix}}_{\text{ions}}}_{\text{Modified PB (ion depletion)}}$$

$$M_{\text{to}} \simeq M^{\text{wat}}_{\text{to}} + M^{\text{el*}}_{\text{to}}$$

Rich phenomenology due to the competition between these 2 terms

Herrero, De San Féliciano, Merabia, Joly, Nanoscale 2022

Predicting thermo-osmosis from MD

Is Derjaguin's framework applicable at the nanoscale?

Comparing Derjaguin's approach and direct non-equilibrium measurements

- **Enthalpy excess route**

$$M_{to} = \frac{1}{\mathcal{H}_0} \int_0^{\infty} (z + b)\delta h(z)\mathrm{d}z$$

$$\delta h(z) = \sum_i n_i(z)[h_i(z) - h_i^{\mathrm{bulk}}]$$

$$h_i(z) = u_i(z) + \frac{p^{\parallel}(z)}{n_{\mathrm{tot}}(z)}$$

But: the local pressure is not well defined

$$\Delta H = \int_0^{\infty} \delta h(z)\mathrm{d}z$$

$$M_{to} = \frac{1}{\mathcal{H}_0} \int_0^{\infty} (z + b)\delta h(z)\mathrm{d}z = \frac{\Delta H}{\mathcal{H}}(\lambda_h + b)$$

with $\lambda_h = \frac{1}{\Delta H} \int_0^{\infty} z\delta h(z)\mathrm{d}z \sim 7$ Å

Ouadfel, Merabia, Yamaguchi, Joly, Molecular Physics 2024

Predicting thermo-osmosis from MD

Derjaguin's formalism:

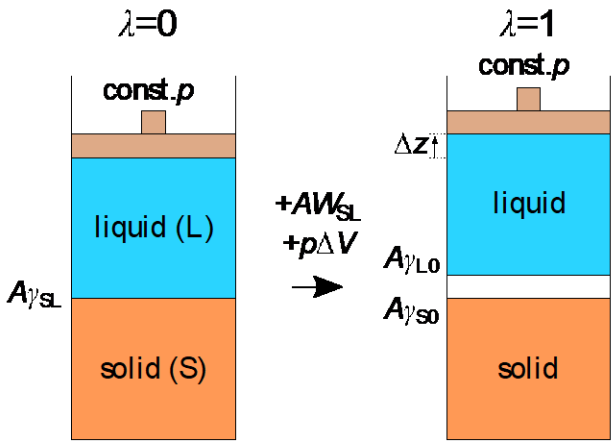
- **Entropy excess route**

$\mu_i = h_i - Ts_i$

$\Rightarrow \quad \delta h(z) = T\delta s(z)$ with $\delta s(z) = \sum_i n_i(z)[s_i(z) - s_i^{\text{bulk}}]$

$\Rightarrow$ $\Delta H = T\Delta S$ ⇒ Thermodynamic integration

Dry surface method: measuring the work of adhesion



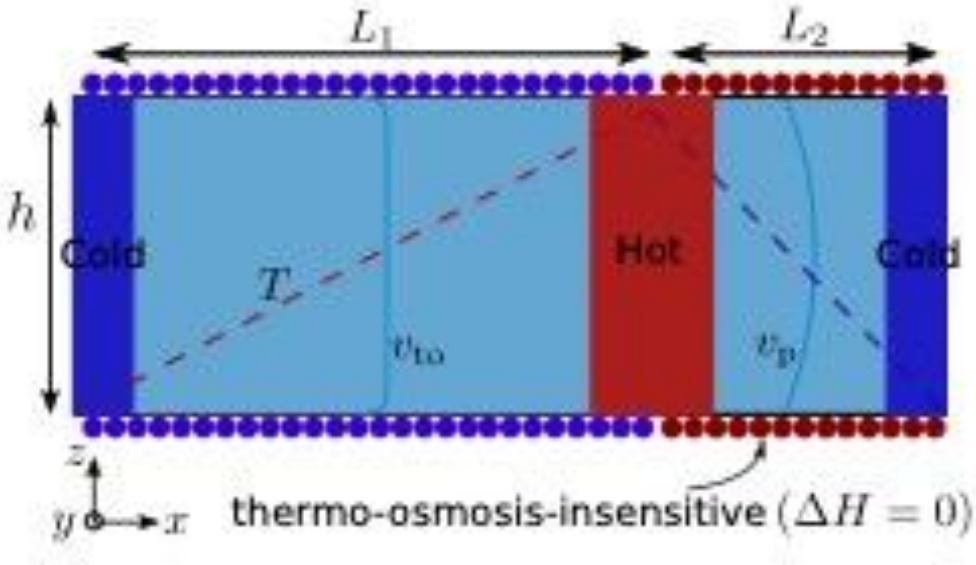
$$W_{sl}(\kappa) = \left(\frac{\Delta F}{A}\right)_{N,V,T} = -\frac{1}{A}[F(\kappa) - F(\kappa_0)] = -\frac{1}{A}\int_{\kappa_0}^{\kappa} \left\langle \frac{\partial \phi(\kappa')}{\partial \kappa'} \right\rangle_{N,V,T} d\kappa'$$

