## Nanofluidics: a joint workshop by GDRs Interfacial Soft Matter and MicroNanofluidics

16-18 Oct 2024 Grenoble France

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### Nanofluidic flows on excitable walls

Lydéric Bocquet $^{1}$ 

<sup>1</sup> Laboratoire de Physique de l'Ecole Normale Supérieure, ENS, Université PSL, CNRS, Sorbonne Université, Université de Paris, 75005 Paris, France.

### The Effect of Water Structure on Hydration forces and the Electrical Double Layer

Hélène Berthoumieux \*  $^{\rm 1}$ 

<sup>1</sup> Gulliver, ESPCI, CNRS – ESPCI Paris, PSL Research University – France

Forces between hydrophilic surfaces mediated by water are important in various systems in naofluidics. Experimental and simulation studies reported the non-monotonic, oscillatory decay in the forces between molecularly smooth surfaces – any other surface exhibits only quasiexponential, monotonous decay. Here we study the hydration force problem using an extended phenomenological Landau-Ginzburg energy model of nonlocal dielectric correlations in water. This model, based on the properties of bulk water, predicts the observed oscillatory decay in hydration force between ideally flat surfaces, the oscillatory mode disappearing with just a tiny roughness of the surfaces. We also investigate the ion distribution in the double layer. More and more experimental studies report a non-monotonous ion distribution at the interface. This is in contrast to the Gouy-Chapman-Stern picture. We show that this behavior can be satisfactorily explained by considering the water polarization modes.

Keywords: Water structure, double layer, Ion distribution at interface

#### Nanofluidics inspired by trees

Olivier Vincent $^*$ , Erik Huber , Théo Tassin , Bastien Marguet , Jiamin Zhang , Eugene Choi $^1,$  Abraham Stroock $^1$ 

 $^1$  School of Chemical and Biomolecular Engineering, Cornell University, Ithaca NY 14853 – United States

Ascent of sap in a tree relies on passive evaporation (transpiration) from nanoporous tissues in the leaf, which generates a suction force that is able to lift the whole water column from the roots. We built synthetic structures that mimic this function, using micro/nano-fabrication techniques with silicon and glass (1, 2).

First, I will show that evaporation-driven flows allow us to finely tune and study capillaryviscous flows in nanopores. Because nanoscale liquid-vapor menisci adapt their curvature to the vapor humidity (Kelvin equation), the magnitude of nanofluidic flows are directly impacted by a control of the external humidity, which translates into a tunable capillary pressure in the pores. We demonstrate this effect both for evaporation-driven flows and condensation-driven flows (spontaneous imbibition).

In a second step, we evaluated how transpiration-driven flows and imbibition are impacted when the nanoporous layer contains microscale channels, in a manner similar to what can be found in trees (xylem tissue). This multiscale structure strongly enhances transport, in a way that depends on the geometry of the microchannels and that can be predicted using effective medium theories. However, other undesirable effects appear, e.g. spontaneous cavitation of the liquid, which results in embolism and conductance loss.

Finally, I will show that interaction between the external humidity and osmotic effects in the nanopores can be used to recover from cavitation, and more generally to drive reversible fill-ing/emptying flows controlled by changes in external humidity.

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(2) Vincent, O., Tassin, T., Huber, E. J. & Stroock, A. D. Tunable transport in bidisperse porous materials with vascular structure. Phys. Rev. Fluids 9, 064202 (2024).

**Keywords:** Evaporation, Imbibition, Negative pressure, Cavitation, Osmosis, Capillary, Kelvin, Xylem, Cavitation

### Capture of using aqueous foam: a 2D case study in microchannel

#### Cécile Aprili \* <sup>1</sup>

<sup>1</sup> Laboratoire Interdisciplinaire de Physique [Saint Martin d'Hères] – Centre National de la Recherche Scientifique, Université Grenoble Alpes, Sous la direction de Elise Lorenceau, Benjamin Dollet et Gwennou Coupier – France

In order to limit global warming, several IPCC scenarios are based on an intensive capture of CO2 from the atmosphere to reduce the greenhouse effect. This objective is technically ambitious since it requires the development of processes to capture the diluted CO2 from air (relative concentration of 0.04%), to separate it from other gases in the atmosphere and to concentrate it in order to limit the storage volumes. Solutions involving absorbing liquid solvents exist (1), and adding microparticles that can fix or consume the CO2 dissolved in the liquid phase increases their efficiency (2, 3, 4). In this context, using aqueous foams to bring CO2 and the absorbing liquid solvent into contact offers several advantages: i) the foams have a large gas/liquid exchange surface, ii) they are fluid and can therefore be destroyed or regenerated on demand iii) their selectivity for the transfer of CO2 compared to nitrogen or oxygen is high and little hindered by the surfactants present at the gas/liquid interfaces (5, 6). Yet, the kinetics of gas transfer through the soap film, quantified using the gas permeability (which encompasses the subtlety of micro-scale transfer), can reveal surprising features, such as a reversible adsorption of a gas onto the self-assembled monolayer (7). To better understand CO2 transfer within an aqueous foam, we follow the evolution of size of the bubbles of a foam confined in a 2D microfluidic geometry. In our experiment, an air bubble is introduced in a CO2 foam. The area and perimeter of the air bubble grows greatly at the expense of the small CO2 bubbles near it. We showed that the experimental results are not compatible with a time-independent permeability. We developed our own model that couples gas transfer through films with additional dynamical features present in the experiments, such as bubble rearrangements and film thinning.

