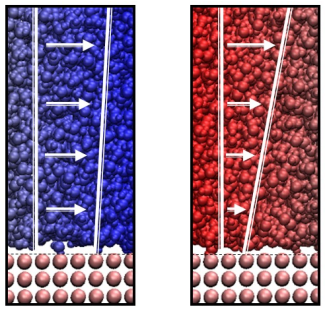
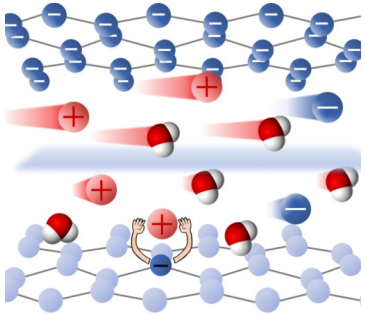




Optimizing liquid-solid slip in nanofluidic systems

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

UNIVERSITÉ DE LYON | Lyon 1

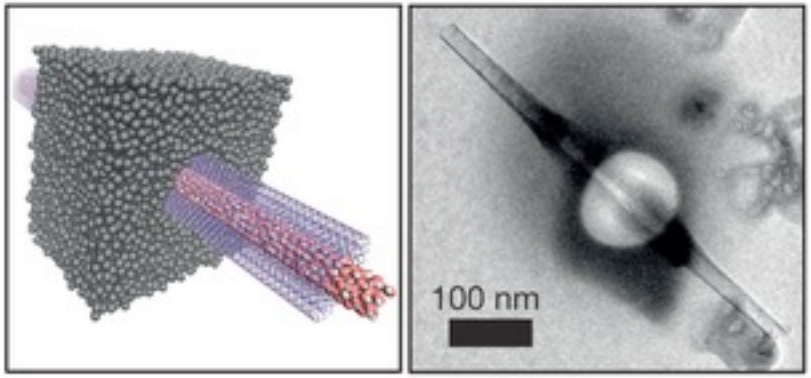
iLM INSTITUT LUMIÈRE MATIÈRE

cnrs

Nanofluidic systems

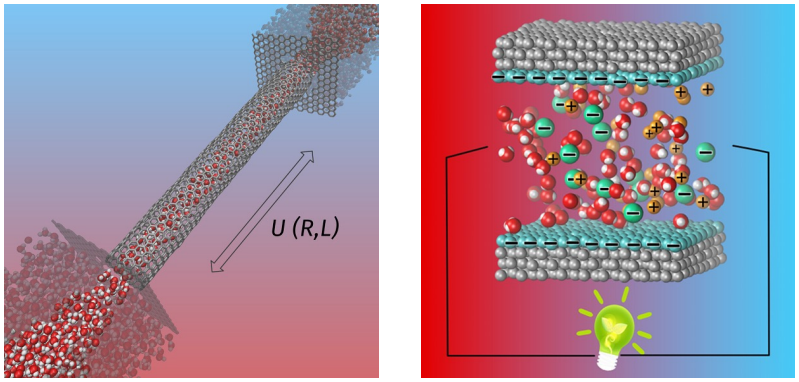
Transport in nanoconfined liquids ➔ present-day applications!

Blue energy harvesting



Siria et al., Nature 2013

Waste heat harvesting



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

Also: water treatment, biology, geology, lubrication, medical/chemical analysis…

Optimizing the performance ➔ **surface effects**

Striolo, Michaelides & Joly, Annu. Rev. Chem. Biomol. Eng. 2016
Kavokine, Netz & Bocquet, Annu. Rev. Fluid Mech., 2021
Herrero, Allemand, Merabia, Biance & Joly, arXiv:2204.13522

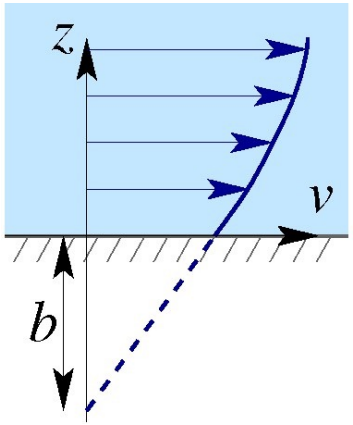
Interfacial hydrodynamics

Partial slip boundary condition

$$\eta \left.\frac{\partial v}{\partial z}\right|_{\text{wall}} = \lambda\, v_{\text{slip}} \quad \Rightarrow \quad v_{\text{slip}} = b \left.\frac{\partial v}{\partial z}\right|_{\text{wall}}$$

(Navier, 1823)