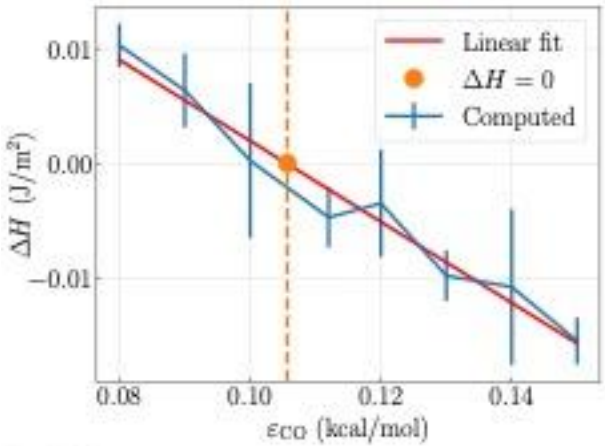
$$W_{sl}(\kappa) = \delta u_{sl}(\kappa) - T\delta s_{sl}(\kappa)$$

Ouadfel, Merabia, Yamaguchi, Joly, Molecular Physics 2024

Predicting thermo-osmosis from MD

Non-equilibrium simulations

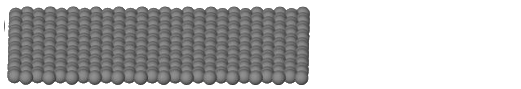


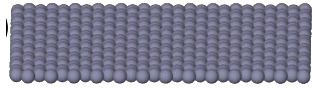


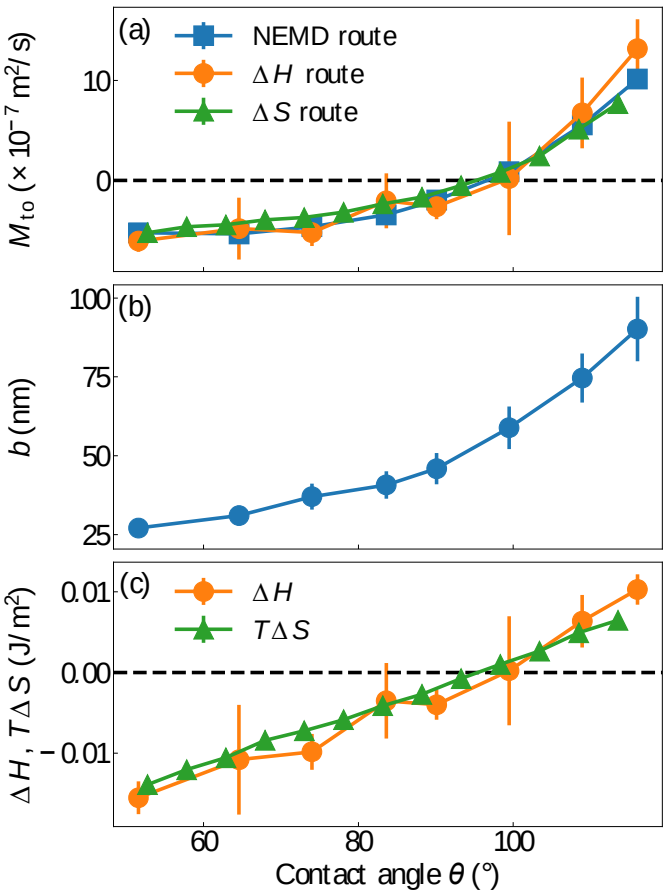
$$M_{to} = -\frac{\overline{v_{tot}}}{\nabla T_1/T}\left[1 + \frac{L_2\,(1+6\,b_1/h)}{L_1\,(1+6\,b_2/h)}\right]$$