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 $<sup>^{*}\</sup>mathrm{Speaker}$ 

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Keywords: Foam, gas transfert, 2D microfluidic geometry

# Entry effects at the scale of ion-exchange membranes

Corentin Trégouët  $^{\rm 1}$ 

<sup>1</sup> ESPCI Paris, PSL Research University, MIE-CBI, CNRS UMR 8231, 10, Rue Vauquelin, 75231, Paris Cedex 05, France.

### Giant mobility of surface-trapped ionic charges following liquid tribocharging

Zouhir Benrahla , Tristan Saide , Louis Burnaz , Emilie Verneuil , Jean Comtet $^{\ast \ 1}$ 

<sup>1</sup> Sciences et Ingénierie de la Matière Molle (UMR 7615) – CNRS, ESPCI Paris, PSL Research University, Sorbonne Université UPMC Paris VI – France

Tribo-electric charging, by which two contacting bodies under relative motion acquire opposite charges, is a puzzling and still misunderstood process. Recent experiments evidenced that such electrification process can also take place when aqueous droplets slide on hydrophobic surfaces, with broad implications ranging from triple-line dynamics to the fabrication of novel energy harvesting devices. While the charges deposited on the solid surface following droplet dewetting are thought to originate from ions originally adsorbed at the solid/liquid interface within the drop, very little is currently known on the nature and dynamics of these trapped ionic surface charges. Here, we take advantage of a scanning-based electrostatic mapping technique, to directly image the dynamics of surface deposited ions following droplet sliding. Surface trapped ionic charges undergo a very slow power-law relaxation, allowing us to follow their dynamics over long timescales of several hours. Remarkably, we evidence an ultra-low friction for these surface-trapped ions, with a bidimensional surface mobility close to that of standard salts in bulk liquid water. While the deposited surface charge can be reversibly tuned by the drop pH pointing to the role of native water self-ions in the charging mechanism, the surface mobility is not, suggesting the hindrance of classical Grotthus-like mechanism generally at play in bulk water. Tuning the concentration and nature of added salt, we further evidence the role of cation co-adsorption and ionic solvation on surface charging and ionic diffusion. Our experiments suggest that surface transport takes place through the diffusion of hydrated ion sliding with low friction on the solid surface. Our observations have general implications for molecular-scale ionic transport at interfaces and electrified matter.

Keywords: triboelectrification, ions at interfaces, surface diffusion

### Electronic response of the SWCNT-FET to distinguish between water confined inside and adsorbed outside carbon nanotube

Said Pashayev \* <sup>1,2,3</sup>, Romain Lhermerout <sup>1,4</sup>, Christophe Roblin <sup>1</sup>, Eric Alibert <sup>1</sup>, Rémi Jelinek <sup>1</sup>, Nicolas Izard <sup>1</sup>, Rasim Jabbarov <sup>2</sup>, Francois Henn <sup>1</sup>, Adrien Noury <sup>1</sup>

<sup>1</sup> Laboratoire Charles Coulomb – CNRS, Université de Montpellier – France
<sup>2</sup> Institute of Physics of the Ministry of Science and Education of the Republic of Azerbaijan – Azerbaijan

<sup>3</sup> Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière – Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière (iLM), UMR 5306, 10 rue Ada Byron, 69622 Villeurbanne Cedex, France – France

<sup>4</sup> Univ. Grenoble Alpes, CNRS, LIPhy – Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble – France

Single walled carbon nanotubes (SWCNTs) have gained interest in the field of nanoscale confinement of the fluids, with a variety of unexpected phenomena such as spontaneous filing, frictionless mas transport, unusual phase diagram, etc. (1). The majority of these phenomena remains unexplored and requires experimental confirmation. In addition, the field requires a sensitive method to carry out measurement in the level of individual and SWCNT, as the confinement is sensitive to the tube diameter. On the other hand, the intrinsic and extrinsic electronic properties of the SWCNT is shown to be sensitive to the diameter, defects, doping, adsorbates, and environment via SWCNT field effect transistors (SWCNT-FET) (2,3).

In this contribution, we show that the electronic response of the individual SWCNT based field effect transistor is an essential tool to study water-CNT coupling mechanism and accurately identify the impact of water confined inside the nanotube. We investigate the charge transfer characteristics of the SWCNT-FET, while exposing several individual SWCNT first unopened, then opened to different environment, such as ambient air, air humidity, vacuum and current annealing under vacuum. We demonstrate that it is possible to assign CNT doping as the main mechanism behind water-CNT coupling, and distinguish between water adsorbed outside of the nanotube from confined inside. Precisely, we found that putting the device under secondary vacuum, after exposing to air humidity, shift the gate voltage neutrality point of opened SWCNT towards more negative values, however, the secondary vacuum has no effect on the same SWCNT when it was closed. We also demonstrate that this behavior is independent CNT metallicity, assuming that the nanotube's surface has been pre-cleaned using current annealing. We will also discuss the water adsorption and desorption kinetics and dynamics.

Our findings open up the possibility of using CNTFET to address long-standing issues in the nanofluidic community regarding the behavior of water confinement at the nanoscale, and also to use them for reliable, sensitive, and selective chemical and biological sensors.

**Reference:** 

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<sup>\*</sup>Speaker

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Keywords: carbon nanotube, CNTFET, nanofluidics

### Fluctuation-induced electro-fluidic couplings at the solid-liquid interface

Baptiste Coquinot \* <sup>1</sup>, Nikita Kavokine <sup>2,3</sup>, Lydéric Bocquet <sup>4</sup>

<sup>1</sup> Laboratoire de Physique de l'Ecole Normale Supérieure, ENS, Université PSL, CNRS, Sorbonne

Université, Université de Paris, 75005 Paris, France.