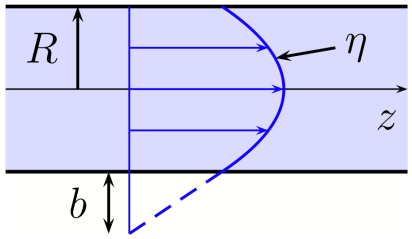
(fluid) friction coefficient



⇒ **Slip length** $b = \eta/\lambda$

Experiments & simulations ➔ *b* from 1 nm to a few 100 nm

⇒ **Large impact on nanoscale transport…**



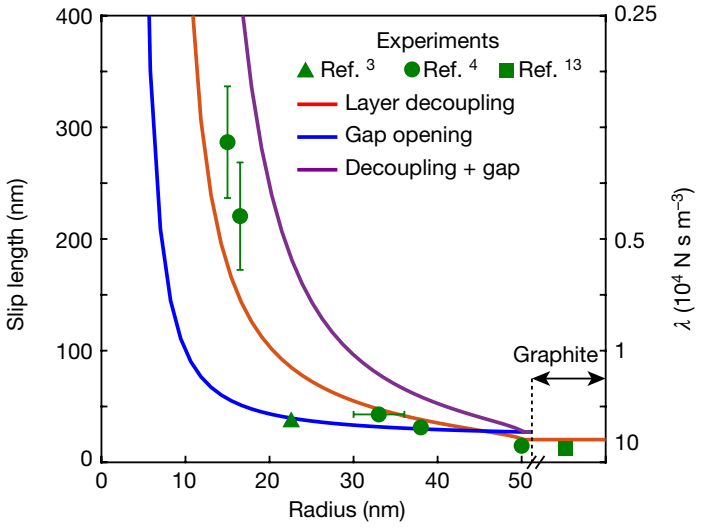
Optimize liquid-solid slip / friction ?

Bocquet & Barrat, Soft Matter 2007

Liquid-solid friction: quantum vs classical

Quantum contribution to friction

- coupling of charge fluctuations in the liquid to electronic excitations in the solid
- marked difference in quantum friction between the water–graphene and water–graphite interface



Kavokine, Bocquet, Bocquet, Nature 2022

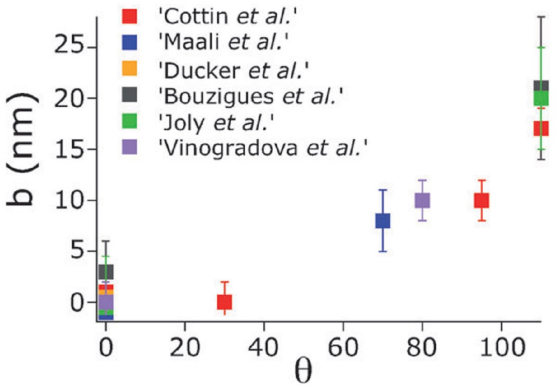
But…

Classical friction still a hot topic!

- most liquid-solid interfaces: classical friction dominates
- a challenging topic of statistical physics of liquids
- Many unsolved mysteries…

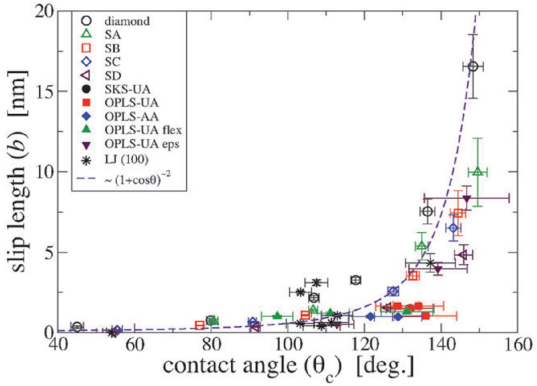
Rizk, Gelin, Biance, Joly, PRL 2022

Experiments

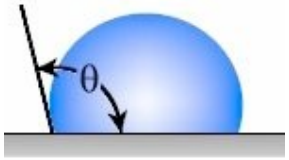


Bocquet & Charlaix, Chem. Soc. Rev. 2010

Simulations



Huang et al., PRL 2008



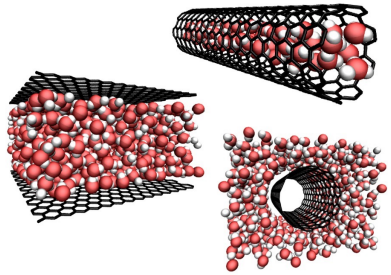
Large quantitative difference!

Molecular dynamics simulations

Fluid friction coefficient

$$b = \eta/\lambda$$

$$F/\mathcal{A} = \lambda\, v_{\mathrm{slip}}$$



Flow measurement

$$\lambda = F/(\mathcal{A}\, v_{\mathrm{slip}})$$

Equilibrium measurement: Green-Kubo formula

$$\lambda_0 = \frac{1}{\mathcal{A} k_{\mathrm{B}} T} \int_0^\infty \langle F(t) F(0) \rangle \, \mathrm{d}t$$

Bocquet & Barrat, PRE 1994, J. Chem. Phys. 2013

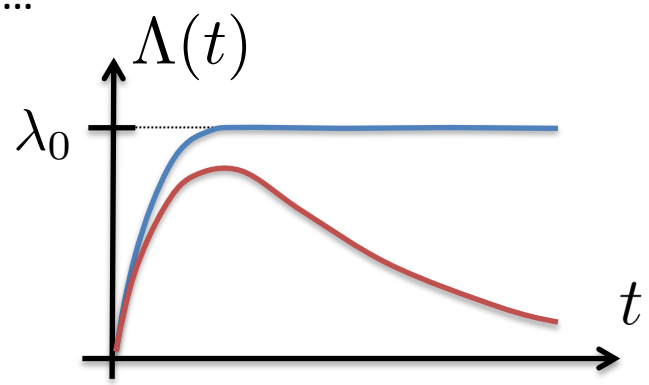
Cf. viscosity:

$$\eta_0 = \frac{\mathcal{V}}{k_{\mathrm{B}} T} \int_0^\infty \langle \tau(t) \tau(0) \rangle \, \mathrm{d}t$$

- Practical implementation in finite-size systems is delicate…

$$\lambda_0 = \lim_{t \to \infty} \Lambda(t) \quad \text{with}$$

$$\Lambda(t) = \frac{1}{\mathcal{A} k_{\mathrm{B}} T} \int_0^t \langle F(t') F(0) \rangle \mathrm{d}t'$$