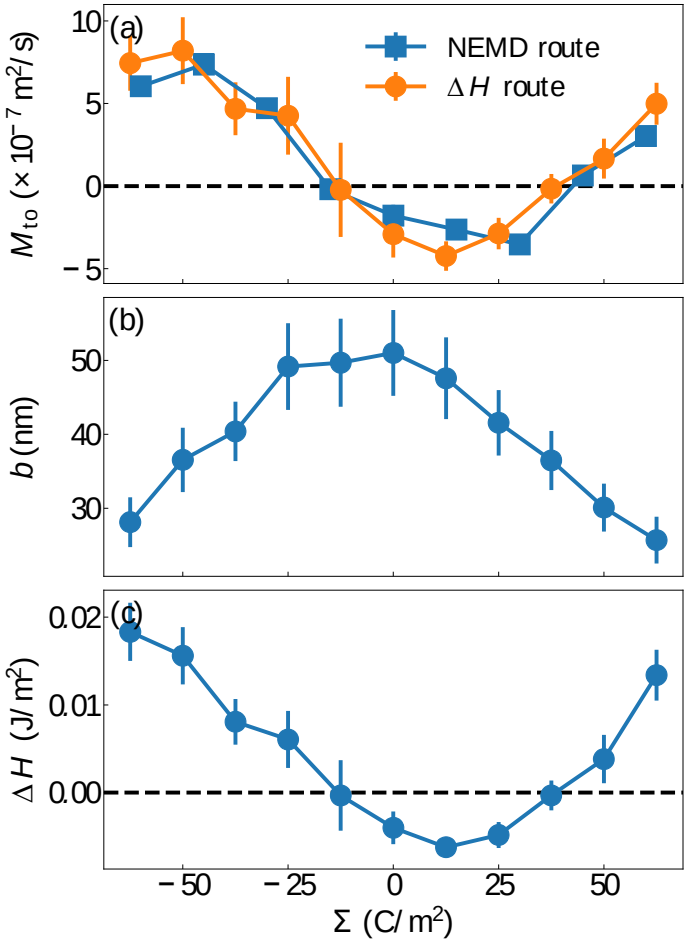
Ouadfel, Merabia, Yamaguchi, Joly, Molecular Physics 2024