<sup>2</sup> Max Planck Institute for Polymer Research – Mainz, Germany

<sup>3</sup> Flatiron Institute – New York, United States

<sup>4</sup> Laboratoire de physique de l'ENS - ENS Paris – Département de Physique de l'ENS-PSL, CNRS –

France

This talk explores couplings at the solid-liquid interface, arising from fluctuations in the microscopic degrees of freedom of both the solid and the liquid. We describe in which contexts these couplings dominate solid-liquid friction, then impacting hydrodynamics at the nanoscale, and how they can be used to engineer the friction coefficient. We show that the solid modes are impacted by a flow at their surface, driving them out of equilibrium. This modifies the friction, so that the study of liquid dynamics now requires describing the dynamics of the solid to which it is coupled. In particular, it becomes possible to engineer the friction by changing the electronic properties of the solid. Moreover, it also becomes possible to transfer a flow throughout a solid and thus to make flows forbidden by standard hydrodynamics. Finally, we prove that it is possible to convert the friction force into an electrical power, thus using these couplings to make a promising hydroelectric generator.

Keywords: Nanofluidics, solid, liquid friction, perturbation theory, fluctuations

### From Metallicity to Motion: Exploring Quantum Friction and Liquid Flow-Induced Currents

Cecilia Herrero \* <sup>1</sup>, Lydéric Bocquet <sup>2</sup>, Benoit Coasne

<sup>1</sup> Institut Laue-Langevin – Institut Laue-Langevin (ILL), Grenoble, France – France

<sup>2</sup> Laboratoire de physique de l'ENS - ENS Paris – Département de Physique de l'ENS-PSL, CNRS – France

Recent theoretical advancements highlight the critical role of quantum effects in nanofluidics, where the intricate coupling between solid and liquid spectra leads to quantum friction (1). Additionally, liquid flow can induce a tunable electric current in the solid, presenting new opportunities for nanoscale sensing and energy generation (2). However, these theories necessitate the development of advanced simulation tools to validate and explore their frameworks, guiding future experiments.

In this presentation, I will show how solid metallicity impacts nanoscale water dynamics by effectively modeling the metal's electrostatic response at the atomic scale. Using large-scale molecular dynamics simulations, we directly measure quantum friction and reveal its complex dependency on metallicity, reflecting the non-trivial nature of the solid's response. Furthermore, we explore how liquid flow can induce an electric current in the solid, providing direct simulation-based evidence for recent theoretical predictions. Overall, our simulation framework accurately reproduces the dynamics of liquids at metal interfaces without solving the electronic structure problem. This enables deeper insights into quantum friction and paves the way for innovative approaches in nanofluidics and nanotechnology.

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(2) Coquinot, B., Bocquet, L., & Kavokine, N. (2023). Quantum feedback at the solid-liquid interface: Flow-induced electronic current and its negative contribution to friction. *Physical Review X*, 13(1), 011019.

(3) Schlaich, A., Jin, D., Bocquet, L., & Coasne, B. (2022). Electronic screening using a virtual Thomas–Fermi fluid for predicting wetting and phase transitions of ionic liquids at metal surfaces. *Nature materials*, 21(2), 237-245.

**Keywords:** nanofluidics, friction, metallicity, solid, liquid coupling, energy generation, nanoscale water dynamics, quantum effects

### On the many ways to translocate through nanopores: from synthetic polymers to proteins

Fabien Montel $^{\rm 1}$ 

<sup>1</sup> Laboratoire de Physique, UMR CNRS 5672, ENS de Lyon, Université de Lyon, Lyon, France.

### Bridging Microscopic Dynamics and Hydraulic Permeability in Mechanically-Deformed Nanoporous Materials

Alexander Schlaich $^{\ast 1,2},$  Matthieu Vandamme $^3,$  Marie Plazanet $^4,$  Benoit Coasne $^5$ 

<sup>1</sup> Hamburg University of Technology – Germany <sup>2</sup> University of Stuttgart – Germany

<sup>3</sup> Laboratoire Navier (NAVIER) – Ecole des Ponts ParisTech, Université Gustave Eiffel, CNRS : UMR8205 – École des Ponts ParisTech, 6-8 avenue Blaise Pascal, 77455 Champs-sur-Marne, France
<sup>4</sup> Laboratoire Interdisciplinaire de Physique [Saint Martin d'Hères] (LIPhy) – Université Joseph Fourier
- Grenoble 1, Centre National de la Recherche Scientifique : UMR5588 – 140 Av. de la physique,BP 8738402 Saint Martin d'Hères, France

<sup>5</sup> Laboratoire Interdisciplinaire de Physique [Grenoble] – Centre National de la Recherche Scientifique, Université Grenoble Alpes, Centre National de la Recherche Scientifique : UMR5588 – France

In the field of nanoconfined fluids, there are striking examples of deformation/transport coupling in which mechanical solicitation of the confining host and dynamics of the confined fluid impact each other. While this intriguing behavior can be potentially used for practical applications (e.g. energy storage, phase separation, catalysis), the underlying mechanisms remain to be understood as they challenge existing frameworks. Here, using molecular simulations analyzed through concepts inherent to interfacial fluids, we investigate fluid flow in compliant nanoporous materials subjected to external mechanical stresses. We show that the pore mechanical properties significantly affect fluid flow as they lead to significant pore deformations and different density layering at the interface accounted for by invoking interfacial viscous effects. Despite such poromechanical effects, we show that the thermodynamic properties (i.e. adsorption) can be linked consistently to Darcy's law for the permeability by invoking a pore size definition based on the concept of Gibbs' dividing surface. In particular, regardless of the pore stiffness and applied external stress, all data can be rationalized by accounting for the fluid viscosity and slippage at the interface independent of a specific pore size definition. Using such a formalism, we establish that the intimate relation - derived using the linear response theory between collective diffusivity and hydraulic permeability remains valid. This allows for linking consistently microscopic dynamics experiments and permeability experiments on fluid flow in compliant nanoporous materials.