Petravic & Harrowell, JCP 2007; Español, de la Torre, & Duque-Zumajo, PRE 2019

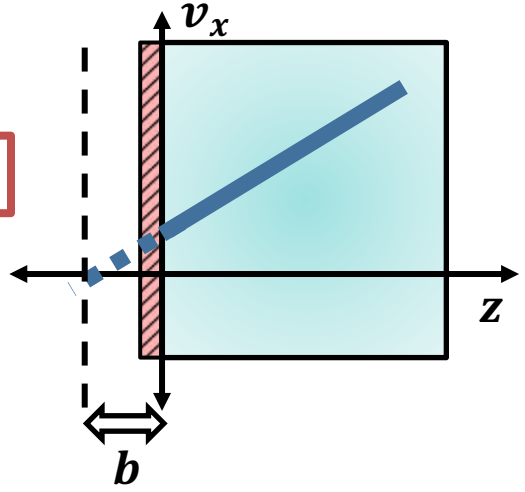
Hydrodynamic wall position

with Cecilia Herrero, Takeshi Omori, and Yasutaka Yamaguchi

- **Slip Boundary Condition**

$$v_{\text{slip}} = \frac{\eta}{\lambda}\partial_z v_x\Big|_{z=z_s} = b\,\partial_z v_x\Big|_{z=z_s}$$

Slip length b



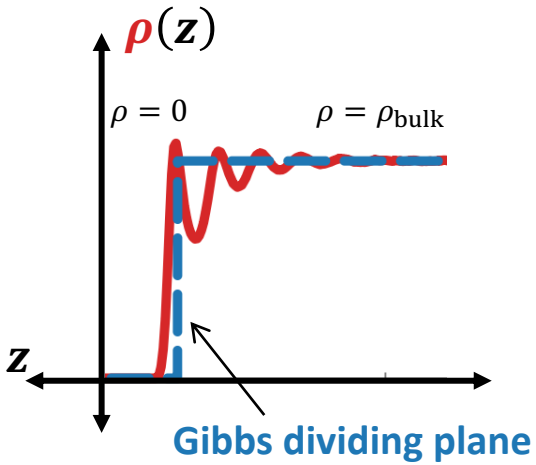
- Continuum perspective: **boundary at $z_s = z_{\text{wall}}$**
- Molecular perspective:
  - z_s position?

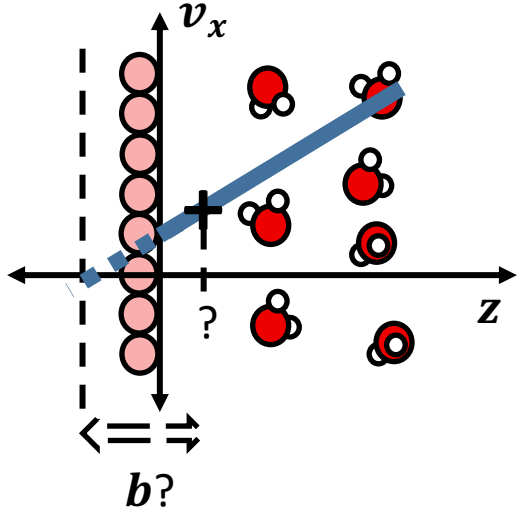
$z_s \equiv$ Gibbs dividing plane

⇩

Equilibrium simulations

C. Herrero et al., *JCP* Comm. (2019)

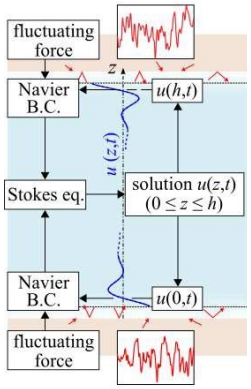




Extending the Green-Kubo formula

with H. Oga, T. Omori, C. Herrero, S. Merabia, and Y. Yamaguchi

Theoretical framework for finite-size systems



- Langevin equation for fluctuating bottom wall + Stokes equation for fluid

Maximum

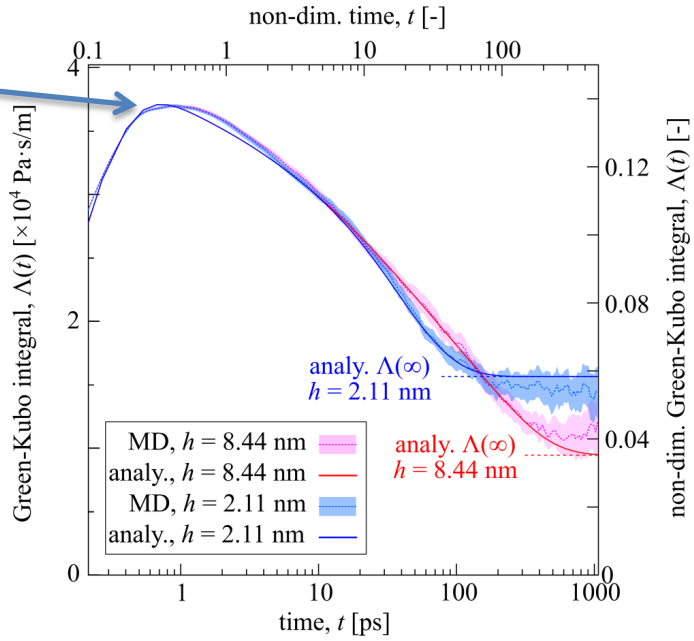
$$\Lambda_{\max} = \lambda \frac{1+u}{1-u}\left[u^{\frac{u}{1-u}} - u^{\frac{1}{1-u}}\right] \qquad u = t_2/t_1$$