Graphitic surfaces





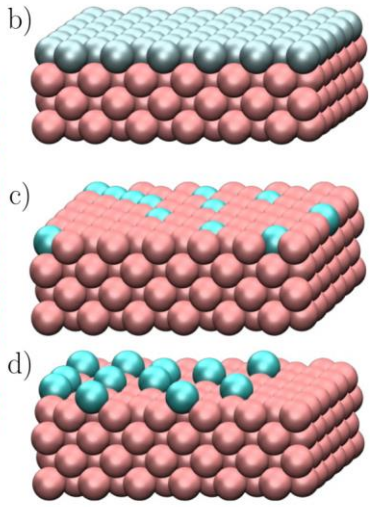


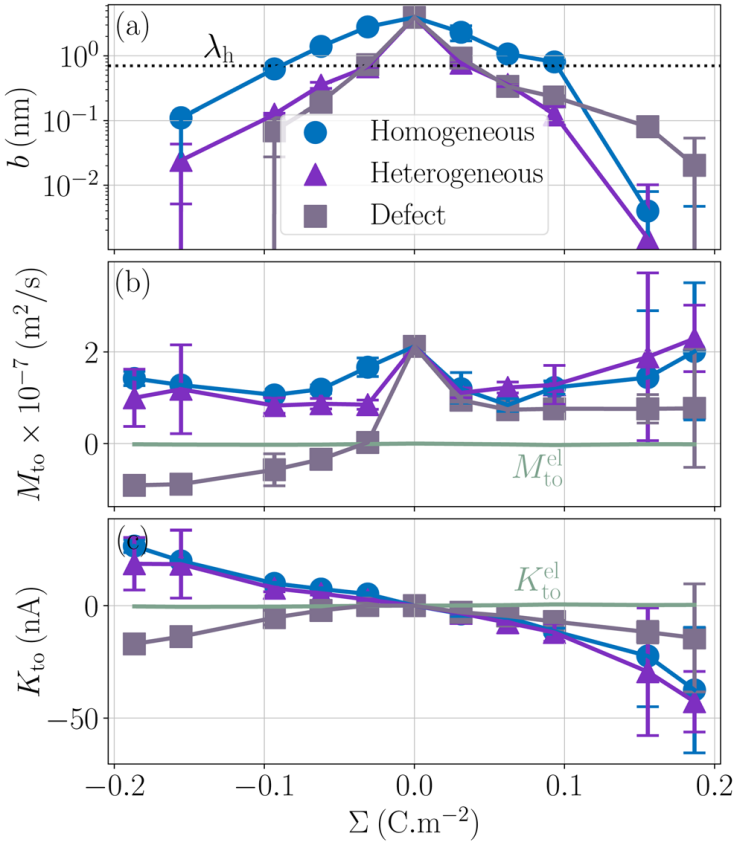


- The 3 methods match very nicely!
- Complex dependence on surface charge

Ouadfel, Merabia, Yamaguchi, Joly, Molecular Physics 2024

Thermo-osmosis vs surface charge





$$M_{to} = \frac{\Delta H}{\eta}(\lambda_h + b)$$

$$K_{to} \approx -\frac{\Sigma \Delta H}{\eta}(\lambda_h + b)$$

- Large impact of surface charge through water enthalpy excess
- Largely depends on surface charge distribution

Ouadfel, De San Féliciano, Herrero, Merabia, Joly, PCCP 2023

Conclusion

Osmotic transport generated in the nanometric vicinity of interfaces

- Molecular **structure** and **dynamics**
- *Interfacial hydrodynamics can control amplitude and sign of the response!*
- *Rich phenomenology originating in specific interactions with the walls*

Molecular dynamics simulations

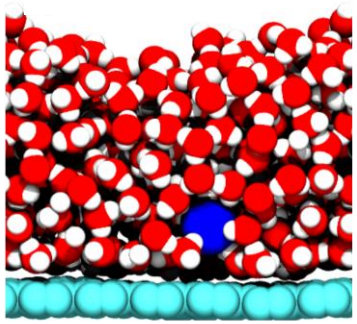
Toward a sustainable future

- Diffusio-osmotic current
- thermoelectricity

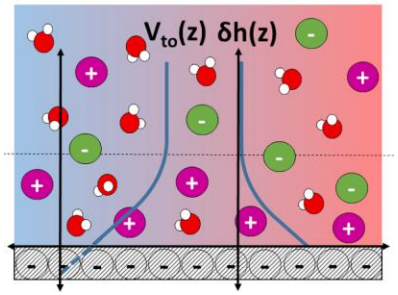
$$\begin{pmatrix} q \\ j_e \\ j_n \\ j_h \\ \vdots \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} & \cdots & & \\ M_{21} & M_{22} & \cdots & & \\ \vdots & \ddots & M_{33} & & \\ & & & M_{44} & \\ & & & & \ddots \end{pmatrix} \begin{pmatrix} -\nabla p \\ -\nabla V \\ -k_B T \nabla c/c \\ -\nabla T/T \\ \vdots \end{pmatrix}$$

Bonhomme, Blanc, Joly, Ybert, Biance, Adv. Colloid Interface Sci. 2017
Hartkamp, Biance, Fu, Dufrêche, Bonhomme, Joly, Curr. Opin. Colloid Interface Sci 2018
Herrero, Allemand, Merabia, Biance, Joly, arXiv preprint arXiv:2204.13522, 2022

Thank you



Electro & diffusio-osmosis
Gabriele Tocci
Marcella Iannuzzi
Robert Meißner
Anne-Laure Biance



Thermo-osmosis
Li Fu
Cecilia Herrero
Michael De San Féliciano
Aymeric Allemand
Mehdi Ouadfel
Samy Merabia

- French National Research Agency, projects EFOAM, NECtAR, smoothE
- Institut Universitaire de France
- Computational resources: GENCI-TGCC

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