**Keywords:** nanofluidics, molecular dynamics, adsorption, compliant nanoporous media, linear response theory, permeability, diffusion

### Direct measurement of the viscocapillary lift force near a liquid interface

Hao Zhang <sup>1</sup>, Zhang Zaicheng , Jha Aditya <sup>1</sup>, Amarouchene Yacine <sup>1</sup>, Salez Thomas <sup>1</sup>, Thomas Guerin <sup>1</sup>, Misbah Chaouqi <sup>2</sup>, Abdelhamid Maali

<sup>1</sup> Laboratoire Ondes et Matière d'Aquitaine (LOMA) – Centre National de la Recherche Scientifique -CNRS : UMR5798, Université de Bordeaux (Bordeaux, France) : UMR5798, Centre National de la Recherche Scientifique - CNRS, Université de Bordeaux (Bordeaux, France) – France <sup>2</sup> LiPHY – Université Grenoble Alpes – France

I will present the first direct measurement of the lift force acting on a particle moving in a viscous fluid along the liquid interface that separates two liquids. The force arises from the coupling between the viscous flow induced by the particle motion and the capillary deformation of the interface. Using an atomic force microscope (AFM), the viscocapillary lift force was measured versus the distance between the sphere and the interface. We investigated various liquid interfaces, working frequencies, sliding velocities, and two different sphere radii. Our measurement results are in good agreement with the theoretical model and numerical calculation developed within the framework of soft lubrication theory. H. Zhang, Z. Zhang, A. Jha, Y. Amarouchene, T. Salez, T. Guérin, C. Misbah, A. Maali, "Direct measurement of the viscocapillary lift force near a liquid interface" https://doi.org/10.48550/arXiv.2406.02374.

**Keywords:** capillary deformation, viscous flow, liquid, liquid interface, Atomic force microscope, Lift force, Viscocapillary coupling

# Molecular origins of thermo-osmotic transport

Laurent Joly<sup>1</sup>

<sup>1</sup> Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, UMR5306, Villeurbanne, France.

# Role of surfactant chemistry on the dynamics of pancake-like droplets.

Lucas Jannin \* <sup>1</sup>, Marie-Caroline Jullien <sup>2</sup>, Isabelle Cantat <sup>3</sup>, Adrien Gans <sup>4</sup>, Jacques-Teïva Baué

<sup>1</sup> Institut de Physique de Rennes – Universite de Rennes 1, Centre National de la Recherche Scientifique – France

<sup>2</sup> Institut de Physique de Rennes – Université de Rennes, Centre National de la Recherche Scientifique – France

<sup>3</sup> Institut de Physique de Rennes (IPR) – Université de Rennes, Centre National de la Recherche

Scientifique – Bâtiment 11A , B, C, E – 10B263 av. Général Leclerc35042 Rennes cedex FRANCE, France

 $^4$ Laboratoire Energies et Mécanique Théorique et Appliquée – Université de Lorraine - UMR CNRS 7563 – France

We report the effect of surfactant solubility on pancake-shaped droplet dynamics travelling in a microfluidic cavity. Previous works (1) have shown that by increasing the continuous phase velocity, the droplet's velocity can either increase or decrease with their radius depending on the solubility of the surfactant, which has important consequences on droplet and emulsion dynamics. As such, the droplet velocity is critically sensitive to the solubility of the surfactant, that depends itself on the carbon chain length. If a model recovering the first behavior was proposed in the literature (2), we are not aware of one predicting the droplet's velocity decrease with its radius in the case of poorly soluble surfactants. In this work, we propose a model, which takes into account the flux of surfactants on both the wetting film and the lateral meniscus, leading to a good agreement with experimental data without adjustable parameter. To complete our understanding, we then investigate the lubrication film topography in both cases, which is an indirect measurement of surfactants flows happening in the nanometric lubrication film.

We focus on oil droplets pushed by an aqueous phase containing surfactants of the same family but of different solubilities. Using an interferometric device, we measure the lubrication film topography in dynamical situations, with droplets velocities up to 15 mm.s-1. Surprisingly we observe a local thickening at the back of the droplets for surfactant with shorter chains (less than 11 carbons), *i.e.* for the more soluble ones, and a flat film when the length of the chain increases. The case of soluble surfactants, i.e. when a local thickening is observed, corresponds to an accumulation of surfactant at the rear and has already been modeled in 1D (4). However, this work could not reproduce the radius dependency of this thickening, which we observe experimentally. We propose a 2D model that accounts for the mass transport of surfactant along the whole lubrication film, including their lateral flux as they approach the stagnation point at the rear.

Despite the lack of universality, with the dynamic changing with only one carbon, which is an important result in itself, our system shows a promising tool for characterizing the interfacial

 $<sup>^*</sup>Speaker$ 

behavior of surfactant locally, and as consequence the global dynamic of droplets.