Oga et al., J. Chem. Phys. 2019

Full expression

$$\frac{\tilde{C}_{\delta F\mathrm{bot}}}{Sk_{\mathrm{B}}T} = \frac{\tilde{\lambda}\eta\zeta[\eta\zeta\,\sinh(\zeta h) + \tilde{\lambda}\cosh(\zeta h)]}{(\tilde{\lambda}^2 + \eta^2\zeta^2)\sinh(\zeta h) + 2\tilde{\lambda}\eta\zeta\,\cosh(\zeta h)}$$

with $\tilde{f}(\omega) \equiv \int_0^\infty f(t)e^{-i\omega t}\,\mathrm{d}t \qquad \zeta = \sqrt{i\rho\omega/\eta}$



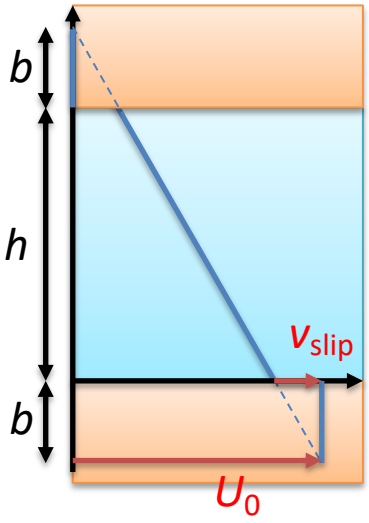
- Fitting the entire curve → frequency dependent / visco-elastic friction
- Final plateau:

$$\Lambda(\infty) = \lim_{\omega\to 0,\ h:\mathrm{finite}} \frac{\tilde{C}_{\delta F\mathrm{bot}}}{Sk_{\mathrm{B}}T} = \frac{\lambda_0}{h/b+2}$$

Oga, Omori, Herrero et al., Phys. Rev. Research 2021

The final plateau

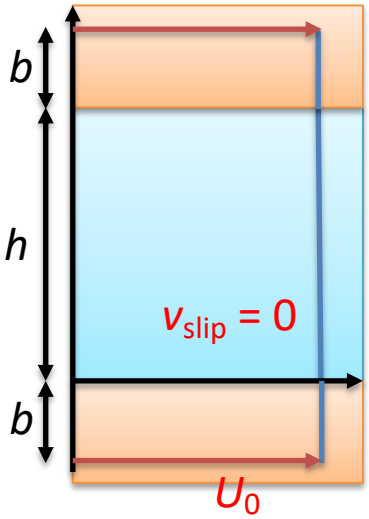
A simple interpretation



- Linear response : $\Lambda(\infty) = \dfrac{F_0/\mathcal{A}}{U_0} = \dfrac{\lambda_0\, v_{\rm slip}}{U_0}$

$$v_{\rm slip} = \frac{U_0}{2 + h/b} \quad \Rightarrow \Lambda(\infty) = \frac{\lambda_0}{2 + h/b}$$

- $h \to \infty : \Lambda(\infty) = 0$
- b>>h: final plateau at $\lambda_0/2$?? (see next slide)



- Considering the total force on the walls:

$$\Lambda(\infty) = \frac{F_0/\mathcal{A}}{U_0} = \frac{\lambda_0\, v_{\rm slip}}{U_0} = 0$$

⇒ vanishing plateau value (cf. cylindrical channel)

Time scales of the Green-Kubo formula

Oga, Omori, Joly, Yamaguchi, J. Chem. Phys. 2023

Three important time scales

t_{k} (friction kernel) $\quad t_{\mathrm{sys}} = h^2/\nu \quad t_{\mathrm{slip}} = b^2/\nu$

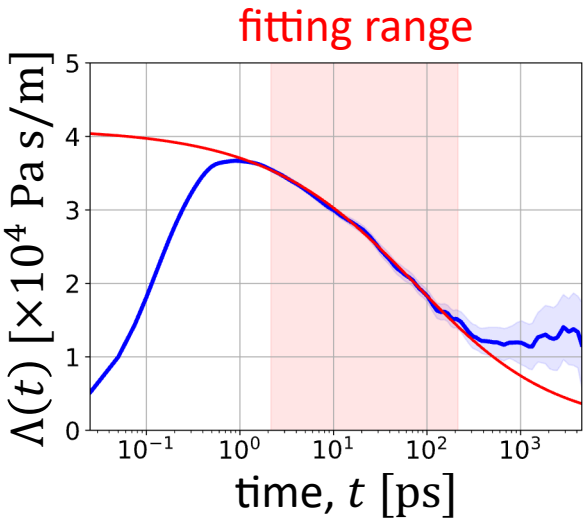
Some typical situations:

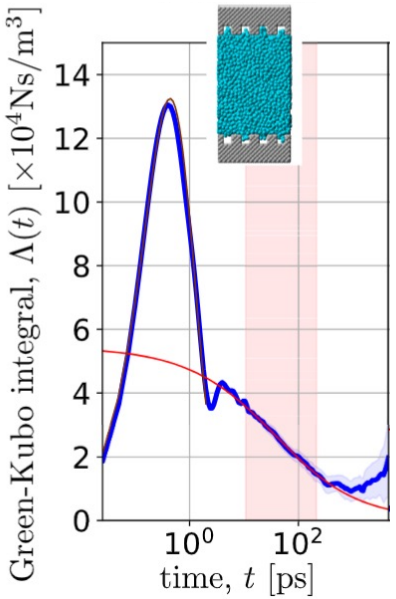
- $t_{\mathrm{k}} < t_{\mathrm{slip}} < t_{\mathrm{sys}}$

  Intermediate times:

$$\Lambda_{\mathrm{mid}}(t) = \lambda_0 \exp\left(\frac{t}{t_{\mathrm{slip}}}\right) \mathrm{erfc}\left(\sqrt{\frac{t}{t_{\mathrm{slip}}}}\right)$$

cf. Bocquet & Barrat JCP 2013
& integral expression with identical result in Nakano & Sasa PRE 2020





- Large slip length $b \gg h \rightarrow t_{\mathrm{k}} < t_{\mathrm{sys}} \ll t_{\mathrm{slip}}$

$t \ll t_{\mathrm{slip}}$:

intermediate plateau at λ_0

(measured in MD simulations)

$t \gg t_{\mathrm{slip}}$:

final plateau at $\lambda_0/2$

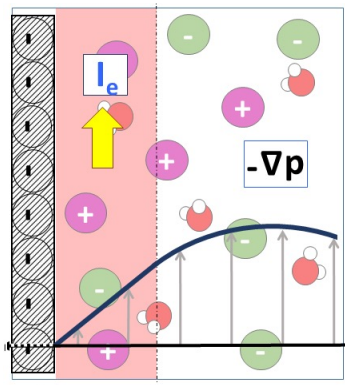
Slip on charged surfaces

with Yanbo Xie, Li Fu, and Thomas Niehaus

Nanofluidic energy conversion

e.g. producing electricity from pressure/salt/temperature gradients

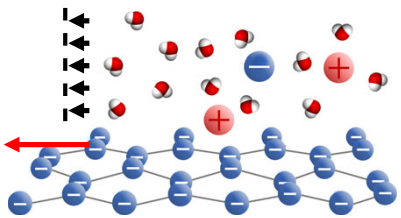
- driven by surface charge
- boosted by slip



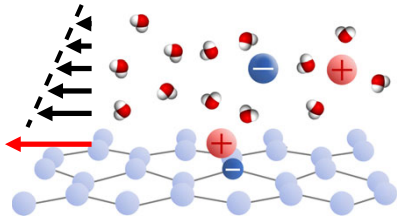
But: slip decreases with increasing surface charge…

Optimize charge-slip coupling?

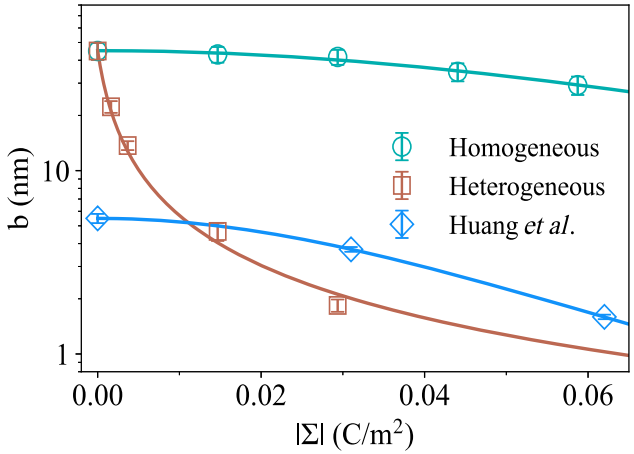
Surface charge distribution: graphene-like surfaces



Homogeneous
(every atom
has a fractional charge)



Heterogeneous
(a fraction of atoms
with a unit charge)



Analytical models

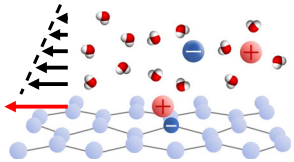
Xie, Fu, Niehaus, Joly, PRL 2020

Slip on charged surfaces

Heterogeneous charge

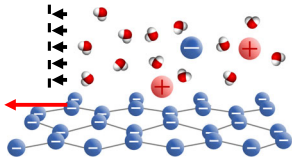
Strongly adsorbed ions -> Stokes drag

$$b = \frac{b_0}{1 + 3\pi\sigma_h b_0(|\Sigma|/e)}$$



Homogeneous charge

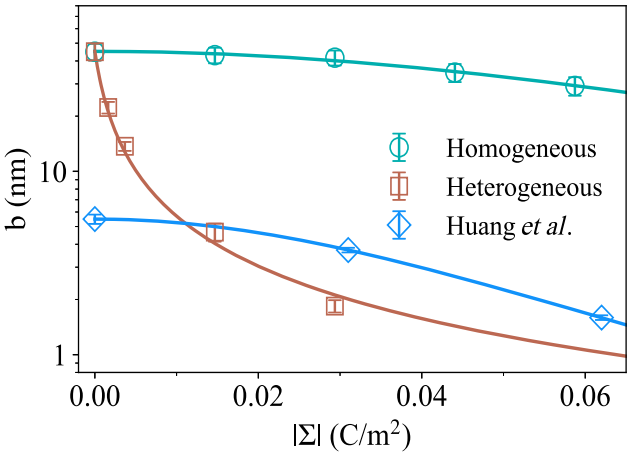
$$\lambda = \frac{1}{Ak_{\mathrm{B}}T}\int_0^\infty \langle F(t)F(0)\rangle \mathrm{d}t \quad \text{with} \quad F(t) = F_{\mathrm{LJ}}(t) + F_{\mathrm{ES}}(t)$$



$$b = \frac{b_0}{(1+\alpha x)^2}, \quad \text{with} \quad x = \left(\frac{3\pi\sigma_\ell b_0}{\sigma_s^2}\right)^{1/2}\left(\frac{\ell_B^i}{\sigma_s}\right)\left(\frac{\Sigma\sigma_s^2}{e}\right)^2$$

α unitless fitting parameter

Consequences?