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(3) A. Huerre et al.: Droplets in Microchannels: Dynamical Properties of the Lubrication Film, Phys. Rev. Lett. **115** (2015), 064501.

(4) B. Reichert et al., Topography of the lubrication film under a pancake droplet travelling in a *Hele-Shaw cell*. Journal of Fluid Mechanics, **850** (2018) 708-732.

Keywords: droplet, lubrication film, surfactant

### Memristive ionic transport in solid-state and $\beta$ -barrel nanopores: toward brain-inspired ionic (bio)computing.

Theo Emmerich \* <sup>1</sup>, Nathan Ronceray <sup>1</sup>, Simon Finn Mayer <sup>1</sup>, Marianna Fanouria Mitsoni <sup>1</sup>, Yunfei Teng <sup>1</sup>, Matteo Dal Peraro <sup>1</sup>, Aleksandra Radenovic

<sup>1</sup> Institute of Bioengineering, Ecole Polytechnique Federale de Lausanne (EPFL), Lausanne, Switzerland

The study of memory in nanofluidic channels is a recent and dynamic research topic  $^{1,2,3}$ . Solid- state electronic memristive devices have been the object of intense research for more than a decade resulting in the rise of brain-inspired, or neuromorphic, computing overcoming the von Neumann bottleneck. In comparison, in-memory processing with fluidic nanodevices relying on ions as information carriers is only starting. It provides however a better analogy with biology as the brain relies on billions of ionic nanochannels to perform information processing at energy costs orders of magnitude lower than electronic digital circuits. Thus, developing nanofluidic neuromorphic systems is an effort aiming at reproducing the extraordinary computing performances displayed by brains of living organisms. In this presentation, I will describe most recent developments regarding brain-inspired nanofluidics. I will shortly introduce primitive nanofluidic memristor, and comment on their limited performances hindering the essential progress towards the circuit-scale<sup>4,5</sup>. Building on initial developments in nanofluidic memristors, I will then present a state-of-the art nanofluidic memristor and show how it has been used to construct the inaugural nanofluidic logic circuit<sup>6</sup>. Finally, I will display an extended study on ionic transport in  $\beta$ -barrel biological porins, which remains poorly understood despite its pivotal role in living organisms and emerging sequencing technologies<sup>7</sup>. In particular, I will demonstrate how these biological nanofluidic channels can function as diodes and memristors with a tuning resolution down to seven single charges, paying the way for versatile nanofluidic biocomputing.

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(2) A. Noy and S.B. Darling, Nanofluidic computing makes a splash, Science, 2023

(3) A. Ismail and B. Radha, Mechano-ionic memristors for nanofluidic logic, Nature Electronics, 2024

(4) P. Robin<sup>\*</sup>, T. Emmerich<sup>\*</sup>, A. Ismail<sup>\*</sup> et al. Long-term memory and synapse-like dynamics in twodimensional nanofluidic channels, Science, 2023

(5) T. Xiong et al. Neuromorphic functions with a polyelectrolyte-confined fluidic memristor. Science. 2023

(6) T. Emmerich<sup>\*</sup>, Y. Teng<sup>\*</sup>, N. Ronceray<sup>\*</sup> et al., Nanofluidic logic with mechano-ionic memristive switches. Nature Electronics, 2024

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 $<sup>^*</sup>Speaker$ 

 ${\bf Keywords:} \ {\rm droplet, \, lubrication \, film, \, surfactant}$ 

# Controlling solid-liquid friction with ionic modes

Damien Toquer \* <sup>1</sup>, Baptiste Coquinot <sup>1</sup>, Lydéric Bocquet <sup>1</sup>

 $^1$ Laboratoire de physique de l'ENS - ENS Paris – Laboratoire de physique de l'ENS - ENS Paris – France

At the solid-liquid interfaces, interactions between fluctuating excitation modes in the solid and in the liquid are expected to be a consequent – when not dominant – part of friction (Kavokine2022, Bui2023). This new contribution, referred to as Van der Waals friction, can be understand in term of coupling between relevant modes of the solid (plasmon, phonon, ...) and of the liquid. In this talk, we extend this effect to the case of an electrolyte and show that ionic modes couple effectively with the solid's modes.

For this purpose, we use classical force-field molecular dynamics simulations of ions and water in nanoconfinement. This allows us to compute the structure factor of the liquid, which is then compared to various theoretical model of ions at different time-scales. We also perform non equilibrium simulations in the same geometry, by using the polarisable Drude oscillator model for the wall. While varying the frequency of the Drude oscillators for the wall, we extract the friction coefficients from the velocities of the species – electrolytes and water.

We find that the dominant mode for ionic friction is a diffusive mode at low frequency (gigahertz). We also obtain a smaller contribution from diffusive modes at larger frequency (hundreds of gigahertz) associated with oscillation of ions in their hydration shell. When the frequency of the wall is chosen to match those modes, we observe an increase of the total friction compared to simulations with pure water. Most strikingly, the frequency at which the friction is maximum depends on the ion diffusion coefficient and radius, leading to ion-specific responses.

Those findings confirm the importance of considering the Van der Waals friction of the ions in nanoconfined systems, which can even exceed the friction of pure water with the wall. More importantly, they lead to an ion specific decoupling of the dynamics between the water and of the interfacial ions, paving the way to applications in ion-separation processes.

**Keywords:** Friction, electrolyte, solid, liquid interface, ionic friction, quantum friction, solid, liquid friction, modes

### Electrokinetics with soap bubbles

Anne-Laure Biance  $^{\rm 1}$ 

<sup>1</sup> Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, UMR5306, Villeurbanne, France.

### Molecular Scope: watching macromolecular dynamics at solid-liquid interfaces at the single-chain level

Malo Velay \*  $^1$ , Jean Comtet  $^2$ 

<sup>1</sup> Laboratoire Sciences et Ingénierie de la Matière Molle – ESPCI Paris, PSL Research University, Sorbonne Universités, UPMC, CNRS – France

<sup>2</sup> SIMM, UMR7615 – ESPCI Paris, PSL Research University, Centre National de la Recherche Scientifique - CNRS, Sorbonne Université UPMC Paris VI – France

Molecular-scale interactions between polymers in solution and solid surfaces govern a large number of macroscopic processes in soft matter, from surface functionalization to hydrogel friction. Despite extensive characterization of these processes at the macroscopic level, our molecular understanding of polymer/surface interactions remains scarce, particularly under out-ofequilibrium situations. Here, we couple state-of-the-art single-molecule microscopy techniques with microfluidic transport, to directly track the nanoscale dynamics of single fluorescently tagged PEG macromolecules at solid/liquid interfaces, allowing to probe their subtle couplings with interfacial hydrodynamic flows.

In the absence of hydrodynamic forces, we uncover an heterogeneous and strongly non-Brownian surface diffusion for individual chains, which alternate between a low-mobility adsorbed state and long desorption-mediated jumps through the solvent (1, 2). The symmetry-breaking effect of the flow leads to a skewed distribution of interfacial displacements, with an unexpected dependence on the nature of the surfaces. On sticky hydrophilic surfaces, the hydrodynamic flow does not affect the chain motion except for an advective effect during solvent-mediated flights. On slippery hydrophobic surfaces, we instead evidence a peculiar regime of mixed macromolecular friction, whereby the adsorbed chain rubs on the solid wall while being continuously dragged by the near-surface hydrodynamic flow, allowing us to finely disentangle chain/wall and chain/solvent frictional molecular interactions. By allowing for direct observations of molecular-scale interfacial dynamics, our approach brings a new molecular vision of macromolecular friction and adsorbate/surface interaction at flowing solid/liquid interfaces.

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(2) C. Yu et al., ACS Nano, 2013, 7, 11, 9735

Keywords: macromolecules, dynamic, super, resolution, adsorption, interface

### Disentangling 1/f noise from confined ion dynamics

Paul Robin $^1,$  Mathieu Lizee \*  $^2,$  Théo Emmerich $^3,$  Qian Yang $^4,$  Alessandro Siria , Lydéric Bocquet $^5$ 

<sup>1</sup> Institute of Science and Technology Austria – Austria

<sup>2</sup> LPENS – Ecole Normale Supérieure de Paris - ENS Paris – 24 rue Lhomond 75005 Paris, France

 $^{3}$  EPFL – Switzerland

<sup>4</sup> Ghent University – Belgium

<sup>5</sup> Laboratoire de physique de l'ENS - ENS Paris – Laboratoire de physique de l'ENS - ENS Paris –

France

Ion transport through biological and solid-state nanochannels is known to be a highly noisy process. The power spectrum of current fluctuations is empirically known to scale like the inverse of frequency, following the long-standing yet poorly understood Hooge's law. Here, we report measurements of current fluctuations across nanometer- scale two-dimensional channels with different surface properties. The structure of fluctuations is found to depend on the channel's material. While in pristine channels current fluctuations scale like  $1/f^{(1+a)}$  with a = 0-0.5, the noise power spectrum of activated graphite channels displays different regimes depending on frequency. Based on these observations, we develop a theoretical formalism directly linking ion dynamics and current fluctuations. We predict that the noise power spectrum takes the form  $1/f \times S_{\text{channel}}(f)$ , where 1/f fluctuations inside it. Deviations to Hooge's law thus allow direct access to the ion transport dynamics of the channel – explaining the entire phenomenology observed in experiments on 2D nanochannels. Our results demonstrate how current fluctuations can be used to characterize nanoscale ion dynamics.

Keywords: fluctuations, liquid, dynamic of ions, noise

### Electromechanical couplings in nanoconfined electrolytes

Julien Allègre \* <sup>1</sup>, Benjamin Cross, Romain Lhermerout

<sup>1</sup> Laboratoire Interdisciplinaire de Physique de Grenoble – Université Grenoble Alpes, CNRS – France

Liquid electrolytes exhibit rich transport phenomena, involving displacements of matter (flow) and charge (electrical current), which are coupled in the presence of charged solid surfaces. These transport processes dictate the mechanical and electrical responses of electrolyte at interfaces and in confinement, which are at the heart of crucial applications such as energy storage (1) (e.g., supercapacitors, batteries, fuel cells) and energy harvesting (osmotic/blue energy) (2). In order to develop technologies with boosted performances, it is necessary to reach a fundamental understanding of the electromechanics of electrolytes under nanoconfinement. My project aims to experimentally probe the electrochemical couplings within an electrolyte under controlled nanoconfinement. The followed approach consists of combining two techniques: the dynamic Surface Force Apparatus (dSFA) which quantifies the nano-rheology of a liquid confined between two solid surfaces (3), and the Electrochemical Impedance Spectroscopy (EIS) which gives access to electrical response of an electrolyte in contact with an electrode (4).

During the talk, I will start by presenting the principle and the implementation of the setup. I will then tell our quest for a model physico-chemical system with high stability and low specific adsorption. I will finally discuss preliminary measurements of electromechanical couplings in nanoconfined electrolytes.