- polarized graphene: large b_0 and weak charge-slip coupling due to small interatomic distance σ_S

Optimal energy conversion

Xie, Fu, Niehaus, Joly, PRL 2020

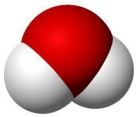
Slip and temperature: water vs methanol

with Cecilia Herrero, Gabriele Tocci, and Samy Merabia

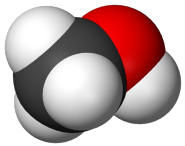
Understanding the mechanisms of liquid-solid slip / friction

Temperature dependence?

- Liquids:



water

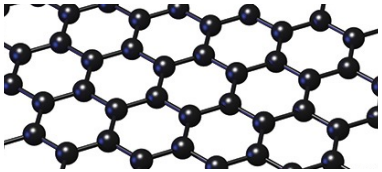


methanol

- walls:

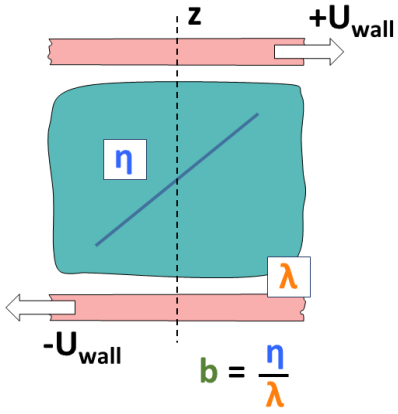


generic apolar wall
(LJ wall)



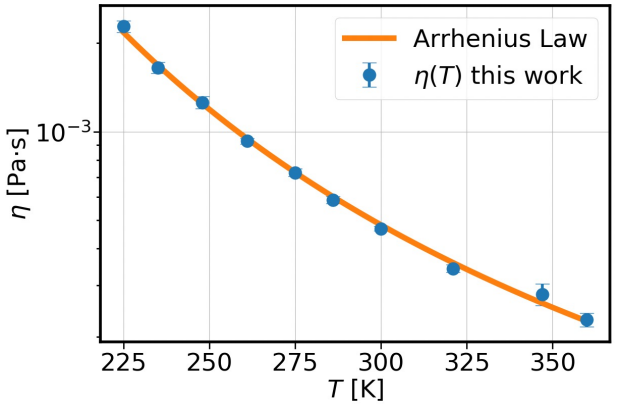
graphene

- Non-equilibrium simulations

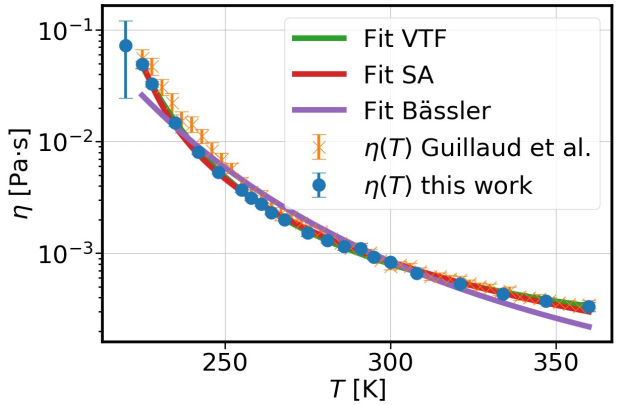


Slip and temperature: water vs methanol

Viscosity



- MeOH: Arrhenius law



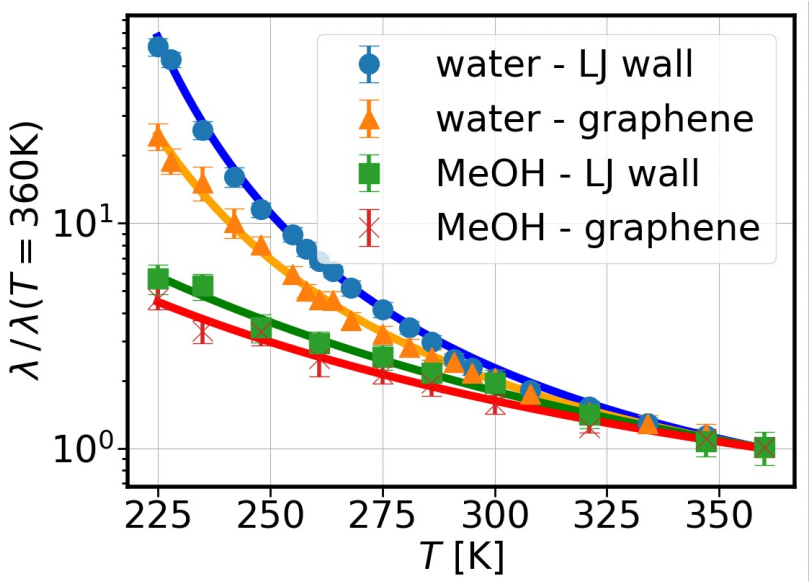
- water: VTF law

$$\eta(T) = \eta_0 \exp\left(\frac{A}{T - T_f}\right)$$

Friction coefficient?