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Keywords: Electrolyte, confinement, electromechanics.

### Contact line in confinement: equilibrium and dynamics

Cyril Picard $^{1}$ 

<sup>1</sup> University Grenoble Alpes, CNRS, LIPhy, F-38000 Grenoble, France.

### Energy dissipation of a contact line moving on a nanotopographical defect

Sylvain Franiatte, Philippe Tordjeman, Thierry Ondarçuhu \* <sup>1</sup>

<sup>1</sup> IMFT, CNRS, Université de Toulouse – CNRS, Université de Toulouse – France

The wetting of a solid substrate by a liquid is extremely sensitive to the presence of surface defects, whether topographical or chemical. This gives rise to a contact angle hysteresis that is still poorly understood, in particular its dynamics. As the droplet spreads, the defects introduce additional energy dissipation that influences the wetting dynamics. It is therefore important to develop methods for studying the interaction of the contact line with nanometric surface defects and, more specifically, the associated dissipation phenomena.

To this end, we carry out experiments based on atomic force microscopy (AFM) measurement of the interaction between a tip terminated by a nanocylinder (1) and a liquid interface. The force measurement enables us to describe the pinning of the contact line on nanometric defects of the surface and thus obtain information about its topography. An original phenomenon of molecular desorption by the contact line has also been demonstrated (2). Here we extend these studies to the dynamic frequency-modulation (FM-AFM) mode. In this mode, the tip is vibrated with a controlled amplitude, allowing to access the system dissipation (3). In our case, a dissipation peak is observed in the curves when the contact line encounters a surface defect, as soon as the oscillation amplitude is greater than a threshold value depending on the defect size.Under this condition, the energy dissipated does not depend on the amplitude of the vibration and corresponds to the capillary energy of the hysteresis cycle (4). It is therefore independent of the speed of the contact line, an essential result for understanding wetting on a real surface.

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Keywords: Wetting, contact line, atomic force microscopy

<sup>\*</sup>Speaker

### Temperature induced phase separation of a binary mixture generating salinity gradients: : opening up to waste heat recovery

Marie-Caroline Jullien \* <sup>1</sup>, Marc Pascual , Axelle Amon , Nicolas Chapuis , Soufiane Abdelghani Idrissi , Alessandro Siria , Lydéric Bocquet

<sup>1</sup> Institut de Physique de Rennes – Université de Rennes, Centre National de la Recherche Scientifique – France

In this work, we report the conversion of low temperature waste heat ( $< 100 \circ C$ ) into salinity gradients which allows harvesting osmotic power. To this end, we focus on a thermoresponsive ionic liquid (IL) solution that has the property of phase separating above a critical temperature, which is well below 100  $\circ$ C, a temperature range known as low grade heat. Interestingly, as the temperature rises, the two phases are progressively purified and the surface tension between the two separated phases increases. We thus took advantage of this property to perform phase separation assisted by a temperature gradient by placing a micro-resistor at the centre of a cavity, 1 cm in diameter and 50  $\mu$ m (circular Hele-Shaw cavity), generating a radial temperature gradient. The advantage of confinement is that it enhances wetting effects, and this actually plays a critical role for the separation to take place. In this experimental configuration, three regimes of separation dynamics as a function of composition are observed, as shown in figure 1.c. These three separation regimes are composed of complex three-dimensional flows. Despite this complexity, we have rationalised all the observed regimes (1). A first regime is essentially composed of flows associated with thermocapillary stresses, a second regime is a thermocapillary instability that we have been able to model, and a third regime corresponds to the migration of water droplets in ionic liquid by thermocapillarity. Interestingly, we end up with two phases with different concentration in ionic liquid, thus generating a salinity gradient. More recently, when the two phases are placed on either side of a commercialized nanoporous membranes, powers of 7 W/m<sup>2</sup> could be reached (2), which is very promising for industrial scale-up. As such, this system reveals very promising to recover low grade heat, known as waste heat, from these salinity gradients.

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Keywords: Phase separation, salinity gradients, waste heat recovery

<sup>\*</sup>Speaker

### Noise in nanopores and the countoscope

Sophie Marbach $^{\rm 1}$ 

 $^1$  CNRS, Sorbonne Université, Physicochimie des Electrolytes et Nanosystèmes Interfaciaux, Paris, F-75005, France.

### Osmotic and phoretic interactions for light-activated hematite

Dolachai Boniface \* <sup>1</sup>, Tierno Pietro

 $^1$ Laboratoire Interdisciplinaire de Physique [Saint Martin d'Hères] – , Universitey of Grenoble Alpes $\rm (UGA)$  – France

Hematites are small colloids  $(\_~\mu m)$  made of iron oxide with an ellipsoid or a peanut shape. They have the property to decompose the hydrogen peroxide when they are exposed to blue light. We studied how the local concentration gradient resulting from the chemical reaction modifies, through diffusiophoresis and difusioosmosis, the interactions between the hematite and its environment. Thus, we observe hematites attract the silica colloids in their vicinity, forming a colloidal raft. Its size is strongly dependent on blue light intensity. Despite the apparent symmetry of the colloidal raft, it self-propels slowly ( $\_~um/min$ ). While the clustering is well explained by difusiophoresis, it seems that the motion of the raft should be attributed to the osmotic flow occurring on the glass substrate. We also investigate the interaction between the hematite field parallel to the substrate, we observe two stable spinning positions: lying or standing. The limits between the two behaviours depend on the magnetic field intensity and frequency. Applying blue light shift toward higher intensity the limit between the two modes, indicating an attractive phoretic/osmotic force.