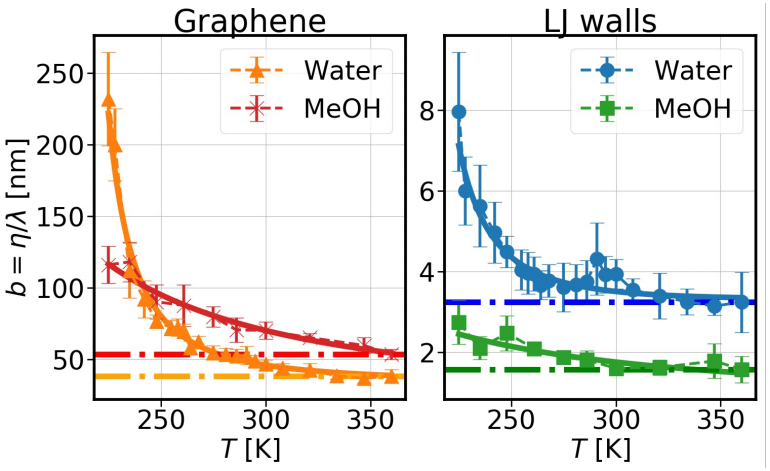
- Temperature evolution mostly controlled by liquid type
- Same laws as viscosity, but with different parameters

Slip length $b(T) = \eta(T)/\lambda(T)$?



Slip and temperature: water vs methanol

Slip length



$$b(T) = \eta(T)/\lambda(T)$$

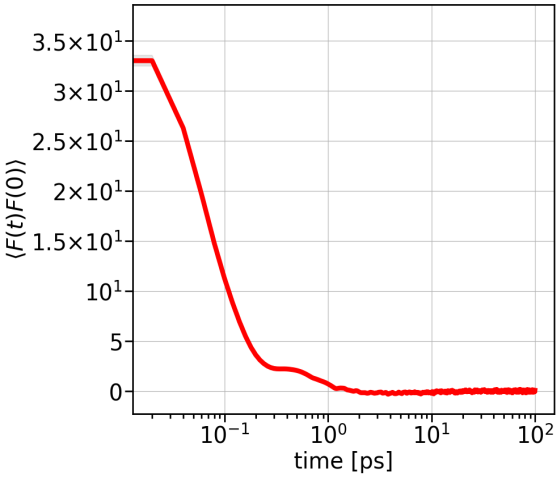
- Strong increase for supercooled water:
- Graphene: x 5, b > 200 nm
- λ increases less than η when T decreases

Origin?

Slip length decomposition

$$\lambda = \frac{1}{S_{\mathrm{wall}} k_{\mathrm{B}} T} \int_0^\infty \langle F(t)F(0)\rangle \, \mathrm{d}t \equiv \lambda_{\mathrm{STAT}} \cdot \lambda_{\mathrm{DYN}}$$

$$\eta = \eta_{\mathrm{STAT}} \cdot \eta_{\mathrm{DYN}}$$



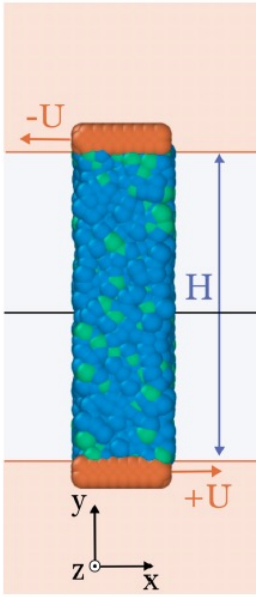
Temperature as a control parameter for slip

Temperature as a way to test molecular models of friction
(traditional models predict a T^2 scaling, see review by Bocquet & Barrat 2007)

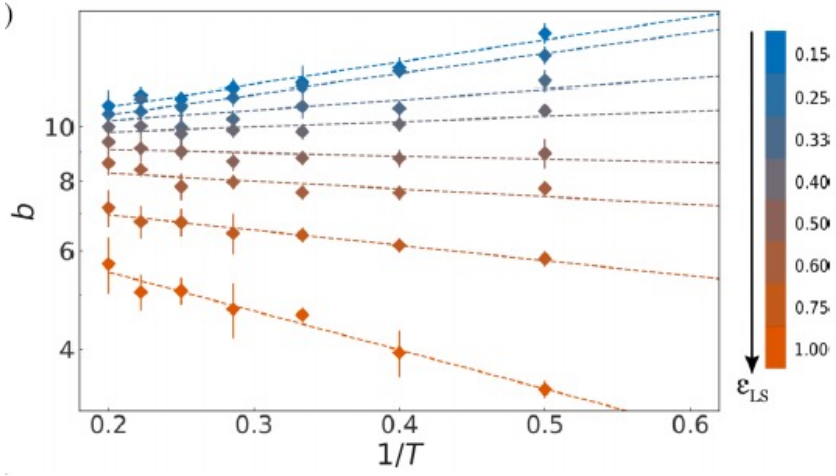
Herrero, Tocci, Merabia, Joly, Nanoscale 2020