Keywords: osmotic flow, diffusiophoresis, diffusioosomis

### The relationship between the contact angle and the microscopic characteristics of the solid and the liquid and the implications for slippage.

Patrick Tabeling \* 1

<sup>1</sup> Chimie-Biologie-Innovation (UMR 8231) – ESPCI Paris, PSL Research University – France

In the framework of a mean field approach, we succeed, by using pairwise summation and perturbing around an exact solution, to calculate analytically, in the limit of weakly compressible Lennard-Jones fluids, the near-wall density profile and the solid-liquid interfacial tension. In the calculation, a dimensionless number  $\Lambda = \rho S \zeta - q(T)$ , where  $\rho S$  and  $\rho L$  are  $\rho L$  the solid and liquid densities,  $\zeta$  a solid/liquid-liquid energy ratio, and q(T) a function of temperature, emerges as a key parameter. We found that the contact angle is controlled by the difference between between the attraction of the solid and the repulsion of the displaced liquid at equilibrium. This finding considerably simplifies the mathematics of the problem. It leads to express the Young contact angle, in a simple manner, in terms of the microscopic characteristics of the solid and the liquid. The analysis brings up the concept of a maximum contact angle, around  $126\circ$  for the 0.7-1 temperature range, independent of the solid properties. The solid-liquid interfacial tension is found equivalent to the energy of adhesion. This validates a number of experimental methods used, without theoretical justification so far, to measure solid-liquid interfacial tensions. The theoretical expression of the contact angle agree remarkably well with the Lennard-Jones molecular simulations reported to date, with a standard type deviation of 6odegree. Agreement is aslso found on the density profiles. The implications of this study on the disjoining pressure, the role of confinement and slippage are discussed.

Keywords: solid, liquid interface, contact angle, slippage, confinement, Lennard, Jones.

### A nanofluidic exchanger for harvesting saline gradients energy

Elisabeth Charlaix $^{1}$ 

<sup>1</sup> University Grenoble Alpes, CNRS, LIPhy, F-38000 Grenoble, France.

### Patterns formed by water condensation or evaporation in a nanoporous medium containing salt

Joachim Trosseille \* <sup>1</sup>, Olivier Vincent

<sup>1</sup> Institut Lumière Matière [Villeurbanne] – Université Claude Bernard Lyon 1, Centre National de la Recherche Scientifique – France

Water condensation and evaporation from saline porous materials has attracted the attention of scientists for years due to a large field of applications: salt weathering of buildings, desalination of water, CO2 sequestration, soil decontamination, etc... (1, 2, 3). A complete understanding of related nanoscale processes is however lacking, in particular concerning the coupling between evaporation/condensation and crystallization/deliquescence in confinement (4). While the comprehension of the phenomenon has progressed in the past few years (4, 5, 6, 7), there are still some challenges remaining in characterizing and understanding these processes. For instance, the interplay between the diffusion of species in the gas phase and in the solution, as well as the influence of concentration gradients on the dynamics of the system, is still no well described. Here we performed experiments to monitor the dynamics of phase change at a macroscopic scale, which is strongly related to diffusion of species and phase change features at a nanoscopic level. On the one hand, at low humidity, salt solution evaporates and can crystallize either inside or outside the porous matrix of the material. On the other hand, at high humidity, crystals deliquesce and can eventually form drops at the surface. Both phenomena form complex patterns whose dynamics are investigated experimentally in the light of the thermodynamics of phase change, known from sorption isotherms measurements. We show that we can account for both thermodynamic and dynamical experiments by using a model involving coupled phase change of the solvent (water evaporation/condensation) and the solute (salt crystallization/deliquescence).

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Keywords: Patterns, crystallization, condensation, phase change, nanoporous

### List of participants

- Alexander Schlaich
- Allègre Julien
- Aprili Cécile
- Berthoumieux Hélène
- Biance Anne-Laure
- Bocquet Lyderic
- Boniface Dolachai
- Boudaoud Abir
- Bureau Lionel
- Calvo Florent
- Camille Scalliet
- $\bullet\,$  Charlaix Elisabeth
- Colin Annie
- Comtet Jean
- Coquinot Baptiste
- Cottin-Bizonne Cecile
- Cramail Caroline
- Cross Benjamin
- Damberg Karina
- Dollet Benjamin
- Emmerich Théo
- Eva Panoni
- Fernandez Contreras Aida Gabriela
- Gravelle Simon
- Grisanti Pablo

- Gutfreund Philipp
- Herrero Cecilia
- Jannin Lucas
- Joly Laurent
- Jullien Marie-Caroline
- Khan Aatir
- Lafon Suzanne
- Lhermerout Romain
- Lizee Mathieu
- Lorenceau Elise
- Maali Abdelhamid
- Marbach Sophie
- Marbach Sophie
- Mariette Guilhem
- Mcgraw Joshua
- Meyer Manon
- Montel Fabien
- Nayak Ananta Kumar
- Noury Adrien
- OndarÇuhu Thierry
- Pashayev Said
- Pashayev Said
- Picard Cyril
- Piednoir Rachel
- Sutter Adrien
- Tabeling Patrick
- Toquer Damien
- Tregouet Corentin
- Trosseille Joachim
- Ugo Heloise
- Velay Malo
- Verdier Claude

- Vincent Olivier
- Vishnu Prasad Kurupath
- Ybert Christophe
- Zavala Martinez Arantza Berenice