Slip and temperature: Kob-Andersen mixture

with Suzanne Lafon, Alexis Chennevière, Frédéric Restagno and Samy Merabia

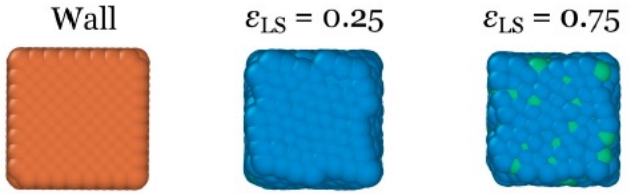


High temperature: effective Arrhenius behavior

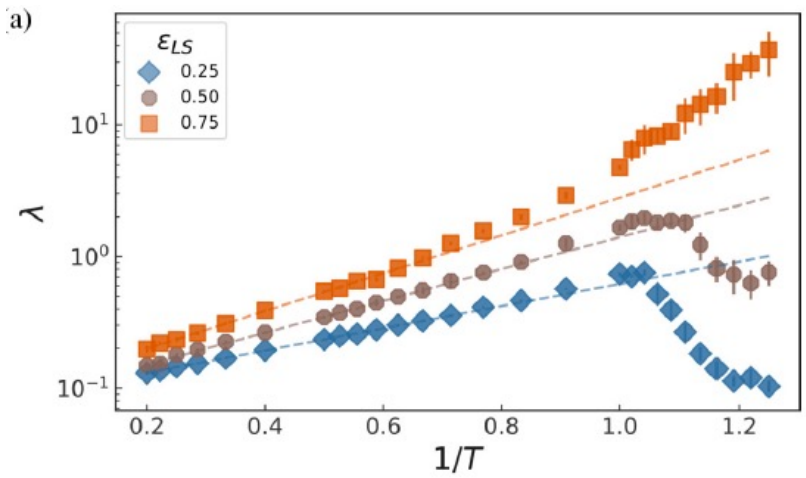


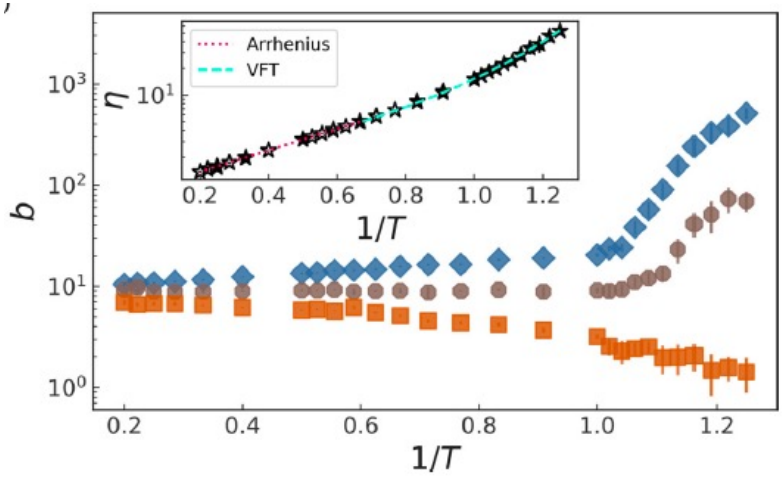
$$b(T) = \eta(T)/\lambda(T)$$

$$\propto \exp\left(\frac{E_{\mathrm{a,viscous}} - E_{\mathrm{a,friction}}}{k_B T}\right)$$



Low temperature: giant slip length



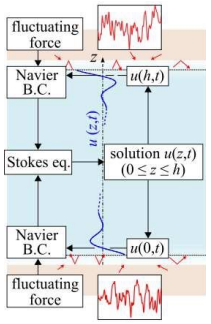


Lafon, Chennevière, Restagno, Merabia, Joly, PRE 2023

Conclusions

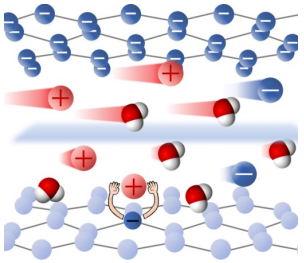
Understanding the molecular mechanisms of liquid-solid slip with molecular dynamics

- Theoretical framework for finite-size systems
- Exploring frequency dependent friction ➔ *toward complex fluids*



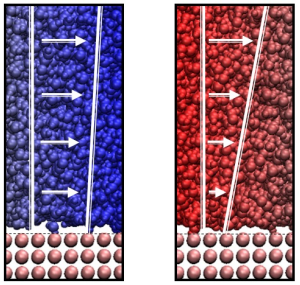
Optimizing the charge-slip coupling

- Dramatic impact of charge distribution on the wall
- Polarized graphene as an optimal surface for energy conversion
- *Toward efficient energy harvesting*

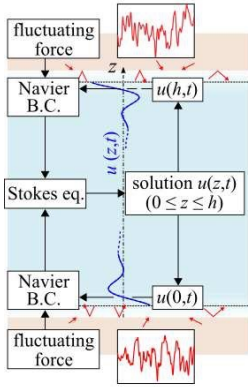


Exploring the temperature dependence of slip

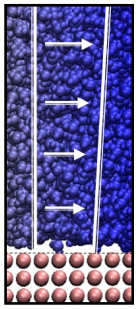
- Large increase of slip in the supercooled state
- Disentangling the bulk/interfacial static/dynamic contributions to slip
- *Toward other exotic behaviors in supercooled nanofluidics*

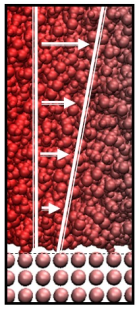


Thank you!

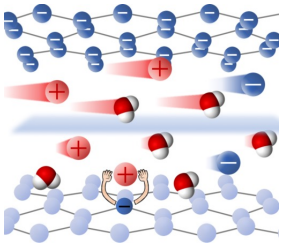


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- Institut Universitaire de France
- Computational resources: GENCI-TGCC

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